

PROGRAM & ABSTRACTS

19th
**General Meeting of the International
Mineralogical Association**

***Expansion to
Nano, Bio, and Planetary Worlds***

*IMA2006-Kobe, Japan, July 23~28, 2006
At International Conference Center Kobe*

<http://www.congre.co.jp/ima2006/>



July 23 Sunday	Welcome Reception											
July 24 Monday	IMA Council and Commissions											
	Registration											
	6 parallel scientific sessions		Lunch time		Opening Ceremony		Plenary Lecture		7 parallel scientific sessions		Commissions	
	Exhibition				Break		Break					
July 25 Tuesday	Registration											
	7 parallel scientific sessions		Lunch time		Plenary Lecture		7 parallel scientific sessions		Poster Session 1			
	Exhibition				Break		Business Meetings, Commissions and Working Groups					
July 26 Wednesday	Registration											
	7 parallel scientific sessions		Lunch time		Plenary Lecture		7 parallel scientific sessions		Break		Banquet	
	Exhibition				Break		IMA Council					
July 27 Thursday	Registration											
	7 parallel scientific sessions		Lunch time		Plenary Lecture		7 parallel scientific sessions		Poster Session 2			
	Exhibition				Break		Business Meetings, Commissions and Working Groups					
July 28 Friday	Registration											
	5 parallel scientific sessions		Lunch time		Plenary Lecture		5 parallel scientific sessions		Closing Ceremony			
	Exhibition				Break		Break					

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Contents

Officers and Council of IMA	3
Welcome Messages from Takamitsu Yamanaka Chairman of IMA2006-KOBE	4
Acknowledgement of sponsorship	5
General information	6
Scientific program	8
Formal events	10
Social programs	12
Exhibition	13
Welcome from Ian Parsons the President of IMA	14
Floor Plan	16
IMA Kobe timetable	18
Scientific program (details)	26

Abstracts

Plenary lecture	96
Session1	102
Session2	108
Session3	114
Session4	120
Session5	125
Session6	132
Session7	137
Session8	141
Session9	153
Session10	160
Session11	164
Session12	171
Session13	179
Session14	182
Session15	185
Session16	192
Session17	201
Session18	205
Session19	216
Session20	225
Session21	232
Session22	239
Session23	243
Session24	248
Session25	258
Session26	268
Session27	275
Session28	282
Session29	288
Session30	291
Session31	298
Session32	307
Session33	310
Session34	316
Session35	320
Session36	326
Session37	330
Authors Index	334

19th General Meeting of the International Mineralogical Association

Expansion to Nano, Bio and Planetary Worlds

July 24 – 28, 2006 Kobe, Japan

Officers and Council of IMA:

President	Ian Parsons, Univ. of Edinburgh, Edinburgh, UK
Past-President	Anthony Naldrett, Surry, UK
1st Vice-President	Takamitsu Yamanaka, Osaka Univ., Osaka, Japan
2nd Vice-President	Nicolai P. Yushkin, Komi Sci. Center, Syktyvkar, Russia
Secretary	Maryse Ohnenstetter, CNRS-CRPG, Nancy, France
Treasurer	Cornelis Klein, Univ. of New Mexico, Albuquerque, USA
Councillors	Alain Baronnet, CRMC2 - CNRS, Case, France
	Ian H. Campbell, ANU, Canberra, Australia
	Werner Schreyer (deceased on Feb. 12th, 2006)
	Kari K.R. Kojonen, Geol. Survey of Finland, Finland
	Marcello Mellini, Univ. di Siena, Siena, Italy

Organized and supported jointly by:

The Science Council of Japan
The Mineralogical Society of Japan (MSJ)
The Japanese Association of Mineralogists, Petrologists and Economic Geologists (JAMPEG)
The Society of Resource Geology (SRG)

Organizing Committee, IMA 2006:

General Chairman		T. Yamanaka (Osaka Univ.)
Secretariat	Chair	E. Ohtani (Tohoku Univ.)
	Vice-chairs	A. Tsuchiyama (Osaka Univ.)
		M. Nedachi (Kagoshima Univ.)
Scientific Program	Chair	K. Fujino (Hokkaido Univ.)
	Vice-chairs	M. Akaogi (Gakushuin Univ.)
		M. Arima (Yokohama National Univ.)
		T. Urabe (Univ. of Tokyo)
Science Excursion	Chair	S. Matsubara (National Sci. Museum)
	Vice-chairs	T. Yoshida (Tohoku Univ.)
		M. Shimizu (Toyama Univ.)
Treasury	Chair	T. Murakami (Univ. of Tokyo)
	Vice-chairs	T. Itaya (Okayama Sci. Univ.)
		M. Enjoji (Waseda Univ.)
Donation Committee	Chair	H. Kaneda (Toho Univ.)
	Vice-chair	Y. Yusa (Fuji Tokoha Univ.)
Publicity	Chair	R. Miyawaki (National Sci. Museum)
	Vice-chairs	M. Aoki (Geol. Survey Jpn)
		T. Nagase (Tohoku Univ.)
Meeting Secretariats and Local Arrangements	Chair	M. Matsui (Univ. of Hyogo)
	Vice-chairs	K. Tomeoka (Kobe Univ.)
		H. Sato (Kobe Univ.)
		S. Taguchi (Fukuoka Univ.)
MSJ, JAMPEG, SRG representatives		
	MSJ	Y. Kudoh (Tohoku Univ.)
	JAMPEG	Y. Osanai (Kyushu Univ.)
	SRG	Y. Seki (Geol. Survey Jpn)
		H. Matsueda (Hokkaido Univ.)
		Y. Morishita (Geol. Survey Jpn)
		Y. Watanabe (Geol. Survey Jpn)

Scientific Program Committee:

Chairman	Kiyoshi Fujino (Japan)	
Secretary	Masaki Akaogi (Japan)	
Members	Makoto Arima (Japan)	Georges Calas (France)
	Giovanni Ferraris (Italy)	Arkady Glikin (Russia)
	Simon L. Harley (UK)	Russell Hemley (USA)
	Soo Jin Kim (Korea)	Anhuai Lu (China)
	Anthony J. Naldrett (Canada)	Andrew Putnis (Germany)
	Tetsuro Urabe (Japan)	Ian S. Williams (Australia)
	Michael Zolensky (USA)	

Welcome Messages

Dear Colleague,

The organizing committee of IMA2006-KOBE is very pleased to have more than thousand overseas and Japanese participants to 19th General Assembly and Science Meeting of the International Mineralogical Association held from July 23rd to 28th, 2006 at Kobe, Japan.

IMA2006-KOBE is organized jointly by The Science Council of Japan (SCJ), The Mineralogical Society of Japan, The Japanese Association of Mineralogists, Petrologists and Economic Geologists and The Society of Resource Geology. We sincerely accept the participation at the conference.

The National Committee for Mineralogy of SCJ took part in IMA since the establishment of IMA in 1958. The IMA Conference in Kobe is held after 36 years from the Kyoto meeting in 1970. The aim of the Kobe Meeting is to assemble scientists and researchers in the field of mineralogy, geochemistry, petrology, resource geology, and related sciences from all over the world and to discuss recent progress and future trends. In consideration of the current and active topics around the mineral science, the catch phrase of the present science program is Nano, Bio, and Planetary Sciences. The International and Local joint Program Committee prepares 37 current and meaningful sessions.

We heartily look forward to providing participants with a wealth of outstanding scientific information and a great opportunity to interact with many colleagues in an excellent environment. We also hope participants will find a New Paradigm for future mineral sciences and this meeting will be an enjoyable and sweet memory for all participants.

Finally, on behalf of the organizing committee of IMA2006-KOBE, we would like to express our gratitude to SCJ and Kobe city for their financial supports and thanks to many cooperative companies for their donation. We also appreciate the great efforts of Congre Co. for their management of the present conference.

Takamitsu Yamanaka
Chairman of IMA2006-KOBE

Acknowledgement of sponsorship

The organizers are grateful for generous financial support from:

Kobe City (Portopia '81 Foundation)

TSUTOMU NAKAUCHI FOUNDATION

The Science Council of Japan

The Mineralogical Society of Japan

The Japanese Association of Mineralogists, Petrologists and Economic Geologists

The Society of Resource Geology

Dowa Mining Co., Ltd.

Gemmological Association of All Japan Co., Ltd.

Geotechnos Co., Ltd.

Hisui Genseki Kan

Mitsubishi Materials Corporation

Mitsui Mining & Smelting Co., Ltd.

Nikko Exploration & Development Co., Ltd.

Nippon Mining & Metal Co., Ltd.

Nittetsu Mining Co., Ltd.

Rigaku Corporation

Sumitomo Metal Mining Co., Ltd.

Syntek Co., Ltd.

Toho Zinc Co., Ltd.

Tokyo Electric Power Services Co., Ltd.

TOTO Ltd.

Mr. Mizota, Tadato

Mr. Takenouchi, Sukune

1. General information

Venue

INTERNATIONAL CONFERENCE CENTER KOBE (ICCK)
6-9-1 Minatojima-nakamachi, Chuo-ku, Kobe 650-0046, Japan
TEL:078-302-5200
FAX:078-302-6485
E-mail:info@kcva.or.jp
URL:http://www.kcva.or.jp

Language

English (no simultaneous interpretation provided)

Registration

The registration desk is located on the first floor, Foyer of the ICCK.

Opening times

Sunday, July 23	13:00-19:00
Monday, July 24	8:00-18:30
Tuesday, July 25	8:30-17:30
Wednesday, July 26	8:30-17:30
Thursday, July 27	8:30-17:30
Friday, July 28	8:30-13:00

Registration fees

Regular	50,000 yen
Accompanying Person	8,000 yen
Banquet	6,000 yen

(Banquet Registration will not be accepted beyond the number of positions available)

Registration Entitlement

All registered participants will be entitled to:

- receive congress materials, including a set of official publications
- participate in all Scientific Sessions /Exhibition
- attend the Welcome Reception, Opening Ceremony and Closing Ceremony
- receive free refreshment services during coffee breaks each day

Entitlement for Accompanying Persons

Those registered as accompanying persons will be entitled to:

- participate in all Scientific Sessions/Exhibition
- attend the Welcome Reception, Opening Ceremony and Closing Ceremony
- receive free refreshment services during coffee breaks each day

Tour desk

The tour desk is located next to the Registration desk and offers a full range of tourist information including hotel accommodations and Optional Tours. The desk will be open as follows:

Sunday, July 23	13:00-19:00
Monday, July 24	8:00-18:30
Tuesday, July 25	8:30-17:30
Wednesday, July 26	8:30-17:30
Thursday, July 27	8:30-17:30
Friday, July 28	8:30-13:00

Badges

All Meeting registrants are required to wear their name badges in order to gain entry to the scientific sessions, the exhibition, and social activities.

Business center

The business center is located on the second floor of the ICCK. Copy machines, computers and access to the Internet will be available. Express deliveries are also available.

Child care

Child care is available at Meeting Room 305 on the third floor of the ICCK during 24 July to 28 July, 2006 by advance registration only.

08:30-13:00 JPY 2,000

13:00-18:00 JPY 2,000

08:30-18:00 JPY 4,000

Cloakrooms

Cloakrooms are available at the Rehearsal Room on the basement floor of the ICCK.

Currency exchange

Most foreign currencies and traveler's checks can be easily exchanged at banks, hotels.

The approximate exchange rate as of April 3 was 1 US dollar = ¥117. The secretariat will only accept cash in Japanese yen (JPY).

Internet access

Internet corners are located on the third floor of ICCK. LAN cable will only be provided.

Please bring your own computer.

Liability

The Meeting organizers shall not be liable for injury or damage to persons or property during the Meetings.

Lunch services

Two kinds of takeout lunch (Japanese box lunch and sandwiches) will be sold at special reduced price at the first floor entrance of the ICCK daily from July 24 through July 28.

Lunch may be taken in the Main Hall as well as in the session meeting rooms on the fourth and fifth floors of the venue.

Mobile phones

Please be aware that mobile phones must be switched off during all sessions.

Public transportation

JR/Subway "Sannomiya" Station — International Conference Center Kobe

Take Port Liner to "Shimin Hiroba" station. (10min. JPY 240)

Tickets for the Port Liner with special discounted rate for the participants of IMA2006-Kobe will be available at the tour desk.

JR "Shin-Kobe" Station — Sannomiya Station

Take subway to "Sannomiya" station. (2min. JPY 200)

JR "Osaka" Station — Sannomiya Station

Take JR Tokaido Line to "Sannomiya" station. (30min. JPY 390)

Coffee break

Coffee, orange juice and mineral water will be served twice a day. During poster session, soft drinks, beer and wine will also be served. These are on a first-come, first-served basis.

Telephones

Pay phones are available at the ICCK for local and long distance calls. Telephone cards can be purchased at the shop in the ICCK and at hotels.

International telephone numbers are as follows:

001-010- Country code – Area code – Telephone number or

0033-010- Country code – Area code – Telephone number

Dial the number exactly as shown above.

Time

Japan Standard Time is 9 hours ahead of UTC (Coordinated Universal Time).

Tipping

A gratuity is always included in the bill at restaurants and in taxi fares. There is no need to offer an additional tip.

Climate

The average temperature in Kobe at the time of the meeting is 27°C (80°F).

2. Scientific program

Timetables are given later in this volume.

2-1. Plenary lectures

Nine plenary lectures are given during the conference. These take place daily, on July 24(14:15-15:15) and July 25-28(13:15-14:15) at the Main Hall and Room 301.

2-2. Oral presentations

37 sessions are given during the conference. These take place concurrently during July 24-28 at the Main Hall, Meeting Room 301 / 401 / 402 / 403 / 503 • 504 / 505.

Instructions for the Oral Presentations

For the oral presentations, basically, speakers must use a Windows computer provided at the venue (for the single-screen projector). We will only accept computer-based PowerPoint presentations. Slide/Overhead/VCR projectors will NOT be available. Please **bring your PowerPoint file to the PC center to upload it on the computer provided one day before your presentation**, as written below.

Exceptionally, speakers may use their own laptop computer, when using some heavy applications such as animations, or using a Macintosh computer.

Please **bring a CD-R or USB memory stick or your computer to confirm the proper operation one day before your presentation to the PC center** which is open as scheduled below. At the PC center, please review your PowerPoint file after operators uploading the file on to the computer provided. Your uploaded PowerPoint file is transferred to your session room by the Program Committee on the day of your presentation.

For speakers using their own laptop computer, please connect your computer to the projector and check your presentation.

Opening times at PC center

Sunday, July 23	13:00-19:00
Monday, July 24	8:30-19:00
Tuesday, July 25	8:30-19:00
Wednesday, July 26	8:30-19:00
Thursday, July 27	8:30-19:00

1. If you bring a CD-R or USB flash memory stick, please follow the instructions below:

- Presentation must be made in PowerPoint readable in Windows.
*Macintosh users should make their presentations as shown in the instruction 2.
- The computers provided for the sessions will be running the following operating system with the following application software installed:
Windows: Windows PowerPoint2000/ PowerPointXP/ PowerPoint2003
- Use the above operating systems' standard fonts.
Windows: Century, Century Gothic, Times New Roman, etc.

2. We strongly recommend you to use the computer provided at the venue. But, if you bring your own laptop computer and make a presentation using your computer at the session room, please follow the instructions below:

- Please bring your computer to the PC center **one day before your presentation** to confirm the proper operation.
- Ensure that your computer is equipped with the proper monitor connector (mini D-sub15 pins) as shown below. If your computer does not have this connection, please bring an appropriate converter with you.



← [mini D-sub 15 pins]

- Be sure to bring an AC adaptor with you. Japanese standard AC voltage is 100V.
- The secretariat is not responsible for any projection troubles caused by computer technical difficulties. We recommend that all presenters bring back-up data.
- Your computer can be placed on a podium for your presentation. Please pick up your computer at the podium in your session room after your presentation.

3. Sound speakers are not available.

4. A computer for presentations will be provided on a podium.

5. Presentation data loaded on the computers provided will be completely deleted by the secretariat.

2-3. Poster presentations

Posters are displayed in the Meeting Room 501, 502 and Foyer on the fifth floor.

Instructions for the Poster presentations

Poster Session 1(Tuesday, July 25)

Session1, 2,3,5,8,14,15,17,18,21,26,28,29,30,31,32,35,37

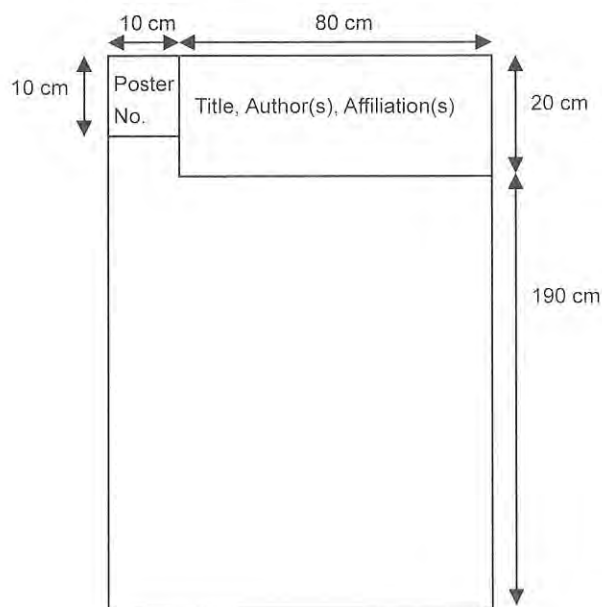
	mounting	session	removing
Monday, July 24	12:00-18:00		
Tuesday, July 25	9:00-12:00	16:30-19:30	19:30-20:00
Wednesday, July 26			9:00-12:00

Poster Session 2(Thursday, July 27)

Session4,6,7,9,10,11,12,13,16,19,20,22,23,24,25,27,33,34,36

	mounting	session	removing
Wednesday, July 26	12:00-18:00		
Thursday, July 27	9:00-12:00	16:30-19:30	19:30-20:00
Friday, July 28			9:00-12:00

1. The Poster board surfaces measure approximately W90cm X H210cm. A poster number (10 cm x 10 cm) is displayed at the top left of the board.
2. A supply of pushpins will be available in the poster area for mounting your poster.
3. Each poster must have a label at the top that indicates the title of the paper, the name(s) of the author(s) and their affiliation(s). The presenting author should be marked with a circle.
4. Authors are required to mount and remove their materials scheduled as above.
5. Authors are expected to be at their poster during the assigned sessions. In particular, authors are expected to make the presentation to the audience at 17:00 -18:30 (core time) in front of their posters.
6. We remind you that you should NOT leave poster tubes or cases in the poster areas. The organizers will not be held responsible for any losses which may be incurred.
7. Posters not removed by the time listed above will be removed and discarded by the congress secretariat.



2-4. Field Excursions

The following field excursions are being held, only to delegates who have pre-registered. Departure and other information are given in the second circular.

FE1: Epithermal gold deposits in southern Kyushu

19th – 22nd July, leaders Koichiro Watanabe and Akira Imai (Kyushu University), Sachihiro Taguchi (Fukuoka University)

FE2: Aso volcano and alkalibasalt including REE-carbonates and zeolites in northern Kyushu

20th – 23rd July, leaders Seiichiro Uehara (Kyushu University), Shinichiro Ikebe (Aso Volcano Museum), Ritsuro Miyawaki (National Science Museum)

FE4 High temperature skarn including new minerals and jadeite-bearing metamorphic rocks in western Honshu

29th – 31st July, leaders Isao Kusachi and Chiyoko Henmi (Okayama University), Shoichi Kobayashi (Okayama University of Science)

FE6 Hydrothermal activity and associated metallic mineralization in Hokkaido

29th July – 2nd August, leaders Hiroharu Matsueda and Shuji Ono (Hokkaido University), Masahiro Yahata (Geological Survey Hokkaido)

FE7 Pb-Zn skarn deposits of the Kamioka mine and jadeitite blocks: Development of the Hida and Hida marginal belts in central Japan

29th July – 1st August, leaders Keitaro Kunugiza and Masaaki Shimizu (Toyama University), Hiroshi Miyajima (Fossa Magna Museum)

FE9 Crustal section and anatexis of lower crust and subduction-related high-pressure type metamorphism in the Hidaka and Kamuikotan metamorphic belts, Hokkaido, Japan

29th July – 4th August, leaders Masaaki Owada (Yamaguchi University), Yasuhiro Osanai (Kyushu University), Toshiaki Shimura (Niigata University), Hideo Ishizuka (Kochi University)

3. Formal events

3-1. Opening and closing ceremonies

The official opening ceremony of IMA 2006 will take place at 13:15 on Monday, July 24 in the Main Hall on the first floor of the ICCK. Delegates will be addressed by Professor Takamitsu Yamanaka (Osaka University, General Chairman of IMA2006 Organizing Committee), Professor Kiyoshi Kurokawa (President of the Science Council of Japan), Professor Ian Parsons (University of Edinburgh, UK, President of IMA) and Mr. Tatsuo Yada (Mayor of Kobe). A message from Prime Minister Jun-ichiro Koizumi will be presented. The ceremony will be followed by a Traditional Japanese music entertainment.

There will be a brief closing ceremony at 17:00 on Friday, July 28 in the Main Hall of the ICCK. Delegates will be addressed by Professor Takamitsu Yamanaka and the Organizing Committee of the next IMA meeting. Shishimai (Lion Dance) Performance will be made by Dragon and Lion Dancing Team of Kobe Municipal Hyogo Commercial High School.

3-2. IMA commissions, business and council meetings

IMA Council at Room 303

Sunday, July 23	13:00-18:00	First Council Meeting
Wednesday, July 26	16:00-18:00	Second Council Meeting
Friday, July 28	12:00-13:00 or after 19:00	Third Council Meeting

Commissions and Working Groups of the IMA

- Commission on New Minerals and Mineral Names (CCNMM) and Commission on Classification of Minerals (CCM), at Room 406
Sunday, July 23 15:30-17:30 (First); Monday, July 24 18:00-20:00 (Second ※)
※ An open discussion on the classification of amphiboles
- Commission on Ore Mineralogy, at Room 407
Tuesday, July 25 16:30 -
- Commission on Applied Mineralogy, at Room 304
Tuesday, July 25 16:30-18:30 (First); Thursday, July 27 16:30-18:30 (Second)
- Commission on Mineral Growth and Interface Processes, at Room 407
Tuesday, July 25 14:00-16:00 (First); Thursday, July 27 18:00- (Second)
- Commission on Gem Materials, at Room 303
Tuesday, July 25 14:30- (First); Thursday, July 27 14:30- (Second)
- Commission on Museums, at Room 406
Tuesday, July 25 15:30-16:45 (First); Thursday, July 27 15:30-16:45 (Second)
- Commission on Physics of Minerals, at Room 303
Tuesday, July 25 16:30 -
- Working Group on Environmental Mineralogy, at Room 404
Tuesday, July 25, 16:30-18:00
- Working Group on Inclusions in Minerals, at Room 405
Tuesday, July 25 16:30-18:00 (First); Thursday, July 27 16:30- 18:00 (Second)

IMA Business Meetings at Main Hall

Tuesday, July 25 16:45-18:45 (First); Thursday, July 27 16:45- 18:45 (Second)

All delegates are encouraged to attend the Business Meetings of the IMA and to contribute to the discussion. If matters arise requiring a vote, under the IMA constitution only delegates nominated by official national representatives are permitted to vote, the number with voting rights being proportional to the size of the member national mineralogical organization.

4. Social Programs

Attention: The starting time and place have been changed from the announced information in the second circular.

4-1. Welcome Reception

Date: Sunday, July 23, 2006

Time: 17:00 - 20:00

Place: 2nd floor of Kobe Chamber of Commerce and Industry, next to the International Conference Center Kobe (Map will be posted at the Registration Desk in the International Conference Center Kobe)

Fee: Included in the registration fee

4-2. Banquet

Date: Wednesday, July 26, 2006

Time: 19:00

Place: Portopia Hotel (near the Conference Center)

Fee: JPY 6,000 per person for registered participants/accompanying persons

JPY 10,000 per person for those not registered as participants/accompanying persons

Taiko (traditional Japanese drums) Performance will be made in the Banquet. Due to limited capacity, on-site sign-up for Banquet may not be accepted.

4-3. Optional Tours

Following optional tours are to be operated during the Meeting. Some of the tours may accept additional reservation at the tour desk.

Mon., July 24	08:00-18:00 T01	Tour of the Ancient Capital of Kyoto(A)
Tue., July 25	10:00-12:00 T03	Tea Ceremony(B)
	09:00-18:00 T04	Temples and Shrines in the Ancient Capital of Nara(A)
Wed., July 26	10:00-12:00 T06	Walking Tour to Pearl Gallery(A)
	08:00-13:00 T07	Tour of Himeji Castle(A)
Thu., July 27	10:00-12:00 T08	Tea Ceremony(B)
	18:30-21:30 T11	Dinner Cruise around Akashi Channel Bridge(C)
Fri., July 28	17:40-21:50 T14	Dinner at Rokkosan Hotel with a Night View of Kobe(D)

Notes:

(A) Please assemble in the lobby (1F) of Portopia Hotel 10 minutes prior to departure time.

(B) Tea Ceremony will take place in the venue (ICCK). Place to meet will be informed at the travel desk.

(C) Please assemble at the passenger terminal (2F of Kobe Merikenpark Oriental Hotel) at 18:30.
Access from the venue will be informed at the travel desk.

(D) DEPARTURE TIME AND PLACE CHANGED.

Please assemble in the lobby (1F) of Portopia Hotel at 17:30.

5. Exhibition

Exhibition will take place at the Reception Hall on the third floor of the ICCK.

	open		close
Monday, July 24	9:00	-	17:00
Tuesday, July 25	9:00	-	17:00
Wednesday, July 26	9:00	-	17:00
Thursday, July 27	9:00	-	17:00
Friday, July 28	9:00	-	12:00

Exhibitors

21st Century COE Program of Kobe University "Origin and Evolution of Planetary Systems"
21st Century COE Program of Tohoku University "Advanced Science and Technology Center for the Dynamic Earth"
21st Century COE Program of Tokyo Institute of Technology "Earth: How to build habitable planets?"
Blackwell Publishing
Crystal Impact
EARTH REMOTE SENSING DATA ANALYSIS CENTER (ERSDAC)
Elsevir B.V.
Gemmological Association of All Japan Co., Ltd.
Geological Museum, Geological Survey of Japan, AIST
Geological Survey of Japan, AIST
HORIBA, Ltd.
HORI MINERALOGY LTD.
JAPAN HIGHTECH CORPORATION LTD.
Japan Oil, Gas and Metals National Corporation
JICOUX DATASYSTEMS INC.
Kyoto University Active Geosphere Investigations for the 21st Century COE Program
MEIJI TECHNO CO., LTD.
Next IMA General Meeting 2010 (Budapest, Hungary)
PANalytical(Spectris Co., Ltd.)
Rigaku Corporation
The International Mineralogical Association
The Japanese Association of Mineralogists, Petrologists and Economic Geologists
The Mineralogical Society
The Mineralogical Society of Japan
The National Science Museum
The Society of Resource Geology
United Publishers Services Limited

WELCOME FROM THE PRESIDENT OF IMA

Welcome to the 19th General Meeting of the International Mineralogical Association! IMA's four-yearly flagship meeting has moved from one island nation, at a passive margin on the western edge of Eurasia, to another at an active margin on its eastern rim. Running a meeting as large as this requires a big team effort and we must all be sincerely grateful for the very hard work of Takamitsu Yamanaka and his colleagues over a period that I know from personal experience stretches over several years. These IMA meetings are important events because they are the only international meetings devoted specifically to mineralogy. The programme the team has put together is extremely exciting and will provide a wonderful show-case for current mineralogical research. Thank you all very much.

There have been many important changes, both internal and external to IMA, since we last met in Edinburgh in 2002. Internally, I have, sadly, to remind delegates of the recent death of one of our most distinguished Council members, Werner Schreyer. His wise advice to Council will be greatly missed. His place on Council has been taken by Walter Maresch, also of Ruhr-University, Bochum. Cornelis 'Kase' Klein, of the University of New Mexico, Albuquerque, decided after many years of devoted service as treasurer of IMA that the time had come to stand down. His role has been taken over by Bob Downs, who is based one American state to the west, in Tucson, Arizona. We must all thank Kase for his work and patience over many years. The repeated difficulty he experienced in getting the national organizations of many countries to pay their annual dues to IMA remains a problem, and one that we shall, I hope, address in Kobe. We are delighted to welcome the mineralogical societies of Uzbekistan and of India to the membership of IMA, which now has 38 supporting organizations.

Following the Edinburgh meeting we began the practice of holding Business Meetings every two years rather than four, and two successful Business Meetings were held during the International Geological Congress in Firenze (Florence). It was particularly appropriate that our competition to choose a logo for IMA, which was carried out by Council without knowledge of the identity or nationality of the designers, was won by a young Italian scientist, Sabrina Nazzareni, of the University of Perugia. The 2nd Business Meeting voted to hold the 20th General Meeting of IMA, in 2010, in Budapest. It will be organized by mineralogists from Austria, Hungary, Romania and Slovakia, under the chairmanship of Ekkehart Tillmanns of the University of Vienna. A collaboration between Christine Lecluse and our Secretary, Maryse Ohnenstetter, in Nancy, France, led to the development of a modern and stylish IMA website (www.ima-mineralogy.org), with links not only to the websites of many of our supporting societies but also to those of many IMA Commissions and Working Groups.

An important external event occurred at the end of 2004, when the first issue of *Elements* magazine appeared. Rod Ewing, of the University of Michigan, introduced the concept of a semi-popular international magazine devoted to mineralogy, geochemistry and petrology, part thematic articles and part news-and-views, to the Mineralogical Society of America (MSA) at the end of 2000. The idea was developed with consultation outside the USA and early in 2003 an international steering committee was formed. At the end of 2003, MSA, the Mineralogical Association of Canada (MAC) and the Mineralogical Society of Great Britain and Ireland agreed to provide start-up funding. Mike Hochella and myself joined Rod as scientific editors and Pierrette Tremblay from MAC as managing editor. We all met for the first time in Michigan in April 2004 and, remarkably, in November the first issue (dated January 2005) appeared. By then the Geochemical Society, the Clay Minerals Society, the European Association for Geochemistry and the International Association of GeoChemistry had joined the consortium. By June 2006 there were eight contributing societies, including Société Française de Minéralogie et de Cristallographie, plus three 'affiliated' societies, IMA, the European Mineralogical Union and the AIPEA, who are provided with space when available but do not pay a subscription. Four other societies have applied to join the contributing consortium in 2007. The editors all hope that other major societies, especially Japan, will join very soon. The print-run is now about 10 000. *Anyone* may view *Elements* at www.elementsmagazine.org.

It is obvious that Elements has been a great success within the international mineralogical and geochemical community. We, as the International Mineralogical Association, have many people to thank for this, particularly Rod Ewing, for his vision and enthusiasm, and Pierrette Tremblay for her style and tireless efficiency. MSA, through its Executive Director, Alex Speer, provides guidance and infrastructure, including the subscription database that only a well-supported, professional scientific society could offer. IMA has capitalised on this unprecedented opportunity to reach its members with news and articles by the President and Secretary and by Chairmen of Commissions. At this meeting I am proposing that we appoint a 'communications officer' to Council to maintain a broader flow of news that might include articles describing the makeup and activities of the smaller Min Socs that make up an important part of IMA, or news and views from their members.

Just recently another very exciting proposal was presented to IMA. One of the most important roles played by IMA is the naming and classification of minerals. The dissemination of this information has been largely accomplished through journals. To provide a new means to present and interact with mineralogical data, Mike Scott, an avid gem collector and founding president of Apple Computer Corporation, is offering funding through the RRUFF project to build a web site and database that will be associated with IMA. The database will present the complete list of minerals, with experimental diffraction patterns, chemistry, spectroscopy, and means to search and identify minerals. The community will be encouraged to contribute and we can build a resource that will educate as well as provide research direction. Bob Downs, our new treasurer, will be talking about the project on Tues afternoon.

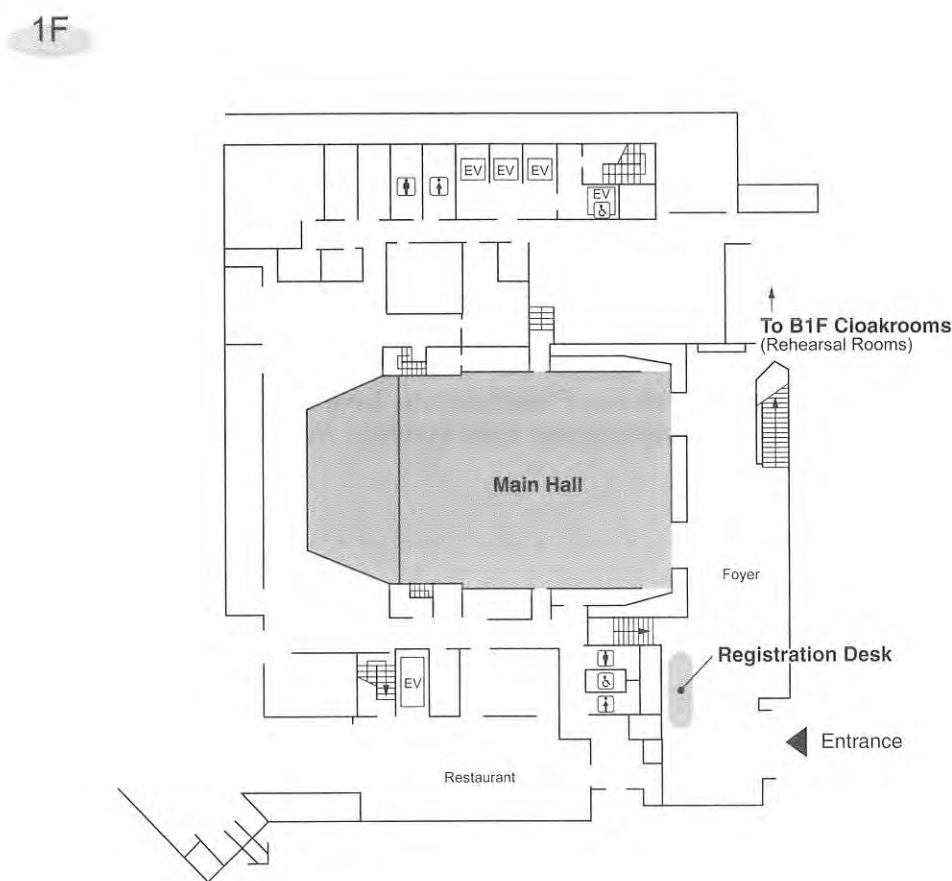
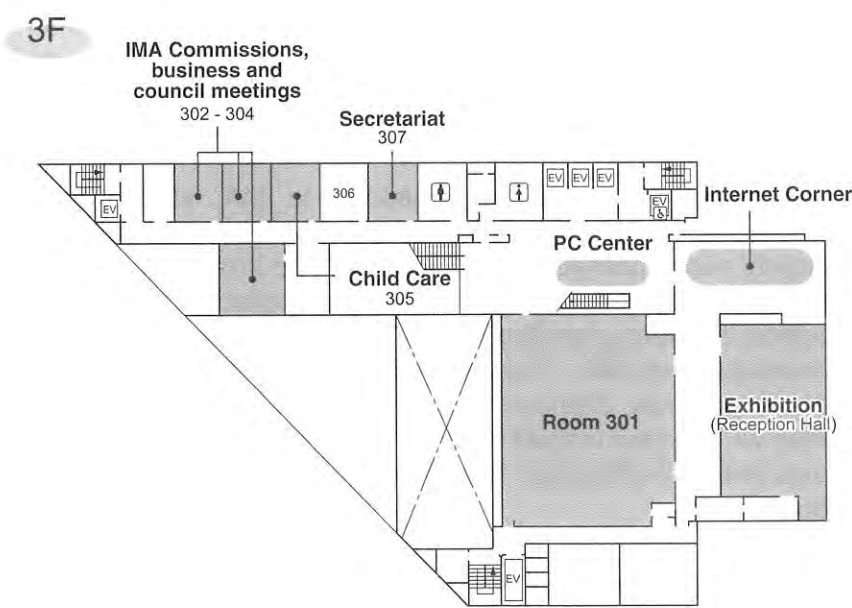
At our Council and Business meetings we shall be discussing further important initiatives that I outlined in the June issue of Elements. The foundation of an IMA medal recognizing international excellence should be a priority. We need to find ways of making the Commissions and Working Groups more pro-active in involving the whole community of mineralogists in their fields, perhaps through the medium of electronic newsgroups resembling MSA-talk. We need a long-term plan to co-organize meetings with other mineralogical and geochemical organizations between IMA General Meetings. We must solve our problems in collecting dues from member countries, perhaps by introducing a flat-rate system in place of the present banded system which makes membership much cheaper for members of the larger, often richer Min Socs than those of the smaller, less well-funded ones. In my view we need to consider shortening the term of office of the President and decoupling the presidency from organization of the General Meeting.

Before I end I must give sincere thanks to our Secretary, Maryse Ohnenstetter, for her tireless efforts over the last four years. Presidents make speeches but it is Secretaries that make organizations like IMA work. Maryse works extremely hard on many aspects of IMA, both on a day-to-day basis and on more time-consuming activities like preparing reports for IUGS (which you can see on the IMA website), providing agendas and supporting papers for meetings like this, and maintaining the website. I shall pass the Presidency to Takamitsu at this meeting confident in the knowledge that he will have unfailing support from Maryse. We all have a great deal to thank her for.

Ian Parsons, President of IMA

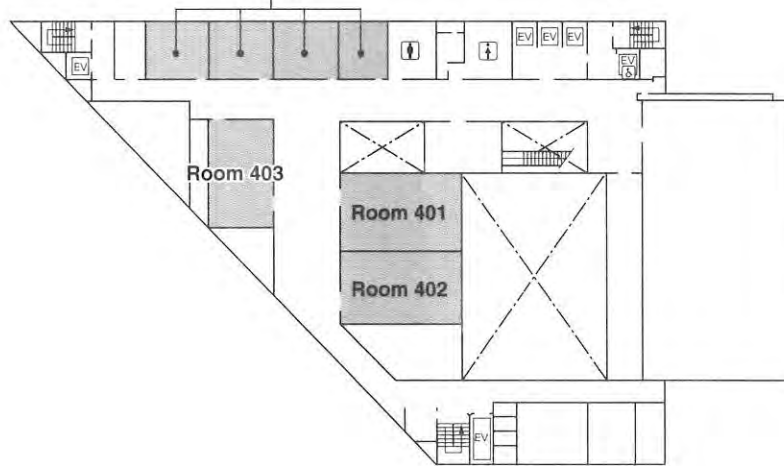
Floor Plan

The International Conference Center Kobe



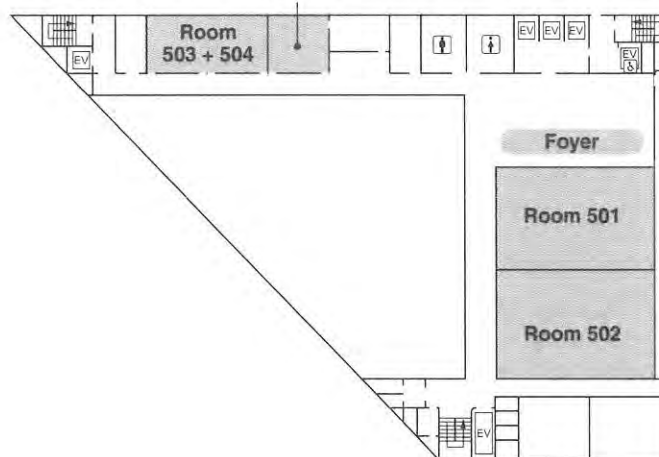
4F

IMA Commissions,
business and
council meetings
404 - 407



5F

Room 505



IMA2006 Kobe : Timetable July 23 Sunday

Date	Room	Floor
	Main Hall	1F
	301	3F
	401	4F
	402	4F
	403	4F
	503, 504	5F
	505	5F
	501, 502 and Foyer	5F
July 23 Sunday	Foyer	1F
	Entrance Hall	3F
	Reception Hall	3F
	303	3F
	304	3F
	404	4F
	405	4F
	406	4F
	407	4F

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IMA2006 Kobe : Timetable July 25 Tuesday

[illegible]

IMA2006 Kobe : Timetable July 26 Wednesday

Date	Room	Floor	7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00
	Main Hall	1F	Plenary Lecture Lindsay P Keller (NASA USA) 5. Mineralogy and dynamics of the mantle and core
	301	3F	Plenary Lecture Lukas Baumgartner (University of Zurich, Switzerland) 20. Oceanic crust and mantle processes
	401	4F	16. Mineralogy of ore deposits
	402	4F	Lunch Time
	403	4F	9. Structure and physical properties of melts and glasses
	503, 504	5F	23. Physical and chemical processes and chronology in the solar system
	505	5F	24. Bio-Geo interface in Minerals
	501, 502 and Foyer	5F	7. Kimberlites, diamonds and mineral inclusions from the mantle
			Mounting (Poster session 2)
July 26 Wednesday	Foyer	1F	Registration
	Entrance Hall	3F	PC Center
	Reception Hall	3F	Exhibition
	303	3F	IMA Council (2nd Council Meeting)
	304	3F	
	404	4F	
	405	4F	
	406	4F	
	407	4F	

IMA2006 Kobe : Timetable July 27 Thursday

Date	Room	Floor	7:00	8:00	9:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00	
	Main Hall	1F				19. Subduction factory and continental evolutions				Please! Lecture Yoshinori Tatsami (JAMSTEC, Japan)	19. Subduction factory and continental evolutions							
	301	3F				25. Mineral-water interactions: from microscopic to macroscopic aspects				Please! Lecture Michael A.Carpenter (Cambridge Univ., UK)	6. Hydrogen, water and volatiles in the deep Earth							
	401	4F				12. Texture formation and crystal growth in geosciences					12. Texture formation and crystal growth in geosciences							
	402	4F				34. Frontier applications of neutron sciences to mineralogy					34. Frontier applications of neutron sciences to mineralogy							
	403	4F				22. Lunar and Martian rocks, differentiated meteorites and planetary missions					22. Lunar and Martian rocks, differentiated meteorites and planetary missions							
	503, 504	5F				4. Computational study of mineral structures and properties					4. Computational study of mineral structures and properties							
	505	5F				10. Mechanisms and kinetics of phase transformations					13. Nucleation and Aggregation of macro- to nano-materials							
	501, 502 and Foyer	5F				Mounting (Poster Session2)							Sessions (Poster session2)			Removing (Poster Session2)		
	July 27 Thursday	Foyer	1F	Registration														
		Entrance Hall	3F	PC Center														
Reception Hall		3F	Exhibition															
303		3F										2nd Commission (Gem Materials)						
304		3F											2nd Commission (Applied Mineralogy)					
404		4F																
405		4F												2nd Working Group (Inclusions in Minerals)				
406		4F											2nd Commission (Museums)					
407	4F														2nd Commission (Mineral Growth and Interface Processes)			
			7:00	8:00	9:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00	

IMA2006 Kobe :Timetable July 28 Friday

Date	Room	Floor	7:00	8:00	9:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00
	Main Hall	1F								Plenary Lecture Sumio Iijima (Meiji Univ., Japan)	25. Mineral-water interactions: from microscopic to macroscopic aspects						
	301	3F									33. New applications of synchrotron radiation in earth and planetary sciences						
	401	4F										12. Texture formation and crystal growth in geosciences					
	402	4F										27. Clays and zeolites: natural and synthetic materials					
	403	4F															
	503, 504	5F									11. Application of novel techniques for "in-situ" observation of crystal growth and nucleation						
	505	5F															
	501, 502 and Foyer	5F									Removing (Poster Session2)						
	Foyer	1F															
	Entance Hall	3F															
July 28 Friday	Reception Hall	3F															
	303	3F														IMA Council (3rd Council Meeting) (tentative)	
	304	3F															
	404	4F															
	405	4F															
	406	4F															
	407	4F															
			7:00	8:00	9:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00



Scientific Program

Plenary lectures

July 24, 14:15-15:15 Main Hall

- PL1 Catherine McCammon (Univ. of Bayreuth, Germany)
"Microscopic properties to macroscopic behaviour: The influence of iron electronic state"

July 24, 14:15-15:15 Room301

- PL2 Christoph A. Heinrich (ETH, Switzerland)
"From fluid inclusion microanalysis to large-scale hydrothermal mass transfer in the Earth's interior"

July 25, 13:15-14:15 Main Hall

- PL3 Eiji Ito (Okayama Univ., Japan)
"Sintered diamond multi-anvil apparatus and its application to mineral physics"

July 25, 13:15-14:15 Room301

- PL4 Jillian F. Banfield (Univ. of California, Berkeley, USA)
"Microbial metabolism and the size- and chemical environment-dependence of the structure and reactivity of nanoparticle products"

July 26, 13:15-14:15 Main Hall

- PL5 Lindsay P. Keller (NASA, USA)
"The nature of early solar system and presolar materials"

July 26, 13:15-14:15 Room301

- PL6 Lukas Baumgartner (Univ. of Lausanne, Switzerland)
"Mineral growth in high and low pressure metamorphic rocks"

July 27, 13:15-14:15 Main Hall

- PL7 Yoshiyuki Tatsumi (JAMSTEC, Japan)
"Operation of subduction factory and production of andesite"

July 27, 13:15-14:15 Room301

- PL8 Michael A. Carpenter (Univ. of Cambridge)
"Structural evolution, strain and elasticity of perovskites at high pressures and temperatures"

July 28, 13:15-14:15 Main Hall

- PL9 Sumio Iijima (Meijo Univ., Japan)
"Nanomaterial research learning from mineralogy"

Scientific Sessions

The scientific sponsor of each session is given between parentheses at the end of the session title. The full names of the abbreviations of the sponsorship are given in the end of the list of the sessions.

principal convener , * corresponding convener , † keynote paper , § invited paper.

01. Phase transitions and thermodynamic modeling of minerals and rocks (WGME)

Conveners: Masaki Akaogi^{#,*} (Gakushuin Univ.), Yingwei Fei (Geophysical Lab.), Stefano Poli (Univ. of Milano), Surendra K. Saxena (Florida International Univ.)

Chairs: Masaki Akaogi (Gakushuin Univ.), Stefano Poli (Univ. of Milano)

Oral presentations

Mon. July 24 9:30~11:50 3F 301

9:30~10:00

- O1-1 § Lars Stixrude, Carolina Lithgow-Bertelloni, Wenbo Xu
Physical properties of multi-phase mantle assemblages

10:00~10:30

- O1-2 § Jibamitra Ganguly, Saxena K. Saxena, Andrew M. Freed
Density variations in subducting slabs and surrounding upper mantle: Understanding stagnation vs. penetration of the slabs at the 670 km discontinuity

10:30~10:50

- O1-3 Andrey V. Bobrov, Hiroshi Kojitani, Masaki Akaogi, Yuriy Litvin
Experimental study of phase relations on the diopside $\text{CaMgSi}_2\text{O}_6$ - hedenbergite $\text{CaFeSi}_2\text{O}_6$ - jadeite $\text{NaAlSi}_2\text{O}_6$ system at 7-24 GPa and 1600-2300°C

10:50~11:10

- O1-4 Daisuke Nakamura
A new formulation of garnet-clinopyroxene thermometer using large number of experimental data with graphite capsules

11:10~11:30

- O1-5 Lin-gun Liu, Ahmed El Goresy
High-pressure phase transitions of the feldspars and further characterization of lingunite

11:30~11:50

- O1-6 Stefano Poli, Jose Francisco Molina, Ettore Franzolin
Fe-Mg-Ca partitioning between carbonates, garnet and clinopyroxene at high pressure: Experimental constraints in mafic systems up to 6 GPa

Mon. July 24 15:30~18:30 3F 301

15:30~16:00

- O1-7 § Tetsuya Komabayashi, Soichi Omori
Thermodynamic modeling of high-pressure hydrous phases and fluid phases in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ up to 35 GPa, 1873K

16:00~16:20

- O1-8 Masaki Akaogi, Harumi Takayama, Asuka Furukawa, Hiroshi Kojitani, Hitoshi Kawaji, Tooru Atake
Thermodynamic properties of high-pressure magnesium silicates and analogue materials and equilibrium phase relations at high pressure

16:20~16:50

O1-9 § Daniel J. Frost

The effects of water content and oxygen fugacity on the olivine to wadsleyite transformation

Break

17:10~17:30

O1-10 Ronald Miletich, Angela Ullrich, Clivia Hejny, Wilson A. Crichton

High-pressure polymorphism, phase transition and elastic behaviour of behoite, $\text{Be}(\text{OH})_2$

17:30~17:50

O1-11 Daisuke Hamane, Yusuke Seto, Kiyoshi Fujino, Takaya Nagai

Fe^{3+} and Al partitioning between silicate perovskites at the lower mantle condition

17:50~18:10

O1-12 Hitoshi Yusa, Nagayoshi Sata, Yasuo Ohishi

Hexagonal perovskites in barium silicates

18:10~18:30

O1-13 Denis Andrault, Nathalie Bolfan-Casanova, Osamu Ohtaka, Hiroshi Fukui, Guillaume Morard, Nicolas Guignot, Ken-Ichi Funakoshi

In-situ determination of Fe-S and Fe-Si high-pressure melting diagrams

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P1-1 Wenjun Yong, Edgar Dachs, Anthony C. Withers, Eric J. Essene
Heat capacity of Si-wadsleyite ($\text{K}_2\text{Si}_4\text{O}_9$) and related phase equilibria
- P1-2 Edgar Dachs, Charles Geiger
Heat capacities and entropies of mixing of pyrope-grossular ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) garnet solid solutions
- P1-3 Hélène Gailhanou, Juan Olives, Marc Amouric, Jacques Rogez, J. C. van Miltenburg, G. J. K. van den Berg, Guy De Weireld, Youssef Belmabkhout, Régis Perbost, Eric Gaucher, A. Inoue, P. Blanc
Nanostructures, thermodynamic functions and hydration of clay minerals
- P1-4 Ayano Ono, Hiroshi Kojitani, Masaki Akaogi
Thermodynamic properties and high pressure phase equilibria of hexagonal phases in the systems MgAl_2O_4 - CaAl_2O_4 and NaAlSiO_4 - MgAl_2O_4
- P1-5 Shuangmeng Zhai, Eiji Ito
Phase relations of $\text{CaAl}_4\text{Si}_2\text{O}_{11}$ at high-pressure and high-temperature conditions
- P1-6 Kenji Hagiya, Masanori Matsui, Takatoshi Sakaguchi, Masahiro Obata
X-ray diffraction studies of high-pressure phases of calcite at room temperature
- P1-7 Shugo Ohi, Akira Miyake, Norimasa Shimobayashi, Masao Kitamura
Stability of high-temperature orthopyroxene in $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ system at atmospheric pressure
- P1-8 Naoya Ishida, Mitsuyoshi Kimata, Norimasa Nishida, Tamao Hatta, Masahiro Shimizu
Polymorphic relation between cavansite and pentagonite: Implications for hydronium and hydroxyl ions in cavansite

02. Physical properties of minerals and rocks at high pressure

Conveners and chairs: Denis Andrault (Univ. of Paris), Tomoo Katsura (Okayama Univ.), Osamu Ohtaka* (Osaka Univ.), Donald J. Weidner# (SUNY, Stony Brook)

Oral presentations

Tue. July 25 9:00~12:00 4F 401

9:00~9:40

O2-1 † Jay Bass

Measurements of velocities and elastic properties at high pressures and temperatures

9:40~10:00

O2-2 § Tetsuo Irifune, Yuji Higo, Toru Inoue, Ken-ichi Funakoshi

Ultrasonic velocities of majorite garnet and mineralogy of the mantle transition region

10:00~10:20

O2-3 § Patrick Cordier, Philippe Carrez, Denise Ferre

Predicting dislocation properties using the Peierls-Nabarro model: the example of the perovskite and post-perovskite phases of MgSiO_3

10:20~10:40

O2-4 § Norimasa Nishiyama, Yanbin Wang, Mark L. Rivers, Steve R. Sutton, David Cookson

High P-T rheological studies of hcp-Fe in its stability field

Break

11:00~11:20

O2-5 Mark D. Welch, Wilson A. Crichton

High-pressure behaviour of hydrous sheet silicates

11:20~11:40

O2-6 Nicolas Guignot, Denis Andrault, Guillaume Morard, Nathalie Bolfan-Casanova, Mohamed Mezouar

Post-Perovskite phase elastic properties at D" layer P-T conditions

11:40~12:00

O2-7 Takehiko Yagi, Etsuko Iida, Hisako Hirai, Nobuyoshi Miyajima, Takumi Kikegawa

High-pressure behavior of SiO_2 clathrate

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P2-1 Akira Kuwata, Masanori Matsui, Tomoo Katsura, Kenji Hagiya, Naotaka Tomioka, Mitsuhiro Sugita, Sho Yokoshi, Akifumi Nozawa, Ken-ichi Funakoshi

High-temperature and high-pressure equation of state of $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ ringwoodite by synchrotron X-ray diffraction

P2-2 Hiroshi Fukui, Hiroshi Arima, Hajime Tanida, Yasuo Ohishi, Denis Andrault, Osamu Ohtaka, Akira Yoshiasa

EXAFS measurement for iron under high-pressure conditions

P2-3 Emil Makovicky, Lars A. Olsen, Tonci Balic-Zunic

Structural changes in the lone electron pair compound PbBi_2S_4 (galenobismutite) at the hydrostatic pressures between 0 and 10 GPa

P2-4 Angela Ullrich, Ronald Miletich

High-pressure behaviour of $\text{NaTi}^{3+}\text{Si}_2\text{O}_6$: Comparative compressibilities of low-clinopyroxenes at hydrostatic pressures

P2-5 Daisuke Yamazaki, Takashi Yoshino, Hiroaki Ofuji, Eiji Ito

Two-phase rheology of the mixture of $(\text{Mg,Fe})\text{SiO}_3$ perovskite and magnesio-wüstite: morphology and lattice preferred orientation

- P2-6 Akira Yoneda, Shunsuke Sakai
High Frequency Resonant ultrasound spectroscopy for sub-millimeter specimens of high pressure phases
- P2-7 Hisako Hirai, Shin-ichi Machida, Taro Kawamura, Yoshitaka Yamamoto, Takehiko Yagi
Stability and transition of methane hydrate up to 86 GPa
- P2-8 Masahiro Osako, Akira Yoneda, Eiji Ito
Measurement of thermal properties of mantle minerals under pressure
- P2-9 Olga B. Kotova
Surface physics of micro- and nanominerals under (P, T) - conditions
- P2-10 Gabriel O. Iancu, Yasunori Miura
Shocked quartz and corona texture at Takamatsu buried crater
- P2-11 Takeshi Kitatani, Masayuki Okuno, Toshiyuki Atou, Kiyoto Fukuoka, Masae Kikuchi, Masashi Kawasaki, Tatsuro Araki, Bruno Reynard, Mikio Koyano, Shin-ichi Katayama
Structural change of sanidine crystal by shock compression
- P2-12 Osamu Ohtaka, Denis Andrault, Pierre Bouvier, Emmanuelle Schultz, Mohamed Mezouar
Phase relations and equation of state of ZrO₂ to 1 Mbar
- P2-13 Maki Okube, Akira Yoshiasa, Eiji Ito, Takuya Matsumoto, Yasuko Terada, Hiroshi Arima, Jun-ichi Matsuda, Satoshi Sasaki
Local structure of noble gas in terrestrial planetary materials
- P2-14 Paul Raterron, Jihua Chen, Li Li, Donald Weidner, Julien Durinck, Patrick Cordier
Pressure-induced slip-system transition in olivine: high-pressure rheological measurements, microstructures and flow laws
- P2-15 Anton F Shatskiy, Tomoo Katsura, Eiji Ito
Crystal growth of MgSiO₃ perovskite in 2KHCO₃-Mg(OH)₂ solvent

03. New applications of spectroscopy in mineral sciences

Conveners and chairs: Georges Calas (Univ. of Paris), Catherine McCammon (Univ. of Bayreuth), Satoru Nakashima[#](Osaka Univ.), Keiji Shinoda^{*}(Osaka City Univ.)

Oral presentations

Mon. July 24 15:30~18:30 4F 402

15:30~16:10

- O3-1 † Yasushi Inouye
Near field spectroscopy for nano and bio-materials

16:10~16:30

- O3-2 § Satoru Nakashima
New visible and infrared spectroscopies for water-rock interactions

16:30~16:50

- O3-3 Hiroyuki Kagi, Satoshi Fukura, Tatsuo Nakagawa, Munenori Nakai, Kazumasa Sugiyama
Development of a built-in scanning near field microscope head for an atomic force microscope system and its applications to natural polycrystalline diamonds and Al₂O₃/ZrO₂ eutectic composites

Break

17:10~17:30

- O3-4 § Yasuko Terada
SR-XRF analysis of mineralogical samples using X-ray microbeam

17:30~17:50

- O3-5 Joanna N. Walsh, Michael A. Carpenter, Jurgen Schreuer, Tim W. Darling
Anomalous elastic behaviour of (Ca, Sr)TiO₃ Perovskite

17:50~18:10

- O3-6 § Jonathan F. Stebbins
NMR studies of high-pressure minerals and glasses: pushing the limits of sensitivity

Tue. July 25 14:30~16:30 4F 401

14:30~14:50

- O3-8 § Georges Calas, Etienne Balan, Laurence Galois, Guillaume Morin
Spectroscopic investigation of transition elements in minerals

14:50~15:10

- O3-9 § Jim R.J. Evans, Denis G. Rancourt, Michael Grodzicki
Electronic structure calculations for Mössbauer spectroscopy of disordered materials

15:10~15:30

- O3-10 Yuta Yamanoi, Satoru Nakashima
In situ high temperature visible microspectroscopy under controlled atmosphere for studying color change processes of volcanic materials

15:30~15:50

- O3-11 Jun Abe, Nobuo Hirano, Noriyoshi Tsuchiya
High temperatures and pressures IR spectroscopy of water at solid-water interface

15:50~16:10

- O3-12 Keiji Shinoda, Naoki Noguchi
Induction heating diamond anvil cell (IH-DAC) for Raman microspectroscopy

16:10~16:30

- O3-13 Robert T. Downs
The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P3-1 Ruth E.A. McKnight, Michael A. Carpenter, Juergen Schreuer, Tim W. Darling
Resonant ultrasound spectroscopy of natural polycrystalline samples
- P3-2 Roberta Oberti, Simona Quartieri, Maria Chiara Dalconi, Federico Boscherini, Massimo Boiocchi
XAS and structure refinement allied to understand site preference and local environment of major and trace elements in garnets
- P3-3 Masato Okui, Sei Fukushima, Michiru Yamashita, Aurel Mihai Vlaicu, Maya Yasui, Muneyuki Motoyama
Chemical state of Fe in igneous rocks using high resolution X-ray fluoresce, HRXRF
- P3-4 Atsushi Tani, Kenji Ishikawa, Kei Takeya, Takahiro Otsuka, Satoru Nakashima
ESR study on methane hydrate
- P3-5 Yevgeniya N. Kotova
Radiospectroscopy of vein quartz of the Subpolar Ural deposits
- P3-6 Masahiro Kayama, Tasuku Okumura, Hirotugu Nishido, Kiyotaka Ninagawa
Effect of sample temperature on cathodoluminescence of tridymite and cristobalite
- P3-7 Hirotugu Nishido, Shotaro Nishizawa, Tasuku Okumura, Kiyotaka Ninagawa
Temperature quenching mechanism of cathodoluminescence in Mn-activated calcite
- P3-8 Tasuku Okumura, Hirotugu Nishido, Arnold Gucsik, Kiyotaka Ninagawa
Cathodoluminescence and 3D Raman spectroscopy of shocked quartz from impact craters

- P3-9 Naoki Noguchi, Keiji Shinoda
Direct observation of the quartz-coesite phase transformation by using IH-DAC
- P3-10 Takashi Sawai, Satoru Nakashima
Infrared spectroscopy of aqueous solutions - effects of dissolved ionic species -
- P3-11 Junichi Fukuda, Keiji Shinoda, Naoya Miyoshi, Nobuyuki Aikawa
Water diffusion into synthetic beryl channel at 500-700°C, 50-150MPa

04. Computational study of mineral structures and properties

Conveners and chairs: Masanori Matsui^{*,*}(Univ. of Hyogo), G. David Price (Univ. College London), Lars Stixrude (Univ. of Michigan)

Oral presentations

Thur. July 27 9:00~12:00 5F 503, 504

9:00~9:20

- O4-1 § Taku Tsuchiya, Jun Tsuchiya
Ab initio investigation of post-perovskite phase change

9:20~9:40

- O4-2 Feiwu Zhang, Artem R. Oganov
Aluminum-bearing post-perovskite in the Earth's D" layer

9:40~10:00

- O4-3 § Ronald E. Cohen, Razvan Caracas, Xianwei Sha
Computational study of mineral structures and properties

10:00~10:20

- O4-4 § Lidunka Vocadlo, Stephen Stackhouse, John Brodholt, David Price
Ab initio calculations of the elasticity of deep mantle and core phases

Break

10:40~11:00

- O4-5 Yigang Zhang, Dapeng Zhao, Masanori Matsui, Guangjun Guo
A molecular dynamics study of the equations of state of CaSiO₃ perovskite

11:00~11:20

- O4-6 § Stephen C. Parker, Jeremy Allen, David J. Cooke, Arnaud Marmier, Dino Spagnoli, Sebastien Kerisit
Atomistic simulations of mineral surface structure and stability

11:20~11:40

- O4-7 Paul A. Madden, Sandro Jahn
Atomistic simulation of minerals and melts using advanced interatomic potentials derived from first-principles DFT calculations

11:40~12:00

- O4-8 § Renata M. Wentzcovitch, Koichiro Umemoto
MgSiO₃ at conditions of the giants' cores and exoplanets

Thur. July 27 14:30~16:30 5F 503, 504

14:30~14:50

- O4-9 Hisako Sato, Toshihiro Kogure, Cliff T. Johnston, Kanta Ono, Akihiko Yamagishi
First-principles calculation studies on mechanical properties and pressure-induced phase transformations of kaolin-polytypes

14:50~15:10

- O4-10 Claro I. Sainz-Diaz, Esther Molina-Montes, Davide Donadio, Alfonso Hernandez-Laguna, Michele Parrinello
Dehydroxylation of pyrophyllite by means of ab initio molecular dynamics and metadynamics

15:10~15:30

- O4-11 § Artem R. Oganov, Colin W. Glass
Crystal structure prediction: new methodology and geologically important results

15:30~15:50

- O4-12 § Lars Stixrude, Bijay Karki
Structure and freezing of MgSiO₃ liquid in Earth's interior

15:50~16:10

- O4-13 Georg Amthauer, Michael Grodzicki, Walter Steiner
The electronic and magnetic structure of Fe-bearing silicates

16:10~16:30

- O4-14 Tonci Balic-Zunic
Geometrical analysis of mineral structures under compression using the centroid approach

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P4-1 Masanori Matsui
MD simulated equations of state of sodium chloride and argon
- P4-2 Akira Miyake, Jun Kawano
Molecular dynamics simulations of MgSiO₃ enstatite and seismic discontinuity in the upper mantle
- P4-3 Tadashi Akamatsu, Katsuyuki Kawamura
Molecular dynamics simulation of CH₄-CO₂ mixed hydrates
- P4-4 Koichi Momma, Toshiro Nagase, Yasuhiro Kudoh, Takahiro Kuribayashi
Molecular dynamics simulation of twin boundaries in quartz
- P4-5 Anne-Line Auzende, Roland J.-M. Pellenq, Bertrand Devouard, Alain J. Baronnet, Olivier Grauby
Atomistic calculations of structural and elastic properties of serpentine (lizardite and antigorite) minerals
- P4-6 Taketoshi Taniguchi, Seturo Ito
Deformation and fracture of NaAlSiO₄ glass with regular arrangement of Al and Si ions using molecular dynamics simulation

05. Mineralogy and dynamics of the mantle and core (CPM)

Conveners and chairs: Jay Bass (Univ. of Illinois), Kei Hirose (Tokyo Inst. of Technology), Eiji Ohtani[#],*(Tohoku Univ.), David C. Rubie (Univ. of Bayreuth)

Oral presentations

Tue. July 25 14:30~16:30 3F 301

14:30~14:50

- O5-1 § David P. Dobson, Almar DeRonde, Florian Heidelbach, Li Li, Donald Weidner, Philip J. Meredith
Deep seismicity triggered by the olivine-wadsleyite transformation: Multi-anvil acoustic-emissions results

14:50~15:10

- O5-2 Hiroaki Ohfuji, Yosuke Tachida, Toru Shinmei, Daisuke Yamazaki, Tetsuo Irifune
Lattice preferred orientation of akimotoite synthesized under deviatoric stress

15:10~15:30

- O5-3 Paola Comodi, Fabio Cera, Leonid Dubrovinsky, Sabrina Nazzareni, Patrizia Fumagalli
Raman spectra of 10 Å phase at simultaneously HP-HT

15:30~15:50

- O5-4 Takehiko Hiraga, David L. Kohlstedt
Equilibrium interface segregation in Earth's mantle

15:50~16:10

- O5-5 Cristiano Ferraris, Jean-Pierre Lorand
Nano domains of Ir-bearing rutile within a Cr-rich spinel from a mantle-derived harzburgite
- First evidence and petrological implications

16:10~16:30

- O5-6 Taku Okada, Takamitsu Yamanaka, Yusuke Seto, Daisuke Hamane-Nishio, Takaya Nagai, Kiyoshi Fujino
Phase relations of aegirine at high pressures and temperatures: Na behavior in the compounds bearing ferric iron

Wed. July 26 14:30~18:30 1F Main Hall

14:30~15:00

- O5-7 † Hokwang Mao, Wendy L. Mao
Core-Mantle Interaction - The Formation, Elasticity, Rheology, and Dynamics of Iron-Rich Silicate in Core-Mantle Boundary Layer

15:00~15:20

- O5-8 § Jung-Fu Lin
Magnesiowustite in the Earth's lower mantle

15:20~15:40

- O5-9 § Feiwu Zhang, Artem R. Oganov
Valence and spin states of iron impurities in lower mantle silicates

15:40~16:00

- O5-10 § Jay Bass, Jan Matas
Mineral Elasticity: Implications for the Temperature and Mineralogy of the Lower Mantle

16:00~16:20

- O5-11 Ryosuke Sinmyo, Kei Hirose, Hugh St.C. O'Neill, Eiji Okunishi
Fe³⁺-bearing post-perovskite phase in a subducted MORB crust

16:20~16:40

- O5-12 § Kei Hirose, Kenji Ohta, Nagayoshi Sata, Yasuo Ohishi
Depth and Sharpness of the Post-perovskite Phase Transition

Break

16:50~17:10

- O5-13 Shigehiko Tateno, Kei Hirose, Nagayoshi Sata, Yasuo Ohishi
High solubility of FeO in perovskite and the post-perovskite phase transition in (Mg_{0.5}Fe_{0.5})SiO₃

17:10~17:30

- O5-14 Tadashi Kondo, Yusuke Kobayashi, Eiji Ohtani, Masaaki Miyawaki, Takeshi Sakai, Takumi Kikegawa
Iron partitioning between (Mg, Fe)SiO₃ post-perovskite, perovskite, and magnesiowustite to core-mantle boundary

17:30~17:50

- O5-15 § Yuki Asahara, David C. Rubie, Daniel J. Frost, Falko Langenhorst
The effects of pressure and temperature on the solubility of oxygen in liquid iron and implications for the composition of the Earth's core

17:50~18:10

- O5-16 Oliver D. Tschauner, Paul D. Asimow, Thomas J. Ahrens, Michael J. Willis
Partitioning of elements between liquid metal and liquid silicate under conditions of a giant impact

18:10~18:30

- O5-17 Kyusei Tsuno, Eiji Ohtani, Hidenori Terasaki
Immiscible two-liquid regions in the Fe-O-S melt up to 21 GPa and implications for the planetary cores

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P5-1 Yuta Kawadai, Tadashi Kondo, Eiji Ohtani, Takehiko Yagi
Phase relation in the hydrogen-helium system at high pressure
- P5-2 Nicheng Shi, Wenji Bai, Guowu Li, Qingson Fang
Core mineralogy, concept, crystal chemistry and its example
- P5-3 Takeshi Sakai, Tadashi Kondo, Eiji Ohtani, Hidenori Terasaki, Masaaki Miyahara, Noriaki Endo, Toshiko Kuba, Toshiaki Suzuki, Kikegawa Takumi
Wetting property at the core-mantle boundary and core signature in plume source region
- P5-4 Takaaki Kawazoe, Eiji Ohtani, Hidenori Terasaki, Konstantin Litasov, Asami Sano, Akio Suzuki, Yoshinori Tange, Ken-ichi Funakoshi
In situ X-ray observation of eutectic temperatures and subsolidus phases in Fe-FeS-FeO system at 23-34 GPa
- P5-5 Naohisa Hirao, Tadashi Kondo, Eiji Ohtani, Takumi Kikegawa
Post-hollandite phase in KAlSi_3O_8 as a possible host mineral of potassium in the Earth's lower mantle
- P5-6 Yusuke Seto, Daisuke Hamane, Takaya Nagai, Kiyoshi Fujino
The fate of carbonates with subducted slabs into the lower mantle and a possible formation of diamonds
- P5-7 Hiroshi Kojitani, Masaki Akaogi
Rietveld analysis of Al-containing MgSiO_3 perovskites
- P5-8 Taku Tsuchiya, Jun Tsuchiya
Effect of iron on the stability of lower mantle phases
- P5-9 Rei Shiraishi, Eiji Ohtani, Kyuichi Kanagawa, Akira Shimojyuku, Masaaki Miyahara
Seismic anisotropy of Akimotoite MgSiO_3 and implications for the structure of the subducting slab
- P5-10 Masaaki Miyahara, Takeshi Sakai, Yusuke Kobayashi, Jung Ho Yoo, Tadashi Kondo, Eiji Ohtani
TEM foil preparation technique by Focused Ion Beam (FIB) system

06. Hydrogen, water and volatiles in the deep Earth

Conveners and chairs: Daniel Frost (Univ. of Bayreuth), Toru Inoue^{*,*} (Ehime Univ.),
Tatsuhiko Kawamoto (Kyoto Univ.), Joseph R. Smyth (Univ. of Colorado, Boulder)

Oral presentations

Wed. July 26 9:00~11:50 5F 505

9:00~9:40

- O6-1 † Eiji Ohtani
Effect of water on dynamics in the upper mantle and transition zone

9:40~10:00

- O6-2 Tetsuya Komabayashi
Water circulation in the Earth's mantle

10:00~10:30

O6-3 § Stefano Poli

High pressure behaviour of hydrates and carbonates and the generation of C-O-H fluids in subduction zones: experimental constraints in mafic systems up to 5 GPa

Break

10:50~11:20

O6-4 § Kenji Mibe, Masami Kanzaki, Tatsuhiko Kawamoto, Kyoko N. Matsukage, Yingwei Fei, Shigeaki Ono

Second critical endpoint and properties of aqueous fluid in a hydrous upper mantle

11:20~11:50

O6-5 § Andreas Audetat, Hans Keppler

Physical and chemical properties of subduction zone fluids - direct insights by experiments in the hydrothermal diamond anvil cell

Thur. July 27 14:30~16:30 3F 301

14:30~14:50

O6-6 Joseph R. Smyth, Christopher M. Holl, Daniel J. Frost, Hans Keppler, Fabrizio Nestola, Katrin Mierdel

Hydration of nominally anhydrous minerals: Melt generation, physical properties, and dynamics of the upper mantle

14:50~15:10

O6-7 Jannick Ingrin, Andreas Kurka, Marc Blanchard, Juliette Forneris, Henrik Skogby

Hydrogen diffusion in garnet: a summary

15:10~15:30

O6-8 Konstantin D. Litasov, Eiji Ohtani, Hiroyuki Kagi, Sujoy Ghosh

Water partitioning between olivine and wadsleyite near 410-km seismic discontinuity

15:30~15:50

O6-9 Toru Inoue, Masanori Katsuta, Tomoyuki Wada, Rumi Sasaki, Tetsuo Irifune, Hisayoshi Yurimoto

Partitioning of H₂O in the mantle

15:50~16:10

O6-10 Jun Tsuchiya, Taku Tsuchiya

First principles studies of hydrous wadsleyite under high pressure

16:10~16:30

O6-11 Xianyu Xue, Masami Kanzaki, Hiroshi Fukui, Eiji Ito, Takafumi Hashimoto

Cation order and hydrogen bonding of delta-AIOOH, phase egg and aluminous stishovite: An NMR and Raman study

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P6-1 Yusuke Yachi

Water activities of aqueous fluid phases at upper mantle conditions

P6-2 § Tatsuhiko Kawamoto, Yoshitaka Kumagai

Raman spectroscopy of LiCl solution: Implications for chemical and physical features of aqueous fluids in the mantle wedge beneath the volcanic arcs

P6-3 Asami Sano, Eiji Ohtani, Tadashi Kondo, Naohisa Hirao, Takumi Kikegawa, Naoyoshi Sata, Yasuo Ohishi

High-pressure stability field of aluminous hydroxide delta-AIOOH

P6-4 Pierfrancesco Zanazzi, Paola Comodi, Sabrina Nazzareni, Nicola Rotiroti

Behavior of 10Å phase at low temperature

- P6-5 Masami Kanzaki, Xianyu Xue, Hiroshi Fukui, Eiji Ito
High-pressure form of topaz-OH: Structure and characterization by NMR and Raman
- P6-6 Henrik Skogby, Roland Stalder
Dehydration reactions in orthopyroxene
- P6-7 Takashi Yoshino, Takuya Matsuzaki, Shigeru Yamashita, Tomoo Katsura
Electrical conductivity of single crystal hydrous olivine
- P6-8 Yu Nishihara, Toru Shinmei, Shun-ichiro Karato
Effect of chemical environments on hydrogen related defects in wadsleyite

07. Kimberlites, diamonds, and mineral inclusions from the mantle

Conveners: Minoru Akaishi (National Inst. for Materials Sci.), Makoto Arima^{*,*} (Yokohama National Univ.), Ben Harte (Univ. of Edinburgh), Nikolai V. Sobolev (Russian Academy of Sci., Novosibirsk)

Chairs: Tim Ivanic (Univ. of Edinburgh), Anna V. Spivak (IEM RAS), Satoshi Fukura (Univ. of Tokyo)

Oral presentations

Wed. July 26 14:30~18:30 5F 505

14:30~15:00

- O7-1 † Daniel J. Schulze, Ben Harte, John W. Valley, Dominic M. DeR. Channer
Diamonds with multiple growth stages and variable fluid sources from the Quebrada Grande region of Guaniamo, Venezuela

15:00~15:20

- O7-2 § Nikolai V. Sobolev, Alla M. Logvinova, Dmitry A. Zedgenizov, Dmitry V. Kuzmin, Alexander V. Sobolev
Olivine inclusions in Siberian diamonds: high precision approach to trace elements

15:20~15:40

- O7-3 Tim J. Ivanic, Ben Harte, John J. Gurney
Multiple events affecting highly chromian, garnet-rich peridotite xenoliths from South African kimberlites

15:40~16:00

- O7-4 § Alla M. Logvinova, Richard Wirth, Nikolai V. Sobolev
Nanometre-sized mineral and fluid inclusions in cloudy Siberian diamonds: new insights on diamond formation

16:00~16:20

- O7-5 § Makoto Arima, Yusuke Kozai
Growth and resorption of diamond by redox reactions in kimberlitic and carbonatitic melts

16:20~16:40

- O7-6 Anastasia V. Shushkanova, Yuriy A. Litvin
Peculiarities of diamond formation in the mantle carbonate-silicate-sulphide melts by experimental evidence

Break

16:50~17:10

- O7-7 Anna V. Spivak, Andrey A. Shiryaev, Yuriy A. Litvin
Growth of diamond in multicomponent carbonate-carbon melts: formation of the mixed C- and A-defects

17:10~17:30

- O7-8 Satoshi Fukura, Hiroyuki Kagi, Tatsuo Nakagawa
Photoluminescence, Raman, and infrared studies of carbonado

17:30~17:50

- O7-9 § Yoshihide Ogasawara
Microdiamonds formation during intraslab UHP metasomatism: An example from the Kokchetav Massif

17:50~18:10

- O7-10 Vadim N. Reutskiy, Ben Harte, EIME, Yuri M. Borzdov, Yuri N. Palyanov
Carbon and nitrogen effects during HTHP diamond crystallization

18:10~18:30

- O7-11 § Ben Harte, Cayzer Nicola
An EBSD study of majoritic garnet inclusions in diamonds

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P7-1 Minoru Kikuchi, Yoshihide Ogasawara
Occurrence and characterization of UHPM microdiamonds from the Kokchetav Massif
- P7-2 Sujoy Ghosh, Eiji Ohtani, Konstantin D. Litasov, Akio Suzuki, Hidenori Terasaki
Solidus of carbonated peridotite to 20 GPa
- P7-3 Rentaro Shimizu, Yoshihide Ogasawara
Characterization of microdiamonds in 'K-tourmaline'-rich UHP rock by Raman spectroscopy
- P7-4 Galina P. Kudryavtseva, Tatiana V. Posukhova, Olga V. Polazchenko
Diamonds from the V. Grib pipe: internal structure and origin

08. Crystal structure, topology and crystal chemistry (CCM)

Conveners and chairs: Robert T. Downs (Univ. of Arizona), Yasuhiro Kudoh^{*,*}(Tohoku Univ.), Massimo Nespolo (Univ. of Henri Poincare Nancy 1), Satoshi Sasaki (Tokyo Inst. of Technology)

Oral presentations

Tue. July 25 9:00~11:55 1F Main Hall

9:00~9:40

- O8-1 † Charles T. Prewitt
Radii of transition-metal ions at high pressures and temperatures

9:40~9:55

- O8-2 Takamitsu Yamanaka, Tetsuro Mine, Sachiko Asogawa, Taku Okada, Yuki Nakamoto
Structure change of $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ spinel solid solution under high pressures

9:55~10:10

- O8-3 Volker Kahlenberg, Biljana Lazic, Juergen Konzett, Kaindl Reinhard
Structural chemistry of high pressure polymorphs of CaAl_2O_4

10:10~10:25

- O8-4 Yasuhiro Kudoh, Takahiro Kuribayashi, Toru Inoue
Crystal structure of hydrous forsterite with 0.38 wt% H_2O

Break

10:45~11:25

- O8-5 † Hiroyuki Horiuchi
Isomorphism: The implications of understanding structural changes at extreme physical conditions

11:25~11:40

- O8-6 Marcus J. Origlieri, Robert T. Downs, Michael D. Carducci, Kevin M. Rosso, G. V. Gibbs
Crystal structure and bonding in the new mineral AsSbO₃

11:40~11:55

- O8-7 Stuart J. Mills, Uwe Kolitsch, William D. Birch
Crystal-chemical behaviour of Ge and Ga in Pb-Fe members of the alunite supergroup

Tue. July 25 14:30~16:30 1F Main Hall

14:30~15:10

- O8-8 † Michael O'Keeffe
Periodic nets and crystal structures

15:10~15:25

- O8-9 Herta Effenberger
Crystal structure topology controlled by hydrogen bonds

15:25~15:40

- O8-10 Takahiro Kuribayashi, Hiroyuki Kagi, Masahiko Tanaka, Yasuhiro Kudoh
High-pressure Single-crystal X-ray diffraction studies using synchrotron radiation and FT-IR observations on norbergite

Break

16:00~16:15

- O8-11 Marcello Mellini, Mihovil Logar, Enrico Mugnaioli, Cecilia Viti
Intrasector radial stacking faults in polygonal serpentine

16:15~16:30

- O8-12 Chiaki Uyeda, Takaaki Abe, Ryoichi Takashima
Magnetic oscillation of ordinary diamagnetic minerals due to weak field of horseshoe magnet originating from bond directions in crystal

Wed. July 26 9:00~12:00 1F Main Hall

9:00~9:40

- O8-13 † Stefano Merlino, Elena Bonaccorsi
Double wollastonite chains: topological/conformational varieties and polytypic forms

9:40~9:55

- O8-14 Masaaki Ohmasa, Kenji Hagiya, Katsuhiro Kusaka
On the structure of the low temperature phase of the incommensurate Ca₂CoSi₂O₇

9:55~10:10

- O8-15 Elena Sokolova, Frank C. Hawthorne
Short-range order, non-linear chemical variation and phase transitions in scapolites

10:10~10:25

- O8-16 Masahide Akasaka, Mariko Nagashima, Kuniaki Makino, Kosuke Onuma
Distribution of Fe³⁺ and Ti⁴⁺ in CaFe_{0.8}Ti_{0.2}Al_{1.2}Si_{0.8}O₆-pyroxene: X-ray and TOF neutron Rietveld study

Break

10:45~11:00

- O8-17 Susan Schorr, Hans-Joachim Hoebler, Michael Tovar
The stannite-kesterite join studied by neutron diffraction

11:00~11:15

- O8-18 Darrell J. Henry
Tourmaline-fluid interactions: Fluorine monitor and the role of tourmaline crystallography

11:15~11:30

- O8-19 John M. Hughes, Bradley L. Jolliff, Mickey E. Gunter
The atomic arrangement of lunar merrillite

11:30~11:45

- O8-20 Maria Sokolov, Robert F. Martin
Plumbian microcline and the Pb-dominant analog of celsian included in amazonitic K-feldspar, Mount Ploskaya, Kola Peninsula, Russia

11:45~12:00

- O8-21 Patrick H.J. Mercier, Yvon Le Page, Pamela S. Whitfield, Lyndon D. Mitchell, Thomas Baikie, Jean Y. Kim, Timothy J. White
Major precision and accuracy benefits from direct least-squares extraction of crystal-chemical parameters in $P6_3/m$ eco-apatites

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P8-1 Massimo Nespolo, Giovanni Ferraris
High-index twins in minerals
- P8-2 Masatomo Yashima, Mohd. Roushown Ali
Crystal structure, space group, phase transition and octahedral tilting of the calcium titanate perovskite
- P8-3 Guowu Li, Nicheng Shi, Ming Xiong, Zhesheng Ma
Incommensurate modulated crystal structure of Ankangite
- P8-4 Satoshi Sasaki, Shin Ishikawa, Koichi Ohkubo, Maki Okube, Makoto Sakata, Eiji Nishibori
Single-crystal maximum-entropy study on the electron-density distribution of orthoenstatite
- P8-5 Makio Ohkawa, Thomas Armbruster, Eugeny V. Galuskin
Symmetry variations of vesuvianite formed by retrograde metamorphism of gehlenite in high-temperature skarn at Kushiro, Tojyo, Hiroshima, Japan
- P8-6 Fumito Nishi, Ritsuro Miyawaki, Takahiro Kuribayashi, Yasuhiro Kudoh
Some kinds of superstructures of (Ge, Si) wollastonite
- P8-7 Naoyuki Kawame, Daijo Ikuta, Kanazawa Hideki, Kazuhiko Ito, Mickey E. Gunter, Osamu Tamada
New monoclinic superstructure of mordenite with $2a \times 2b \times c$ cell
- P8-8 Atsushi Kyono
Guanacoite, $Mg_2(Mg,Cu)_3(OH)_4(H_2O)_4(AsO_4)_2$, low-temperature crystal structure and revised chemical formula
- P8-9 Galina N. Lysiuk, V. Rogov
Structure and composition of Baltic Sea manganese nodules
- P8-10 Kuniaki Makino, Daisuke Dogomi, Kentaro Fujiwara
Hydrogen deficiency in volcanic and plutonic biotite
- P8-11 Kiyonori Michiba, Kyoko Shirai, Takeshi Tahara, Akiko Hokura, Izumi Nakai, Ritsuro Miyawaki, Satoshi Matsubara
Hydrothermal synthesis and crystal structure analysis of $RE(CO_3)OH$ with the hydroxyl-bastnasite-type structure
- P8-12 Andrew C. McCarthy, Robert T. Downs, Ren Lu, Hexiong Yang
Reexamination of yedlinite, $Pb_6(Cl,OH)_6Cr^{3+}(OH,O)_8$, using single-crystal X-ray diffraction and Raman spectroscopy, and redetermination of the chemical formula
- P8-13 John F. Rakovan, Yun Luo, Evert Elzinga, Yuanming Pan, Marian Lupulescu, John M. Hughes
Site distribution and structural state of Th in fluoroapatite determined by single crystal XRD and EXAFS

- P8-14 Giovanni Battista Andreozzi, Paolo Ballirano, Antonio Gianfagna, Simona Mazziotti Tagliani, Biagio Maria Bruni
Crystal chemistry of the new asbestiform fluoro-edenite amphiboles of volcanic origin from Biancavilla (Sicily, Italy)
- P8-15 Klaus Bente, Ronny Kaden, Gerald Wagner
Architecture and physical properties of Cylindrite $\text{Fe}_{1\pm m}\text{Sn}_{4\pm x}\text{Pb}_{3\pm y}\text{Sb}_{2\pm z}\text{S}_{14}$
- P8-16 Atsuyuki Ohta, Hiroshi Tsuno, Hiroyuki Kagi, Masaharu Nomura
XAFS characterization of REE adsorbed on ferrihydrite and manganese dioxides
- P8-17 Seiichiro Uehara, Fred J. Wicks
Detailed Structure and Microchemistry of 15-sectored Polygonal Serpentine
- P8-18 Akihito Uchida, Takamitsu Yamanaka, Eiji Ito
Single-crystal X-ray diffraction study of high-pressure and high-temperature phase of MgFe_2O_4 - post-spinel phase structure -
- P8-19 Hiroaki Sugita, Takamitsu Yamanaka, Eiji Ito
Study of the site symmetry change of high-pressure phase of ZnFe_2O_4 by single-crystal structure analysis
- P8-20 Nenad Tomasic, Andreja Gajovic, Vladimir Bermanec, Masa Rajic Linaric, Dangsheng Su, Theodoros Ntafos, Gunnar Raade
Relics of samarskite structure in a metamict ABO_4 mineral and its high-temperature transformations
- P8-21 Daijo Ikuta, Naoyuki Kawame, Shohei Banno, Takao Hirajima, Kazuhiko Ito, John F. Rakovan, Robert T. Downs, Osamu Tamada
First in situ X-ray identification of coesite and retrogressed quartz on a glass thin section of ultrahigh-pressure metamorphic rock and their crystal structure details
- P8-22 Hiroki Mashima, Junji Akai
Reexamination of rengerite and strontio-orthojoaquinite from Ohmi-Itoigawa region, central Japan by TEM
- P8-23 T.M. Khobaer, Kazuki Komatsu, Takahiro Kuribayashi, Yasuhiro Kudoh
In situ high temperature single crystal X-ray diffraction study of natural heulandite at 150°C
- P8-24 Hikaru Hirata, Akihiro Ida, Hiroki Okudera, Tomoaki Morishita, Kuniaki Kihara
Anharmonic thermal vibrations and disorder of atoms in tourmaline
- P8-25 Thomas A. Laetsch, Robert T. Downs
Software for identification and refinement of cell parameters from powder diffraction data of minerals using the RRUFF project and American mineralogist crystal structure databases
- P8-26 Tamas G. Weiszbarg, Erzsebet Toth, Dana Pop
Continuous crystal chemical space in the dioctahedral iron-rich micas and related phases (celadonite, glauconite, Fe-illite)
- P8-27 Erzsebet Toth, Dana Pop, Tamas G. Weiszbarg
Graphical representations systems for TOT layer silicates: A case study for iron-rich dioctahedral phases (celadonite, glauconite)

09. Structure and physical properties of melts and glasses (CPM)

Conveners and chairs: Grant S. Henderson (Univ. of Toronto), Masami Kanzaki^{*,*}(Okayama Univ.), Daniel R. Neuville (Univ. of Paris), Xianyu Xue (Okayama Univ.)

Oral presentations

Wed. July 26 9:00~12:00 4F 402

9:00~9:30

O9-1 § Xianyu Xue, Masami Kanzaki

Dissolution mechanisms of water in depolymerized aluminosilicate melts (glasses): a comprehensive one- and two-dimensional ^1H , ^{29}Si and ^{27}Al NMR study

9:30~10:00

O9-2 § Laurent Cormier, Daniel R. Neuville, Dominique Massiot

Structural environment and aluminum coordination in calcium and magnesium aluminosilicate glasses

10:00~10:20

O9-3 Sarah J. Gaudio, Sabyasachi Sen, Ping Yu, Charles E. Lesher

Densification of vitreous MgSiO_3 and formation of high-coordinated silicon

Break

10:30~10:50

O9-4 Sung Keun Lee, Bjorn O. Mysen, George D. Cody, Yingwei Fei, Ho-Kwang Mao, Peter Eng

Structural Origins of Transport Properties of Silicate Melts at High-Pressure: Solid-State NMR and Synchrotron X-ray Study

10:50~11:10

O9-5 Jonathan F. Stebbins, Lin-Shu Du

Oxygen sites and germanium coordination in alkali germanate glasses: oxygen-17 triple-quantum MAS NMR

11:10~11:30

O9-6 Makoto Urushihara, Tokuro Nanba, Shinichi Sakida, Yoshinari Miura

Ab Initio Calculation of ^{17}O NMR Parameter of Oxygen Sites in Borosilicate Glasses

11:30~12:00

O9-7 § Koji Saito

Industrial application of multi nuclear solid state NMR (^{17}O , ^{25}Mg , ^{27}Al , ^{43}Ca) to glassy slags at high field (16.4T) and super high field (21.8T)

Wed. July 26 14:30~18:40 4F 402

14:30~15:10

O9-8 † Bjorn O. Mysen

Structure and properties of hydrous silicate melts

15:10~15:30

O9-9 Tetsuji Yano, Nobusuke Kabashima, Shuichi Shibata

Local structure of sulfate ions in Na_2O - CaO - SiO_2 glasses and melts: High-temperature raman spectra

15:30~15:50

O9-10 Wim J. Malfait, Valentina P. Zakaznova-Herzog, Werner E. Halter

New experimental approach to determine Raman scattering profiles for Q^n species in silicate glasses and melts: Preliminary results

15:50~16:10

O9-11 Valentina P. Zakaznova-Herzog, Florian Herzog, Wim J. Malfait, Werner E. Halter

Quantitative raman spectroscopy: Mathematical procedure for the treatment of spectral data in silicate glasses and melts

16:10~16:30

- O9-12 Grant S. Henderson, Delphine Cabaret
O K-edge XANES: An indirect probe of cation coordination?

Break**16:50~17:10**

- O9-13 Sandro Jahn
Atomic structure and transport coefficients of Mg-Al-Si-O melts at high pressures and temperatures: A molecular dynamics simulation study

17:10~17:40

- O9-14 § Daniel R. Neuville
Structure and mixing properties in soda and alkaline-earth silicate melts

17:40~18:00

- O9-15 Eozen Strukelj, Daniel R. Neuville
Viscosity and mixing in the system $M_2O-Al_2O_3-SiO_2$ with M= Li, K, Na

18:00~18:20

- O9-16 Taishi Matsushita, Seshadri Seetharaman
Physical properties of molten slags and fluxes in steelmaking process

18:20~18:40

- O9-17 Tatsuya Sakamaki, Eiji Ohtani, Akio Suzuki, Satoru Urakawa, Yoshinori Katayama
Density measurement for MORB melts by X-ray absorption method

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P9-1 Toru Sugawara
Calorimetric enthalpy of multicomponent silicate melts
- P9-2 Marcel Potuzak, Alex R. L. Nichols, Donald B. Dingwell, David A. Clague
The behavior of basaltic glasses during DSC experiments across the glass transition: Evidence for hyperquenching
- P9-3 Hidemi Ishibashi, Hiroaki Sato
Viscosity measurement of subliquidus magmas : Alkali olivine basalt from the Higashi-Matsuura district, SW Japan
- P9-4 Francesco Vetere, Harald Behrens, Francois Holtz, Juergen Koepke, Hiroaki Sato
Viscosity of andesite melts - implication for magma mixing prior to Unzen 1991-1995 eruption
- P9-5 Keisuke Nishida, Hidenori Terasaki, Eiji Ohtani, Akio Suzuki
The effect of sulphur content on the liquid Fe-S density at high pressure
- P9-6 Akane Inoue, Masayuki Okuno, Hiroki Okudera, Toshiyuki Atou, Kiyoto Fukuoka, Masae Kikuchi, Masashi Kawasaki, Mikio Koyano, Shin-ichi Katayama
Vitorification of opal by shock compression
- P9-7 Charles E. Lesher, Sarah J. Gaudio, Yanbin Wang, Norimasa Nishiyama, Mark Rivers, Jean A. Tangeman
P-V-T equation of state of refractory silicate glasses and melts by X-ray microtomography and absorption
- P9-8 Keiji Shimoda, Yasuhiko Tobu, Takahiro Nemoto, Koji Saito
Structural investigation on Mg local environments by high field ^{25}Mg MQMAS NMR spectroscopy
- P9-9 Akihiro Yamada, Toru Inoue, Satoru Urakawa, Nobumasa Funamori, Ken-ichi Funakoshi, Takumi Kikegawa, Tetsuo Irifune
In situ X-ray experiment on the structure of melt in the system $MgO-SiO_2-H_2O$ under high-pressure and temperature

10. Mechanisms and kinetics of phase transformations

Conveners and chairs: Michael A. Carpenter[#](Univ. of Cambridge), Kiyoshi Fujino^{*}(Hokkaido Univ.), Tomoaki Kubo (Kyushu Univ.)

Oral presentations

Thur. July 27 9:00~12:00 5F 505

9:00~9:30

O10-1 † Takamitsu Yamanaka

Pressure-induced sequential transformations of oxides and silicates with electron-lattice interactions

9:30~9:50

O10-2 § Christopher J. Howard

Symmetry considerations in structural phase transitions

9:50~10:10

O10-3 Kiyoshi Fujino, Hiroyuki Izumi, Daisuke Hamane, Yusuke Seto, Takaya Nagai

High pressure phase transformations of CaSiO_3 , FeSiO_3 and MnSiO_3 in relation to the perovskite structure

10:10~10:30

O10-4 Kuniaki Kihara, Takeshi Nakagawa, Tadayuki Hirose

Disorder and structural transitions in melanophlogite and tridymite

Break

10:40~11:00

O10-5 § Tomoaki Kubo, Takumi Kato, Makoto Kimura, Masayuki Nishi, Aiko Tominaga, Takumi Kikegawa

An in-situ X-ray diffraction study on kinetics of plagioclase breakdown at high pressure

11:00~11:20

O10-6 Jun-ichi Ando, Naotaka Tomioka, Kazunari Matsubara, Toru Inoue, Tetsuo Irifune

Mechanism of the olivine-ringwoodite transformation in the presence of aqueous fluid

11:20~11:40

O10-7 Simon A.T. Redfern

Mechanical properties of minerals: the role of transformation microstructures

11:40~12:00

O10-8 Corentin Le Guillou, Fabrice Brunet, Jean N. Rouzaud, Tetsuo Irifune, Hiroaki Ohfuji

New experimental constraints on nanodiamond formation mechanisms from carbon nanoparticles at high pressure

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P10-1 Simona Quartieri, Cinzia Medici, Giovanna Vezzalini, Maria Cristina Betti, Ettore Fois, Gloria Tabacchi

Gismondine under HP: deformation mechanism and re-organization of the extra-framework species

P10-2 Francesco Princivalle, Fedora Martignago, Alberto Dal Negro

Kinetics of cation distribution in synthetic $\text{Mg}(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$ spinels

P10-3 Akira Shimojuku, Tomoaki Kubo, Eiji Ohtani, Tomoki Nakamura, Ryuji Okazaki

Silicon diffusivity in ringwoodite at the transition zone conditions

P10-4 Yuki Nakamoto, Takahiro Yabuuchi, Katsuya Shimizu, Takumi Kikegawa

Structure transitions of calcium metal under high pressure

- P10-5 Young-Boo Lee, Youn-Joung Kim, Jung-Hoo Lee, Hyang-Ran Mun
Convergent beam electron diffraction study on Si-Al ordering of albite by energy filtered transmission electron microscopy
- P10-6 Yasunori Miura
Spinodal crystallization from impact glasses of labradorite feldspars

11. Application of novel techniques for "*in-situ*" observation of crystal growth and nucleation (CMGIP)

Conveners: Andreas Luttge (Rice Univ.), Katsuo Tsukamoto#*(Tohoku Univ.)
Chairs: Katsuo Tsukamoto (Tohoku Univ.), Andreas Luttge (Rice Univ.), Toshiya Abe (Yamaguchi Univ.)

Oral presentations

Fri. July 28 9:00~12:00 5F 503, 504

9:00~9:40

- O11-1 † Alexander A. Chernov, James J. DeYoreo, Christine A. Orme, Leonid N. Rashkovich
Revisiting basic concepts of crystal growth to meet in situ AFM data - Gibbs-Thomson law, BCF theory, stoichiometry

9:40~9:55

- O11-2 Hitoshi Shindo, Tamon Kose, Musun Kwak
Stabilities of crystal faces of calcite and aragonite compared by atomic force microscopic observation of dissolution processes in aqueous acetic acid

9:55~10:10

- O11-3 Andreas Luttge, Rolf S. Arvidson
Vertical scanning interferometry - A review of applications and future possibilities

10:10~10:25

- O11-4 Izumi Yoshizaki, Seijiro Fukuyama, Haruhiko Koizumi, Masaru Tachibana, Kenichi Kojima, Long Rong, Satoshi Adachi, Shinichi Yoda
Impurity induced defect and its effect on protein crystal perfection

Break

10:45~11:10

- O11-5 † Kazuhiko Kuribayashi, Kosuke Nagashio
Metastable phase formation from undercooled melt in containerless processing

11:10~11:25

- O11-6 Yuko Inatomi
Microscopic visualization of solid/liquid interface in crystal growth at high temperature under reduced convection condition

11:25~11:40

- O11-7 Masahito Watanabe, Akitoshi Mizuno, Kensuke Higuchi, Kousuke Nagashio, Kazuhiko Kuribayashi, Yoshinori Katayama, Shinji Kohara
In-situ observation of structure and properties of undercooled melts by using high energy x-ray diffraction combined with containerless levitation technique

11:40~12:00

- O11-8 § Lukas P. Baumgartner, Thomas Mueller, Benita Putlitz, Martin Robyr, Susanne Skora, Anke Wohlers
The use of computed X-ray micro-tomography in deciphering growth kinetics

14:30~14:55

- O11-9 † Gen Sazaki, Masashi Okada, Guoliang Dai, Alexander Van Driessche, Fermin Otarora, Takuro Matsui, Katsuo Tsukamoto, Kazuo Nakajima
Molecular level in-situ observations of elementary growth processes of protein crystals by advanced optical microscopy

14:55~15:15

- O11-10 § Patricia Acero, Jordi Cama, M. Pilar Asta, Andreas Luttge
Surface mechanisms that control the dissolution and oxidation of sulphides

15:15~15:30

- O11-11 Hisao Satoh, Yoshihiro Nishimura, Katsuo Tsukamoto, Akira Ueda, Shinzo Ueta
Phase shift interferometry on macro-particles of smectite in alkaline solutions

15:30~15:50

- O11-12 § Yoshinori Furukawa, Salvador Zepeda, Hiroyuki Nakaya, Yukihiro Uda, Etsuro Yokoyama
Self-oscillatory growth of ice crystals in antifreeze glycoprotein solutions

15:50~16:05

- O11-13 Mu Wang, Guobin Ma, Jianmin Zhu, Nai-Ben Ming
In-situ high resolution transmission electron microscopy study of aggregation and coalescence of TiO₂ nanocrystals

16:05~16:20

- O11-14 Gareth G. E. Seward, Steve Celotto, David J. Prior, John Wheeler, Robert C. Pond
Phase transformation in titanium observed in-situ using electron backscatter diffraction

16:20~16:35

- O11-15 Katsuo Tsukamoto, Ken Nagashima, Hidekazu Kobatake, Jun Nozawa, Hisao Satoh
Crystallization of cosmic materials in space

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P11-1 Ryuichi Komatsu, Etsuro Asakura
Characterization of alite crystal growth from high temperature solution by using in-situ observation
- P11-2 Koji Maiwa, Hiroaki Nakamura, Hideo Kimura, Akimitsu Miyazaki
In situ observation of crystal growth and dissolution in peritectic system
- P11-3 Masayuki Kawasaki, Kazuo Onuma, Ichiro Sunagawa
Growth mechanism of synthetic quartz crystals
- P11-4 Shinzo Ueta, Akira Ueda, Katsuo Tsukamoto, Norikazu Yamada
Application of nano-scale mineralogical investigation to radioactive waste repository design
- P11-5 Akiko Ozawa, Akira Ueda, Yoshihiro Nishimura, Hisao Satoh, Katsuo Tsukamoto
Geochemical monitoring of calcite precipitation and dissolution in Ca rich ground waters with a newly developed interferometer
- P11-6 Mihoko Maruyama, Katsuo Tsukamoto, Nishimura Yoshihiro, Sazaki Gen
Calcite step velocity in the presence of chiral amino acid
- P11-7 Wataru Erikawa, Makoto Yonezawa, Yoshihiro Nishimura
Development of laser confocal phase-shift interference microscopy for in situ observation
- P11-8 Yoshihiro Nishimura, Hisao Satoh, Katsuo Tsukamoto, Akira Ueda, Shinzo Ueta, Koich Kato
Application of phase-shift interference microscopy to the measurement of faint dissolution rate
- P11-9 Wei Qing Jin
Mass transport in a laminar boundary of oxide crystal growth

- P11-10 Takehiko Ishikawa, Paul-Francois Paradis
Thermophysical property measurements of molten high temperature materials using an electrostatic levitator
- P11-11 Karl Thomas Fehr, Michael Huber
Growth and kinetics of Al-tobermorite under hydrothermal conditions: An *In-situ* neutron diffraction study

12. Texture formation and crystal growth in geosciences (CMGIP)

Conveners: Michihiko Nakamura (Tohoku Univ.), Tadao Nishiyama* (Kumamoto Univ.),
Andrew Putnis[#] (Univ. of Münster)

Chairs: Andrew Putnis (Univ. of Münster), Michihiko Nakamura (Tohoku Univ.),
Tadao Nishiyama (Kumamoto Univ.), Takao Hirajima (Kyoto Univ.)

Oral presentations

Thur. July 27 9:00~12:00 4F 401

9:00~9:35

- O12-1 † Viatcheslav S. Solomatov
Grain size and mantle dynamics

9:35~9:55

- O12-2 Tomohiro Ohuchi, Michihiko Nakamura
Grain growth kinetics in the system forsterite-diopside-water

9:55~10:20

- O12-3 § John Wheeler, J. M. Ford
Local stresses and texture evolution during metamorphism

Break

10:40~11:05

- O12-4 § Rainer Abart, Lukas Kelller, Ralf Milke
Transport and rheological controls on metamorphic crystallization

11:05~11:25

- O12-5 Julia E. Hammer
Lattice preferred orientations of co-crystallizing igneous pyroxene and titanomagnetite at high degrees of undercooling

11:25~12:00

- O12-6 † Ian Parsons, Martin R. Lee, Michael Shelley
Intra-crystal textural and chemical reorganization during dissolution-reprecipitation reactions in alkali feldspars

Thur. July 27 14:30~16:30 4F 401

14:30~14:50

- O12-7 Barb Dutrow
Consequences of thermal input on metamorphic textures in contact and regional-contact metamorphic terranes

14:50~15:10

- O12-8 Kazuhiro Miyazaki
Metamorphic mineral growth and pattern transition from random distribution to cluster

15:10~15:40

- O12-9 § Christine V. Putnis
Texture development in coupled dissolution-reprecipitation reactions

15:40~16:10

- O12-10 Daniel W. Schmid, Yuri Yu Podladchikov
Computational modeling of mineral unmixing and growth

16:10~16:30

- O12-11 Elsa Pupier, Stephanie Duchene, Mikeal J. Toplis
An experimental study of plagioclase crystal size distribution during cooling of basalts

Fri. July 28 14:30~16:30 4F 401

14:30~14:50

- O12-12 Tadao Nishiyama, Kazuhiro Miyazaki, Kazuhiko Ito, Hiroki Sato, Hideki Kanazawa, Osamu Tamada
Oscillatory zoning in a synthetic Fe-Mg olivine single crystal

14:50~15:10

- O12-13 Jeanne Paquette, Michelle Deakin, Azin Zangooi, Kristy Thornto, Don Baker
Comparing growth microtopography and sector zoning in natural hydrothermal and synthetic magmatic clinopyroxenes

15:10~15:30

- O12-14 Ichiro Sunagawa
Morphogenesis of quartz crystals twinned after Japan Law

15:30~15:50

- O12-15 Ivan K. Bonev, Radostina Atanassova
Crystallography and origin of colloform pyrite

15:50~16:10

- O12-16 Nikolay P. Yushkin
New radial dendritic oolites: Constitution and crystallization evolution

16:10~16:30

- O12-17 Gioacchino Tempesta, Eugenio Scandale, Nicola Melone
Striations and hollow channels in rounded beryl crystals by X-Ray diffraction topography

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P12-1 Takashi Hoshide, Masaaki Obata, Takashi Akatsuka
Magmatic differentiation processes in the Murotomisaki gabbroic complex: Segregation of plagioclase-rich crystal mush from the crystallization boundary layer
- P12-2 Hiroaki Sato, Francois Holtz, Roman Botcharnikov, Harald Behrens, Setsuya Nakada
Crystallization behavior of hydrous groundmass composition of the 1991-1995 dacite of Unzen volcano at 100 MPa
- P12-3 Takashi Yuguchi, Tadao Nishiyama
Cooling process of a granitic body deduced from the reaction textures during two sub-solidus stages: An example from the Okueyama granitic body, Kyushu, Japan
- P12-4 Masao Kitamura, Masatoshi Nonogaki
Chemical zoning formed by crystal growth of a solid solution controlled by the interface kinetics
- P12-5 Toshiya Abe
Growth patterns on Ilmenite crystals in pyroclastic deposits
- P12-6 Michihiko Nakamura, Tomohiro Ohuchi
Cation exchange between fluid and olivine in dunite controlled by grain boundary migration: Implications for mantle metasomatism
- P12-7 Mutsuko Inui
The effect of limited material transport in the matrix of the metamorphic rocks on the chemical composition trend of garnet

- P12-8 Takao Hirajima, Yoshikuni Hiroi, Martin Svojtka, Kyuichi Kanagawa
Andalusite formation after kyanite and sillimanite in sheared HP Gföhl Granulites of southern bohemia massif, Czech Republic: Typical example of strain-assisted polymorphic reactions?
- P12-9 Hiroshi Isobe, Kimitoshi Tanaka
Sulfide recrystallization experiments from hydrothermal solution circulating by thermal convection
- P12-10 Gilla Simon, Ralph-Uwe Barz, Tatyana B. Bekker
Characterization of defects in hydrothermally grown and natural beryl single crystals: A comparison
- P12-11 Satoshi Nakano
Ripple textures in volcanic alkali feldspars
- P12-12 Ewa Krzeminska, Ian S. Williams, Janina B. Wiszniewska
Zircon textural and chronological evidence for Mesoproterozoic and Carboniferous mafic igneous complexes in the crystalline basement of NE Poland
- P12-13 Hisashi Sekiguchi, Miho Watanabe, Mamoru Enjoji
On the diverse etch patterns of magnetite by hydrochloric acid
- P12-14 Giovanna Agrosi, Nicola Melone, Alessandro Monno, Eugenio Scandale, Gioacchino Tempesta
On the striated prism faces of the tourmaline crystals

13. Nucleation and Aggregation of macro- to nano-materials (CMGIP)

Conveners and chairs: Lukas Baumgartner (Univ. of Lausanne), Masamichi Ishikawa^{#,*}(Tokyo Inst. of Technology)

Oral presentations

Thur. July 27 14:30~17:00 5F 505

14:30~15:00

- O13-1 † Ryo Kobayashi, James A. Warren
Modeling of the evolution of 3 dimensional polycrystalline structures

15:00~15:15

- O13-2 Askhab M. Askhabov
Quataron concept for crystal growth and nanomaterials formation

15:15~15:30

- O13-3 Masamichi Ishikawa
Self-assembling of colloidal particles and nucleation problems

15:30~15:45

- O13-4 § Tsutomu Sawada
Formation of single-domain colloidal crystals by strong shear-flow

15:45~16:15

- O13-5 † Juan Manuel Garcia Ruiz
Self-assembly of nanocrystals into non-crystallographic morphologies

16:15~16:30

- O13-6 § Mu Wang, Da-jun Shu, Ru-wen Peng, Nai-ben Ming
Self-organization growth in diffusion-limited system

16:30~16:45

- O13-7 § Xiang Yang Liu
From nucleation-mediated assembly/aggregation to micro/nano scale architecture of new functional materials

16:45~17:00

- O13-8 § Kenji Waizumi
Nucleation and growth of insulin crystals

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P13-1 Guobin Ma, Mu Wang, Ting Zhang, Nai-Ben Ming
Synthesis and growth mechanism of rutile TiO₂ spherulites
- P13-2 Radostina Atanassova, Ivan K. Bonev, Juan Manuel Garcia-Ruiz
Filamentary and skeletal sulphide (pyrite and galena) crystals embraced in large contemporaneously growing calcite crystal
- P13-3 Jun Nozawa, Katsuo Tsukamoto, Hisao Satoh
Self-assemblage of extraterrestrial nano-magnetite particles

14. Sea-floor hydrothermal systems: Present and past examples

Conveners: Rodney Allen[#] (Univ. of Lulea), Munetomo Nedachi (Kagoshima Univ.),
Tetsuro Urabe* (Univ. of Tokyo)

Chairs: Munetomo Nedachi (Kagoshima Univ.), Tetsuro Urabe (Univ. of Tokyo)

Oral presentations

Mon. July 24 9:30~12:00 5F 505

9:30~9:45

- O14-1 Tetsuro Urabe
An overview of seafloor hydrothermal activity in arc/backarc systems of the western Pacific

9:45~10:15

- O14-2 § Jun-ichiro Ishibashi, Ryohei Suzuki, Miwako Nakaseama, Hitoshi Chiba, Kaul Gena, Satoru Ohkubo, Urumu Tsunogai
Diversity in fluid chemistry and mineralization caused by phase separation in the active seafloor hydrothermal field at the Yonaguni Knoll IV, Okinawa Trough, southwest Japan

10:15~10:30

- O14-3 Katsumi Marumo, Tetsuro Urabe
Mercury and lead isotope ratios of the Suiyo seafloor hydrothermal system and Kuroko deposits

10:30~10:45

- O14-4 Ryohei Suzuki, Jun-ichiro Ishibashi, Tetsuro Urabe, Takuro Noguchi, Itoh Michihiro, Tamotsu Oomori
Seafloor hydrothermal mineralization at the off-axial vent sites of the southern Mariana Trough

10:45~11:00

- O14-5 Nikolay S. Bortnikov, Vladimir A. Simonov, Serafim V. Ikorskii, Olga V. Stavrova, Igor D. Krinov, Ekaterina O. Terenya, Igor L. Kamenskii, Anaid A. Avedisyan, Anatoly M. Sagalevich
Chemistry, isotope composition and temperature of fluids at East Pacific Rise ⁹⁰ and ²¹⁰N

11:00~11:15

- O14-6 Krister L Sundblad, Tom Andersen, Monica Beckholmen, Odd Nilsen
Recognition of ordovician escanaba type VMS deposits in the scandinavian caledonides

11:15~11:30

- O14-7 Gregor Borg, Fernando Tornos
From SEDEX to VMS -the Skorpion-Rosh Pinah massive sulphide district, Namibia

11:30~11:45

- O14-8 Munetomo Nedachi, Yoko Nedachi, Harutoki Sakaki, Kazuya Terashima
Hydrothermal alteration in the 2.77 Ga Mt Roe basalt, Pilbara, Western Australia

11:45~12:00

- O14-9 Takuya Echigo, Mitsuyoshi Kimata, Teruyuki Maruoka
The isotopic and structural implications for the hydrothermal formation of karpatite from Picacho Peak, San Benito Country, California

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P14-1 Hiromasa Ishikawa, Tsukasa Ohba, Hirokazu Fujimaki
Diversity of chemical and strontium isotopic compositions of land water from Bandai area, Japan
- P14-2 Hirotaka Ishizeki, Daizo Ishiyama, Toshio Mizuta, Norihiko Kobayashi, Yoshihiro Watanabe
Alteration of felsic volcanics hosting gas reservoirs in the Minami-Nagaoka gas field, Niigata Prefecture, Japan -Comparison of the alteration styles of rhyolite on gas reservoirs with dacite associated with kuroko deposits -

15. Precious and base-metal deposits in magmatic arcs

Conveners and chairs: John Dilles[#] (Oregon State Univ.), Akira Imai (Kyushu Univ.), Yasushi Watanabe^{*} (AIST, Tsukuba)

Oral presentations

Mon. July 24 15:30~18:30 5F 503504

15:30~16:00

- O15-1 † Douglas J. Kirwin
Unidirectional solidification textures, miarolitic cavities and orbicles: Field evidence for the magmatic to hydrothermal transition in intrusion-related mineral deposits

16:00~16:20

- O15-2 § Jeffrey W. Hedenquist
Transitions from porphyry environments: Ore versus barren epithermal systems determined by magma history?

16:20~16:40

- O15-3 § Andreas Audetat, Thomas Pettke
Evolution of sulfur and copper in the magmas associated with porphyry-Cu mineralization at Santa Rita, New Mexico (U.S.A.)

16:40~17:00

- O15-4 § John H. Dilles, Mark H. Reed, Brian G. Rusk, Robert A. Houston, Lihua Zhang, Mark W. Martin, Larry W. Snee, Holly J. Stein, Cyrus W. Field, Adam J. Kent
Porphyry Cu-Mo and base metal lodes at butte, Montana: A world class ore deposit produced by millions of years of magmatic-hydrothermal activity

Break

17:15~17:30

- O15-5 Akira Imai, Kentaro Masaki, Yukiko Ohbuchi, Takayuki Tanaka, Seiya Morita, Masanori Furuno, Kentaro Yasunaga, Hiroyuki Takahata
Porphyry Cu Mineralization in Namosi District (Waivaka and Waisoi), Viti Levu, Republic of the Fiji Islands

17:30~17:45

- O15-6 Leilanie O. Suerte, Sho Nishihara, Akira Imai, Koichiro Watanabe, Graciano P. Yumul, Jr., Victor B. Maglambayan
The occurrences of ore minerals and fluid inclusions in the Kingking porphyry copper deposit, Eastern Mindanao, Philippines

17:45~18:00

- O15-7 Yasushi Watanabe, Xiaofeng Li
Tectonic setting of the Dexing porphyry Cu-Mo deposit in south China: Transition from magmatic arc to contraction zone

18:00~18:15

- O15-8 Xiaofeng Li, Yasushi Watanabe
Hydrothermal alteration and mineralization of the Dexing porphyry copper deposit, South China

18:15~18:30

- O15-9 Jargalan Sereenen, Yasushi Watanabe
Geochemical variation caused by hydrothermal alteration at Oyu Tolgoi Cu-Au porphyry deposit

Tue. July 25 14:30~16:30 4F 402

14:30~14:45

- O15-10 Yong Ui Kim, Takuya Ooi
Hydrothermal activity for auriferous vein and associated porphyry stock, in the sea shore side Ugusu -Arari, west Izu Peninsula

14:45~15:00

- O15-11 Syafrizal, Akira Imai, Koichiro Watanabe
Characteristics of the ciurug and cikoret veins: Genetic reconstruction of the pongkor epithermal deposit, West Java, Indonesia

15:00~15:15

- O15-12 Ryohei Takahashi, Hiroharu Matsueda, Victor M. Okrugin
Gold and silver mineralization and magnetic susceptibility of host rock at the asachinskoe deposit in South Kamchatka, Russia

15:15~15:30

- O15-13 Balmer Echeverri, Hiroto Ohira
Genesis and thermal history of gold mineralization in the Remedios-Segovia mining district of Northern Colombia

15:30~15:45

- O15-14 Jeffrey D. Keith, Elizabeth O. Hunter, Jacob Hunter, Elizabeth Ryskamp, Nichelle Baxter, Michael Dorais, David Tingey
The smallest base- and precious-metal deposits in the world and why we should care: Vesicle-hosted Cu-Sn-Co-Ag alloys

15:45~16:00

- O15-15 Elizabeth Ryskamp, Jeffrey Abbott, Jeffrey D. Keith, Eric H. Christiansen
Petrogenesis of Eocene-Oligocene magmatism of the sulphur spring range, central Nevada: The role of magma mixing

16:00~16:15

- O15-16 Shunso Ishihara, Kinichi Hoshino, Hiroyasu Murakami, Yuji Endo
Why is indium rich in the Japanese island-arc magmatic belts?

16:15~16:30

- O15-17 Tetsuichi Takagi, Katsuhiko Tsukimura
Genesis of metallogenic provinces from the viewpoint of global material recycling

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P15-1 Daizo Ishiyama, Naoyuki Sugawara, Toshio Mizuta, Takeyuki Ogata
Origin of iron on Miocene Fe skarn mineralization of the Oohinata deposit in the active uplifting region of central Japan

- P15-2 Yuki Nagai, Akira Imai
A study on the quartz veins and associated ore minerals at the deep part of the Batu Hijau porphyry copper deposit, Sumbawa, Indonesia
- P15-3 Koichi Michimasa, Hiroharu Matsueda, Norio Tsushima
The time and spatial distribution of mineralization at the southeastern part of Toyoha deposits in southwest of Hokkaido
- P15-4 Hiroharu Matsueda, Toru Shimizu, Aki Sato
Mineralization process of Au-Ag deposit at the Koryu mine, southwest Hokkaido, Japan
- P15-5 Miyuki Furusawa, Munetomo Nedachi
Chlorine geochemistry of volcanic rocks in the Hokusatsu gold mining district in Kyushu, Japan
- P15-6 Kenzo Sanematsu, Akira Imai, Koichiro Watanabe
Gangue minerals associated with the precipitation of gold at the Hishikari low-sulfidation epithermal gold deposit, Japan
- P15-7 István Márton, Robert Moritz, Peter Marchev, Nikolay Bonev, Sean Hasson, Torsten Vennemann
Tertiary sedimentary rock-hosted, low-sulfidation epithermal deposits and prospects in the Eastern Rhodopes, Bulgaria: New geological, stable isotope and fluid inclusion constraints
- P15-8 Kotaro Yonezu, Takushi Yokoyama, Akira Imai, Koichiro Watanabe
Spectroscopic study of gold(I) and silver(I) thiosulfate adsorbed on Al₂O₃
- P15-9 Hiroyasu Murakami, Shunso Ishihara, Yasushi Watanabe
Rare earth mineralizations in clay sediments related to weathered granitic rocks in Japan

16. Mineralogy of ore deposits (COM)

Conveners: Nigel J. Cook[#](Univ. of Oslo), Kari Kojonen (Geological Survey of Finland), Hiroharu Matsueda (Hokkaido Univ.), Roland K. W. Merkle (Univ. of Pretoria), Masaaki Shimizu^{*}(Univ. of Toyama)

Chairs: Masaaki Shimizu (Univ. of Toyama), Kari Kojonen (Geological Survey of Finland), Roland K. W. Merkle (Univ. of Pretoria), Alan P. Boyle (Univ. of Liverpool), Jeffrey L. Mauk (Univ. of Auckland), Nigel J. Cook (Univ. of Oslo)

Oral presentations

Wed. July 26 9:00~12:00 4F 401

9:00~9:30

- O16-1 † Roland Merkle, Roger D. Dixon
Possibilities and limitations of trace element characterization (fingerprinting) of precious materials

9:30~10:00

- O16-2 § Alan P. Boyle
New insights into pyrite textures from the application of electron backscatter diffraction

10:00~10:20

- O16-3 Alba Nury Gallego, Masahide Akasaka
The silver-bearing and related minerals in El Zancudo deposit, Antioquia, Colombia and their genetic processes

10:20~10:40

- O16-4 Jeffrey L. Mauk
Distribution of Cu-Ag-S-Se phases in epithermal deposits of the Hauraki Goldfield, New Zealand

Break

11:00~11:20

- O16-5 Chihiro Fukuda, Masahide Akasaka
Mineralogical and genetic characteristics of the Dohgamaru skarn and vein type ore deposits, Shimane Prefecture, Japan

11:20~11:40

- O16-6 Cristiana L. Ciobanu, Allan Pring, Nigel J. Cook, Peter Self
High-resolution transmission electron microscopy study of natural Bi-chalcogenides of the tetradymite group

11:40~12:00

- O16-7 Nigel J. Cook, Cristiana L. Ciobanu, Allan Pring, Gheorghe Damian
Another look at nagyágite from Săcărimb (Romania)

Wed. July 26 14:30~18:20 4F 401

14:30~15:00

- O16-8 § Werner H. Paar, Hubert Putz, Dan Topa, Ricardo J. Sureda, Milka Brodtkorb, Volker Lüders
Breccias with high-grade Ag-Sn mineralization at Pirquitas, Argentina

15:00~15:30

- O16-9 § Toshio Mizuta, Daizo Ishiyama
Kuroko and Besshi-type volcanogenic massive sulfide deposits in Japan

15:30~15:50

- O16-10 Tsubasa Otake, David J. Wesolowski, Anovitz M. Lawrence, Allard F. Lawrence, Ohmoto Hiroshi
Non-redox transformation of magnetite - hematite under H₂-rich hydrothermal conditions

15:50~16:10

- O16-11 James Thom, Greg Anderson
The role of reaction kinetics in the growth of sphalerite in MVT deposits

16:10~16:30

- O16-12 Tatiana L. Evstigneeva
Some crystallochemical peculiarities of PGM with As, Te, Sb, and Sn

Break

16:40~17:00

- O16-13 § Emin Ciftci, Abdurrahman Lermi, Richard D. Hagni
Ore mineral paragenesis and sulfur isotope characteristics of volcanogenic massive sulfide deposits of Turkey occurring in the Eastern Pontides (NE Turkey): Are they true Kuroko-type deposits?

17:00~17:20

- O16-14 Domenico Cozzupoli, Caterina De Vito, Vincenzo Ferrini, Federico Rossetti
Structural control and rheological properties of the hydrothermal mineralization: A case of a mineralized mafic dike outcropping near Lula, Sardinia, Italy

17:20~17:40

- O16-15 Farahnaz Daliran, Gregor Borg, Richard Armstrong
Metallogenic constraints on the origin of hypogene zinc ores at Angouran Mine, Iran

17:40~18:00

- O16-16 Mark P. Simpson, Jeffrey L. Mauk
Alteration minerals in adularia-sericite epithermal deposits as indicators of mineralisation potential: Examples from the Hauraki Goldfield, New Zealand

18:00~18:20

- O16-17 Kari K. Kojonen, Mahmud Tarkian, Vladimir V. Knauf, Ragnar Törnroos, Stephanie Heydrich
Placer platinum-group minerals from Ivalojoiki and Lemmenjoki rivers, Finnish Lapland

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P16-1 Klaus Robl, Werner H. Paar, Dan Topa, Ricardo J. Sureda, Milka Brodtkorb
Ore mineralogy of a high-grade epithermal silver mineralization at El Quevar, Argentina
- P16-2 Hubert Putz, Werner H. Paar, Dan Topa
Microparagenesis of germanium mineralization in polymetallic deposits of Bolivia and Argentina
- P16-3 Milan Drabek, Milan Rieder
The Os-Mo-S system, a crystal-chemical and experimental approach
- P16-4 Michael Preuschoff
Bieber - a widely unknown ancient Ore - Deposit in the Spessart - Mountains (Germany)
- P16-5 Hiroyuki Miura, Keiji Wada, Yoshio Katsui
Tephrochronology of the manganese wad deposit at the Akan Yunotaki hot spring
- P16-6 Cassian Pirard, Frederic B.R. Hatert
Uranyl-selenites, unique minerals of Musonoï Mine, Katanga, DRC
- P16-7 Asahiko Sugaki, Arashi Kitakaze
New phase relations of the system Fe-Ni-S at temperatures from 875 to 400°C as the pentlandite ore-genesis
- P16-8 Masaaki Shimizu, Yasutake Kato, Marina Shimizu, Hideto Yoshida, Lehmann Bernd
Sodalite from Cerro Sapo, Bolivia: Bridge between archeology and mineral sciences
- P16-9 Ken-ichiro Hayashi, Tomohito Wada, Kosei Komuro
Cathodoluminescence study of gold ore at the Harmony mine, Witwatersrand Basin, South Africa
- P16-10 Toru Shimizu, Hiroharu Matsueda
Structural and textural variations of epithermal Au-Ag vein quartz -Koryu deposit in Hokkaido, Japan
- P16-11 Gleb Baturin, Viktor Dubinchuck, Elena Ozhogina, Alexandre Rogozhin
Geochemistry and species of major and rare elements in Fe-Mn crusts from sub-sea mountains of NW Pacific Ocean
- P16-12 Takahiko Ogawara, Junji Akai
Mineralogical description and their Biosignatures of Kuroko Ore minerals
- P16-13 Elena Yu. Anikina, Gennady N. Gamyagin, Nickolay S. Bortnikov
Bismuth-bearing minerals in some tin-silver-lead-zinc deposits of Verkhoyansk fold belt (Sakha-Yakutiya, Russia)
- P16-14 Berna Yavuz, Ahmet Atac, Emin Ciftci, Richard D Hagni
Sulfur Isotope Characteristics of Carbonate-Hosted Pb-Zn Deposits Occurring in the Central Taurus Mountains (Southern Central Turkey)
- P16-15 Yosuke Kanai, Junji Akai
TEM mineralogy of Mn oxide in sedimentary and biogenic manganese ore in relation to origin of trilling in todorokite
- P16-16 Gyorgyi Tuba, Ildiko Cora, Tamas G. Weiszbarg, Peter Pekker
Micro-scale Mineralogical Study on the Toarcian Manganese Ore Deposit, Úrkút, Hungary
- P16-17 Volker Hoeck, Corina Ionescu
PT constraints on the formation of large brucite deposits: a case study from the Apuseni Mnts., Romania

17. Fluid and melt inclusions (WGIM)

Conveners: Mamoru Enjoji (Waseda Univ.), Christoph A. Heinrich (ETH, Zürich),
Sergey Smirnov (Russian Academy of Sci., Novosibirsk), Zhaolin Li[#] (Zhongshan Univ.), Takayuki Sawaki* (AIST, Tsukuba)
Chairs: Zhaolin Li (Zhongshan Univ.), Kenichi Hoshino (Hiroshima Univ.)

Oral presentations

Mon. July 24 9:30~11:30 4F 403

9:30~10:10

- O17-1 † Andreas Audetat, Thomas Pettke, Christoph A. Heinrich
The magmatic-hydrothermal transition in barren vs. mineralized intrusions

10:10~10:30

- O17-2 Zhaolin Li
Study on melt inclusions in zircon in igneous rocks from various regions in China

10:30~10:50

- O17-3 Andrew Putnis, Ruth Hinrichs, Christine V. Putnis, Ute Golla-Schindler
The significance of hematite-filled nano-inclusions in feldspar

10:50~11:10

- O17-4 Andrzej Kozłowski, Janina B. Wiszniewska
Origin of the fluorite mineralization in the Tajno alkaline Massif (NE Poland)

11:10~11:30

- O17-5 Kenichi Hoshino, Tomoe Hirotaka, Ai Nagatomi, Makoto Watanabe
Nahcolite and carbonaceous matters in fluid inclusions in quartz veins from the Ryoke metamorphic belt, SW Japan

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P17-1 Hiroki Nagaseki, Ken-ichiro Hayashi
The effect of sulfur on the vapor-liquid distribution of Cu and Zn in boiling hydrothermal fluid by SRXRF microanalysis of synthetic fluid inclusions
- P17-2 Alexander R. L. Nichols, Richard J. Wysoczanski
Analyzing volatiles in silicate melt inclusions by FTIR spectrometry
- P17-3 Hiroto Ohira, Daisuke Negi, Toshihiro Tanaka, Sachihito Taguchi
Thermal history of the Nabeyama sericite mine, NE Shimane, SW Japan, based on fission track and fluid inclusion studies
- P17-4 Masanori Kurosawa, Sadayoshi Shimano, Satoshi Ishii, Kimikazu Sasa
Fluid inclusion compositions of the Kofu granite body, central Japan: significance for chemistries of deep groundwater in the granite body
- P17-5 Ryo Nishimura, Mamoru Enjoji
The thermal properties of the crystallized inclusions in minerals from Kogarasu-yama granodiorite, Kofu, Japan
- P17-6 Mamoru Enjoji, Ryo Nishimura, Hiromu Nomura
The formation of rhyolite from Nagahama Volcano, Kozu-shima, Tokyo, Japan
- P17-7 Hiroyuki Ohyama, Toshiaki Tsunogae
Fluid inclusions in the high-grade Abukuma metamorphic rocks from Hanazono district, northeast Japan
- P17-8 Junji Torimoto, Hiroharu Matsueda, Sachihito Taguchi
Characteristics and significant role of fluid inclusion from high-grade metamorphic rocks in Sri Lanka

18. Metamorphism under extreme P-T conditions

Conveners: Masaki Enami^{#,*}(Nagoya Univ.), Simon Harley (Univ. of Edinburgh),
Anand Mohan (Baranas Hindu Univ.), Yasuhito Osanai (Kyushu Univ.),
Jian-Jun Yang (Chinese Academy of Sci.)
Chairs: Jian-Jun Yang (Chinese Academy of Sci.), Anand Mohan (Baranas Hindu Univ.),
Yasuhito Osanai (Kyushu Univ.), Masaki Enami (Nagoya Univ.)

Oral presentations

Tue. July 25 9:00~12:00 3F 301

9:00~9:40

- O18-1 † Takao Hirajima, Daisuke Nakamura, Kousuke Naemura, Hiroyoshi Sai, Martin Svojtka
Missing link between ultra-high pressure (UHP) and ultra-high temperature metamorphism (UHT); A case study in the Bohemian massif

9:40~10:00

- O18-2 Michael Brown
Do ultrahigh temperature and ultrahigh pressure metamorphic belts record secular change in tectonic regime on Earth?

10:00~10:20

- O18-3 Anand Mohan, Yasuhito Osanai
Art of petrography: An amazing tool for snap-shots of the journey of UHT rocks

Break

10:40~11:00

- O18-4 Yasuhito Osanai, Nobuhiko Nakano, Masaaki Owada, Tran N. Nam, Pham Binh, Tomoharu Miyamoto, Nguyen T. Minh
Collision zone metamorphism under extreme P-T conditions in Vietnam and adjacent SE-Asia

11:00~11:20

- O18-5 Tran N. Nam, Yasuhito Osanai, Nobuhiko Nakano, Masaaki Owada
Multiple tectonothermal events in high-grade gneisses of the Kontum massif, central Vietnam: Geochronological constraints and geodynamic implications

11:20~11:40

- O18-6 Masaaki Owada, Yasuhito Osanai, Nobuhiko Nakano, Tomokazu Hokada, Hiroo Kagami
Ultrahigh-temperature metamorphism and crustal anatexis caused by mantle plume in collision zone, the Kontum Massif, Central Vietnam

11:40~12:00

- O18-7 Divya Prakash, Makoto Arima
Madurai Block, Southern India: A classic terrain for petrotectonic implication

Wed. July 26 9:00~12:00 3F 301

9:00~9:20

- O18-8 Edward S. Grew, Thomas Armbruster, Olaf Medenbach, Martin G. Yates, Christopher J. Carson
Ferromagnesian phosphates as products of anatexis in granulite-facies paragneisses from the Larsemann Hills, Prydz Bay, East Antarctica

9:20~9:40

- O18-9 Madhusoodhan Satish-Kumar, Yoichi Motoyoshi
Garnet-scapolite intergrowths and multistage garnet coronas in UHT calc-silicate boudins from Rundvågshetta, East Antarctica: Insights for P-T-X-fO₂ evolution

9:40~10:00

- O18-10 Kosuke Naemura, Takao Hirajima, Martin Svojtka
Pressure-temperature path of spinel-garnet peridotite at the Plesovice quarry in the Blansky les granulite massif, Southern Bohemia

10:00~10:20O18-11 Tomokazu Hokada

Perrierite in sapphirine-quartz gneiss: geochemical and geochronological features and implications for accessory phase paragenesis of UHT metamorphism

Break**10:40~11:00**O18-12 Tatsuki Tsujimori, Virginia B. Sisson, Juhn G. Liou, George E. Harlow, Sorena S. Sorensen

Windows to the very-low-temperature subduction process: A review of worldwide lawsonite eclogites

11:00~11:20O18-13 Masaki Enami, Tadao Nishiyama, Takashi Mouri

Laser Raman microspectrometry of metamorphic quartz: A simple and effective method for comparison of metamorphic pressures

11:20~11:40O18-14 Jian-Jun Yang

Ca-rich garnet-clinopyroxene rocks at Hujialin in the Su-Lu terrane (Eastern China): deeply subducted arc cumulates?

11:40~12:00O18-15 Fabrice Brunet, Tetsuo Irifune, Vincent Bonneau, Takeshi Sanehira

Crystal-chemistry of phosphorus at ultra high pressures : Petrological implications

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P18-1 Kaushik Das, Sankar Bose, Subrata Karmakar, Somnath Dasgupta

Meso-Neoproterozoic compressional reworking of UHT metamorphosed granulites: First petrological evidence from the Eastern Ghats Belt, India

P18-2 Makoto Shimpō, Toshiaki Tsunogae, Santosh M.

Pan-African high-pressure and ultrahigh-temperature metamorphism in the palghat-cauvery shear zone system: Implications for crustal evolution in Southern India

P18-3 Sankar Bose, Kaushik Das, Somnath Dasgupta, Hiroyuki Miura

New textural evidences of anomalously high thermal conditions in deep continental crust from Eastern Ghats granulite belt, India

P18-4 Hiroyuki Tadokoro, M. Santosh, Yasutaka Yoshimura

Metamorphic evolution of the Kodaikanal metapelite belt, Southern India

P18-5 Akira Yamada, Toshiaki Tsunogae, M. Santosh, Norimasa Nishida

Fluid-rock interaction in high-grade calc-silicate rocks from the madurai granulite block, Southern India: Evidence from scapolite chemistry

P18-6 Shunsuke Ishii, Toshiaki Tsunogae, Santosh M.

Metamorphism and fluids of ultrahigh-temperature garnet-orthopyroxene-cordierite granulites from the achankovil zone, Southern India

P18-7 Tetsuo Kawakami, David J. Ellis, Andrew G. Christy

Sulfide evolution in high-temperature to ultrahigh-temperature metamorphic rocks from Lützow-Holm Complex, East Antarctica

P18-8 Yasutaka Yoshimura, Tomoharu Miyamoto, Yoichi Motoyoshi

Metamorphic evolution and partial melting under ultrahigh-temperature conditions: The Howard Hills UHT rocks, Napier Complex, East Antarctica

P18-9 Tomoharu Miyamoto, Yasutaka Yoshimura, Kei Sato, Daniel J. Dunkley, Yoichi Motoyoshi, Christopher J. Carson

Time tracks of cooling after UHT metamorphism in Howard Hills, Napier Complex, east Antarctica

- P18-10 Toshiaki Tsunogae, Dirk D. van Reenen
Sapphirine + quartz corona around Mg-staurolite in garnet granulite from the Limpopo Belt, Southern Africa: Evidence for ultrahigh-temperature metamorphism?
- P18-11 Tomoyuki Kobayashi, Takao Hirajima, Svojtka Martin
Precursor high-pressure evidence in the Grt-Bt-Sil-Crd gneiss in the Lhenice shear zone (Moldanubian Zone of the southern Bohemian Massif), Czech Republic, and its geological significance
- P18-12 Yuki Beppu, Takamoto Okudaira
Low-pressure metamorphism on the Ryoke metamorphic rocks from Kasado-jima Island, SW Japan
- P18-13 Lukas Keller, Christoph Anton Hauzenberger, Rainer Abart
Interphase boundary diffusion rates and their effect on retrograde zoning patterns of metamorphic minerals
- P18-14 Kei Sato, Yasutaka Yoshimura, Naoto Hirano, Takafumi Hirata
Experimental studies of melting phase relation of garnet-sillimanite felsic gneiss and distribution of minor elements between garnet and melt under ultrahigh-temperature metamorphic condition
- P18-15 Nirihaja Othon Thierry Rakotonandrasana, Makoto Arima, Ritsuro Miyawaki, Roger Andriamparany Rambeloson
First Report of h gbomite from ultrahigh temperature metapelite along the Ranotsara Shear Zone in Southern Madagascar
- P18-16 Yoshikuni Hiroi, Yoichi Motoyoshi, Simon R. Wallis
Corundum replacing Al₂SiO₅ minerals in the vicinity of quartz in both high-pressure and high-temperature metamorphic rocks: Evidence for brief partial melting during exhumation
- P18-17 Nobuhiko Nakano, Yasuhito Osanai, Masaaki Owada, Sachihiko Taguchi, Tomokazu Hokada, Nam Ngoc Tran
Ultrahigh-pressure metamorphism recorded in ultrahigh-temperature mafic granulite from the Kontum Massif, central Vietnam
- P18-18 Kazuhiko Otsuka, Takao Hirajima
Pressure and temperature trajectory obtained by Gibbs' Method for the kyanite-quartz eclogite from the Sambagawa metamorphic belt, Japan
- P18-19 Yasuo Miyagi, Takeyoshi Yoshida, Akira Takasu
Protolith and polymetamorphic evolution of the Tonaru eclogite-bearing metagabbro body in the Sambagawa belt, central Shikoku, Japan
- P18-20 Taro Ubukawa, Akiko Haranaka, Keisaku Matsumoto, Takao Hirajima
Two generations of talc in the Sanbagawa metamorphic rock at the Kotsu area, eastern Shikoku, Japan
- P18-21 Yukihisa Osada, Hirokazu Maekawa, Koshi Yamamoto
The origin of jadeite-quartz rocks in the Kamuikotan metamorphic terrane, Japan
- P18-22 Keisaku Matsumoto, Takao Hirajima
Phase relationships of the eclogite in the southern eclogitic micaschist complex of the Sesia zone, Italy
- P18-23 Fred Gaidies, Rainer Abart, Christian de Capitani, James Alexander Connolly
Characterization of polymetamorphism in the Austroalpine basement east of the Tauern Window using garnet isopleth geothermobarometry
- P18-24 Akira Takasu, M. Tagiri, A. B. Bakirov, K. S. Sakiev, A. A. Orozbaev, A. A. Bakirov, A. A. Togonbaeva, J. U. Baslakunov, T. Sakurai, M. M. Satybaev
Eclogites and UHP metamorphic rocks in the Kyrgyz Tien-Shan
- P18-25 Delia A-M. Androne, Haino Uwe Kasper, Nicolae Buzgar
The garnet from Contu-Negovanu pegmatitic field (Lotru-Cibin Mts.-Romania)
- P18-26 Andrey Y. Lysiuk, G. Yurgenson, Nikolay Yushkin
Phytotfulgurites: New type of atmogenic electric-discharge metamorphism

19. Subduction factory and continental evolutions

Conveners: Yoshihiko Tamura^{*,*}(JAMSTEC, Yokosuka), Graciano P. Jr. Yumul (Univ. of the Philippines, Quezon)

Chairs: Osamu Ishizuka (Geological Survey of Japan/AIST), Jun-ichi Kimura (Shimane Univ.), Yoshiaki Yamaguchi (Shinshu Univ.), Yoshihiko Tamura (JAMSTEC, Yokosuka), Takeyoshi Yoshida (Tohoku Univ.), Richard Wysoczanski (JAMSTEC)

Oral presentations

Thur. July 27 9:00~12:00 1F Main Hall

9:00~9:20

O19-1 § Jun-Ichi Kimura, Takeyoshi Yoshida

Contributions of slab fluid, wedge mantle, and crust to the origin of quaternary lavas in the NE Japan arc

9:20~9:40

O19-2 Masao Ban, Yutaka Iai, Shiho Hirotani

Magma feeding system beneath the Gassan volcano, NE Japan

9:40~10:00

O19-3 Maria Luisa G. Tejada

Evolving mantle source regions and crustal growth in the Philippines

10:00~10:20

O19-4 Lucas D. Setijadji, Yasuyuki Kohno, Shigeo Kajino, Akira Imai, Koichiro Watanabe

Petrochemical variations of island arc volcanics and sources for these discrepancies: observation from Java island, Sunda arc, Indonesia

Break

10:40~11:00

O19-5 § Osamu Ishizuka, Rex N. Taylor, Yasuhiko Ohara

Spatial and temporal variability of intra-oceanic island arc magma sources: new observations from Oligocene Izu-Bonin arc

11:00~11:20

O19-6 Kantaro Fujioka, Saneatsu Saito

History of volcanism of the Izu-Bonin Arc deduced from the chemical composition of heavy minerals of volcaniclastics

11:20~11:40

O19-7 Yoshihiko Tamura, Kenichiro Tani, Qing Chang, Osamu Ishizuka, Hiroshi Shukuno, Hiroshi Kawabata, Richard S. Fiske

Magmatic evolution in the central Izu-Bonin arc: a 3-D perspective and the possible role of phengite

11:40~12:00

O19-8 Ikuo Katayama, Shun-ichiro Karato

Experimental constraints on olivine LPO under water-rich conditions and implications for seismic anisotropy in subduction zones

Thur. July 27 14:30~16:30 1F Main Hall

14:30~14:50

O19-9 Mihoko Hoshino, Mitsuyoshi Kimata, Yoji Arakawa, Norimasa Nishida, Masahiro Shimizu

Allanite as an indicator of origin and tectonic setting for granitic rocks, Japan: Implications for fractionation in manganese and rare earth elements, and for difference in Sr-Nd isotope compositions

14:50~15:10

O19-10 Yoshiaki Yamaguchi, Tamami Yamaguchi, Yasushi Ohta

Large sulfur supplies by mafic magma injection into the magma systems of the volcanic front of the northeast to Central Japan arc: Melt inclusion evidence

15:10~15:30

- O19-11 Rustam T. Orozbaev, Akira Takasu, Michio Tagiri, Apas B. Bakirov, Kadyrbek S. Sakiev
Polymetamorphism of the Aktyuz eclogites in the Northern Tien-Shan, Kyrgyzstan

15:30~15:50

- O19-12 Fernando Bea, Pilar Montero, Cristina Talavera, Francisco G. Lodeiro, Martin J. Whitehouse
Zircon thermometry and inheritance kinetics reveal ultra-fast magma generation processes during Cambro-Ordovician times in Iberia

15:50~16:10

- O19-13 Michael Burchard, Walter V. Maresch, Thomas Fockenberg
Modeling silicate-rich fluids at high pressures: The system $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-H_2O$ (KNCASH)

16:10~16:30

- O19-14 Hao Cheng, Katsura Kobayashi, Eizo Nakamura
Origin of atoll garnets in eclogite and its implication for the mobility of trace elements in continental subduction zone

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P19-1 Chisato Nagai, Takeyoshi Yoshida, Ryoichi Yamada
Temporal and spatial variation of petrochemistry of the tertiary volcanic rocks in the Oga peninsula, NE Honshu arc
- P19-2 Tsukasa Ohba, Yuki Kitade, Yasuyuki Kimura, Hiromasa Ishikawa, Hirokazu Fujimaki, Kenichi Ishikawa
Decompression-induced phenocryst crystallization in arc basalt magma from Hakkoda, Northern Japan
- P19-3 Takeyoshi Yoshida, Ryoichi Yamada, Keizo Yanai, Nobutaka Tsuchiya, Takeshi Ohguchi, Toshio Mizuta, Nobuo Doi
Evolution of the Northeast Honshu Arc - Arc volcanism from cretaceous to present -
- P19-4 Yasuyuki Kimura, Tsukasa Ohba, Hirokazu Fujimaki
High-magnesian andesite produced by two-stage magma mixing at Ebisumori of Hachimantai, Northern Honshu, Japan
- P19-5 Osamu Ujike, Reina Mashimo
Petrologic significance of magmatic enclaves on the origin of Hakusan volcanic rocks, Central Japan
- P19-6 Hiroshi Kawabata, Naoto Takafuji
Origin of garnet crystals in calc-alkaline volcanic rocks from the Setouchi volcanic belt, Japan
- P19-7 Mitsuo Makita, Tomoaki Morishita, Shoji Arai, Yoshito Ishida
Origin of orthopyroxene in the Horoman peridotite complex, Japan: A natural example of products after partial melting of heterogeneous mantle materials
- P19-8 Richard J. Wysoczanski, Yoshiyuki Tatsumi, Kenichiro Tani
Melt inclusions from the Higashi-Izu monogenetic volcano group
- P19-9 Norie Fujibayashi, Hiroo Kagami, Naoyuki Ishida, Hiroko Kondo
Petrology and mineral isochron age of ultramafic to mafic xenoliths from the NE Japan Arc.
- P19-10 Ushio Honma
Petrology and geochemistry of quaternary Oginosen monogenic volcano, eastern part of Southwest Japan
- P19-11 Masaru Taga
Petrology of the Hijikai pluton, Okayama prefecture, Southwest Japan
- P19-12 Daiki Sunada, Masayuki Sakakibara, Sakae Sano
Various fluid-rock interaction and tourmalinization in the Sanbagawa high-P/T metamorphic rocks, Central Shikoku, Japan.

- P19-13 Eriko Nitta, Mitsuyoshi Kimata, Mihoko Hoshino, Takuya Echigo, Satoshi Hamasaki, Hiroshi Shinohara, Norimasa Nishida, Tamao Hatta, Masahiro Shimizu
High-temperature sublimate minerals from Iwodake volcano, Satsuma-Iwojima, Kyusyu, Southwestern Japan
- P19-14 Yasuko Okuyama, Akiko Kawabata, Akira Uyeda
Migmatite as a seal of magmatic fluid in Tanohata thermal aureole, NE Japan
- P19-15 Toru Ryu, Mitsuyoshi Kimata, Norimasa Nishida, Masahiro Shimizu
Chemical evolution of ferrocolumbites and their paragenesis with ixiolites from the Ishikawa-yama granitic pegmatites, Fukushima, Japan
- P19-16 Pilar G. Montero, Fernando Bea, Francisco Gonzalez-Lodeiro, Cristina Talavera, Martin Whitehouse
Zircon crystallization age and protolith history of the metavulcanites and metagranites of the olo de Sapo Domain in Central Spain. Implications for the neoproterozoic to early-paleozoic evolution of Iberia
- P19-17 George E. Harlow, Nancy A. Price, Tatsuki Tsujimori
Serpentinites of the Motagua fault zone, Guatemala: A mineralogical assessment
- P19-18 Alfonso Pesquera, Jose Torres-Ruiz, Pedro P. Gil-Crespo, Encarnacion Roda-Robles
Tourmaline in the Alamo complex (Central Iberian Zone, Spain): Evidence for boron recycling in the continental crust and petrogenetic implications
- P19-19 Hideki Murakami, Andre E. Lalonde
Significance of elevated contents of $\square\text{Si}_4\text{O}_8$ and $\text{AlAl}_3\text{SiO}_8$ end-members in black clouded plagioclase from the Lac Saint-Jean anorthosite: Evidence for oxidation-induced postmagmatic exsolution of Fe-Ti oxide inclusions from plagioclase

20. Oceanic crust and mantle processes

Conveners: Shoji Arai*(Kanazawa Univ.), Georges Ceuleneer# (CNRS, Toulouse)
Chairs: Eiichi Takazawa (Niigata Univ.), Natsue Abe (JAMSTEC), Georges Ceuleneer (CNRS, Toulouse), Shoji Arai (Kanazawa Univ.)

Oral presentations

Wed. July 26 14:30~18:20 3F 301

14:30~15:00

- O20-1 † Georges Ceuleneer
Melt migration processes in the mantle and their geochemical consequences: A review based on evidence from ophiolites

15:00~15:20

- O20-2 § Susumu Umino, Laura Crispini, Paola Tartarotti, Damon A.H. Teagle, Banerjee R. Neil, IODP Expedition 309&312 Scientific Parties
Contrasting upper crustal structures revealed by deep ocean crust drilling --- insights into shallow magma plumbing systems beneath intermediate versus superfast spreading ridges

15:20~15:40

- O20-3 Natsue Abe, Daniel Brunelli, Heidi-Elisabeth Hansen, Eric Hellebrand, Satoko Ishimaru, Kevin T.M. Johnson, Akihiro H. Tamura
A preliminary result of an oceanic lithosphere drilling IODP expedition 304 and 305 at the Atlantis massif, the Mid-Atlantic ridge 30°N

15:40~16:00

- O20-4 § Juergen Koepke, Sandrin T. Feig
Magmatic processes in the deep oceanic crust triggered by water: Experimental constraint

Break

16:20~16:40

- O20-5 Sumio Miyashita, Yoshiko Adachi, Azusa Akimoto, Takashi Tomatsu
Magma processes beneath fast-spreading ridges: Constraints from petrological evidence in gabbroic unit of the Oman ophiolite

16:40~17:00

- O20-6 § Eiichi Takazawa, Nami Kanke
Kilo meter-scaled highly refractory zone found in the mantle section of the northern Oman ophiolite (Fizh block): implications for remelting of oceanic lithospheric mantle

17:00~17:20

- O20-7 Marie Python, Georges Ceuleneer
High magnesian diopsidite dykes in the Oman ophiolite: Evidence for high temperature hydrothermal circulation in the oceanic mantle

17:20~17:40

- O20-8 Eric S. Andal, Shoji Arai, Tomoaki Morishita, Masako Yoshikawa
Fertile peridotites from the Isabela ophiolite: Fragments of the lower part of a cretaceous oceanic lithosphere

17:40~18:00

- O20-9 Tomoaki Morishita, Eric S. Andal, Shoji Arai, Yoshito Ishida
Hydrous metasomatic overprinting in mantle section of the Isabela ophiolite, Philippines

18:00~18:20

- O20-10 Masaaki Obata, Eiichi Takazawa
High-pressure mafic layers of gabbroic origin embedded in mantle-derived orogenic peridotite: The Horoman peridotite and other examples

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P20-1 Toshio Nozaka, Michael W. Abratis, Muriel Andreani, James S. Beard, Adelle Delacour, Marion Drouin, Bryce R. Frost, Patricia B. Fryer, Andrew M. McCaig, Yasuhiko Ohara
Multiple vein/dike-related alteration, metasomatism and thermal metamorphism of the oceanic lower crust at IODP site U1309, Mid-Atlantic ridge
- P20-2 Jinichiro Maeda, Yukari Suzuki, Tomoaki Morishita, Hidenori Kumagai, Natsuki Neo, Shoji Arai, Sumio Miyashita, Toru Yamasaki, Yukiko Ohtomo
Evidence for primitive magmatism at segment-end on ultraslow spreading ridges: A case study from the Atlantis II Fracture Zone, Southwest Indian Ridge
- P20-3 Hidenobu Okamura, Shoji Arai, Kazuyuki Kadoshima
Dunite-wehrlite-olivine clinopyroxenite series rocks from the North Fiji basin as deep-seated rocks from the Backarc basin
- P20-4 Keiko Murata, Hirokazu Maekawa, Teruaki Ishii
A speculation on thermal history of forearc peridotites in the Mariana arc-trench system
- P20-5 Shoji Arai, Kenji Suzuki
Petrological structure of the uppermost mantle beneath a mid-ocean ridge: An example from Wadi Rajmi, northern Oman ophiolite
- P20-6 Yoshitoshi Takemoto, Shoji Arai
Late intrusive rocks in the Oman ophiolite as a peridotite/melt reaction product"
- P20-7 Graciano P. Yumul, Jr., Leilanie O. Suerte, Rodolfo A. Tamayo, Jr., Carla B. Dimalanta
The Tacloban Ophiolite Complex: A petrological and geochemical characterization of a supra-subduction zone basement complex in Central Philippines
- P20-8 Akihiro Tamura, Shoji Arai
Geochemistry of clinopyroxene in peridotites from the Nukabira complex, northern Japan: residues of multi-stage melting
- P20-9 Satoko Ishimaru, Shoji Arai
Geochemical and petrological features of fine-grained peridotite xenoliths from Avacha volcano, the Southern Kamchatka

- P20-10 Yoshito Ishida, Shoji Arai, Douglas Smith
Trace-element mineral chemistry of peridotite xenoliths, Green Knobs
- P20-11 Murad A. Ali, Shoji Arai
Petrological feature of mantle xenoliths from Bir Ali Area, Yemen: An implication for mantle processes related to the rifted continental margin
- P20-12 Yoshihiro Sawada, Yoshikazu Sampei, Ichiro Matsumoto, Yukinobu Sakaguchi, Go Aratani, Koji Seto, Kiyoaki Niida
Carbonaceous materials in wedge mantle: A case study of the Horoman peridotite complex, Hokkaido, NE Japan
- P20-13 Kazuyasu Shindo, Ken-ichiro Hayashi
Sulfide minerals in the Horoman and Nikanbetsu complexes, Hokkaido, Japan
- P20-14 Sandrin T. Feig, Juergen Koepke, Jonathan E. Snow
Effect of H₂O and fO₂ on the phase equilibria in a primitive basaltic system
- P20-15 Sulaiman A. Alaabed
Carbonate bodies in the ophiolitic ultramafic rocks, where they came from?

21. Primitive meteorites, interplanetary dust and sample return missions (WGA)

Conveners: Tomoki Nakamura (Kyushu Univ.), Kazushige Tomeoka^{#,*}(Kobe Univ.),
Michael E. Zolensky (NASA JSC)

Chairs: Michael E. Zolensky (NASA JSC), Keiko Messenger (NASA), Kazushige Tomeoka (Kobe Univ.), Tomoki Nakamura (Kyushu Univ.), Naotaka Tomioka (Kobe Univ.)

Oral presentations

Mon. July 24 15:30~18:25 1F Main Hall

15:30~16:05

O21-1 † Ulrich Ott

Heavy trace elements in presolar silicon carbide grains: Isotopic and elemental signatures

16:05~16:20

O21-2 Makoto Kimura, Jeff N. Grossman, Mike K. Weisberg, Haruna Nakajima

Metamorphic conditions of unequilibrated chondrites

16:20~16:35

O21-3 Kazushige Tomeoka, Noriko Ishizaki, Ichiro Ohnishi

Silicate darkening in CK chondrites: A possible indicator of shock on a heated parent body

16:35~16:50

O21-4 Ichiro Ohnishi, Kazushige Tomeoka

Hydrothermal alteration experiments of enstatite under various pH, temperature and run duration conditions: Implications for aqueous alteration of carbonaceous chondrites

16:50~17:05

O21-5 Tomoki Nakamura, Ryuji Okazaki, Gary R. Huss

Mineralogical and noble-gas isotopic signatures of thermally metamorphosed hydrous carbonaceous chondrites

Break

17:25~17:40

O21-6 Naotaka Tomioka, Kazushige Tomeoka, Keiko Nakamura, Toshimori Sekine

Heating effects on the matrix of experimentally shocked Murchison CM chondrite: Comparison to micrometeorites

17:40~17:55

- O21-7 Andreas Morlok, Melanie M. Köhler, Monica M. Grady
Infrared absorption spectroscopy of chondrules from Allende (CV)

17:55~18:10

- O21-8 Mitsuhiro Sugita, Kazushige Tomeoka
Unusual matrix mineralogy and texture in the Ningqiang carbonaceous chondrite: Evidence for parent-body processes

18:10~18:25

- O21-9 Kentaroh Kudoh, Hirokazu Fujimaki
Petrography and mineralogy of a unique spherical CAI in the Murchison(CM2) meteorite

Tue. July 25 9:00~12:00 4F 403

9:00~9:20

- O21-10 § George J. Flynn
Composition analysis of the Wild-2 samples collected by Stardust

9:20~9:40

- O21-11 § Michael E. Zolensky
Mineralogy of the comet Wild2 nucleus samples returned by the Stardust mission

9:40~10:00

- O21-12 § Lindsay Keller
Optical spectroscopy of Stardust samples

10:00~10:20

- O21-13 § Masanao Abe, the Hayabusa Science Team
Nature of asteroid (25143) Itokawa observed by Hayabusa spacecraft

Break

10:40~11:00

- O21-14 Ryuji Okazaki, Nobuo Takaoka, Tomoki Nakamura, Keisuke Nagao
Primordial noble gases in enstatite chondrites: Implication for their parent bodies

11:00~11:15

- O21-15 Sachio Kobayashi, Hisayoshi Yurimoto
Presolar silicates in Kainsaz CO3.1 chondrite

11:15~11:30

- O21-16 Keiko Messenger, Scott R. Messenger, Lindsay P. Keller, Michael E. Zolensky
Interstellar signatures of organic globules in Tagish Lake meteorite: Nanoscale measurements of its chemical composition and isotopic properties

11:30~11:45

- O21-17 Shingo Ebata, Kazuhide Nagashima, Sachio Kobayashi, Naoya Sakamoto, Shoichi Itoh, Timothy J. Fagan, Hisayoshi Yurimoto
Presolar silicate grains in enstatite chondrites

11:45~12:00

- O21-18 Ken Nagashima, Katsuo Tsukamoto, Hisao Satoh
Chondrule formation from a hypercooled melt by levitation method

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P21-1 Tomoaki Aoki, Shoichi Toh, Yoshihiro Nakamuta
TEM observation of olivine crystals in a chondrite focused on dislocation density in relation to apparent strain of a lattice

- P21-2 Akiko Takayama, Kazushige Tomeoka
Fine-grained chondrule rims in the Tagish Lake chondrite: Evidence for formation by parent-body alteration processes
- P21-4 D. Nakashima, S. Herrmann, U. Ott, A. El. Goresy, T. Nakamura
Noble gases and nitrogen in the KLE98300 EH3 chondrite
- P21-5 Akiko Suzuki, Yoko Kebukawa, Satoru Nakashima, Tomoki Nakamura
Infrared microspectroscopy of organic and hydrous components in Antarctic micrometeorites
- P21-6 Yukari Wada, Kazushige Tomeoka, Akiko Nakamura, Naru Hirata, Kouki Kani
Shock experiments of serpentine powder: An attempt to simulate dust formation by asteroidal impacts
- P21-7 Chisa Nishizaki, Yoshihiro Nakamura
Mineralogical properties of Sahara 98222 L6 chondrite: Implications for the thermal history
- P21-8 Yoko Kebukawa, Satoru Nakashima, Michael E. Zolensky
In-situ micro-FTIR study of thermal changes of organics in carbonaceous chondrites - Behavior of aliphatic hydrocarbons and effects of minerals -
- P21-9 Masayuki Uesugi, Takeshi Akaki
A new constraint on the formation of compound chondrules
- P21-10 Seiji Yasuda, Taishi Nakamoto
Possible maximum size of porphyritic chondrules in the shock-wave heating model

22. Lunar and Martian rocks, differentiated meteorites and planetary missions

Conveners and chairs: Timothy J. Fagan (Waseda Univ.), Kazuto Saiki (Osaka Univ.), Akira Yamaguchi^{*,*}(National Inst. of Polar Research)

Oral presentations

Thur. July 27 9:40~12:00 4F 403

9:00~9:40

- O22-1 † Paul G. Lucey
The quiet revolution in lunar science: Lunar meteorites, global remote sensing and the magma ocean hypothesis

9:40~10:00

- O22-2 § Junya Terazono
SELENE - A pathfinder for new era of lunar exploration

10:00~10:20

- O22-3 Yasuhiro Yokota, Jun'ichi Haruyama, Makiko Ohtake, Tsuneo Matsunaga
Lunar imager / spectro meter (LISM) for the SELENE project

10:20~10:40

- O22-4 Hideaki Okuno, Yuta Yamanoi, Kazuto Saiki
Mg-number mapping of mare serenitatis with a hyper-spectral telescope

Break

11:00~11:20

- O22-5 Tomoko Arai
Can orbital data distinguish Mg-rich crustal rocks from Mg-rich basalt cumulates?

11:20~11:40

- O22-6 Hiroshi Takeda, Tomoko Arai, Yuuki Yazawa, Tatsuaki Yamaguchi, Makiko Ohtake, Hiroshi Kanamori
Na-Ca-bearing planetary minerals and preparation of lunar simulants for lunar bases

11:40~12:00

- O22-7 John H. Jones, Stephen J. Mackwell
Experimental partitioning of Cr³⁺ and Sc³⁺ into olivine: Mechanisms and implications

Thur. July 27 14:30~16:30 4F 403

14:30~15:10

- O22-8 § Gordon A. McKay, Loan Le, Takashi Mikouchi, Junichi Makishima, Craig Schwandt
Pyroxenes in martian meteorites as petrogenetic indicators

15:10~15:30

- O22-9 Takashi Mikouchi, Gordon McKay, Masamichi Miyamoto
Mineralogy of nakhlite martian meteorites: Implications for their relative burial depths

15:30~15:50

- O22-10 Naoya Imae, Yukio Ikeda
Crystallization experiments for nakhlite martian meteorites

15:50~16:10

- O22-11 Falko Langenhorst, J. R. Smyth, H. Kroll
Guinier-Preston exsolutions in extraterrestrial orthopyroxene

16:10~16:30

- O22-12 Yoshihiro Nakamuta
Lonsdaleite, doubt on the existence in meteorites

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P22-1 Timothy J. Fagan
Fe-enrichment vs. Si-enrichment in two samples from the moon
- P22-2 Kazuto Saiki
Development and comparison of two types of telescopic imaging spectrometer for the moon
- P22-3 K. Saito, K. Saiki, H. Okuno, A. Suzuki, R. Nakamura
The estimation of the lunar absolute radiance and reflectance by ground-based observation using a tunable liquid-crystal filter
- P22-4 Akira Yamaguchi, Mitsuru Ebihara, Okamoto Chisato
Mineralogy and chemical compositions of several eucrites: Implication for impact processing of the HED parent body

23. Physical and chemical processes and chronology in the solar system (WGA)

Conveners and chairs: Guy Libourel (CNRS, Nancy), Akira Tsuchiyama^{#,*} (Osaka Univ.), Hisayoshi Yurimoto (Hokkaido Univ.)

Oral presentations

Tue. July 25 14:30~16:30 4F 403

14:30~15:10

- O23-1 † Hiroko Nagahara
Evaporation and condensation kinetics for minerals and silicate melt

15:10~15:30

- O23-2 Naoko Matsumoto, Hiroko Nagahara, Kazuhito Ozawa, Shogo Tachibana, Haruka Kawasaki, Shinnosuke Tamada
Evaporation anisotropy of olivine

15:30~15:50

- O23-3 Maho Yamada, Shogo Tachibana, Hiroko Nagahara, Kazuhito Ozawa, Naoko Matsumoto
Evaporation of forsterite in vacuum: anisotropy in rates and Mg isotopic fractionation

15:50~16:10

- O23-4 Akira Tsuchiyama, Kazuhiro Itou, Tomoki Nakamura
Condensation experiments of metallic iron and accompanied isotopic mass fractionation

16:10~16:30

- O23-5 Yuki Kimura, Joseph A. Nuth III, Subrata Chakraborty, Mark H. Thiemens
Non-mass dependent oxygen isotopic fractionation of silicate grains during grain formation in various environments

Wed. July 26 14:30~18:30 4F 403

14:30~14:50

- O23-6 § Martin Bizzarro
Nickel isotopes in meteorites: Evidence for live ^{60}Fe and distinct Ni isotope reservoirs in the early solar system

14:50~15:10

- O23-7 Hisayoshi Yurimoto, Kiyoshi Kuramoto
Origin and evolution of oxygen isotopic compositions of the solar system

15:10~15:30

- O23-8 Miwa Yoshitake, Hisayoshi Yurimoto
Time interval of formation for a type B2 CAI

15:30~15:50

- O23-9 Shoichi Itoh, Sara Russell, Kazuhide Nagashima, Hisayoshi Yurimoto
Oxygen and Al-Mg isotopic compositions of a barred olivine chondrule from NWA1152 C3-ungrouped chondrite

15:50~16:10

- O23-10 Keisuke Murata, Takashi Takakura, Hiroki Chihara, Chiyoe Koike, Akira Tsuchiyama
Crystallization experiment of amorphous silicates with the CI chondritic composition

Break

16:30~16:50

- O23-11 § Akira Kouchi, Hideyuki Nakano, Yuki Kimura, Chihiro Kaito
Diamond formation in interstellar clouds and parent bodies of carbonaceous chondrites

16:50~17:10

- O23-12 § Guy Libourel, Alexander N. Krot
Origin of olivines in type I chondrules

17:10~17:30

- O23-13 Hitoshi Miura, Taishi Nakamoto
Shock-wave heating model for chondrule formation: Relation between external shapes of molten droplets and non-spherical chondrules

17:30~17:50

- O23-14 Taishi Nakamoto
Compound chondrule formation in shock-wave heating model

17:50~18:10

- O23-15 Bertrand Devouard, Nicolas Cluzel, Didier Laporte, Hugues Leroux
Experimental investigation of wetting textures in the Fe-Ni-S system: Application to Bencubbin-like (CB) meteorites

18:10~18:30

- O23-16 Ryoichi Takashima, Takaaki Abe, Chiaki Uyeda
Magnetic alignment of enstatite and forsterite detected by weak field of a horseshoe magnet and determination of field structure in young stellar objects

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P23-1 Haruka Kawasaki, Shinnosuke Tamada, Shogo Tachibana, Hiroko Nagahara, Kazuhito Ozawa, Naoko Matsumoto
Fe-Mg interdiffusion in olivine at 1 atm and in vacuum: Temperature dependence and anisotropy
- P23-2 Birgit Kreher-Hartmann, Falko Langenhorst, Alexander Deutsch, Ulrich Bläß, Klaus Heide
Volatile signatures and geochemical characteristics of impact melt products from the Lake Bosumtwi impact structure, Ghana, W. Africa, and Ivory Coast tektites
- P23-3 Naoya Sakamoto, Hisayoshi Yurimoto
High sensitive ion imaging system using direct combination of stacked-type solid-state imager and microchannel plate

24. Bio-Geo interface in minerals (WGOM, ICAM)

Conveners: Danielle Fortin[#](Univ. of Ottawa), Motoharu Kawano^{*}(Kagoshima Univ.),
Kazue Tazaki (Kanazawa Univ.)

Chairs: Danielle Fortin (Univ. of Ottawa), Kazue Tazaki (Kanazawa Univ.),
Toshihiko Ohnuki (Japan Atomic Energy Agency), Motoharu Kawano (Kagoshima Univ.)

Oral presentations

Wed. July 26 9:00~12:00 5F 503, 504

9:00~9:40

- O24-1 † Jennifer A. Roberts, Charles Knapp, Andrew O'Neill, Ezra Kulczycki, David Fowle, Lindsey Simon, Michail Alterman, Rachel O'Brien, David Graham
Sequestration of Cu from mineral sources by type II methanotrophs

9:40~10:00

- O24-2 § Gordon Southam, Maggy F. Lengke, Bruce Ravel, Mike E. Fleet
The role of bacteria in secondary gold formation

10:00~10:20

- O24-3 § Maria Dittrich, Martin Obst, Bernhard Wehrli
Cyanobacterial calcite nucleation: Driven by photosynthesis or mediated by cell surfaces?

Break

10:40~11:00

- O24-4 § Annette S. Engel, Kelli W. Randall
Microbial colonization and weathering of carbonates in deep subsurface settings

11:00~11:20

- O24-5 § Kazue Tazaki, Hiroaki Watanabe, Ryuji Asada, Koichi Shiraki, Takamasa Iwai, Rie Wakimoto, Majura A. M. Songo, Sospeter M. Muhongo
Clays and bacteria carry important role to release Hg from small scale Au mine near Lake Victoria, Tanzania

11:20~11:40

- O24-6 § Yoshio Takahashi, Danielle Fortin
Rare earth element patterns as biomineralization probes

11:40~12:00

- O24-7 § Yohey Suzuki, Takeshi Suko
Geomicrobiological factors controlling uranium mobility in natural systems

Wed. July 26 14:30~18:30 5F 503, 504

14:30~15:10

- O24-8 † Jon R. Lloyd
Redox transformations at the mineral-microbe interface; mechanisms, environmental impact and biotechnological applications

15:10~15:30

- O24-9 § Toshihiko Ohnuki, Takahiro Yoshida, Ozaki Takuo, Sakamoto Fuminori, Naofumi Kozai, Takuya Nankawa, Yoshinori Suzuki, Arokiasamy J. Francis
Microbial impacts on the environmental behavior of actinides

15:30~15:50

- O24-10 § Yuri A. Gorby
Bacterial nanowires and their role in mineral transformation

15:50~16:10

- O24-11 § David A. Fowle, Arne Sturm, Sean A. Crowe
Microbial controls on heavy metal release from ferrihydrite and iron rich sediments

16:10~16:30

- O24-12 § Sean Langley, Danielle Fortin
Reduction of biogenic iron oxides by *Shewanella putrefaciens* CN32

Break

16:50~17:10

- O24-13 Yoko Masue, Thomas Borch, Ben Kocar, Scott Fendorf
Arsenic attenuation upon bioreduction of ferrihydrite

17:10~17:30

- O24-14 § Asfaw Zegeye, Christian Mustin, Christian Ruby, Frederic Jorand
Factors controlling the biomineralization pathways of γ -FeOOH into green rust vs magnetite

17:30~17:50

- O24-15 § Xavier Châtellier, Mohamad Fakihi, Laurence Bourcereau, Joseph Le Lannic, Philippe Vandenkoornhuys
Bacteria and the oxidation of iron at neutral or near neutral pH

17:50~18:10

- O24-16 § Mihály Pósfai, Takeshi Kasama, Edward T. Simpson, Ryan K.K. Chong, Ilona Kósa, André Scheffel, Dirk Schüller, Rafal E. Dunin-Borkowski
Spatial arrangements and magnetic properties of oxide and sulfide magnetosomes in magnetotactic bacteria

18:10~18:30

- O24-17 Katja Etzel, Jan Toporski, Wulf Depmeier, Harald Huber, Reinhard Rachel, Michael Thomm, Gottfried Schmalz
Pyrite surface alteration as effect of microbial activity and crystallographic orientation

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P24-1 Kazue Tazaki, Hiroaki Watanabe, Siti K. Chaerun, Koichi Shiraki, Ryuji Asada
Hydrocarbon-degrading bacteria and paraffin from the Nakhodka oil spill-polluted seashores in the Sea of Japan after 9 years of bioremediation

- P24-2 Katsuaki Watanabe, Ohfuji Hiroaki, Ando Jun-ichi, Kitagawa Ryuji
Elemental behavior during the corrosion process of *sekishu* roof-tile glaze affected with *Lecidea* s.lat. sp
- P24-3 Jinghua Shi, Fei Liu, Honghan Chen, Ye Li
Degradation of tetrachloroethene by several co-metabolism substrates in groundwater
- P24-4 Ye Li, Fei Liu, Honghan Chen, Jinghua Shi, Yufan Wang
Anaerobic biodegradation of tetrachloroethylene with acetic acid as cometabolism substrate
- P24-5 Tomoyuki Matsui, Kazuko Saruwatari, Michio Suzuki, Hiromichi Nagasawa, Toshihiro Kogure
New insight into the nucleation and growth mechanism of nacreous aragonite in pearl oyster
- P24-6 Haruhiko Seyama, Yukinori Tani, Naoyuki Miyata, Mitsuyuki Soma, Keisuke Iwahori
Analysis of pebble surfaces coated with biogenic manganese oxides
- P24-7 Motoharu Kawano, Katsutoshi Tomita
Rate enhancement of kaolinite dissolution by interaction with proteins released from bacterial cells
- P24-8 Masayuki Okuno, Yuka Kitagawa, Ryuji Asada, Kazue Tazaki
Structural change of non-crystalline biogenic silica of diatoms by heat treatment
- P24-9 Adrijana Bocek, Vladimir Bermanec, Ivan Sondi
Precipitation of calcium carbonate polymorphs effectuated through catalytic decomposition of urea in solutions of calcium salts
- P24-10 Milan Rieder, Jiri Fryda, Patricie Tycova, Jakub Haloda, Mariana Klementova
Texture of aragonite in nacre: The potential of different diffraction techniques
- P24-11 Seigo Sato, Kakegawa Takeshi
Fossilized chemoautotrophic microorganism in artificial drilled holes at the suiyo submarine hydrothermal field, Izu-Bonin arc, Western Pacific, Japan
- P24-12 Noboru Furukawa, Koji Kameo
Crystallographic direction of coccolith elements of the marine alga *Braarudosphaera* and its fossil group, *discoaster* spp.
- P24-13 Sang Soo Lee, Kathryn L. Nagy, Paul A. Fenter, Changyong Park, Neil C. Sturchio
In-situ X-ray reflectivity study of the mica-fulvic acid interface in aqueous solutions containing barium and mercury
- P24-14 Masaharu Nakagawa, M. Santosh, C.G. Nambiar, G.N. Hariharan, J. Imadate
Morphology and chemistry of placer gold from Chaliyar River, Southern India
- P24-15 Norio Kitadai, Satoru Nakashima
Changes in secondary structures of dissolved polypeptides with pH, salts and temperature as analyzed by attenuated total reflection infrared spectroscopy (ATR-IR)
- P24-16 Hiroki Imanishi, Kazue Tazaki
Characteristics of black and reddish brown microbial mats in spring water
- P24-17 Issei Morii, Kazue Tazaki
The shell nacre of *Sinohyaliopsis schlegeli* recorded water environmental factor
- P24-18 Takuya Nankawa, Yoshinori Suzuki, Takuo Ozaki, Toshihiko Ohnuki, Arokiasamy Joseph Francis
Effect of trivalent actinides on the degradation of malic acid by *pseudomonas fluorescens*
- P24-19 Tatsuya Shirotori, Kazue Tazaki
Radioactive biofilm in Tamagawa Hot Springs at Akita prefecture
- P24-20 Yul Roh, Hee-Dong Jang, Ji-Hoon Lee, Hor-Gil Hur
Biomining of magnetite nanoparticles by fermentative processes

- P24-21 Jun Aizawa, Kazuhisa Yoshimura, Kousuke Kurisaki
Origin and genesis of phosphate and related minerals from Senbutsu-do cave, Fukuoka prefecture, Southwest Japan
- P24-22 Fa-qin Dong, Qun-wei Dai, Jian-jun Deng
Effect of several kinds of mineral dusts to the growth of silicate bacteria S35
- P24-23 Shengrong Li, Yonghua Gao, Liangfeng Yang, Ye Cao, Junyan Luo, Jinggui Tong
A new way for evaluation of lake water quality: Mineralogical study of fish otoliths

25. Mineral-water interactions: from microscopic to macroscopic aspects (ICAM)

Conveners: Jordi Cama (CSIC, Barcelona), Takashi Murakami^{*,*}(Univ. of Tokyo),
Arthur F. White (U. S. Geological Survey)

Chairs: Takashi Murakami (Univ. of Tokyo), Jordi Cama (CSIC, Barcelona), Andreas Lutge
(Rice Univ.), Willem Van Riemsdijk (Wageningen Univ.), Katsuhiro Tsukimura
(AIST)

Oral presentations

Thur. July 27 9:00~12:00 3F 301

9:00~9:40

O25-1 † Roland Hellmann

The role of near-surface alteration at the fluid-mineral interface: evolving views on the mechanisms of dissolution

9:40~10:00

O25-2 § Claudine Noguera, Bertrand Fritz, Alain Clement, Alain Baronnet

NANOKIN: A geochemical computer model for dissolution, nucleation and growth of minerals in aqueous solutions

10:00~10:20

O25-3 Osamu Tamada, Gerald V. Gibbs, Monte B. Boisen, Kazuhiko Ito, Keiko Kuzawa,
Donald J. Rimstidt

Simulated water attack modeled for silica

10:20~10:40

O25-4 Katsuhiro Tsukimura

Predicting mineral phases formed at low temperatures

Break

11:00~11:20

O25-5 § Michael A. Velbel

Natural weathering processes and surface textures of pyroxenes and amphiboles

11:20~11:40

O25-6 Zainuddin M. Yusoff, Ian Parsons, Bryne T. Ngwenya, Steve Hillier

Mechanisms of feldspar dissolution in the tropics

11:40~12:00

O25-7 § Takashi Murakami, Bulusu Sreenivas, Subrata Das Sharma

Relation of redox-sensitive elements in Precambrian paleosols to atmospheric oxygen evolution

Fri. July 28 9:00~12:00 1F Main Hall

9:00~9:20

O25-8 § Tjisse Hiemstra, Willem H. Van Riemsdijk, Liping Weng

Linking a microscopic approach to macroscopic observations for ion adsorption on mineral surfaces

9:20~9:40

- O25-9 Jeffrey G. Catalano, Changyong Park, Zhan Zhang, Paul Fenter
Simultaneous inner- and outer-sphere As(V) adsorption on iron and aluminum oxide surfaces

9:40~10:00

- O25-10 Mathias Flörsheimer, Krause Kruse, Ahmed Abdelmonem, Jae-II Kim, Thomas Fanghanel
Speciation of the functional groups at mineral surfaces in situ under water by sum frequency vibrational spectroscopy

10:00~10:20

- O25-11 Thorsten Stumpf, Silvia Stumpf, Maria Marques Fernandes, Clemens Walther, Andreas Bauer, Thomas Fanghanel
Elucidation of geochemical reactions at the water-mineral interface on a molecular level by time resolved laser fluorescence spectroscopy with Cm(III)

Break

10:40~11:00

- O25-12 § Andreas Luttge, Rolf S. Arvidson, Li Zhang, Michael D. Vinson
Time and length scales of crystal dissolution kinetics

11:00~11:20

- O25-13 Pete Morris, Roy A. Wogelius
Conditioning film formation: Bonding environment, crystallographic and chemical controls

11:20~11:40

- O25-14 David Brown, Caroline L. Smith, Maureen MacKenzie, Mark E. Hodson, Roland Hellmann, Martin R. Lee
High-resolution characterization of naturally weathered mineral surfaces by focused ion beam and transmission electron microscopy

11:40~12:00

- O25-15 Tadashi Yokoyama, Satoshi Okumura, Satoru Nakashima
Water distribution profile in a weathered rhyolitic glass as measured by IR microspectroscopy

Fri. July 28 14:30~16:10 1F Main Hall

14:30~14:50

- O25-16 Fei Liu, Yuanying Huang, Weihua Cui
Impact factors on removal of perchloroethylene with nano-Ni/Fe methodology

14:50~15:10

- O25-17 Chun-Jung Chen, Wei-Teh Jiang
Precipitation of iron oxyhydroxide compounds in relation to stream and seawater chemistry in the Chinkuashih acid mine drainage area, Northern Taiwan

15:10~15:30

- O25-18 Dieter Rammlmair, Torsten Graupner, Markus Furche, Andrea Kassahun, Antonio Romero Baena
Processes of hardpan formation in extreme pH environments

15:30~15:50

- O25-19 Marek Michalik, Wanda Wilczynska-Michalik
Minerals formed in weathering reactions zones on rocks in polluted atmosphere (examples from SE Poland)

15:50~16:10

- O25-20 Wanda Wilczynska-Michalik, Marek Michalik
Weathering of the upper Jurassic limestone in polluted urban atmosphere: Results of mineralogical and isotopic study

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P25-1 Norio Yanagisawa, Matsunaga Isao, Sugita Hajime, Sato Masatake, Okabe Takashi
Calcite and anhydrite precipitation in the geothermal test field at Hijiori, Yamagata, Japan
- P25-2 Munetake Sasaki
A preliminary study on numerical modeling of seawater-sedimentary rock interaction for CO₂ sequestration
- P25-3 Yohei Yoshimura, Daizo Ishiyama, Osamu Matsubaya, Kazuhiko Kano, Masatsugu Yamamoto, Takeshi Ohguchi, Naoya Miyoshi, Nobuyuki Aikawa, Toshio Mizuta
Hydration mechanism of glassy rhyolite, pleistocene Katsuma-Yama volcano, Okushiri Island, Hokkaido, Japan
- P25-4 Hinako Satoh, Daizo Ishiyama, Toshio Mizuta, Osamu Matsubaya
Characteristic features of radium-lead-strontium-bearing Tamagawa thermal water related to a deep-seated magmatic system in Akita prefecture, Japan
- P25-5 Satoru Suzuki, Katsuyuki Kawamura
Study of molecular structure of water in tiny clay minerals by the variable-angle polarized IR spectroscopy
- P25-6 § Elodia Musu, Jordi Cama, Stefania DaPelo, Pierfranco Lattanzi, Giovanni DeGiudici, Luca Fanfani
AFM study of enargite-solution interface at basic pH
- P25-7 M. Pilar Asta, Stefania Da Pelo, Mario Lorrai, Elodia Musu, Carlo Ricci, Jordi Cama, Giovanni De Giudici, Luca Fanfani, Pierfranco Lattanzi
Kinetics of arsenopyrite oxidative-dissolution: A multiscale approach
- P25-8 Hirokazu Sugimori, Takashi Murakami
Dissolution of Fe-bearing silicate minerals under low P_{O₂} conditions and implications for late archean - early paleoproterozoic weathering
- P25-9 Yoshihiro Kuwahara
In-situ observations of the dissolution of muscovite and smectite under alkaline conditions at 25-50°C by AFM with an air/fluid heater system
- P25-10 Takeshi Tomita, Shoichi Kobayashi, Takabumi Sakamoto
Alteration process of gabbroic building stone by CO₂ saturated water
- P25-11 Eiki Ogura, Shoichi Kobayashi, Takabumi Sakamoto
Artificial chemical weathering of olivine under earth surface conditions
- P25-12 Yasuhiko Takaya, Tamao Hatta, Seiko Nemoto, Yukinori Matsukura
Surface analytical approaches to artificial weathering of granite and its constituent minerals by AFM and XPS
- P25-13 Masao Sorai, Takashi Ohsumi, Masamichi Ishikawa, Katsuo Tsukamoto
Measurement of feldspar dissolution rate and its implication to the underground CO₂ storage
- P25-14 Nobuo Hirano, Yosuke Ota, Noriyoshi Tsuchiya
Critical point measurements of binary and ternary fluid mixture by direct observation using the visible-type autoclave
- P25-15 Akiko Ito, Tsutomu Sato, Kenichi Ito
Removal and immobilization of hazardous anions by blast furnace slag
- P25-16 Laurent J. Michot, Isabelle Bihannic, Karine Devineau, Frédéric Villières, Dimitri Prêt, Jean-Charles Robinet, P. Sardini, Stéphane Sammartino, Marco Stamponi, Nicolas Michau
In situ neutron diffraction and synchrotron X-Rays tomography analyses of the influence of geometric confinement on the crystalline swelling of montmorillonites

- P25-17 Yoshihisa Iida, Tetsuji Yamaguchi, Fumika Yamada, Toshikatsu Maeda, Yoshifumi Sakamoto, Tsuyoshi Mizuno, Tadao Tanaka, Shininchi Nakayama
Modeling of pore-water chemistry as a common base for understanding dissolution of montmorillonite and mass transport in compacted bentonite
- P25-18 Fumika Yamada, Tetsuji Yamaguchi, Toshikatsu Maeda, Tsuyoshi Mizuno, Yoshifumi Sakamoto, Kumi Negishi, Tadao Tanaka, Yoshihisa Iida
Development of a coupled mass-transport / chemical reaction code for simulating variation in hydraulic conductivity of bentonite buffer in radioactive waste disposal

26. Environmental and medical mineralogy (ICAM, WGEM)

Conveners: Anhuai Lu (Pekin Univ.), Mihaly Posfai (Univ. of Veszprem),
Tsutomu Sato^{*,*} (Kanazawa Univ.), David J. Vaughan (Univ. of Manchester),
Roy Wogelius (Univ. of Manchester)

Chairs: Anhuai Lu (Pekin Univ.), Mihaly Posfai (Univ. of Veszprem), Tsutomu Sato
(Kanazawa Univ.), David J. Vaughan (Univ. of Manchester)

Oral presentations

Tue. July 25 9:00~12:00 5F 503, 504

9:00~9:30

- O26-1 † Peter R. Buseck, Kouji Adachi, Trudi Semeniuk, Matthew E. Wise
New approaches to studying individual small particles

9:30~9:45

- O26-2 Mihály Pósfai, Renáta Simonics, Viktória Kovács Kis, János Lábár
Compositions, structures, and surface properties of carbonaceous aerosol particles from the continental atmosphere

9:45~10:00

- O26-3 Yuka Kishikawa, Tomoko Kojima
Hygroscopicity of sulfate coated mineral-dust particles: Experiments using an environmental scanning electron microscope

10:00~10:15

- O26-4 Anhuai Lu, Shanshan Huang, Rui Liu, Dongjun Zhao, Shan Qin
Environmental effects of micro- and ultramicro-channel structures of natural minerals

Break

10:35~10:55

- O26-5 § John L. Jambor, John E. Dutrizac, Mati Raudsepp
Quantitative mineralogy applied to the prediction of acid mine drainage

10:55~11:10

- O26-6 David J. Vaughan, Rebeca Alvarez, Nick Bryan, Marina Fomina, Geoff Gadd, Stephanie Handley, Miranda Keith-Roach, Francis Livens, Jon Lloyd
Geochemical and Microbial controls of the decomposition and dispersion of depleted uranium in the environment

11:10~11:30

- O26-7 § Georges Calas, Guillaume Morin
Arsenic in soils, mine tailings, and former industrial sites

11:30~11:45

- O26-8 Andrew G. Gault, John Waters, John M. Charnock, Roy A. Wogelius, David G. Kinniburgh, David A. Polya
Ferrihydrite precipitates aged over 25 years: Structural evolution and reactivity with dissolved arsenic

11:45~12:00

- O26-9 Jayappa Manjanna, Tamotsu Kozaki, Naofumi Kozai, Seichi Sato
Use of Fe(II)-montmorillonite for the reduction of aqueous Cr(VI)

Tue. July 25 14:30~16:20 5F 503, 504

14:30~14:50

- O26-10 § H. Catherine W. Skinner
Minerals and disease: asbestos and apatite

14:50~15:05

- O26-11 Michele C. Warren, Katie J. Finch, Alexander I. R. Stark, Paul L. Wincott, David J. Vaughan
Surface structure, growth and Ca²⁺ incorporation on barite (001) and (210)

15:05~15:20

- O26-12 Maggie L. White, David A. C. Manning
Use of stable isotopes to distinguish mechanisms of calcite precipitation in response to different landfill operational environments

15:20~15:35

- O26-13 Friedlinde Goetz-Neunhoeffer, Matthias Goebbels, Ralph Enderle
Investigation of the β - α TCP phase transformation in dependence of Mg-content

15:35~15:50

- O26-14 Chelo S. Pascua, Tsutomu Sato, Hirohisa Yamada, Atsushi Asai
Low temperature formation of clay minerals from aqueous starting materials

15:50~16:05

- O26-15 Tsutomu Sato, Masato Kuroda, Shingo Yokoyama, Keisuke Fukushi
Kinetics of smectite dissolution for safety assessment of radioactive waste disposal

16:05~16:20

- O26-16 Hassan M. Baioumy, Hajime Kayanne, Ryuji Tada, Yozo Hamano, Mohamed M. Abu El-Hassan, Gad M. Al-Qady
Clay minerals from Lake Qarun sediments, Egypt and their climatic implications

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P26-1 Vera Cardile, Armanda Pugnali, Antonio Gianfagna, Simona Mazziotti Tagliani, Laura Lombardo, F. Giantomassi, Luigi Paoletti, Biagio Maria Bruni, Alessandro Pacella
In vitro toxicity of the new fluoro-edenite amphibolic fibres from Biancavilla (Mt Etna, Sicily, Italy).
- P26-2 Biagio Maria Bruni, Alessandro Pacella, Simona Mazziotti Tagliani, Antonio Gianfagna, Luigi Paoletti
Nature and extent of the exposure to fibrous amphiboles in Biancavilla (Sicily, Italy).
- P26-3 Takuma Yoshida, Akira Sasahira, Kenji Noshita, Keita Okuyama, Kazuyuki Kato, Katsuhito Futakuchi, Takeo Kaneko, Shinya Nagasaki, Toshiaki Ohe
Development of "in-situ" measurement device for geochemical diagnosis
- P26-4 Chie Kwaragi, Tetsuro Yoneda, Yusuke Nakamura, Kouki Kashiwaya, Katsuhiko Kaneko
Micro-structural modeling of bentonite barrier for solid waste disposal by means of X-ray computerized tomography and near-infrared spectroscopy
- P26-5 Yusuke Otani, Sato Tsutomu
Kinetics of smectite dissolution at highly alkaline condition: Effect of dissolved silica and aluminum
- P26-6 Yukie Ota, Tsutomu Sato, Syohei Ohara, Syui Tamamura, Takeshi Kakegawa
Adsorption and polymerization of amino acid on mineral surface
- P26-7 Kazuya Morimoto, Tsutomu Sato
Complexation reactions of anions on hydrotalcite surface

- P26-8 Shuji Tamamura, Tsutomu Sato, Yukie Ota, Ning Tang, Kazuichi Hayakawa
Decomposition of PAHs on mineral surfaces under relative humidity controlled conditions
- P26-9 Morio Takada, Tsutomu Sato
Kinetics of transformation from schwertmannite to goethite
- P26-10 Wei-Teh Jiang, Chun-Jung Chen
An EXAFS study of arsenate sorption in synthetic and natural schwertmannite
- P26-11 Kenichi Ito, Sato Tsutomu, Fukushi Keisuke, Hashimoto Koichi, Katagiri Ayumi, Ito Akiko, Minato Mio, Ota Yukie
A novel remediation method learnt to natural attenuation processes in acid mine drainage
- P26-12 Norimichi Suzuki, Ayako Tamura, Junji Akai
Absorbed characteristics of arsenic in holocene sediments: Comparison of drilling core samples from Niigata plain, Japan and Bangladesh

27. Clays and zeolites: natural and synthetic materials (ICAM)

Conveners: Toshihiro Kogure^{*,*}(Univ. of Tokyo), Osamu Terasaki (Stockholm Univ.),
Atsushi Yamazaki (Waseda Univ.)

Chairs: Stephen Guggenheim (Univ. of Illinois at Chicago), Toshihiro Kogure (Univ. of Tokyo), Bruno Lanson (Univ. Grenoble-CNRS), Alain Baronnet (CRM-CN-CNRS)

Oral presentations

Fri. July 28 9:00~12:00 4F 402

9:00~9:30

- O27-1 § Alain J. Baronnet, Olivier Grauby, Muriel Andreani, Bertrand Devouard, Nina Krasnova
A TEM/AEM survey of serpentine microstructures

9:30~10:00

- O27-2 § Bruno Lanson, Victor A. Drits, Alain Manceau
Crystal-chemistry of lamellar manganese oxides

10:00~10:20

- O27-3 Toshihiro Kogure, Jun Kameda, Tomoyuki Matsui, Ritsuro Miyawaki
Stacking structure in disordered talc: Interpretation of its X-ray diffraction pattern by using pattern simulation and high-resolution transmission electron microscopy

Break

10:40~11:10

- O27-4 § Osamu Terasaki, Juanfang Ruan, Zheng Liu, Tetsu Ohsuna
Fine structures of zeolites: TEM study

11:10~11:40

- O27-5 § Tatsuya Okubo, Toru Wakihira
Crystal growth of zeolites observed by atomic force microscopy

11:40~12:00

- O27-6 Charles A. Geiger, Boris A. Kolesov
Molecule-mineral interactions in micro- and nanoporous silicates: A vibrational study using IR and raman spectroscopy

Fri. July 28 14:30~16:20 4F 402

14:30~15:00

- O27-7 § Stephen Guggenheim, August F. Koster van Groos
Complexes of methane hydrate and clay

15:00~15:20

- O27-8 Bum Han Lee, Sung Keun Lee
Interactions between kaolinite siloxane surfaces and benzyl alcohol: Quantum chemical calculations

15:20~15:40

- O27-9 Hideo Minato
New remediating technology for contaminated soils and new barrier material for waste sites in urban areas with applications of mineral compounds, clays and zeolites

15:40~16:00

- O27-10 Jun Kameda, Ritsuro Miyawaki, Ryuji Kitagawa, Toshihiro Kogure
Investigation of the stacking structure in sudoite by using high-resolution electron microscopy

16:00~16:20

- O27-11 Bruno Lanson, Boris A. Sakharov, Francis Claret, Victor A. Drits
Diagenetic evolution of clay minerals in Gulf Coast shales: New insights from X-ray diffraction profile modeling

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P27-1 Ryuji Kitagawa, Kouich Suemine, Mayumi Jige, Tetsurou Hirono, Toshihiko Shimamoto
Clay mineralogical characteristics of decollement zone at the Nankai trough (ODP; Leg190-site1174)
- P27-2 Gulzhan A. Kudaikulova
Investigation of Kazakhstan bentonite
- P27-3 Ildiko Cora, Erzsebet Toth, Tamas Weiszbarg
Mineralogical study of upper cambrian glauconites from Texas, USA
- P27-4 Hirohisa Yamada, Shingo Yokoyama, Kenji Tamura, Takashi Watanabe
Synthesis of interstratified clay minerals from (K, Na)-saponite glass at hydrothermal conditions
- P27-5 Kiyotaka Ishida
Crystal chemistry of ^{IV}Si-for-^{IV}Ge substituted phlogopites with interlayer K and Rb: Similarities and differences for their evolutions
- P27-6 Shoji Higashi, Akihide Tsubomoto
Interstratified system of Illite-tobelite for NH₄-bearing mica clay minerals
- P27-7 Il Mo Kang, Ja Lang Gu, Won Pyo Lee, Yongjae Lee, Yungoo Song, Hi-Soo Moon, Youn Joong Kim
Derivation of an equation to quantify the layer proportion of randomly interstratified illite-smectite using the peak width of X-ray basal reflection
- P27-8 Judit Toth, Mariann Kallai, Andrea Lukacs
Gasoline pollution modelling in laboratory
- P27-9 Anastasia Dewi Titisari, Lucas D. Setijadji, Widiasmoro, Koichiro Watanabe
Natural zeolite deposits from Lower Tertiary volcanic formations in Southern Mountains region, central Java, Indonesia
- P27-10 Inkook Bae, Yongnam Jang, Soochun Chae, Sungki Lee, Kyoungwon Ryu
Synthesis and characterization of zeolite using slag melted from municipal incineration ash
- P27-11 Takaaki Wajima, Takeshi Hirai, Tomoe Shimizu, Kazuharu Yoshizuka, Yasuyuki Ikegami
Synthesis of zeolitic material from waste sandstone filler using alkali fusion method
- P27-12 Anna G. Turchkova, Igor V. Pekov, Igor A. Bryzgalov
Cation-exchange properties of natural zeolite-like sodium zirconosilicates: an experimental study in aqueous solutions at 80-90°C and 1 atm

- P27-13 Libing Liao, Zhenyu Huang
Preparation and characterization of epoxy resin/vermiculite nanocomposites
- P27-14 Fumihiko Ohashi, Hiroko Hase, Shin-Ichiro Wada
Characterization and photocatalytic properties of synthetic allophane-coated titanium dioxide nanocomposites

28. Crystals, ceramics and glasses with advanced physico-chemical properties (CAM, ICAM)

Conveners: Georges Calas (Univ. of Paris), Richard Hagni (Univ. of Missouri-Rolla), Falko Langenhorst (Jena Univ.), Masatomo Yashima (Tokyo Inst. of Technology), Akira Yoshiasa*(Kumamoto Univ.), Satoshi Uda (Tohoku Univ.)

Chairs: Falko Langenhorst (Jena Univ.), Georges Calas (Univ. of Paris), Masatomo Yashima (Tokyo Inst. of Technology), Satoshi Uda (Tohoku Univ.), Akira Yoshiasa (Kumamoto Univ.)

Oral presentations

Mon. July 24 9:30~12:00 4F 402

9:30~10:00

- O28-1 † Hans-Joachim Kleebe
Phase separation in carbon-rich SiOC glasses: The evolution of nano-domains

10:00~10:30

- O28-2 † Laurence Galois, Georges Calas, Laurent Cormier
The environment of transition elements in oxide glasses

10:30~10:45

- O28-3 Georges Calas, Laurence Galois, Laurent Cormier, Odile Majerus
Spectroscopy of chromium in borate and borosilicate glasses: Local structure, redox states and thermal expansion

10:45~11:00

- O28-4 Dario Manara, Agnes Grandjean, Daniel R. Neuville
Structural factors governing the sulphate incorporation in borosilicate glasses

Break

11:10~11:30

- O28-5 § Akira Yoshikawa, Tsuguo Fukuda
Synthesis of novel single crystalline materials for electrical, optical and medical applications using the advanced crystal growth technique

11:30~11:45

- O28-6 Satoshi Uda, Xinming Huang, Shinji Koh
Conversion of the melting state of langasite from incongruent into congruent by an external electric field

11:45~12:00

- O28-7 Armando H. Shinohara, Kazumasa Sugiyama
Characterization of synthetic quartz crystals grown on cylindrical and V-notched seeds by the X-ray topography

Tue. July 25 14:30~16:30 5F 505

14:30~14:50

- O28-8 § Masatomo Yashima
Precise structural analysis and phase transition of inorganic materials through high-temperature neutron and synchrotron diffraction techniques

14:50~15:05

- O28-9 Matthias Göbbels, Andreas Wesselsky, Nico Langhof
Crystal chemistry of La- and Co-doped Sr-Hexaferrites

15:05~15:20

- O28-10 Kazumasa Sugiyama, Yasutaka Takemaru, Masatoshi Saito
The structural analysis of disordered materials by the anomalous X-ray scattering coupled with reverse monte carlo simulation

Break

15:30~15:45

- O28-11 Akihiko Nakatsuka, Yuya Miyake, Noriaki Nakayama, Ikuta Yasuaki, Hiroki Okudera, Akira Yoshiasa, Kazuake Iishi
Correlation between atomic thermal vibrations and cation-cation repulsions in vanadate garnets $\text{NaA}_2\text{M}_2\text{V}_3\text{O}_{12}$ (A = Ca, Pb; M = Mg, Mn, Co, Ni, Cu, Zn)

15:45~16:00

- O28-12 Herbert Pöllmann
Measurement and description of water in synthetic ettringite and kuzelite

16:00~16:15

- O28-13 Maria G. Krzhizhanovskaya, Rimma S. Bubnova, Stanislav K. Filatov, Valeriy L. Ugolkov
New members of zeolite family, $(\text{Cs,Rb})\text{BSi}_5\text{O}_{12}$ borosilicates: Preparation and Cs-Rb substitution

16:15~16:30

- O28-14 Axel Müller, Peter M. Ihlen
Trace element geochemistry of pegmatitic quartz and associated minerals in the Froland pegmatite field, Norway

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P28-1 Karolina Schwendtner, Uwe Kolitsch, Ekkehart Tillmanns
 $\text{Al}(\text{H}_2\text{AsO}_4)(\text{H}_2\text{As}_2\text{O}_7)$ - a novel strongly acidic structure type and the first structural characterization of a diprotonated diarsenate group
- P28-2 Hiroki Okudera
Precipitation of amorphous silica from alcohol solution of Si-tetraethoxide
- P28-3 Shunsuke Sakai, Akira Yoshiasa, Kazumasa Sugiyama, Riturou Miyawaki
Structures and properties of $\text{CaCu}(\text{AsO}_4)(\text{OH})$ and related minerals
- P28-4 Kei-ichiro Murai, Yasuhiro Akune, Toshihiro Moriga
Local structure analysis of rutile-type RuO_2 and TiO_2 by X-ray spectroscopy
- P28-5 Takahumi Hashimoto, Akira Yoshiasa, Maki Okube, Masatomo Yashima, Hiroki Okudera, Akihiko Nakatsuka
XAFS study of the local structure changes in ATiO_3 , A_2TiO_4 and TiO_2 (A=Mg, Ca, Ba, Pb, Nb, Fe) compounds
- P28-6 Qi Xu, Masatomo Yashima, Akira Yoshiasa
Crystal structure and phase transition of the fast-ion conductor CuI
- P28-7 Hideki Kanazawa, Kazuhiko Ito, Hiroki Sato, Mizuho Kumatoriya, Kazuhiro Miyazaki, Seiichiro Uehara, Naoyuki Kawame, Keiko Kuzawa, Osamu Tamada
Growth of forsterite single crystal doped by Cr and their optical properties
- P28-8 Akira Yoshiasa, Maki Okube, Hiroshi Fukui, Hiroshi Arima, Yoshinori Katayama, Kei-ichiro Murai, Osamu Ohtaka
EXAFS and diffraction study of AgI under high pressure and high temperature

29. Process mineralogy (CAM, ICAM)

Conveners: Henrique Kahn (Univ. of Sao Paulo), Tadato Mizota (Yamaguchi Univ.),
Kazumasa Sugiyama^{*,*} (Univ. of Tokyo)
Chairs: Richard D. Hagni (Univ. of Missouri-Rolla), Kazumasa Sugiyama (Univ. of Tokyo),
Alfonso G. Trudu (CSIRO Minerals)

Oral presentations

Mon. July 24 15:30~18:30 5F 505

15:30~16:00

- O29-1 † Alfonso G. Trudu, James R. Manuel, Jason M. Young
Geometallurgy of Australian iron ores, and a comparison with their Brazilian counterparts

16:00~16:20

- O29-2 § Dogan Paktunc
Influence of arsenic on the recovery of gold from refractory gold ores evidenced from SIMS and XAFS studies

16:20~16:40

- O29-3 § Kiyoshi Okada, Yoshikazu Kameshima, Chengala D. Madhusoodana, Kenneth J.D. MacKenzie
Functional materials prepared by processing kaolin minerals

Break

17:00~17:15

- O29-4 Sabine M. C. Verryn, Johan P. R. de Villiers
Quantitative X-Ray powder diffraction analysis of iron-ore sinters

17:15~17:30

- O29-5 Richard D. Hagni
Application of cathodoluminescence microscopy to fluorspar ores and concentrates: Fluorspar deposits, Okorusu, Namibia

17:30~17:45

- O29-6 Roger Meier
The referenced rietveld analysis, a key tool to reduce energy consumption and CO₂ emissions in cement production

17:45~18:00

- O29-7 Joe Zhou, Inna Dymov, Chris Martin, Chris Fleming
Gold in refractory ores: Deportment and its impact on metallurgical processing

18:00~18:15

- O29-8 Ying Gu, Debra Burrows
Quantitative ore texture characterization

18:15~18:30

- O29-9 Robert Schouwstra, Dieter Rammlmair
Detailed chemical stratigraphy of PGE bearing horizons of the bushveld complex, SA

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P29-1 Kari Moen, Terje Malvik, Lisbeth Alnæs, Jarle Hjelen
Quantification of marble microstructure - a model for predicting the deterioration of marble

30. Mineralogical and geological museums (CM)

Conveners: William D. Birch[#](Museum of Victoria), George E. Harlow (Amer. Museum of Natural History), Ritsuro Miyawaki^{*}(National Science Museum)

Chairs: William D. Birch (Museum of Victoria), George E. Harlow (Amer. Museum of Natural History)

Oral presentations

Mon. July 24 9:30~12:00 5F 503, 504

9:30~10:00

O30-1 † Michiaki Bunno

Mineral collections and mineralogical museums in Japan - a review

10:00~10:20

O30-2 § Igor V. Pekov

Classic mineral localities of Russia: History and present day

10:20~10:40

O30-3 § Mark Mauthner, George E. Harlow, Carl Francis

Toward mineral database standards for world-wide-web utilization

10:40~11:00

O30-4 Dermot A. Henry, William D. Birch

Fake gold but real history: The gold nugget replica collection of Museum Victoria

11:00~11:20

O30-5 Boris M. Shmakin

Slyudyanka region at Baikal as a natural mineral museum

11:20~11:40

O30-6 Lydie Touret

From mineralogy to petrography: A new trend for education at the Ecole Impériale des mines

11:40~12:00

O30-7 Yuhua Li, Zhongpeng Jia

The GMC: A centre of mineral collections, fine displays and communications

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P30-1 Kay Uwe Schüermann, Peter Koenigshof

The mineral collection of the Senckenberg Museum: An ancient collection - a new approach

P30-2 Hans-Peter Scherl, Gilla Simon, Kay Uwe Schüermann

Mineral collections and museums in Germany: Past, presence, future

P30-3 § Yoshihiro Nakamuta, Seiichiro Uehara

Ko collection of minerals and the Kyushu University Museum, Japan

P30-4 § Yasuyuki Banno, Michiaki Bunno, Masahiro Aoki, Makoto Haruna, Yasuko Okuyama-Kusunose, Chisayo Matsue

The mineralogical collections of the Geological Museum, geological survey of Japan

P30-5 Satoshi Matsubara, Kazumi Yokoyama, Ritsuro Miyawaki, Yukiyasu Tsutsumi

Special exhibition, "Jadeite", and collection of jadeite-bearing rocks in NSM

P30-6 Osamu Nishikawa, Takahiko Maruyama

Mineral Industry Museum, Faculty of Engineering and Resource Science, Akita University

P30-7 Akira Ueda

The Mitsubishi Wada mineral collection

P30-8 Daiji Hirata, Hiroyuki Yamashita, Akira Kato

Outline of Kanagawa Prefectural Museum of natural history, Japan

- P30-9 Tatsuo Obayashi
Nakatsugawa Mineral Museum and the Nagashima mineral collection
- P30-10 § Hiroshi Miyajima, Ko Takenouchi, Yosuke Ibaraki
Fossa Magna Museum in Itoigawa, Central Japan
- P30-11 Tohru Sakiyama
Application of mineralogy and petrology to lifelong education in the Museum of Nature and Human Activities, Hyogo
- P30-12 § Mamoru Adachi, Hidekazu Yoshida
Japan's oldest rocks and minerals stored at Nagoya University Museum
- P30-13 Wataru Koike
Detailed records and sketching of minerals by collector, Nambu Mineral Collection of Ibaraki Nature Museum
- P30-14 Yasushi Mori
Kitakyushu Museum of Natural History and Human History: Activities on mineralogy and petrology
- P30-15 Takashi Fujiwara, Ai Nagatomi
Introduction of Masutomi Geology Museum
- P30-16 Toshiaki Kitagaki, Kenichi Sunohara
Introduction of The Kiseki Museum of World Stones
- P30-17 § Toshiro Nagase
Mineral collections of Natural History Museum of Tohoku University
- P30-18 Naoki Takahashi
Introduction of the Natural History Museum and Institute, Chiba
- P30-19 § Hiroharu Matsueda, Kiyooki Niida, Hiroyuki Miura, Makoto Kawamura, Ryohei Takahashi, Yuuki Komata
Geological exhibition of the Hokkaido University Museum and the database for the collection of rocks, minerals and ores
- P30-20 Yurika Tachibana, Tokuhei Tagai
The Wakabayashi mineral collection

31. New minerals and mineral classification (CNMMN, CCM)

Conveners: Giovanni Ferraris (Univ. of Torino), Satoshi Matsubara^{*,*}(National Science Museum), Zhuming Yang (Chinese Academy of Sci.)
Chairs: Giovanni Ferraris (Univ. of Torino), Zhuming Yang (Chinese Academy of Sci.), Satoshi Matsubara (National Science Museum), Ekkerhart Tillmanns (Univ. Wien, Geozentrum)

Oral presentations

Tue. July 25 9:00~12:00 4F 402

9:00~9:30

- O31-1 † Ernst A.J. Burke
Giving names is not as easy as one thinks (J.W. von Goethe, 1807)

9:30~9:50

- O31-2 Igor V. Pekov
Alkali and hydrous sulfide minerals: Classification and genetic aspect of crystal chemistry

9:50~10:10

- O31-3 Gunnar Raade, Ole Johnsen
Crystal chemistry of the vicanite group

10:10~10:30

- O31-4 Frederic B.R. Hatert, André-Mathieu Fransolet, Encarnación Roda-Robles, François Fontan
The wyllieite group of minerals: Crystal chemistry, nomenclature and stability

Break

10:40~11:00

- O31-5 Ian Grey, William D. Birch, Catherine Bougerol, Stuart J. Mills
Nano-scale phase intergrowths in crystals of a 'new' tungstate mineral from Pittong, Victoria, Australia

11:00~11:20

- O31-6 Daniel Atencio, Jose Coutinho
Menezesite from Cajati, São Paulo, Brazil

11:20~11:40

- O31-7 Fumihiko Matsuyama, Kaoru Kiyota
Kintoreite-Corkite solid solution mineral from Japan

11:40~12:00

- O31-8 § Ru Chen Wang, Huan Hu, François Fontan
Cs analogue of polyolithionite from rare-element granitic rocks in China

Wed. July 26 9:00~12:00 4F 402

9:00~9:30

- O31-9 † Frank C. Hawthorne, Roberta Oberti
On the classification of amphiboles

9:30~9:50

- O31-10 § Christian Chopin
Heterovalent substitutions in mineral nomenclature: The dominant-ion rule revisited

9:50~10:10

- O31-11 § Sergey V. Krivovichev, Andrey A. Zolotarev, Victor N. Yakovenchuk, Thomas Armbruster
Does cation ordering justify approval of new mineral species? New data on labuntsovite-group minerals

10:10~10:30

- O31-12 § Joel D. Grice, Marc Leblanc, Vincent Maisonneuve
Natural and synthetic fluoride carbonates: Structural classification, properties and uses

Break

10:40~11:00

- O31-13 Giovanni Ferraris, Svetlana V. Soboleva
Modelling and classifying modular structures - A second member of the nafertiste group

11:00~11:20

- O31-14 Stanislav K. Filatov, Lidia P. Vergasova
Crystal chemistry of new exhalative minerals (to 30th anniversary of great fracture tolbachik eruption, Kamchatka, Russia)

11:20~11:40

- O31-15 § Nikita V. Chukanov
Contribution of the IR spectroscopy to the characterization of new mineral species

11:40~12:00

- O31-16 Jean-Marie R. Genin, Christian Ruby
Deprotonation of Fe^{II-III} hydroxycarbonate green rust and fougérite mineral in gley soils; structure and thermodynamics

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P31-1 Masayuki Ohnishi, Isao Kusachi, Shoichi Kobayashi, Junji Yamakawa
Numanoite, $\text{Ca}_4\text{CuB}_4\text{O}_6(\text{OH})_6(\text{CO}_3)_2$, a new mineral, the Cu-analogue of borcarite from the Fuka mine, Okayama prefecture, Japan
- P31-2 Uwe Kolitsch, Ekkehart Tillmanns
A new mineral: PbHPO_4 , the phosphate analogue of schultenite
- P31-3 Arashi Kitakaze
Sugakiite $\text{Cu}(\text{Fe,Ni})_8\text{S}_8$, a new mineral
- P31-4 Marco Pasero, Paolo Orlandi
Two new minerals from Italy: Ardennite-(V) and allanite-(La)
- P31-5 Elena Bonaccorsi, Stefano Merlino, Paolo Orlandi
New minerals from Italy: Zincalstibite and a new member of the cancrinite-sodalite group
- P31-6 Yasuhiro Takai, Seiichiro Uehara
Rare earth carbonates and an unknown Ca-Y carbonate mineral in the Higashimatsuura basalts
- P31-7 Yasuyuki Banno, Ritsuro Miyawaki, Toshihiro Kogure, Satoshi Matsubara, Toshiaki Kamiya, Shigeo Yamada
Aspidolite, the Na analogue of phlogopite, from Japan
- P31-8 Antonio Gianfagna, Fernando Scordari, Simona Mazziotti Tagliani, Gennaro Ventruti
Fluorophlogopite from Biancavilla (Mt Etna, Sicily, Italy): Crystal chemistry of a new F-dominant analogue of phlogopite
- P31-9 Ritsuro Miyawaki, Kazumi Yokoyama, Satoshi Matsubara, Yukiyasu Tsutsumi, Atsushi Goto
A Mn-analogue of allanite-(Ce) in granite from Japan
- P31-10 Irina Galuskina, Evgeny Galuskin, Piotr Dzierzanowski
Scandian garnet from Wiluy River, Sakha-Yakutia Republic, Russian Federation - a potential new mineral species in the garnet group
- P31-11 Takashi Yamada, Satoshi Matsubara, Ritsuro Miyawaki, Akira Harada, Yasuhiro Kosuge
A Bi-Te-S-O mineral and Al-rich phosphates in epithermal quartz veins from the Kawazu mine, Izu peninsula, Central Japan
- P31-12 Marcelo B. Andrade, Daniel Atencio
Pyrochlore-group minerals: Brazilian occurrences
- P31-13 Mehmet F. Taner, Robert F. Martin, Robert A. Gault
Occurrence of Spurrite-Tilleyite-Rustumite-Hillebrandite (Spurrite-Merwinite Facies) within the Limestone-Granite Contact in the Güneyce-Ikizdere Area, Eastern Black Sea (Pontides), Turkey
- P31-14 Hiroshi Miyajima, Satoshi Matsubara, Ritsuro Miyawaki, Kazumi Yokoyama, Kazuo Hirokawa, Kanako Ito
Strontium-dominant new minerals found in jadeitite and related rocks from Itoigawa, Central Japan
- P31-15 Alexander P. Khomyakov
Endemic Minerals as Products of Geocatalysis and Indicators of Highly Productive Ore-generating Processes
- P31-16 Christian Chopin, Roberta Oberti, Fernando Camara
Arrojadites: New formula, new structure and constraints on crystal-chemistry
- P31-17 Zhuming Yang, Milan Liu, Franz Pertlik
Crystal chemistry of iron atoms in non-metamict chevkinite-(Ce): Valence state and site occupation proportions
- P31-18 Giancarlo Della Ventura, Fabio Bellatreccia, Massimo Piccinini, Gian Carlo Parodi
The channel constituents of vishnevite

- P31-19 Eriko Sato, Izumi Nakai, Akiko Hokura, Kiyonori Michiba, Ritsuro Miyawaki, Satoshi Matsubara
Study of isomorphous substitution in alunite-beudantite group minerals

32. Natural and artificial gem materials (CGM)

- Conveners: Lee A. Groat[#](Univ. of British Columbia), Corina Ionescu (Babes-Bolyai Univ. of Cluj-Napoca), Hisao Kanda (National Inst. for Materials Sci.), Takeshi Miyata^{*}(Yamanashi Inst. of Gemmology & Jewellery Arts)
Chairs: Lee A. Groat (Univ. of British Columbia), Corina Ionescu (Babes-Bolyai Univ. of Cluj-Napoca), Takeshi Miyata (Yamanashi Inst. of Gemmology & Jewellery Arts) and/or Hisao Kanda (National Inst. for Materials Sci.)

Oral presentations

Mon. July 24 15:30~18:30 4F 403

15:30~16:00

- O32-1 † James E. Shigley
HPHT-treated colorless and colored gem diamonds

16:00~16:30

- O32-2 § Emmanuel Fritsch, Laurent Massi, Thomas Hainschwang, Alan Collins
The first color center related to the brown graining in type Ia natural diamonds

16:30~16:45

- O32-3 Tatiana V. Posukhova, Nastya Malakhova, Galina I. Dorokhova
X-ray Computer Microtomography - effective method of the investigation of the inclusion in diamond

16:45~17:00

- O32-4 Corina Ionescu, Onuc Cozar, Volker Hoeck, Monica Culea, Nicolae Leopold, Sorin Usurelu
Cenozoic fossil resins used in gemmology: Towards a practical grouping

Break

17:15~17:45

- O32-5 † Lee A. Groat, David Turner, Heather L.D. Neufeld, Anthony N. LeCheminant, Mary L. Garland
The Mineralogy and Geology of Canadian Gem Deposits

17:45~18:00

- O32-6 Carlo Aurisicchio, Luisa Ottolini, Inessa Morotz, Caterina De Vito
Archaeological emerald provenance: A contribution from trace elements analysis by secondary ion mass spectrometry

18:00~18:15

- O32-7 Jun Kawano, Muneyuki Okuyama, Miyata Takeshi
Behavior of beryllium diffusion in corundum

18:15~18:30

- O32-8 Ahmadjan Abduriyim, Hiroshi Kitawaki
Application of LA-ICP-MS (Laser Ablation System with Inductively Coupled Plasma Mass Spectrometry) to the gemological field

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P32-1 Stefanos Karampelas, Emmanuel Fritsch, Spyros Sklavounos, Triantafyllos Soldatos
Pigments in cultured freshwater pearls: Identification using Raman scattering and UV-Vis spectroscopy
- P32-2 Hisao Kanda, Kenji Watanabe
Two Types of the Blue Band-A Luminescence of Natural Diamond

- P32-3 Norimasa Shimobayashi, Akira Miyake, Yusuke Seto, Sachio Ohtaki, Masao Kitamura
Iridescent andradite garnets (*Rainbow Garnets*), newly-found from the Tenkawa area in the Yoshino district, Nara prefecture, Japan

33. New applications of synchrotron radiation in earth and planetary sciences

Conveners: Fabrice Brunet (Ecole Normale Supérieure, Paris), George J. Flynn (SUNY, Plattsburgh), Tetsuo Irifune^{#,*} (Ehime Univ.), Kenneth Kemner (Argonne National Lab.), Izumi Nakai (Tokyo Univ. of Sci.), Akira Tsuchiyama (Osaka Univ.)
Chairs: Tetsuo Irifune (Ehime Univ.), Akira Tsuchiyama (Osaka Univ.), Fabrice Brunet (Ecole Normale Supérieure, Paris), Izumi Nakai (Tokyo Univ. of Sci.)

Oral presentations

Fri. July 28 9:00~12:00 3F 301

9:00~9:40

- O33-1 † Osamu Shimomura
Mineral physics and synchrotron radiation

9:40~10:00

- O33-2 § Andrew G. Gault, David A. Polya, Farhana S. Islam, John M. Charnock, Helen A. L. Rowland, Victoria S. Coker, Richard L. Pederick, Roy A. Wogelius, Jonathon R. Lloyd
Mechanisms of arsenic mobilization in SE Asian aquifers: Shedding synchrotron light on a natural disaster

10:00~10:20

- O33-3 § Yoshio Takahashi
Sensitive measurement of fluorescence XAFS using bent crystal analyzer and its application to radiogenic osmium in molybdenite

Break

10:40~11:00

- O33-4 § George J. Flynn, Susan Wirick, Chris Jacobsen, Lindsay P. Keller
Mineral location and identification using a scanning transmission X-Ray microscope

11:00~11:20

- O33-5 § Kentaro Uesugi, Akihisa Takeuchi, Yoshio Suzuki, Akira Tsuchiyama, Tsukasa Nakano
Development of high-resolution X-ray micro-tomography system with fresnel zone plate optics at spring-8

11:20~11:40

- O33-6 Jacques Roux, Daniel R. Neuville, Laurent Cormier, Anne-Marie Flank, Dominique De Ligny, Grant Henderson, Pierre Lagarde
In situ high temperature X-ray absorption investigation at the Al, Si and Ca K-edges in melts

11:40~12:00

- O33-7 Tatsuhiko Kawamoto, Masami Kanzaki, Kenji Mibe, Kyoko Matsukage, Shigeaki Ono
Second critical endpoint between aqueous fluids and a high-magnesian andesite by high-pressure and high-temperature X-ray radiography

Fri. July 28 14:30~16:30 3F 301

14:30~14:50

- O33-8 § Yanbin Wang, T. Uchida, N. Nishiyama, R. B. von Dreele, K. Funakoshi, A. Kaneko, H. Nozawa, A. Yamada, T. Kunimoto, I. Ohnishi
CAESAR diffraction and the symmetry of CaSiO₃ perovskite with and without Al₂O₃

14:50~15:10

- O33-9 Tomoo Katsura, Anton Shatskiy, Shuangmeng Zhai, Hiroshi Fukui, Daisuke Yamazaki, Eiji Ito, Naotaka Tomioka, Mitsuhiro Sugita, Kennichi Funakoshi, Akifumi Nozawa
Thermal expansion of mantle minerals at high-pressures

15:10~15:30

- O33-10 Yoshinori Tange, Eiichi Takahashi, Tetsuo Irifune, Ken-ichi Funakoshi
Phase relations in the system MgO-FeO-SiO₂ up to 50 GPa and 2000°C

15:30~15:50

- O33-11 Hans J. Mueller, Frank R. Schilling, Christian Lathe
Triple H experiments - MAX200x - HASYLAB HARWI-II High pressure experiments

15:50~16:10

- O33-12 Yuji Higo, Toru Inoue, Tetsuo Irifune
Precise measurement of elastic wave velocities combined X-ray and ultrasonic measurements

16:10~16:30

- O33-13 Baosheng Li, Wei Liu, Jennifer Kung
Sound velocity measurements on partial melting and melts at mantle pressures using combined ultrasonics and synchrotron X-radiation

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P33-1 Toshiro Sakae, Yasushi Hayakawa, Takao Kuwada, Takeshi Sakai, Kyoko Noguchi, Toshinari Tanaka, Ken Hayakawa, Isamu Sato
Detection of Sr in dinosaur eggshell by wavelength tunable LEBRA-PXR
- P33-2 Tetsu Kogiso, Katsuhiko Suzuki, Toshihiro Suzuki, Kentaro Uesugi, Akihisa Takeuchi, Yoshio Suzuki
Detection of platinum-group-element nuggets in terrestrial rock samples by X-ray absorption and fluorescence imaging using synchrotron radiation
- P33-3 Takahide Okazaki, Hajime Yano, Akira Tsuchiyama, Kentaro Uesugi, Tsukasa Nakano, Takaaki Noguchi, Kyoko Okudaira
Three-dimensional structures of dust samples and their tracks captured in silica aerogel onboard EuReCa using SR micro-tomography
- P33-4 Hiroshi Arima, Osamu Ohtaka, Yoshinori Itakura, Katsuyuki Kubo, Akira Yoshiasa, Shinobu Nishimiya, Yuki Furukawa, Yoshinori Katayama, Hiroshi Fukui
High-pressure XAFS Study of germanate melts
- P33-5 Hidenori Terasaki, Satoru Urakawa, Norimasa Nishiyama, Yanbin Wang
Application of high pressure X-ray microtomography: Measurement of interfacial energy of liquid Fe-alloy under pressure
- P33-6 Akifumi Nozawa, Ken-ichi Funakoshi
Development of the density measurement of liquid sulfur at high pressure using the falling sphere method
- P33-7 Masahiko Tanaka, Tomoki Nakamura, Takaaki Noguchi
Quantitative-phase and crystal-structure simultaneous analysis of multi-mineral phase micro samples by synchrotron Gandolfi method
- P33-8 Nagayoshi Sata, Kei Hirose, Yasuo Ohishi
Preliminary test experiments for Au pressure scales
- P33-9 Yann Le Godec, Gerard Hamel, Domingo Martinez, Tahar Hammouda, Vladimir L. Solozhenko, Guillaume Morard, Wilson Crichton, Mohamed Mezouar, Stefan Klotz
Compact multianvil device for in situ angular-dispersive X-ray diffraction studies at high pressures and temperatures
- P33-10 Yuichiro Sueda, Tetsuo Irifune, Toru Shinmei, Takehiko Yagi, Ken Niwa, Ken-ichi Funakoshi
The high pressure and high temperature phase relations and the elastic properties of the calcium ferrite and calcium titanite-type structures in MgAl₂O₄

34. Frontier applications of neutron sciences to mineralogy

Conveners: Hiroyuki Kagi^{*,†} (Univ. of Tokyo), Takaya Nagai (Hokkaido Univ.), John B. Parise (SUNY, Stony Brook), Romano Rinaldi (Univ. of Perugia)

Chairs: Hiroyuki Kagi (Univ. of Tokyo), Romano Rinaldi (Univ. of Perugia), Takaya Nagai (Hokkaido Univ.)

Oral presentations

Thur. July 27 9:00~12:00 4F 402

9:00~9:20

O34-1 Romano Rinaldi

Neutron diffraction applied to Mineralogy, an overview

9:20~10:00

O34-2 † Yasuhiko Fujii

Material science to be explored by advanced neutron beam technology

10:00~10:20

O34-3 § Yann Le Godec, Martin T. Dove, Simon A.T. Redfern, Thierry Strässle, Matthew G. Tucker, William G. Marshall, Gerard Hamel, Stefan Klotz

Recent developments using the Paris-Edinburgh cell for neutron diffraction at high pressure and high temperature

Break

10:40~11:00

O34-4 § Yusheng Zhao, L. L. Daemen, J. Zhang, D. He. K. Lokshin, J. Qian, C. Pantea, K. Tait, H. Xu, D. Williams, S. Vogel

Scientific achievements and technological advances of high P-T neutron diffraction at LANSCE, Los Alamos

11:00~11:20

O34-5 § Mark D. Welch

High-P neutron diffraction studies of hydrous minerals: Progress and prospects

11:20~11:40

O34-6 Takaya Nagai, Hiroyuki Kagi, John B. Parise

Hydrogen bonding of goethite (α -FeOOD) at high pressure

11:40~12:00

O34-7 Kazuki Komatsu, Hiroyuki Kagi, William G. Marshall, Takahiro Kuribayashi, John B. Parise, Yasuhiro Kudoh

Powder neutron diffraction for topaz-OD under high pressure

Thur. July 27 14:30~16:10 4F 402

14:30~14:50

O34-8 § Simon A.T. Redfern

High-P/T studies of mineral transformations by neutron scattering

14:50~15:10

O34-9 § Isabelle Bihannic, Laurent J. Michot, Karine Devineau, Manuel Pelletier, Elise Rotureau, Frédéric Viliéras, Giovanna Fragneto, Bruno Demé, Nicolas Michau

Hydration of compacted bentonite: A neutron scattering and diffraction study

15:10~15:30

O34-10 § Jan Pleuger

Tectonic studies of the Alps by means of neutron texture goniometry

15:30~15:50

O34-11 § Florian Kargl, Andreas Meyer

Silicate melts and glasses: Alkali ion transport and structure

15:50~16:10

O34-12 § Laurent Cormier, Georges Calas

Neutron diffraction coupled with isotopic substitution in the study of glasses and melts

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

P34-1 Kimberly T. Tait, Frans R. Trouw, Marcus P. Hehlen, Alan H. Shapiro, Yusheng Zhao, Robert T. Downs

Inelastic neutron study of THF + D₂ clathrates

35. Micro-chronology of minerals

Conveners: C. Mark Fanning (Australian National Univ.), Tetsumaru Itaya^{#,*}(Okayama Univ. of Sci.), Simon P. Kelley (Open Univ.), Kazuhiro Suzuki (Nagoya Univ.)

Chairs: Tetsumaru Itaya (Okayama Univ. of Sci.), Kazuhiro Suzuki (Nagoya Univ.), C. Mark Fanning (Australian National Univ.)

Oral presentations

Mon. July 24 9:30~12:00 4F 401

9:30~10:00

O35-1 † Kazuhiro Suzuki

Permian metamorphism in the Yeongnam and Gyeonggi massifs of the Korean Peninsula, revealed by the CHIME dating of monazite and zircon

10:00~10:20

O35-2 Daniel J. Dunkley, Kazuhiro Suzuki, Monika A. Kusiak

Cretaceous monazite ages in migmatites of the Higo terrane, Japan: The importance of petrogenetic associations in accessory mineral geochronology

10:20~10:40

O35-3 Krishnan Sajeew, Kazuhiro Suzuki

Monazite age-mapping and PTt evolution of Kodaikanal metapelite belt, Southern India

Break

11:00~11:20

O35-4 Yoichi Motoyoshi, Yoshikuni Hiroi, Tomokazu Hokada, Kazuyuki Shiraishi

EMP dating on monazite from the western rayner complex, east antarctica: Implications for the metamorphic evolution

11:20~11:40

O35-5 Monika A. Kusiak, Kazuhiro Suzuki, Janusz Lekki, Nonna Bakun-Czubarow

EPMA and PIXE dating of granulites from Gieraltow Bohemian massif, Poland

11:40~12:00

O35-6 Noriko Hasebe, Koji Aratake, Masayuki Okuno, Shoji Arai, Isamu Sinno

Radiation damage or chemical composition? Raman spectroscopy of zircon

Mon. July 24 15:30~18:30 4F 401

15:30~16:00

O35-7 § Christopher Mark Fanning, Richard A. Armstrong, Peter Holden, Ian S. Williams

An update of "More SHRIMP for the Geological Feast"; new developments and future trends

16:00~16:20

- O35-8 Tsuyoshi Iizuka, Kenji Horie, Tsuyoshi Komiya, Shigenori Maruyama, Takafumi Hirata, Hiroshi Hidaka
 Reworking of Hadean continental crust into Acasta gneisses in Northwestern Canada: Evidence from in-situ zircon U-Pb and Lu-Hf isotope analyses

16:20~16:40

- O35-9 Nam Ngoc Tran, Mitsuhiro Toriumi, Kentaro Terada
 Tectonothermal events in high-grade metamorphic complexes in Vietnam: Evidence from SHRIMP U-Pb zircon dating

Break**17:00~17:20**

- O35-10 Tony I. Kemp, Toshiaki Shimura
 Ion microprobe U-Pb (zircon) geochronology of the Hidaka metamorphic belt, Hokkaido, Japan: New results and implications for granite generation at convergent margins

17:20~17:40

- O35-11 Alain Cocherie, Michele Robert, Mark C. Fanning
 Recent development of LA-MC-ICPMS and a multi-ion counting system for micrometer scale U-Pb chronology of complex zircon grains

17:40~18:10

- O35-12 § Hironobu Hyodo
 From 2000 to over 16 giga years by laser probe $^{40}\text{Ar}/^{39}\text{Ar}$ dating: A review

18:10~18:30

- O35-13 Tetsumaru Itaya, Hironobu Hyodo, Tatsuki Tsujimori, Simon Wallis, Mutsuki Aoya, Tetsuo Kawakami
 Excess argon wave trap zone in Barrovian type metamorphic belt, Eastern Tibet

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P35-1 Takenori Kato
 Comparison of EPMA Correction Procedures in CHIME Dating
- P35-2 Takashi Nakajima, Ian S. Williams, Hironobu Hyodo, Kazuhiro Miyazaki, Allah B. Kausar
 Micro-chronology of Kohistan lower crustal tonalite, Northern Pakistan: Implication to the timing of India-Eurasia collision
- P35-3 Yukiyasu Tsutsumi, Kazumi Yokoyama, Ritsuro Miyawaki, Satoshi Matsubara, Hiroshi Hidaka
 Ion microprobe U-Pb dating of zircons in jadeitites and jadeite-bearing rocks from Japan
- P35-4 Hassan A.E. Ibrahim, Ibrahim M. Khalaf, Wolfgang Siebel, Friedrich Finger, Tetsumaru Itaya
 U-Pb zircon dating of Neoproterozoic anorthosites from Wadi Dib, North Eastern desert, Egypt
- P35-5 Nuong Dieu Nguyen, Tetsumaru Itaya, Yujiro Nishimura
 K-Ar phengite age - temperature relations in the Ishigaki high-pressure schist belt of the Southern Ryukyu arc, Japan
- P35-6 Thanh Xuan Ngo, Tetsumaru Itaya, Talat Ahmad, Satoru Kojima, Tomoyuki Ohtani, Masayuki Ehiro
 Late Cretaceous igneous activity predating Ladakh batholith in Northern India: K-Ar ages of Hunder granite - diorite complex in the Shyok Suture Zone
- P35-7 Lalu Prasad Paudel, Tetsumaru Itaya, Kazunori Arita
 K-Ar ages of white micas in metapelites from the Lesser Himalaya, Central Nepal: Implications for the timing of metamorphism
- P35-8 Trung Minh Nguyen, Nuong Dieu Nguyen, Tetsumaru Itaya
 Rb-Sr isochron and K-Ar ages of igneous rocks from the Samnua depression zone in Northern Vietnam

- P35-9 Shin Toyoda, Kosei Komuro, Hirotugu Nishido, Tasuku Okumura
 Dating of uranium ore by cathodoluminescence: Experimental basis by He ion implantation in relation to the radiation effects detected by ESR

36. Minerals relating to the origin and distribution of life in the Universe

Conveners: George Cody (Geophysical Lab.), Takeshi Kakegawa^{*,*}(Tohoku Univ.),
 Kensei Kobayashi (Yokohama National Univ.)
 Chairs: Takeshi Kakegawa (Tohoku Univ.)

Oral presentations

Fri. July 28 9:00~12:00 4F 401

9:00~9:30

- O36-1 † Michael J. Russell
 Mineral clusters as ready-made catalysts in the emergence of life and oxygenic photosynthesis

9:30~9:45

- O36-2 Hiromoto Nakazawa, Yoshihiro Furukawa, Shohei Ohara, Takeshi Kakegawa
 A universal phylogenetic tree having roots

9:45~10:00

- O36-3 Yoshihiro Furukawa, Hiromoto Nakazawa, Toshimori Sekine, Takeshi Kakegawa
 Impact vaporization of extraterrestrial objects: Importance of liquid water and implication to the early Earth

10:00~10:15

- O36-4 Shohei Ohara, Takeshi Kakegawa, Hiromoto Nakazawa
 Pressure dependence of peptide formation in solid-state: Implications for the chemical evolution under the deep crust

Break

10:30~10:50

- O36-5 § George D. Cody, Nabil Boctor
 Transition metal sulfides, organosynthesis, and the emergence of life

10:50~11:10

- O36-6 § Kensei Kobayashi, Hironari Kurihara, Neubeck Anna, Takeo Kaneko, Hiroshi Yanagawa
 Roles of metal ions in chemical evolution in submarine hydrothermal systems

11:10~11:25

- O36-7 Hidekazu Yoshida, Mamoru Adachi
 Genesis of biogenic iron-oxide nodules (takashikozo) in reducing sediments

11:25~11:40

- O36-8 Takeshi Kakegawa, Ohtomo Yoko
 Origin of graphite in 3.8 Ga Isua supracrustal belt: three different origin?

11:40~12:00

- O36-9 § Masamichi Hoashi, Munetomo Nedachi, Hiroshi Ohmoto
 Bio-activity in the 3.46 Ga hydrothermal system; ferruginous marble bar chert, Pilbara, Western Australia

Poster presentations

Thur. July 27 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P36-1 Taku Iwamoto, Dai Shiota, Tadashi Yokoyama, Satoru Nakashima
 Hydrothermal formation of organic globules in the presence of porous rocks

- P36-2 Kohsuke Okihara, Tadashi Yokoyama, Satoru Nakashima
Instability of adenosine in the presence of hydroxyapatite under hydrothermal conditions
- P36-3 Yuichi Iwai, Takeshi Kakegawa
Thermal stability of nucleotide and formation of ATP: Importance of temperature and phosphate concentrations
- P36-4 Yoko Ohtomo, Takeshi Kakegawa
Metamorphic and metasomatic effects on carbon isotope and REE compositions in 3.8 Ga metasedimentary rocks in Isua supracrustal belt
- P36-5 Keiichi Yagishita, Junji Akai, Nozomu Sekiguchi, Munetomo Nedachi
Mineralogical examination of archean biosphere drilling project samples of marble bar chert, Australia
- P36-6 Masataka Haikawa, Takeshi Kakegawa, Sachiko Niituma
Geochemical study of 3.0 Ga Steep Rock group in Canada: Microbial diversity corresponding to the redox change in 3.0 Ga Steep Rock ocean

37. Recent progress of nano particles studies in earth and planetary sciences

Conveners: Junji Akai^{*,} (Niigata Univ.), Jillian F. Banfield (Univ. of California, Berkeley),
Toshihiro Kogure (Univ. of Tokyo)
Chairs: Junji Akai (Niigata Univ.), Benjamin Gilbert (Lawrence Berkeley National Lab.),
Toshihiro Kogure (Univ. of Tokyo)

Oral presentations

Tue. July 25 9:00~12:00 5F 505

9:00~9:30

O37-1 † Benjamin Gilbert

Nanoparticles in the earth sciences: Making the link between size dependent properties and reactivity

9:30~9:50

O37-2 § R. Lee Penn, Amy J. Anschutz, Jasmine Erbs, Rachel Gabor, Jentzsch Teresa

Reactivity of iron oxide nanoparticles

9:50~10:10

O37-3 § Denis G. Rancourt

Nature and genesis of ferrihydrite

10:10~10:30

O37-4 § Satoshi Utsunomiya

Migration of trace elements via nanoscale processes

Break

10:45~11:00

O37-5 Mami Kurumada, Chihiro Kaito, Sunagawa Ichiro

High-resolution electron microscopy on topological amphibole whisker

11:00~11:15

O37-6 Junji Akai, Yohsuke Kanai, Takahiko Ogawara

Nano to micro scale mineral structures in 'biogenic' ores

11:15~11:30

O37-7 Takaaki Abe, Chiaki Uyeda

Magnetic alignment of diamagnetic presolar grains above 1000°C detected by weak field of horseshoe magnet orientated to the estimation of stellar field

11:30~11:45

- O37-8** Takayuki Aoki, Junji Akai
Nano carbon minerals in carbonaceous chondrites observed by HRTEM

11:45~12:00

- O37-9** Denis G. Rancourt
Advances in characterization methods for environmental mineralogy

Poster presentations

Tue. July 25 16:30~19:30 (core time 17:00~18:30) 5F 501, 502 and Foyer

- P37-1** Rustam Koneev
Natural nanotechnologies in the process of formation of mineral deposits
- P37-2** Chihiro Kaito, Masahiro Ueda, Osamu Kido, Mami Kurumada, Hitoshi Suzuki, Yuki Kimura, Yoshio Saito
Direct observation on phase transition of copper sulfide produced by solid-solid reaction
- P37-3** Sachiko Niitsuma, Takeshi Kakegawa, Toshiro Nagase, Munetomo Nedachi
Occurrence of meta-stable sulfide minerals in black shale of the 2.77 Ga Mt. Roe basalt in Western Australia

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Plenary lectures

PL1

Microscopic properties to macroscopic behaviour: The influence of iron electronic state

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Iron is not only the most abundant element in the Earth, but it is also the only major element with multiple electronic configurations (oxidation and spin state). The loss of a single electron or a change in the distribution of electrons between orbital states may appear minor at the atomic scale, but at the macroscopic level the effects can be profound. The oxidation state of iron varies through the mantle, from predominantly Fe^{2+} in the upper mantle and transition zone to roughly 50% Fe^{3+} in the lower mantle due to the strong affinity of $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ perovskite for Fe^{3+} . This presentation will examine the effect of both oxidation state and spin state on physical and chemical properties of the mantle, as well as dynamic processes, including a consideration of the post-perovskite phase transformation. The movement of material into the lower mantle must involve redox reactions to balance charge, which in the bulk mantle likely occurs through Fe^{2+} disproportionation to produce Fe^{3+} (which goes into the perovskite phase) and metallic iron, while in subducting slabs charge balance may involve reduction of volatile species, potentially giving rise to deep diamonds. Recent models reported in the literature show that the growth of an $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ perovskite-rich lower mantle during core formation would progressively oxidise the mantle to present levels as a portion of the disproportionated iron-rich metal phase became incorporated into the core, and the increase in oxygen fugacity during the later stages of Earth accretion would alter the partitioning behaviour of elements between mantle and core, resolving puzzles such as the siderophile element anomaly and the discrepancy between U-Pb and Hf-W systematics in the early Earth. The rise of atmospheric oxygen approximately 2.3 Ga ago might be related to a mantle avalanche in the late Archean that disturbed the balance of volatile element cycles.

PL2

From fluid inclusion microanalysis to large-scale hydrothermal mass transfer in the Earth's interior

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This paper illustrates how the recent development of micro-analytical techniques for major- and trace-elements in fluid and melt inclusions contributes to quantitative understanding of lithosphere-scale chemical transport by hydrothermal fluids, including the formation of mineral deposits. After an introductory remark on aspects of instrumentation and data quality assessment, the first-order controls of crustal fluid compositions are discussed, indicating that trace-element concentrations broadly follow silicate rock buffered conditions. Field-based studies of ore-forming liquid and vapor-like fluid inclusions in upper-crustal magmatic centres emphasise, however, that effective ore formation is a disequilibrium process, requiring deviations from the crustal fluid buffers. Microanalytical techniques are also changing experimental approaches in the laboratory, allowing fluid trapping experiments to investigate mineral solubilities, melt–fluid distribution constants, and the nature of fluids responsible for selective element transfer from the downgoing slab to the melting region of calc-alkaline magmas in the mantle wedge.

Sintered diamond multi-anvil apparatus and its application to mineral physics

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The Kawai-type multi anvil apparatus, in which an octahedral pressure medium in eight cubic anvils (the Kawai-cell) is compressed by external force, has been widely used in the mineral physics field because of its versatile abilities such as large sample volume and pressure environment of high hydrostaticity due to compression from multi-directions despite usage of solid pressure media. These features make it possible to heat a sample of few milligrams to higher than 2300 K by employing a internal heater, which are in some sense complementary to those of the diamond anvil cell (DAC). However, it has been realized in last two decades that the maximum attainable pressure is limited to ca. 28 GPa, almost one order of magnitude lower than in DAC, so far as tungsten carbide (WC) is used as the anvil material. Fortunately, sintered diamond (SD) has become available for the cubic anvils in the late 1980s. As the hardness of SD is at least twice harder than that of WC, attainable pressure range of the Kawai-type apparatus has been extended preserving the abilities mentioned above. Pressures up to 63 GPa are generated over a volume larger than 2 mm³ using SD cubes with an edge length of 14 mm and a truncation of 1.5 mm. The phase equilibrium and melting studies of the mantle materials have become possible to pressures corresponding to conditions of the mid mantle. By compressing the Kawai-cell equipped with SD anvils in a cubic press (DIA type press) at Spring-8, in situ X-ray observation has been carried up to 60 GPa and 2000 K. The technical innovations make it possible to determine phase boundaries between unquenchable high pressure phases and equations of state of geophysically important minerals. The electrical conductivity of minerals has also been measured up to 60 GPa at room temperature and up to 30 GPa at higher than 1000 K.

Microbial metabolism and the size- and chemical environment-dependence of the structure and reactivity of nanoparticle products

Goodell, C.M.¹, Michael J. Finnegan¹, Moreau J.¹, Gilbert, B.², Zhang, H.¹, Huang, F.¹, Chen, B.¹, and Banfield, J.F.¹

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Microbial metabolism, such as sulfate reduction or iron oxidation, can result in the production of very abundant nanometer-scale particles. As a consequence of the relatively large concentration of surface sites, the structure, stability, and reactivity of these small particles can differ significantly from those of the equivalent bulk compounds. For over a decade, we have studied the interplay of size, structure stability, and crystal growth kinetics. We have learned that nanoparticles can grow by aggregation-based mechanisms, yielding novel crystal morphologies. Recently, we have focused on analysis of how the environment of a nanoparticle can influence its structure and properties. Processes such as the adsorption of ions to surfaces can induce internal ordering and can drive aggregation. In fact, particle-particle interactions induced by aggregation can lead to structural transformations that are reversible upon disaggregation. Both experiments and simulations show that adsorption of water molecules to ZnS nanoparticle surfaces leads to an irreversible increase in structural order. However, because water adsorption also induces aggregation, the kinetics of the water adsorption-driven transformation are difficult to evaluate. In order to separate the effects of adsorption and aggregation and to determine the activation energy for the adsorption-driven reaction, we fixed the aggregation state by vacuum-drying nanoparticles before exposure to water vapor at different temperatures. The results confirmed that the adsorption of water molecules is a stronger determinant of the nanoparticle structure than the aggregation state. In order to further evaluate structure-directing surface interactions, nanoparticles have been exposed to a variety of inorganic and organic ligands. Higher degrees of crystallinity were associated with chemical binding and electrostatic interactions rather than van der Waals interactions. High-resolution analyses of natural biologically generated ZnS nanoparticles have documented isotopic fractionation attributed to fluctuations in metabolic rate and revealed the presence of surface adsorbed protein that is inferred to have played a role in aggregate formation. Thus, interactions among biologically-formed nanoparticles and between nanoparticles and surface adsorbed molecules may be important in determining the physical, chemical, and biological reactivity, and thus the fate, of nanoparticles in aqueous or hydrophobic organic-rich terrestrial environments.

The nature of early solar system and presolar materials

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The application of transmission electron microscopy (TEM) analysis to research on extraterrestrial materials has provided fundamental new information of the origin and evolution of solid materials in the solar system. This is especially true for the fields of interplanetary dust, presolar grains, and matrices of primitive chondrites. Transmission electron microscopy is the only technique that provides mineralogical and crystallographic and chemical data on the individual submicrometer constituent phases in IDPs and other samples. With advances in sample preparation techniques, it is now routine to obtain mineralogical and petrographic data, isotopic compositions, light element geochemistry, infrared spectra, trace element data, and X-ray absorption data on the same 70–100 nm ultramicrotome thin section of a 10 micrometer in diameter ID.P

Abundant silicate stardust has recently been discovered in meteorites and interplanetary dust particles (IDPs) as well as grains of silicate supernova dust. These grains were previously undetected owing to their small sizes (0.2 – 1.0 μm). These silicate grains are known to have an extrasolar origin because of their extremely anomalous isotopic compositions that reflect nucleosynthetic processes in their stellar sources. Major questions remain regarding their detailed mineralogy, and so a major focus of our IDP studies is the identification of the host phase(s) that carry these highly anomalous isotopic signatures through coordinated transmission electron microscopy, ion microprobe and spectroscopic measurements. We study the mineralogy of the isotopically anomalous grains and characterize their microstructures in order to learn more about their formation conditions and histories from their origin in the outflows of evolved stars, through processing in the interstellar medium, accretion in the presolar molecular cloud, and finally their interaction with materials formed in the early solar nebula. These questions become even more important with the return of samples from Comet Wild-2 by the Stardust mission.

Mineral growth in high and low pressure metamorphic rocks

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The study of metamorphism of rocks investigates the mineralogical changes induced by temperature, pressure, and fluid compositions in the earth's crust. The crystallization of new minerals occurs typically within a static or deforming solid rock matrix, with the exception of growth of minerals in open veins which crystallize in a fluid dominated domain. The purpose of the present communication is to demonstrate the usefulness of mineral kinetic approaches to understanding the geo-tectonic history of metamorphic terrains. To this end, studies in regional metamorphic and contact metamorphic terrains are presented.

Garnets are important minerals in regional metamorphic rocks in many mountain ranges, since they are often used to determine the pressure and temperature conditions that lead to the formation of metamorphism. Existing new developments in rare earth element (REE) geochemistry over the last decade have opened up the possibility to obtain the age and duration of garnet growth. The research of e.g. Carlson and co-workers have proposed that diffusion limited growth seems most likely for many garnets in meta-pelitic rocks (e.g. Carlson et al., 1995). In contrast, we (and other workers) have been finding that garnet growth in high pressure meta-basic rocks is in agreement with surface kinetic control. In contrast, the uptake of trace elements seems to be governed by diffusion. The latter seriously hampers the dating of these garnets.

Kinetics of mineral growth in thermal aureoles of shallow intrusions has been a contentious problem, with some workers arguing that major (prograde) mineral growth might happen after peak metamorphism, during actual cooling, since slow kinetics might have prevented equilibration during the fast heating stage which followed the intrusion of magmas. Arguments are reviewed and new data presented which indicate significant disequilibrium. Crystal size distributions, stable isotope data, and petrologic data are presented for the infiltration driven formation of periclase are presented to illustrate the effect of disequilibrium in fluid rich environments. These data are modeled using a combined infiltration-reaction-nucleation- growth code to assess the amount of disequilibrium needed during crystallization.

In summary, it is apparent that mineral growth and nucleation are fundamentally important factors to understand metamorphism. At present the metamorphic community is starting to understand quantitatively the growth and nucleation rates during metamorphism. This understanding will eventually be used to calibrate tectonic models with a much higher precision than it is currently possible using equilibrium thermodynamic approaches.

Carlson, W. D., Denison, C., and Ketcham, R. A. (1995) Controls on the nucleation and growth of porphyroblasts; kinetics from natural textures and numerical models. *Geol. J.* 30; 3-4, 207-225.

Operation of subduction factory and production of andesite

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The subduction factory processes raw materials such as oceanic sediments and basaltic crust, selectively extracts particular subduction components and manufactures magmas, their solidified materials and continental crust as products. The waste materials from the factory, such as chemically modified oceanic materials and delaminated mafic arc lower crust are transported down to the deep mantle modified their compositions and ultimately recycled as mantle plumes. Andesite composes the bulk continental crust and therefore is the major product in the subduction factory. Two types of andesites, calc-alkalic and tholeiitic series, are commonly recognized in a single arc volcano. We propose a new mechanism for production of these two magma series on the basis of data obtained by Sr isotopic micro-analyses of plagioclase in volcanic rocks from Zao Volcano, NE Japan. Tholeiitic magmas having constant and enriched isotopic signatures are produced by anatexis of the preexisting mafic lower crust, whereas calc-alkalic magmas, having compositions similar to the bulk continental crust, are products of mixing a mantle-derived, hence isotopically depleted, basaltic magma and crust-derived felsic tholeiites.

Structural evolution, strain and elasticity of perovskites at high pressures and temperatures

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Octahedral tilting transitions in perovskites are usually identified by the significant lattice distortions which accompany them. The underlying mechanism of coupling between the tilts and the macroscopic strain also gives rise to large anomalies in single crystal and bulk elastic moduli. Landau theory provides an effective framework for describing these different changes in properties and relating them, quantitatively, to the evolution of the driving order parameter for the transition. This approach has been used to analyse the overall elastic behaviour of perovskites belonging to the CaTiO_3 - SrTiO_3 solid solution, which is expected to be closely analogous to the behaviour of silicate perovskites at higher pressures and temperatures. $\text{Pm-3m} \rightarrow \text{I4/mcm}$ and $\text{I4/mcm} \rightarrow \text{Pnma}$ transitions in CST perovskites are marked by changes in the shear modulus of ~ 10 -30 %. The evolution of the order parameter and, hence, of the octahedral tilt angles through these can be followed through the variations of spontaneous strains extracted from high resolution lattice parameter data. Contributions to the elastic softening which are due to strain/octahedral tilt coupling have been calculated using a fully parameterised Landau model of the $\text{Pm-3m} \rightarrow \text{I4/mcm}$ transition as a function of temperature, pressure and composition. Differences between calculated elastic constants and experimental data from Dynamical Mechanical Analysis, pulse-echo ultrasonics and Resonant Ultrasound Spectroscopy show that a proportion of the total softening in tetragonal samples is due to anelastic effects. The anelastic contributions are observed at frequencies of both a few Hz and 10's of MHz, and can be understood in terms of strain contributions arising from movements of transformation twin walls in response to an externally applied shear stress. Similar transitions in other perovskites are likely to display small anomalies in the bulk modulus, due to weak coupling between octahedral tilts and volume strain, but much larger anomalies in the shear modulus. The elastic properties of tetragonal and orthorhombic structures are likely to be quite different due to different anelastic contributions from twin wall displacements.

Nanomaterial research learning from mineralogy

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In recent years high resolution transmission electron microscopy (HRTEM) has been playing an important role in the research on nano-materials and nano-devices. In the early 1970s the present author developed the microscopy method and examined many fine structures of minerals during my stay at Arizona State University. First I, like to introduce some of those historical works (1). I would like to emphasize the point that my all experiences with mineralogical studies and others during that period led me to the discovery of carbon nanotubes (CNTs) in 1991. Second, after introducing briefly carbon nanotubes in general, I like to speak about recent progress in carbon nanotube research particularly in terms of tubule growth and its control. The factor controlling the growth, which includes diameter, chirality, length, orientation, quantity etc, is the most important issue in both nanoscience and nanotechnology of carbon nanotubes (2). Third, I like to point out the powerfulness of HRTEM in structural characterization of CNTs and their modifications such as so-called "peapod" of doped CNTs with fullerene and other molecules. The microscopy allows us to visualize even atomic defects such as vacancies and interstitials of carbon atoms to be visualized. Direct structure determination of individual single walled CNTs, that is (n, m) indices by HRTEM observation became possible in recent development of spherical aberration corrected HRTEM. Lastly (3). Lastly I like to show some possible application of nano-carbon materials to bio-technology such as bio-recognition and drug delivery systems, where another type of carbon nanotubes, called 'carbon nanohorns', are utilized (4).

References

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Scientific Sessions

Oral & Poster

O01-01

Physical properties of multi-phase mantle assemblages

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In the upper 1000 km of Earth's mantle, phase transformations are ubiquitous; their influence on the physical properties are comparable to those of pressure and temperature over this depth range. Accounting for the effects of phase transformations on properties such as the thermal expansion and temperature dependence of elastic velocities is essential for the construction of accurate geodynamical models and for the interpretation of seismological observations. We have developed a new thermodynamic model of mantle assemblages that treats phase equilibria and physical properties on an equal footing. The method is based on the idea of fundamental thermodynamic relations, suitably generalized to the case of non-hydrostatic stress and strain. Given a pressure, temperature, and bulk composition, this method yields thermodynamically self-consistent values of equilibrium phase proportions and compositions, isotropic thermodynamic properties such as density and enthalpy, and anisotropic properties such as the full elastic constant tensor. The parameters of the model are constrained by experimental data, or when none is available, by first principles quantum mechanical calculations. We will show several applications of the method to an understanding of the structure of the mantle, including: 1) the origin of the low velocity zone via comparison of the elastic wave velocities of a model mantle to those of seismic models 2) scaling of lateral variations in seismic wave velocity to temperature for the interpretation of tomographic models and 3) the influence of super-grain scale compositional heterogeneity on elastic wave velocities particularly in the vicinity of the boundary between upper and lower mantle.

O01-02

Density variations in subducting slabs and surrounding upper mantle: Understanding stagnation vs. penetration of the slabs at the 670 km discontinuity

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It is commonly accepted that the 670 km seismic discontinuity in the Earth's mantle is primarily due to the ringwoodite/perovskite transformation that has a slightly negative P-T slope, which causes the cooler slab to be somewhat lighter than the surrounding mantle, thus resisting its further subduction. Seismic tomographic images, however, show both stagnation of the slab at this depth and penetration to greater depths. The latter phenomenon suggests that at least under some conditions a slab might be heavier than the surrounding mantle below the 670 km discontinuity. In order to understand the fate of subducting slabs, we estimate the density of slabs and surrounding mantle (just below normal mantle transition to perovskite) taking into consideration all major mineralogical transformations, and integrate these density data with the thermal structure within and around specific slabs, calculated using an advection code based on a plate model. The mantle is assumed to be pyrolite, whereas the slab to be compositionally stratified with a lherzolite bottom layer, followed upward by harzburgite and basalt. The stable mineralogy and bulk density is calculated by minimizing the Gibbs energy for these compositions in the system MgO-FeO-CaO-Al₂O₃-SiO₂. The results suggest that lherzolite is denser than harzburgite below 875 °C so that the lherzolite to harzburgite ratio of a cold slab (e.g. Mariana) would have important effect on its density profile. A slab that has maintained an interior temperature of ≤ 750 °C, and is comprised of 55% lherzolite, 35% harzburgite, and 10% basalt, would have a net density greater than that of the surrounding pyrolite mantle. However, even young slabs with warm interiors cool the immediately surrounding mantle, thereby raising its density. Thus, the net density for the relatively warm Nazca slab (internal thermal minimum ~ 950 °C) and the surrounding thermally perturbed mantle (TPM) is greater than that of the ambient mantle. This is consistent with observations of direct penetration of the Nazca slab into the lower mantle. For much older, colder slabs, such as that found beneath the Marianas trench (which is also observed to penetrate the 670), the density increase is more significant, suggesting an easier path to further subduction. Of course, other factors such as slab roll back, viscosity jump and dip angle also influence the fate of subducting slabs, which may explain why some slabs appear to stagnate at the 670 despite our general finding of negative net buoyancy for slab + TPM.

O01-03

Experimental study of phase relations on the diopside CaMgSi₂O₆ - hedenbergite CaFeSi₂O₆ - jadeite NaAlSi₃O₆ system at 7-24 GPa and 1600-2300°C

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Phase relations on the diopside (Di) - hedenbergite (Hd) - jadeite (Jd) system modeling mineral associations of natural eclogites were studied for the compositions (mol.%) Di₇₀Jd₃₀, Di₅₀Jd₅₀, Di₃₀Jd₇₀, Di₂₀Hd₃₀ + Di₄₀Hd₁₀Jd₅₀ using anvil-with-hole Bridgman-type (7 GPa) and split-cylinder type 8 multi-anvil high-pressure apparatus (12–24 GPa). At 7 GPa and 1800–2000°C Di and Jd form complete solid solution, which is molten congruently, addition of Hd does not change melting relations in the pyroxene system. Melting temperature was estimated for the Di₅₀Jd₅₀ composition at 15.5 GPa (2270°C). The appearance of garnet is clearly dependent on initial clinopyroxene composition: at 1600°C first "embryonic" garnet crystals are observed at 13.5 GPa in jadeite-rich part of the system (Di₃₀Jd₇₀), whereas diopside-rich starting material (Di₇₀Jd₃₀) produces garnet only above 17 GPa. The proportion of garnet increases rapidly above 18 GPa as pyroxene dissolves in the garnet structure and pyroxene-free garnetites are produced from diopside-rich starting materials. Garnet in all experiments is accompanied by stishovite; Di₇₀Jd₃₀ and Di₅₀Jd₅₀ starting materials also produce CaSiO₃ with perovskite structure (Ca-Pv). At a pressure above 18 GPa pyroxene is completely replaced by an assemblage of majorite (Maj) + St + Ca-Pv in Ca-rich systems, whereas majorite is associated with almost pure jadeite up to a pressure of 21.5 GPa. Above ~22 GPa, Maj and St are associated with NaAlSi₃O₄ with calcium ferrite structure (Cf). We established, that Hd component also spread the field of pyroxene stability up to 20 GPa. In the Di₇₀Jd₃₀ system at 24 GPa we obtained an assemblage of Maj+Ca-Pv+MgSiO₃ with ilmenite structure (Mg-Il). Correlation between Na, Si, and Al contents in Maj with pressure was established experimentally, that in Grt (Maj) - pyroxene assemblages may be the base for "majorite" geobarometer. Results of our experiments are applicable to transitional zone of the Earth (400–670 km) demonstrating a wide range of transition from eclogite to garnetite. In addition, mineral associations obtained model parageneses of inclusions in diamonds formed under the conditions of transitional zone and lower mantle.

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O01-04

A new formulation of garnet-clinopyroxene thermometer using large number of experimental data with graphite capsules

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Previous experimental data including garnet and clinopyroxene as run products are accumulated, and a new formulation of garnet-clinopyroxene thermometer is created using those data. The total number of the used data is 333-pair experiments, and all of them are carried out with graphite capsules. Experiments without using graphite capsules are not used because of difficulty in estimation of Fe²⁺ content of clinopyroxene. For the calibration, regular solution model is adopted to express the non-ideality of garnet. The magnitudes of excess interaction parameters (W_{ij}) for garnet are adopted from independent experimental data. In a provisional regression of the above data, non-ideality between Fe and Mg in clinopyroxene was evaluated and a slightly negative value was obtained (W_{FeMg}^{Cpx} = -4340 J/mol). This is clearly inconsistent with other independent experimental data (W_{FeMg}^{Cpx} is positive), and hence clinopyroxene is treated as ideal solution in this calibration. Pressure correction is simply treated as linear, and difference of volume of Fe-Mg exchange reaction between garnet and clinopyroxene is fixed to be -120.72 (J/kbar.mol). The regressed and obtained thermometer formulation is as follows: T (°C) = {2922 + 14.52 P (kbar) - 191.6 (X_{ppp} - X_{alm}) + 1626.6 X_{grs} + 173.2 X_{sp5}} / (lnK_D + 1.544 + 0.740 X_{grs}) - 273, where T = temperature, P = pressure, X_{ppp} = Mg / (Fe²⁺ + Mn + Mg + Ca)^{Grt}, X_{alm} = Fe / (Fe²⁺ + Mn + Mg + Ca)^{Grt}, X_{grs} = Mn / (Fe²⁺ + Mn + Mg + Ca)^{Grt}, X_{sp5} = Ca / (Fe²⁺ + Mn + Mg + Ca)^{Grt}, K_D = (Fe²⁺/Mg)^{Grt}/(Fe²⁺/Mg)^{Cpx}. Similar calibrations using large number of data have been recently carried out (Ai, 1994, CMP 115, 467–473; Krogh-Ravna, 2000, JMG 18, 211–219), but their calibrations also use experimental data without graphite capsules. In addition, their formulations are quite empirical forms to express non-ideality of garnet. When the above accumulated data set are applied to their thermometers, temperatures are overestimated at high-T conditions. Furthermore, famous thermometers favored by many researchers (e.g. Powell, 1985, JMG 2, 33–42) are inconsistent with the accumulated data; they underestimate temperatures at high-T conditions and overestimate at low-T conditions. The above formulation of thermometer is the best fit to the accumulated data. When we apply this thermometer to natural rocks, slightly lower temperatures (by about 50°C) tend to be obtained, for example, comparing with the Powell's (1985) thermometer.

High-pressure phase transitions of the feldspars and further characterization of lingunite

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All known high-pressure phase transitions of the feldspar end-members of albite (NaAlSi₃O₈), anorthite (CaAl₂Si₂O₈) and orthoclase (KAlSi₃O₈) were reviewed and summarized. Although all these end-members crystallize in the feldspar structure at ambient conditions, the high-pressure phase behavior of these feldspars is rather different from each other except for the formation of the pair of NaAlSi₃O₈-hollandite and KAlSi₃O₈-hollandite. Yet, the maximum solubility of NaAlSi₃O₈-hollandite in KAlSi₃O₈-hollandite was found to be limited to ~40 mol% at 23 GPa and below ~1500 °C. Among all new Na⁺, K⁺ and Ca²⁺ aluminosilicates found in these end-members (6 in total) at high pressures, only NaAlSi₃O₈-hollandite (or lingunite) and KAlSi₃O₈-hollandite have so far been discovered in shocked meteorites. Raman spectrum is available only for natural lingunite, and it has been compared with those of synthetic KAlSi₃O₈-hollandite, NaAlSi₃O₈-glass and stishovite.

Thermodynamic modeling of high-pressure hydrous phases and fluid phases in the system MgO-SiO₂-H₂O up to 35 GPa, 1873K

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Phase relations in the system MgO-SiO₂-H₂O (MSH) are essentially important for the discussion of water circulation at the deep mantle, since this system can represent a simplified hydrous peridotite. At lower temperatures in this system, stability relations of high-pressure hydrous phases are key for water transportation by the subducting slab because they carry water into the deep mantle. Although the system has been investigated for 40 years, stability relations of high-P hydrous phases have not been clarified. This is because the phase relations are quite complicated and they have been studied by high-pressure experiments only. One of the promising methods for understanding the complicated phase relations is to construct an internally consistent thermodynamic data set for the phases and calculate the phase equilibria. In this talk, we will summarize our recent results of thermodynamic modeling of the high-pressure hydrous phases based on the high-pressure experiment.

We performed fluid-absent high-pressure experiments in the system MSH in a multi-anvil apparatus from 11.0 to 21.5 GPa, and from 800 to 1200°C in order to constrain fluid-absent solid-solid reactions. From the experimentally constrained fluid-absent phase equilibria, thermodynamic parameters for high-pressure hydrous phases were retrieved by a linear programming method. Together with dry mantle minerals from the existing data set, an internally consistent set of thermochemical and thermophysical parameters for seven high-P hydrous phases was evaluated. High-pressure hydrous phases involved in the data set are, phase A, phase E, clinohumite, phase D, superhydrous phase B, hydrous wadsleyite, and hydrous ringwoodite. Using this new data set with Schreinemaker bundle method, we calculated the petrogenetic grid consisting of 89 univariant reactions including these hydrous phases up to 35 GPa and 1873K. In addition, by calculating water-bearing reactions we have estimated water activities in the fluid phase. The water activity decreases with increasing pressure or temperature, suggesting the amount of silicate component dissolved in the fluid phase increases with pressure or temperature.

Fe-Mg-Ca partitioning between carbonates, garnet and clinopyroxene at high pressure: experimental constraints in mafic systems up to 6 GPa

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Element partitioning between carbonates and coexisting high pressure phases plays a critical role in unraveling petrogenetic processes of eclogitic rocks, diamond-bearing rock suites, and carbonatitic magmas. Experiments were carried out on three model MORB bulk compositions, from gel starting materials, at variable Mg/(Mg+Fe) using piston-cylinder and multi-anvil machines at P from 1 to 6 GPa and T from 650 °C to 800 °C, in the presence of a fluid at variable C-O-H ratios ranging from aqueous fluids to mixtures of oxalic acid dihydrate and silver oxalate. fH₂ was buffered at NNO, OH (X, COH) and hematite-magnetite HM, OH (X, COH) buffers using a double capsule technique (notation after Eugster H.P. and Skippen G.B. 1967, *Researches in Geochemistry* 2, 492-526).

Phase assemblages are discussed in a companion contribution presented at this meeting. Dolomite and magnesite coexist with eclogitic assemblages from 2 GPa 680°C at NNO, OH (X, COH) to 4.2 GPa, 730 °C at HM, OH (X, OH), being replaced by Mg-calcite at 4.6 GPa and 5.0 GPa, 800 °C at HM, OH (X, OH). Graphite is ubiquitous above 1.8 GPa at both hydrogen fugacities. Graphite is the dominant carbon compound at fH₂ buffered by NNO above 2 GPa.

Although element partitioning is examined in synthesis experiments and reversals are hindered by low-reactivity of starting materials composed of crystalline mixtures, excellent T-P correlation of Mg/Fe partitioning between garnet and clinopyroxene reveals approach to equilibrium conditions.

Negative linear correlations between log[X_{Mg}(magnesite)/X_{Mg}(dolomite-Mg-calcite)] vs. 1/T, log [X_{Mg}(garnet)/X_{Mg}(dolomite-Mg-calcite)] vs.

1/T, log[X_{Mg}(clinopyroxene)/X_{Mg}(dolomite-Mg-calcite)] obtained integrating these new results with a dataset from other high pressure synthesis experiments recently published on carbonate-bearing mafic rocks suggest their potential usage as geothermometers in a variety of bulk compositions. Observed carbonate compositions as well as partitioning properties cannot be reproduced using currently available solution models which largely underestimate compositional variability of disordered dolomite and Mg-calcite series. The development of a new solution model for ternary carbonates profiting of high pressure data is in progress.

Thermodynamic properties of high-pressure magnesium silicates and analogue materials and equilibrium phase relations at high pressure

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Olivine(α)-wadsleyite(β) transition and postpyroxene transition of ringwoodite(γ) are accepted to be responsible to the 400 and 660 km seismic discontinuities, respectively. Recently, postperovskite transition in MgSiO₃ was found at pressure corresponding to the D'' layer of the mantle. Studies on high-pressure transitions in Mg₂SiO₄ and MgSiO₃ are very important to clarify the nature of these discontinuities. Calorimetric measurements of high-pressure phases are useful to constrain thermodynamic properties that can be used for thermodynamic modeling of the high-pressure transitions. In contrast to enthalpies, entropies of most of high-pressure silicates have not yet been directly measured, because adiabatic method used for low temperature heat capacity measurement requires a sample of one to several grams. Recently, thermal relaxation method was developed to measure low temperature C_p of samples of milligram quantity. In this study, we determined entropies of high-pressure magnesium silicates by the thermal relaxation C_p measurement, and also enthalpies of the magnesium silicates and analogue materials by high-temperature calorimetry. Using the measured thermodynamic data, high-pressure phase relations were calculated in comparison with experimental determinations.

Sintered polycrystalline β- and γ-Mg₂SiO₄ were synthesized to measure heat capacities at 2-305 K with the thermal relaxation method using a PPMS apparatus. Drop-solution enthalpies of the Mg₂SiO₄ phases were measured using a Calvet-type microcalorimeter at 978 K. For CaIrO₃ perovskite and postperovskite phases, analogue materials to MgSiO₃, enthalpies for dissociation into CaO + Ir + oxygen were measured by a high temperature drop calorimeter at 1573 K. At 298 K, entropy and enthalpy of the α-β transition in Mg₂SiO₄ were -7.7 J/molK and 28.9 kJ/mol, respectively, and those of β-γ transition were -3.6 J/molK and 12.9 kJ/mol, respectively. The enthalpy of CaIrO₃ perovskite-postperovskite transition was measured as -34 kJ/mol. Using the measured entropy and enthalpy data, equilibrium transition boundaries were calculated. Though the dP/dT of the calculated boundary depends in part on adopted heat capacity equations at high temperature, the α-β and β-γ transition slopes in Mg₂SiO₄ are less steep than those by in situ X-ray observations. The calculated boundary of the CaIrO₃ perovskite-postperovskite transition has a large slope, about 0.04 GPa/K, which is generally consistent with that by experiments and is comparable with that of MgSiO₃ by recent experimental and theoretical studies.

The effects of water content and oxygen fugacity on the olivine to wadsleyite transformation

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It is generally accepted that the olivine to wadsleyite phase transformation causes the "410" km seismic discontinuity. A number of seismological studies provide evidence that the depth and depth interval over which this transformation takes place vary regionally within the Earth. These variations have been ascribed to variations in temperature and/or H₂O content of the mantle. But variations in oxygen fugacity could also affect the transformation as ferric iron readily dissolves in the wadsleyite structure whereas it is almost totally excluded from olivine.

The effect of H₂O on the olivine to wadsleyite transformation has been examined in a multianvil by determining the extent to which the Mg₂SiO₄ wadsleyite stability field expands under H₂O-saturated conditions. The effect of oxygen fugacity has been determined by examining the extent of the olivine to wadsleyite stability field at an oxygen fugacity buffered by Re-ReO₂. In both cases experiments were performed with a second capsule containing an (Mg,Fe)₂SiO₄ assemblage buffered by the presence of metallic Fe from which the experimental pressure can be accurately determined by comparison with the known olivine-wadsleyite phase relations. The results have been used to refine a thermodynamic model that can determine the wadsleyite stability field over a range of mantle H₂O and redox conditions.

Results show that the wadsleyite stability field expands by over 1.5 GPa at 1200°C under water saturated conditions. This expansion decreases rapidly, however, with increasing temperature to less than 0.3 GPa at 1600°C, which is consistent with the observed decreasing solubility of hydroxyl in the wadsleyite structure with increasing temperature. H₂O concentrations on the order of 500 ppm at ambient mantle conditions would have very little effect on the position and sharpness of the 410. H₂O can only cause a significant broadening of the 410 at lower temperatures, for example, in areas of subduction. For redox conditions buffered by Re-ReO₂, however, the wadsleyite stability field expands by over 0.5 GPa at ambient mantle conditions. Although ferric Fe concentrations are >10% of total Fe at these conditions, typical mantle ferric Fe contents may also slightly broaden the transformation. The dilution of the mantle's ferric Fe content in wadsleyite will cause the transition zone to be more reduced than the upper mantle. Simple calculations predict a strong influence of redox state on the speciation of C-O-H fluids and melts, resulting in volatile species such as CH₄ and even H₂ becoming more important in the transition zone.

High-pressure polymorphism, phase transition and elastic behaviour of behoite, Be(OH)₂

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The elastic properties of hydrous minerals and OH-bearing phases play an important role for understanding the magnitude of effects resulting from hydrous components in mineral structures. Synthetic behoite, Be(OH)₂ beryllium hydroxide (space-group symmetry P2₁2₁2₁, Z=4, a=4.5861 Å, b=7.0512 Å, c=4.4914 Å), has been subject of a high-pressure static compression study at room temperature. Diffraction pattern from a polycrystalline sample loaded in a ETH-type diamond-anvil cell (0.6 mm culets, methanol-ethanol pressure medium, ruby pressure-calibration) were recorded using synchrotron radiation at ESRF (beamline ID27, λ=0.37380 Å, MAR345 image-plate detector, 358.4 mm sample-to-detector distance, 50x50 μm beam cross-section, 120 s exposure time, patterns recorded between 1 bar and 10.9 GPa). The static compression data reveal an orthorhombic-to-orthorhombic phase transition at around 2.4 GPa with a ~1.7% volume discontinuity at the critical transition pressure. The high-pressure polymorph follows an orthorhombic lattice symmetry (Z=8, a=6.5977 Å, b=7.3374 Å, c=5.9774 Å at 2.6 GPa). The bulk modulus and its pressure derivative (K=45.6 GPa, dK/dP=3.4) of the high-P polymorph is similar to that of the low-P form (K=43.7 for a second-order BM equation of state). The compressibility data for the low-P phase show features of elastic softening on approaching the critical transition pressure, indicating the structural instability of low-P behoite at high pressures. The mechanism of the structural transition will be discussed based on the results of the experimental high-pressure diffraction study.

Fe³⁺ and Al partitioning between silicate perovskites at the lower mantle condition

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Perovskites with MgSiO₃ and CaSiO₃ are thought to be the major silicate minerals in the Earth's lower mantle. MgSiO₃ perovskite (Mg-Pv) incorporates Fe³⁺ and Al as Fe³⁺₂O₃, Fe³⁺AlO₃ and Al₂O₃ components. CaSiO₃ perovskite (Ca-Pv) also accommodates as Fe³⁺₂O₃ and Al₂O₃. Therefore, these perovskites are known as the host phases of Fe³⁺ and Al in the lower mantle. Previous study also indicated that Fe³⁺ associated with Al in Mg-Pv as Fe³⁺AlO₃ component. Therefore MgSiO₃-CaSiO₃-Fe³⁺AlO₃ system is important to understand the distribution of Fe³⁺ and Al in the Earth's lower mantle. Here, we report the partitioning of Fe³⁺ and Al between Mg-Pv and Ca-Pv at the lower mantle condition.

A gel with CaMgSi₂O₆ : Fe³⁺AlO₃ = 85 : 15 (85CM) were used as the starting materials. High pressure and temperature experiments for 85CM at 27-100 GPa and 1600-2500 K were conducted by using a laser-heated diamond anvil cell. Analytical transmission electron microscopy and high pressure *in-situ* X-ray experiment were also demonstrated.

The product phases in 85CM were Mg-Pv, Ca-Pv and small amount of stishovite up to 30 GPa and 1600 K, and then stishovite disappeared at higher pressure and temperature. Mg-Pv incorporated most Fe³⁺ and Al, and the composition of Ca-Pv was nearly pure, Fe³⁺/Al ratio in Mg-Pv was almost 1 in all condition. Therefore, Fe³⁺ and Al are dominantly incorporated into Mg-Pv mostly as Fe³⁺AlO₃ component. Although the dominant substitution scheme is the coupled substitution (Fe³⁺Al → MgSi) at all condition, the occurrence of stishovite suggests partly oxygen vacancy forming substitution (Fe³⁺Al → 2Si) at lower pressure and temperature. The partition coefficient of Fe³⁺ and Al, K^D = (X^{FeAl}_{Ca-Pv})/(X^{FeAl}_{Mg-Pv}), were almost constant, around 0.1-0.2 at 27-100 GPa and 1600-2500 K.

When Mg-Pv coexists with Ca-Pv at lower mantle condition, Fe³⁺ and Al are likely to be incorporated to Mg-Pv as Fe³⁺AlO₃ component. For incorporation of Fe³⁺AlO₃, the oxygen vacancy forming substitution is relatively important at pressures corresponding to the uppermost part of the lower mantle and then the coupled substitution seems to be increasingly favored at higher pressure.

Hexagonal perovskites in barium silicates

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Silicate perovskites in A²⁺SiO₃ have been widely surveyed as the key materials in the Earth's interior. In such silicate perovskites, only cubic (*Pm3m*) and orthorhombic (*Pbnm*) forms have been recognized for a long time except for a minor tetragonal modification of CaSiO₃ perovskite (Shim et al. 2002). Recently, the presence of hexagonal perovskite (6H-BaTiO₃ type: *P6₃/mmc*) was confirmed in strontium silicates at 35 GPa (Yusa et al. 2005). On the crystallographic aspect, the symmetry of such perovskites is associated with the ionic radii of divalent cations. The tolerance factor, $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$, where r denotes the ionic radii of each element, has been viewed as such a indicator. The cubic structure in perovskite (e.g. CaSiO₃; $t = 0.99$) exhibits the value close to 1.0. In case of the hexagonal perovskite in SrSiO₃, the value ($t = 1.04$) is greater than unity. In the present study, we note the high tolerance factor ($t = 1.11$) of BaSiO₃. We carried out high-pressure experiments to explore the perovskite structure in BaSiO₃.

The *in-situ* x-ray experiments have been done at BL-10XU (SPring-8) using a diamond anvil cell (DAC) combined with a continuous wave Nd:YLF laser. The starting sample of BaSiO₃ (high-temperature BaGeO₃ type) mixed with a small amount of platinum was compressed without pressure medium in the DAC. After laser heating at 32 GPa and 52 GPa, 9R (*R-3m*) and 6H (*P6₃/mmc*) hexagonal perovskites appeared, respectively. Both perovskites decomposed to amorphous during decompression to ambient pressure as does SrSiO₃ hexagonal perovskite. The structural difference of 9R and 6H perovskites is explained by the periodicity of face-sharing SiO₆ octahedron. In the direction of *c* axis, 9R perovskite exhibits (chl)₃; whereas, 6H perovskite exhibits (cel)₃ sequence, where *c* and *h* correspond to corner- and face-sharing octahedral, respectively. Present results suggest that the large divalent cation of barium can incorporate into the 9R perovskite structure with increasing the number of face-sharing octahedra even at comparable pressure to stabilize 6H perovskite in SrSiO₃.

In-situ determination of Fe-S and Fe-Si high-pressure melting diagramsD. Andraut¹, N. Bolfan-Casanova², O. Ohtaka³, H. Fukui³, G. Morard⁴, N. Guignot⁶, and K.I. Funakoshi⁵¹ Institut de Physique du Globe de Paris, Université Paris 7, Paris, France
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The Earth's inner core crystallizes slowly with time as a consequence of the secular cooling of our planet. This process is affected by the presence of light elements which decrease the melting temperature of iron and have a higher affinity for liquid iron. Understanding the thermal and chemical state at the inner core boundary (ICB) relies on the knowledge of the high-pressure melting diagrams of iron-alloys, which are poorly constrained. We report *in-situ* observations of the melting behavior of iron alloyed with 10 to 20 atom% Si, S, or C, at pressures between 15 and 60 GPa, using synchrotron radiation at Spring8 using the multi-anvil press, and at the ESRF using laser heated diamond anvil cell. Oxygen fugacity was controlled by choosing specific chemical compositions for the starting materials. Melting or recrystallization was evidenced by the diffraction peak disappearance or apparition, and we have also quantified the degree of partial melting of the iron-alloys from the analysis of the diffuse x-ray scattering visible in the diffraction patterns.

Coupled with micro-analysis of recovered samples, the *in-situ* observations bring direct constraints on the shape and positions of the main boundaries (eutectic, solidus, liquidus) in the melting diagrams. Our results evidence that the compatibility of Si and C with solid iron remains at least 5 times greater than that of S in our experimental pressure range. Extrapolations to the ICB pressure conditions remain speculative, but confirm that S can hardly explain the density jump at the ICB, because its compatibility with solid iron increases with pressure. On the other hand, all our experiments show a larger melting temperature depression (ΔT_m) than expected, which strengthen the dominant effect of the light elements for the temperature determination at the Earth's ICB. An other importance of very low eutectic temperature is the slow crystallization of an inner core in smaller planets like Mars or Moon.

P01-01

Heat capacity of Si-wadeite (K₂Si₄O₉) and related phase equilibriaW. Yong¹, E. Dachs², A.C. Withers¹, E.J. Essene³¹ Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA

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Synthesis of 21.4 mg Si-wadeite (K₂Si₄O₉) was undertaken at 3 GPa and 1273 K using a piston-cylinder apparatus at the University of Minnesota. The heat capacity (Cp) of Si-wadeite was then measured over the range of 5-303 K using a physical properties measurement system (PPMS). The low-temperature Cp data measured in this study fit smoothly with previously measured Cp data between 195 K and 598 K by DSC. The standard entropy of Si-wadeite is calculated to be 253.8±0.2 Jmol⁻¹K⁻¹ by integration of the fitted function in the form of $C_p = k_0 + k_1T^{0.5} + k_2T^{-2} + k_3T^{-3} + k_4T + k_5T^2 + k_6T^3$. With the help of this new entropy data, totally independent calculations of the phase transition boundaries involving Si-wadeite can be carried on using Perple_x. Our calculated phase boundaries in the system K₂O-Al₂O₃-SiO₂ are in good agreement with previous experimental work within 0.2 GPa. However, our calculation doesn't favor previous thermodynamic calculation that suggested sanidine would dissociate first to kalsilite (KAlSiO₄) + coesite instead of Si-wadeite + kyanite + coesite. This discrepancy is mainly caused by the inaccurate entropy value of Si-wadeite in their study.

P01-02

Heat capacities and entropies of mixing of pyrope-grossular (Mg₃Al₂Si₃O₁₂-Ca₃Al₂Si₃O₁₂) garnet solid solutionsE. Dachs¹, Ch. Geiger²¹ Department of Material Science, Division of Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria.

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The low-temperature heat capacities for a series of synthetic pyrope-grossular (Py-Gr) garnets along the Py-Gr join were measured with the heat capacity option of the Physical Properties Measurement System (PPMS) produced by Quantum Design®. The measurements were performed between 5 and 300 K on milligram-sized polycrystalline garnets that have been well characterized in previous studies. The Cp measurements indicate positive excess heat capacities (ΔC_p^{ex}) for all solid-solution compositions at temperatures < 50 K with a maximum value of 2.31±0.18 J/(mol K) for the composition Py50Gr50 at about 35 K. Pyrope-rich garnets (i.e., Py90Gr10 and Py75Gr25) have no or slightly positive ΔC_p^{ex} at higher temperatures, whereas grossular-rich garnets (i.e., Py10Gr90 and Py25Gr75) show negative ΔC_p^{ex} values in the temperature range between 50 and 150 K. At T > 150 K ΔC_p^{ex} values scatter around zero for all compositions and the experimental error is too large to permit a clear determination on whether ΔC_p^{ex} is different from zero within 2σ uncertainty. Excess entropies (ΔS^{ex}), calculated from the Cp data of the various solid solution members, at 298.15 K are asymmetric in nature with the largest positive deviations in pyrope-rich compositions. An asymmetric Margules mixing model was found to be inappropriate for modeling the ΔS^{ex} -X data and, thus, a two-parameter Redlich-Kister model was used to describe the excess entropy-composition relationship. Using this macroscopic mixing model for the excess entropy, a T-X diagram for Py-Gr garnets was calculated using different published values for the excess enthalpies of mixing. The effect of short range Ca-Mg order in the solid solution was also considered in the calculations. The calculations give a solvus for the pyrope-grossular join with a higher critical temperature in the range 850-1330 °C at $X_{\text{Gr}} = 0.35$ compared to previous thermodynamic models ($T_{\text{crit}} < 600$ °C) that use symmetric mixing models to describe the excess entropy. Unmixing of garnets in nature, as documented from occurrences in ultramafic diatremes may, therefore, have occurred at higher temperatures than previously thought. The atomistic and lattice-dynamic properties of Py-Gr garnets are reviewed and compared to the macroscopic Cp data. Published IR and Raman spectra are consistent with the occurrence of positive ΔC_p^{ex} values at low temperatures.

P01-03

Nanostructures, thermodynamic functions and hydration of clay mineralsH. Gailhanou¹, J. Olives², M. Amouric², J. Rogez³, J. C. van Miltenburg⁴, G. J. K. van den Berg⁵, G. De Weireld⁵, Y. Belmabkhout⁵, R. Perbost⁵, A. Inoue⁶, E. Gaucher¹, and P. Blanc¹¹ BRGM, av. Claude Guillemin, 45060 Orléans cedex 2, France.² CRM-CNRS, Campus de Luminy, 13288 Marseille cedex 9, France.

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For the first time, nanostructural characterization and all the thermodynamic functions of international reference clays — illite IMt-2, Silver Hill, USA; smectite MX-80, Wyoming, USA; mixed-layer illite-smectite ISCZ-1, Slovakia; mixed-layer illite-smectites from Shinzan, Japan — are presented, at any temperature between 0 K and 500 K, for (i) anhydrous and (ii) highly hydrated minerals. The nanostructural study (HRTEM-EDX) of illite IMt-2 is very original: it reveals the presence of a « trioctahedral illite », interlayered with dioctahedral illite. In smectite MX-80 sample, an important amount of SiO₂ impurities, 20 wt.%, is detected and the smectite mineral is not a montmorillonite, as usually referred: it is a mixing of beidellite and beidellite-montmorillonite. Dissolution isothermal calorimetry is used to determine the enthalpies of formation of the minerals. They are obtained by dissolution in a HF-HNO₃ solution at 25°C of (1) the clay sample and (2) the mechanical mixture of the (oxide or hydroxide) constituents of the clay mineral (+ the impurities). Heat capacities from 0 K to 500 K, obtained by adiabatic calorimetry and differential scanning calorimetry, are corrected by subtracting the contribution of impurities. Entropies, Gibbs free energies of formation and all the thermodynamic functions are finally obtained. At low temperatures, water in smectite or illite-smectite is a glass: one or two glass transitions are observed between 150 and 270 K; and it is liquid water, above 273 K. Clay minerals are more stable than the assemblage of their oxide constituents, and hydrated clay minerals more stable than the assemblage of the anhydrous clay mineral and water. Hydration of smectite and mixed-layer illite-smectite is also studied with the help of water vapor adsorption isotherms, obtained at various temperatures, from 25°C to 105°C, and fitted with a modified BET model. Gibbs free energies of hydration are determined: they are in agreement with the above calorimetric values. The enthalpies of mixing of illite and smectite « layers », obtained by dissolution isothermal calorimetry, on the Shinzan illite-smectite series, are found to be slightly negative (minimum -3 kJ.mol⁻¹). Mixed-layer illite-smectites are then slightly more stable than the assemblage of the two phases, illite and smectite. Energy modelling, based on interatomic potentials, shows that mixed layering occurs as a stacking of O₁₂TiO₁₂ units (and not of TOT layers; T, O, I = tetrahedral sheet, octahedral sheet, interlayer, respectively) of illite and smectite, and the calculated energy of mixing is in agreement with the preceding experimental value.

P01-04

Thermodynamic properties and high pressure phase equilibria of hexagonal phases in the systems $\text{MgAl}_2\text{O}_4\text{--CaAl}_2\text{O}_4$ and $\text{NaAlSi}_3\text{O}_8\text{--MgAl}_2\text{O}_4$ A. Ono¹, H. Kojitani¹, and M. Akaogi¹¹Department of Chemistry, Gakushuin Univ., Mejiro, Toshima-ku, Tokyo, 171-8588, Japan.

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An aluminous hexagonal phase (hp) which is sometimes called a NAL phase has been proposed as one of possible major host phases for alkali elements in the lower mantle. However, thermodynamic properties and stability relations of the hexagonal phase have not yet been clarified in detail.

In this study, using a 6-8 type multianvil apparatus phase relations at high pressures and high temperatures were examined, and the transition pressures from mixture of CaAl_2O_4 (calcium ferrite) and MgAl_2O_4 (spinel) to $\text{Mg}_{0.67}\text{Ca}_{0.33}\text{Al}_2\text{O}_4$ (Mg-Ca hp) and from mixture of $\text{NaAlSi}_3\text{O}_8$ (jadeite), $\alpha\text{-NaAlO}_2$, and MgAl_2O_4 (sp) to $\text{Na}_{0.5}\text{Mg}_{0.5}\text{Al}_{1.5}\text{Si}_{0.5}\text{O}_4$ (Na-Mg hp) were determined. Enthalpies of these phases were measured using a twin Calvet-type microcalorimeter. Drop-solution calorimetry method with gas bubbling technique was adopted to measure the enthalpies. A lead borate ($2\text{PbO} \cdot \text{B}_2\text{O}_3$) solvent was used for the enthalpy measurements. Raman spectra of these hexagonal phases were obtained using a micro-Raman spectroscopy system. The obtained Raman spectra were applied to C_p calculation using the Kieffer model.

The enthalpies of transition for the hexagonal phases of $\text{Mg}_{0.67}\text{Ca}_{0.33}\text{Al}_2\text{O}_4$ and $\text{Na}_{0.5}\text{Mg}_{0.5}\text{Al}_{1.5}\text{Si}_{0.5}\text{O}_4$ were 36.8 ± 2.6 and $54.7 \pm 1.9 \text{ kJ mol}^{-1}$, respectively. Using the measured enthalpies and transition pressures, entropies of transition for the Mg-Ca and Na-Mg hexagonal phases were calculated to be 1.45 and $-1.13 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The vibrational entropies at 298K of the Mg-Ca and Na-Mg hexagonal phases calculated using the Kieffer models were 86.1 and $81.6 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. By considering configurational entropies of these hexagonal phases, transition entropies of the Mg-Ca and Na-Mg hexagonal phases were 2.39, $0.46 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The phase boundaries calculated thermodynamically were in good agreement with those determined by the high pressure experiments.

P01-05

Phase Relations of $\text{CaAl}_4\text{Si}_2\text{O}_{11}$ at high-pressure and high-temperature conditionsS. Zhai^{1,2} and E. Ito¹¹Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken, 682-0193, Japan.

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An alumina-rich calcium aluminosilicate (CAS) phase, $\text{CaAl}_4\text{Si}_2\text{O}_{11}$, occurs in rocks formed from sediments and continental crust at pressures corresponding to those in the upper mantle and transition zone. Previous a few high-pressure experimental works have revealed that this phase is stabilized under pressures higher than 14 GPa. Therefore, the CAS phase would be an important constituent of slab in the deep mantle as a product of crust materials subduction. It is highly likely that the CAS phase is an important host phase of Al and Ca in the deeply subducted slab. Natural occurrence of the CAS phase, on the other hand, was discovered in a shocked Martian meteorite, which contained a significant amount of sodium expressed as $(\text{Ca}_x\text{Na}_{1-x})\text{Al}_{3+x}\text{Si}_{3-x}\text{O}_{11}$.

As a little is known on the stability of the CAS phase at high-pressure and high-temperature conditions, quantitative phase relations determined in the present study are urgently required to understand slab mineralogy and dynamics in the deep mantle.

We determine the stability of the calcium aluminosilicate (CAS) phase, $\text{CaAl}_4\text{Si}_2\text{O}_{11}$, especially examining a possible transformation of the phase at high pressures and high temperatures. The experiments were carried out up to 40 GPa and 2000K using the Kawai-type high-pressure apparatus. Based upon the results, we try to make clear the mineralogical structure of subducted slab down to the lower mantle and discuss dynamics of the slab in deep mantle.

P01-06

X-ray diffraction studies of high-pressure phases of calcite at room temperature

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At room temperature, calcite transforms to calcite II at about 1.4 GPa, and further to calcite III at about 1.8 GPa (Bridgman, 1939; Singh and Kennedy, 1974). The crystal structure of calcite III has not been known. Recently we determined the crystal data of calcite III (monoclinic *C*-centered lattice, *Z*=8) using single-crystal X-ray diffraction methods at room temperature and pressures above 2.3 GPa (Hagiya et al., 2005). By increasing the sample pressure, a new high-pressure phase of calcite has been found by single-crystal X-ray diffraction methods. The present studies have been carried out to determine the crystal data of the new phase and calcite III at room temperature.

The specimens used in the present studies are single crystals of natural calcite from Creel, Chihuahua, Mexico. The Merrill-Bassett type diamond-anvil-cells were used for high-pressure experiments. Pressures were estimated based on the ruby-fluorescence method. X-ray diffraction measurements were performed using an Enraf-Nonius CAD-4 diffractometer with $\text{MoK}\alpha$ radiation monochromatized by graphite. A flat cassette for imaging plates was attached on the diffractometer to measure diffraction patterns.

On the oscillation photographs taken at 2.5 GPa, all the reflections could be well assigned as calcite III. By increasing the sample pressure to 4.5 GPa, several reflections disappeared and the remained reflections could not be assigned by monoclinic cell. Then, the remained reflections were re-indexed and the cell parameters were determined with the angular data of 25 reflections. The new high-pressure phase at 4.5 GPa is triclinic, $a=3.855(3)$, $b=4.815(2)$, $c=6.165(5) \text{ \AA}$, $\alpha=84.10(4)$, $\beta=72.15(5)$, $\gamma=88.73(5)$, $Z=2$. The relationship between the lattice vectors of calcite III (a_m , b_m , c_m) and the triclinic new phase (a_t , b_t , c_t) are determined as $a_t=(a_m-b_m+2c_m)/4$, $b_t=(a_m-b_m-2c_m)/4$ and $c_t=(3a_m+b_m+2c_m)/4$. The phase transition from calcite III to the new phase may occur at 3.7-3.9 GPa and the new phase back-transform to calcite at ambient conditions with a remarkable hysteresis.

P01-07

Stability of high-temperature orthopyroxene in $\text{Mg}_2\text{Si}_2\text{O}_6\text{--CaMgSi}_2\text{O}_6$ system at atmospheric pressureS. Ohi¹, A. Miyake¹, N. Shimobayashi¹, and M. Kitamura¹¹Department of geology and Mineralogy, Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

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In the Mg-rich portion of $\text{Mg}_2\text{Si}_2\text{O}_6\text{--CaMgSi}_2\text{O}_6$ system, there had been the controversy about the appearance and stability of the orthopyroxene phase at high temperatures other than protoenstatite Foster and Lin (1975). Late in the 1980's, after going through the discussion on the relationship with orthoenstatite, Carlson (1988) concluded that Ca-bearing high-temperature orthorhombic pyroxene (HT-OPx) was a thermodynamically distinct phase from orthoenstatite. However, there was no obvious experimental evidence that stands by his conclusion and there has been no direct observation of any transition into the HT-OPx. In recent years, Jackson et al. (2004) and Miyake et al. (2004) independently reported the transition to the high-temperature orthoenstatite although both of them used Ca-free starting materials. However, an inconsistency was about the symmetry; Jackson et al. (2004) determined the space group as *Cmca* whereas Miyake et al. (2004) as *Pbca*. The purposes of the present study are (1) to elucidate the stability of HT-OPx near 1400 °C using Ca-bearing starting materials and (2) to determine the space group of the HT-OPx. At first, the stability field of HT-OPx near 1400 °C was confirmed by synthesis experiments. 30 samples were synthesized from gels with 3 kinds of compositions in enstatite-diopside-forsterite system at different 10 temperatures between 1360 and 1450 °C. Run durations were about 7 days to 14 days. They were analyzed with an optical microscope, X-ray powder diffractometer (XRD), a scanning electron microscope and energy dispersive X-ray spectrometer and an electron backscattered diffraction. The composition of PEn was about $X_{\text{Di}} < 3 \text{ mol\%}$, HT-OPx was $5 < X_{\text{Di}} < 8 \text{ mol\%}$ and Pig was $9 \text{ mol\%} < X_{\text{Di}}$. The stability field of HT-OPx phase was restricted between 1370 and 1442 °C. The sample in the phase of HT-OPx ($\text{Ca}_{0.06}\text{Mg}_{1.94}\text{Si}_2\text{O}_6$) + forsterite + liquid was used as a starting material for the examination of high-temperature in-situ X-ray powder diffractometer (HT-XRD) at the temperature between 790 and 1364 °C. (210), (321) and (610) peaks prohibited by the extinction rule of *C* lattice always appeared and Carlson et al. (1988) also observed these peaks at 1425 °C. HT-OPx wasn't the space group of *Cmca* which was suggested by Jackson et al. (2004). HT-OPx was thought to be the space group of *Pbca* because all peaks except (121) didn't show any change. Therefore, HT-XRD examinations showed the isosymmetric phase transition between LT- and HT-OPx ($\text{Ca}_{0.06}\text{Mg}_{1.94}\text{Si}_2\text{O}_6$, space group, *Pbca*) was observed between 1170 and 1364 °C.

Polymorphic relation between cavansite and pentagonite: implications for hydronium and hydroxyl ions in cavansite

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Rare hydrous vanadosilicate minerals, cavansite and pentagonite, are known as dimorphs of $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10})\cdot 4\text{H}_2\text{O}$ (Staples et al. 1973). Their crystal structures were characterized by silicate layer arrangements, where cavansite with a network of 4- and 8-fold rings is different from pentagonite with that of 6-fold rings (Evans 1973). Cavansite and pentagonite used in this study are from Wagholi in India, where there are associations of these two minerals with mordenite, heulandite, and stilbite. The chemical compositions of cavansite and pentagonite, including water contents and oxidation states of vanadium, were determined by thermogravimetric and differential thermal analysis (TG-DTA), electron spin resonance (ESR) and EMPA. Dehydration mechanisms and hydrous species (H_2O , H_3O^+ and OH^-) in both minerals have been examined by means of TG-DTA, high-temperature X-ray diffraction (HT-XRD) analysis, and Fourier-transformed infrared (FT-IR) spectroscopic analysis. Water contents in cavansite and pentagonite were estimated at 15.95 and 16.07 wt%, respectively, which correspond to ideal water content (15.96 wt%). Vanadium cations in both minerals were identified as only V^{4+} by ESR measurements. TG-DTA and HT-XRD analyses demonstrated that the reversible transition between cavansite and pentagonite never occurs by heating on air condition and that there exists no intermediate amorphous phase between both minerals. Cavansite turned out to preserve the crystal structure up to 400°C and to have three zeolitic waters. On the other hand pentagonite was interpreted to exhibit the crystal structure up to 550°C, and all four water molecules of pentagonite exist as a zeolitic water. Gradual dehydrations of cavansite in the temperature ranging between 225 and 550°C were attributed to removal of hydronium ion, H_3O^+ , and hydroxyl ion, OH^- . The IR absorption bands at 3186 and 3653 cm^{-1} of cavansite were assigned to H_3O^+ and OH^- , respectively. Since neither excess water nor deficiency of Ca^{2+} was recognized in cavansite, the possible exchange reaction (Wilkins et al. 1974) is as follows: $\text{H}_3\text{O}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$. Thus, the new structural formula $\text{Ca}(\text{VO})(\text{Si}_4\text{O}_{10})\cdot 2\text{H}_2\text{O}(\text{H}_3\text{O})(\text{OH})$ is proposed for cavansite. The difference in structural formula between cavansite and pentagonite suggests that hydrous species characterize the polymorphic relation between both minerals. Therefore, the difference in condition of crystallization between cavansite and pentagonite may be caused by whether the hydrothermal fluid yielding either the former or the latter is in super critical condition or not. Resultantly cavansite and pentagonite can be regarded as of a low-temperature form and of a high-temperature one, respectively, from a polymorphic viewpoint.

O02-01

Measurements of velocities and elastic properties at high pressures and temperatures

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The best-resolved properties of Earth's interior are the sound velocities V_p and V_s , and the density. Beyond average radial properties, seismological studies now reveal lateral heterogeneity and anisotropy of the mantle, yielding a fully 3-D view of mantle structure and properties. A major challenge at the interface of mineral physics and seismology is to understand this new view of the mantle, the causes of seismic heterogeneity, and their likely geodynamical implications. Indeed, it appears that both variations in chemical composition and thermal structure contribute to the observed velocity heterogeneity at all levels in the mantle.

In order to fully exploit the information emerging from seismic investigations, it is essential to know shear properties of mantle constituents as well as their bulk moduli (K). While the bulk modulus (and its P and T derivatives) provides necessary information on the density at depth, in many cases the shear modulus and V_s are more sensitive to compositional variations. An example is the substitution of aluminum in Mg-silicate perovskite, where the addition of only 5% Al substantially reduces the shear modulus while having a much smaller (if any) effect on K . Shear properties can therefore provide much tighter constraints on the range of acceptable chemical and thermal models for the mantle. However, relatively few direct experimental measurements have been available on the relevant shear properties. This situation has changed dramatically in the past few years. Shear velocities and moduli at high P and/or T have been measured using several techniques, including light scattering (eg., Brillouin scattering, laser phonon spectroscopy or LIPS), ultrasonic interferometry and resonance, and x-ray diffraction with the diamond cell. We review a selection of the results, emphasizing measurements at high pressures and/or temperatures. An additional technical challenge in high-pressure experimentation is accurate determination of pressure. Combining acoustic measurements of velocity with density measurements by diffraction provides a means for defining primary pressure scales. For that purpose, a Brillouin spectrometer has been interfaced with synchrotron radiation at sector 13 (GSECARS) of the Advanced Photon Source. Techniques that are likely to play an increasingly important role in determination of sound velocities under extreme conditions are those developed at third-generation synchrotron sources, such as inelastic scattering of phonons by x-rays, and nuclear resonant inelastic x-ray scattering.

O02-02

Ultrasonic velocities of majorite garnet and mineralogy of the mantle transition region

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We have developed techniques for precise measurements of elastic wave velocities for polycrystalline sintered bodies of high-pressure phases at pressures to 19 GPa and temperatures to 1700K, equivalent to those of the middle part of the mantle transition region (MTR), by a combination of Kawai-type multianvil apparatus, ultrasonic interferometry, and synchrotron radiation. First such attempts on $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ ringwoodite yielded satisfactory results, consistent with those reported in earlier studies based on different measurements at high pressure and room temperature, or at high temperature and ambient pressure. Here we report the measurement of elastic wave velocities of majorite with a "pyrolyte minus olivine" composition using the same techniques. We found the velocities of the majorite are substantially lower than the earlier estimates based on the measurements for simpler compositions under lower P - T conditions. The present results on the majorite, combined with those of ringwoodite, strongly suggests that pyrolyte yields seismic velocities consistent with those of typical seismological models in the middle part of the MTR, while the bottom ~100km part of this region may have an alternative chemical composition.

O02-03

Predicting dislocation properties using the Peierls-Nabarro model: the example of the perovskite and post-perovskite phases of MgSiO_3

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$(\text{Mg, Fe})\text{SiO}_3$ perovskite (Pv) is widely believed to be the most abundant mineral of the lower mantle. The recently reported post-perovskite (pPv) phase transition provides a potential explanation for the seismic properties exhibited by the region above the core-mantle boundary. The elastic properties of these minerals are necessary, but not sufficient to interpret the seismic observations. In particular, seismic anisotropy, where observed, need to take into account potential lattice preferred orientations induced by convective flow. It is thus necessary to model dislocations properties in these phases to elucidate the structure and dynamic processes in the deep mantle.

The rapid increase in efficiency and power of computers, coupled with methodological advances allow quantum mechanics-based studies of reasonably sized systems. However, the direct modeling of dislocations in minerals (with often large unit cells, low symmetries and complex crystal chemistries) is still a challenging issue. The so-called Peierls-Nabarro (PN) model is a fundamental concept of the dislocation theory which describes the resistance of the lattice to dislocation motion (also called lattice friction). The PN model also provides a analytical description of the dislocation core and of its potential spreading in the glide plane. Known for several decades, the PN model has triggered a renewed interest when Christian and Vitek (1970) showed that realistic models of dislocations could be built by incorporating calculations of generalized stacking faults (GSF) into the Peierls model. Today, GSF can be calculated on minerals from the first-principles.

In this study, we use the *ab initio* total-energy calculation package VASP to calculate GSF for MgSiO_3 perovskite and post-perovskite at 0, 30, 100 GPa (Pv) and 120 GPa (pPv). The GSF are calculated for several potential slip systems suggested by the crystal structure of these phases. These results are incorporated into the PN model to provide for each slip system a model of the dislocation core profile and the value of the stress required to move a dislocation rigidly: the so-called Peierls stress.

O02-04

High P - T rheological studies of hcp-Fe in its stability field

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The Earth's inner core is believed to be made up primarily of hexagonal-closed-packed (hcp) iron. It has been suggested that the observed seismic anisotropy of the inner core arises from lattice preferred orientation of hcp-iron caused by plastic deformation. However deformation experiments of hcp-iron under controlled pressure, temperature, and strain rate have not been possible so far because of experimental difficulties. Here we report the first controlled deformation experiments on hcp-iron using in-situ X-ray diffraction and radiography experiments, within the stability field of this important earth material. Deformation experiments were carried out at the GSECARS 13-BM-D beamline (APS) using a deformation-DIA with monochromatic X-ray diffraction and radiographic imaging. We used four tungsten carbide and two sintered diamond (SD) anvils with truncated edge length of 2 mm. Pressure medium was a mixture of boron and epoxy and a cylindrical graphite furnace was employed. The starting material was a bcc-iron cylinder (0.5 mm in diameter and 0.5 mm long). Two deformation pistons made of alumina were situated above and below the sample. First, the cell assembly was compressed uniformly at room temperature up to about 13 GPa. Then the sample was heated to about 700 K to transform the sample to hcp-iron. After the transformation, several deformation cycles were repeated. We obtained ten independent stress-strain curves at about 12 GPa, three different temperatures (600, 400, and room temperature), with axial strains in excess of 15 percent and strain rates between 10^{-7} and 10^{-5} s^{-1} . In some cases, steady-state deformation has been achieved. The differential stresses at the steady state flow were 2-3 GPa and tend to decrease with increasing temperature and with decreasing strain rate. Systematic comparison with other hexagonal metals, like cobalt and rhenium, and implications for deformation of the inner core will be discussed.

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The responses of hydrous sheet silicates to compression are varied. Important crystal-chemical factors controlling the way these minerals compress include:

- 1) Cross-interlayer cation superpositions;
- 2) Interlayer structure (low-charge cations, hydrogen bonding, Van der Waals);
- 3) Polyhedral structure (e.g. di-octahedral versus tri-octahedral sheets);
- 4) Oxygen packing efficiency.

While these factors are each conceptually obvious, how they interact to determine the compressional behaviour of hydrous sheet silicates is often not so clear and it is necessary to tease out the effects by relating elastic moduli (e.g. axial moduli) to structure, and by comparing topologically-related minerals. Due to the highly anisotropic structure of sheet silicates, their bulk moduli are not very informative in this respect. Based upon our recent synchrotron XRD studies, this presentation will compare the compressional behaviour of chlorite, lizardite and dickite in order to gain insights into the roles of the different factors listed above. The isosymmetric polytypic transformation in dickite at 2.6 GPa, driven by the removal of unfavourable cross-interlayer cation superpositions, is an instructive example and will be described in some detail. It involves restructuring of the interlayer hydrogen bonding, but perhaps surprisingly, there is also a marked in-plane softening of the di-octahedral sheet, which in high-pressure dickite-II is almost twice as compressible in the plane as the tri-octahedral sheet of lizardite. Ditrigonal rotation (and possibly buckling) of the tetrahedral sheet to match the dimensions of the shrinking di-octahedral sheet will reach a limit at high pressures and further compression of the di-octahedral sheet will result in a significant mismatching between octahedral and tetrahedral sheets that could lead to high-pressure amorphisation, as occurs in muscovite at ~18 GPa. Such behaviour contrasts markedly with that of tri-octahedral sheet silicates.

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Compressibility, stability, and interactions with guest molecules were studied on melanophlogite, a natural SiO₂ clathrate, up to about 25 GPa. Many elements and molecules, such as carbon, silicon, and ice, crystallize into clathrate structure and numerous studies have been made to clarify their high-pressure behaviors, from a viewpoint of both basic science and practical applications. Melanophlogite is a rare mineral formed by the volcanic activities and has clathrate structure formed by the combination of SiO₂ cages and guest gas molecules such as CO₂ and CH₄. By heating it in air above 700 °C, we can expel these guest gases from the SiO₂ cages and prepare SiO₂ clathrate with no gas molecules in it. We have studied both of these unheated and heated samples to see the role of guest gases in this structure. Experiments were made using high-pressure in situ X-ray observation and Raman spectroscopy. Several different kind of pressure-transmitting medium, methanol-ethanol-water mixture, CH₄, helium, and hydrogen, were used to compress the sample. In many cases, irreversible amorphization occurred under pressure but the compressibility and stability limit varied widely depending on the pressure-transmitting medium and heat treatment. Small molecules such as helium and hydrogen can get into the SiO₂ cages and alter their property considerably. Present study provides many interesting information about the interaction of host SiO₂ cage and guest gas molecules in clathrate structure.

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The recent discovery of a new MgSiO₃ high pressure polymorph ([1][2]) has a huge impact on our understanding of the structure and dynamics of the deep Earth. This phase with Cmcm CaIrO₃ type-structure, and now commonly named post-perovskite phase, is produced from Pbnm-perovskite MgSiO₃ in the 110-125 GPa pressure range ([3]). This roughly corresponds to the depth of appearance of Earth's D'' layer. This lowermost part of the lower mantle is the probable destination of a non negligible part of downwelling subducted slabs, the probable source of superswells and mantle plumes, and the site of chemical exchanges with the core, all of this being ruled by the very steep temperature gradient near the core-mantle boundary. It displays very complex seismic signatures, mainly due to a high lateral heterogeneity and shear-wave splitting ([4]). Knowing that (Al,Fe)-MgSiO₃ perovskite phase is the major constituent of the lower mantle, it is mandatory to clarify what are the effects of the post-perovskite phase production, i.e. the Clapeyron slope dP/dT of the transition and of course the post-perovskite phase elastic properties. It is therefore necessary to provide precise data on the post-perovskite phase compressibility at D'' layer pressure and temperature conditions. The new ID27 beamline facilities of ESRF (Grenoble) were used to collect in-situ high temperature angle-dispersive x-ray diffraction spectra at high pressure. After a short presentation of the experimental setup, details on post-perovskite phase P-V-T equation of state will be provided.

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Ringwoodite (Mg,Fe)₂SiO₄ is considered to be the most dominant mineral in the lower part of the mantle transition zone. Therefore, it is of great importance to characterize the temperature-pressure-volume (*T-P-V*) equation-of-state (EOS) of ringwoodite at high-*T* and high-*P* conditions found in the deep Earth. Here we present the EOS of (Mg_{0.8}Fe_{0.2})₂SiO₄ ringwoodite based on in situ high-*T* and high-*P* synchrotron X-ray diffraction experiments up to 1700 K and 20 GPa with a multi-anvil apparatus at SPring-8. The third-order Birch-Murnaghan equation was applied to the data between 300 and 900 K, while a constant ($\partial P/\partial T$)_V fitting at temperatures higher than 900 K. We obtained the EOS parameters of (Mg_{0.8}Fe_{0.2})₂SiO₄ ringwoodite using least squares as ($\partial K_T/\partial P$)_T = 4.57(7) and ($\partial K_T/\partial T$)_P = -0.0283(13) GPa/K between 300 and 900 K, and ($\partial P/\partial T$)_V = 0.00535(11) GPa/K at temperatures above 900 K. These values compare very well with previously measured data for Mg₂SiO₄ ringwoodite by Katsura et al. (2004) of ($\partial K_T/\partial P$)_T = 4.6(2), ($\partial K_T/\partial T$)_P = -0.029(1) GPa/K, and ($\partial P/\partial T$)_V = 0.0052 - 0.0055 GPa/K at high temperatures. At *P* = 20 GPa and *T* = 1800 K, as representative conditions in the lower part of the mantle transition zone, the relative *V* and *K_T* values of (Mg_{0.8}Fe_{0.2})₂SiO₄ ringwoodite with respect to the values at 300 K and 0 GPa are found to be *V*/*V*₀ = 0.9424, *K_T*/*K*_{0,300K} = 1.263, based on the present EOS, while those of Mg₂SiO₄ ringwoodite as *V*/*V*₀ = 0.9420, *K_T*/*K*_{0,300K} = 1.239, by Katsura et al. (2004). Thus the effects of Fe substitution for Mg on the *T-P-V* EOS of ringwoodite with (Mg_{0.9}Fe_{0.1})₂SiO₄, thought to be the composition in the mantle transition zone, are virtually negligible for *V*/*V*₀, and within 1% for *K_T*/*K*_{0,300K}.

EXAFS measurement for iron under high-pressure conditions

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Iron is considered as a main component of the Earth's core. The behavior of its high-pressure phase, hexagonal close-packed iron, is very interesting because the physical properties of hcp-iron can be considered as those of the core roughly. We have performed XAFS measurement for Fe *K*-edge at in-situ high-pressure condition using diamond anvil cells with thin diamond anvils in order to obtain inter-atomic potential for iron. This information will yield elastic wave velocity and isochoric heat capacity by combining crystallographic information. Experiments have been conducted at BL37XU of SPring-8. Pressure generating devices used were clock-type diamond anvil cells made of SUS or Cu-Be alloy. Iron powder mixed with boron nitride or iron foil with helium was put into a hole on a rhenium gasket. Generated pressure was determined by ruby fluorescence. Though obtained spectra have some apparent absorption spikes due to diffraction of single crystal diamonds, which make it difficult to analyze EXAFS oscillations, quantitative analysis has been performed with synthesized spectra from a few spectra obtained at each condition. From the analyzed results, we obtained inter-atomic distances of iron at various pressure conditions successfully. We will discuss Debye-Waller factor for hcp-iron and its pressure dependence.

Structural changes in the lone electron pair compound PbBi₂S₄ (galenobismutite) at the hydrostatic pressures between 0 and 10 GPa

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Galenobismutite, PbBi₂S₄, is isostructural with CaFe₂O₄ and with the mantle-pressure polymorph of NaAlSiO₄. In galenobismutite, however, all three distinct cation sites are occupied by cations, which exhibit lone electron pair activity. The M1 site has a slightly distorted octahedral coordination, the polyhedron of M2 is a lying monocapped trigonal coordination prism, and M3 is a standing, bicapped trigonal coordination prism. Pinto et al. (2005) found M1 to be a Bi position whereas M2 and M3 sites are mixed sites, with predominance of Bi and Pb, respectively.

High-pressure experiments were performed in an ETH-type diamond anvil cell with a mixture of methanol:ethanol=4:1 as medium, and quartz as a pressure indicator. A CCD-equipped Bruker AXS four-circle diffractometer with an appropriate structure solution program package was employed.

The 3rd order Birch-Murnaghan equation gives a zero-pressure volume of 700.6(2) Å³, bulk modulus *K*₀ 43.9(7) and its derivative *K*' 6.9(3). The large M3 polyhedron is most compressible, the rigidity of M1 polyhedra slackens at 6 GPa. Eccentricity of the M2 position remains preserved to the highest pressures, unlike the situation in bismuthinite Bi₂S₃ (Lundegaard et al. 2005), and bond lengths separate into two tight groups. This behaviour is shared by M1. The longer bonds are reduced to 2.9 Å as a lower limit; the short bonds are compressed much less, to 2.7–2.6 Å.

The coordination polyhedron of the M3 site appears to accommodate the configurational differences between different isotopes of CaFe₂O₄. In PbBi₂S₄ the highly asymmetric character of this polyhedron remains preserved under compression and M1 approaches a 7-fold coordination at high pressures.

Our studies show that the behaviour of lone electron pairs under pressure depends on the structure type. In the framework-approaching structure of galenobismutite, the lone electron pairs of Bi remain stereochemically active up to at least 10 GPa.

High-pressure behaviour of NaTi³⁺Si₂O₆: Comparative compressibilities of low-clinopyroxenes at hydrostatic pressures

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As pyroxenes are major phases in the Earth's upper mantle, the knowledge of compression behaviour is necessary for understanding properties and behaviour of the Earth's mantle. In this study high-pressure X-ray diffraction experiments were conducted on a synthetic single crystal of the C2/c-clinopyroxene NaTi³⁺Si₂O₆. An ETH-type diamond anvil cell with a 4:1 methanol:ethanol mixture as pressure-transmitting medium was used to achieve hydrostatic pressures up to 10.1 GPa. Unit-cell data were collected at 29 individual pressure points on a Huber four-circle diffractometer. Isothermal equation-of-state parameters were obtained by fitting the pressure-volume data to a 3rd order Birch-Murnaghan equation of state. With a zero-pressure unit-cell volume of *V*₀=437.92(3) Å³, a bulk modulus of *K*₀=107.6(6) GPa and its pressure derivative *K*'=6.53(16) the alkali-metal clinopyroxene fits well into the negative correlation between the size of the M1 cation and the bulk modulus observed in isostructural NaM³⁺-clinopyroxenes with M³⁺=Cr, Fe, Al. Axial compressibilities (*a*₀=9.7183(5) Å, *K*₀=299(4) GPa, *K*'=38.9(1.5); *b*₀=8.8939(3) Å, *K*₀=271.7(1.8) GPa, *K*'=13.2(5); *c*₀=5.2826(2) Å, *K*₀=312(3) GPa, *K*'=19.2(9)) indicate anisotropic compression. A strain ellipsoid was generated with unit strain axial ratios of 1.0:2.6:2.7 and the most compressible direction almost perpendicular to the (-3 0 2) plane direction. These values are consistent with those observed in aegirine and kosmochlor. Regarding the pyroxene structure based on a cubic close-packing of oxygen atoms, the direction of highest compression is approximately perpendicular to (-1 0 1) which resembles the direction of the largest spacing within the close-packed layers.

Two-phase rheology of the mixture of (Mg,Fe)SiO₃ perovskite and magnesio-wüstite: morphology and lattice preferred orientationD. Yamazaki¹, T. Yoshino¹, H. Ohfuji², and E. Ito²¹Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193, Japan

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Earth's lower mantle is mainly composed of mixture of (Mg,Fe)SiO₃ perovskite and magnesio-wüstite. Therefore, the nature of the mixture should control the dynamics of the lower mantle. However, most of previous works have been focused on the physical and chemical properties of each phase. Here, we propose the importance of morphology such as geometry and microstructure of the (Mg,Fe)SiO₃ perovskite and magnesio-wüstite mixture.

We carry out two series of high pressure experiments using a Kawai-type apparatus at 24 GPa and 1400–2000 degree C: i) static experiment to observe the connectivity of weak phase (magnesio-wüstite) to assess the real viscosity of lower mantle rocks, ii) dynamic (pseudo-deformation) experiments to observe the crystallographic preferred orientation for understanding the deformation mechanism and for interpretation of seismic anisotropy. We used San Carlos olivine and forsterite powders as a starting material, which transformed to (Mg,Fe)SiO₃ perovskite and magnesio-wüstite at the present high pressure and high temperature conditions. After experiments, the recovered samples are examined by SEM, EBSD, EDS and X-ray diffraction techniques. Especially, FE-SEM is used for more detailed microstructural observation.

From preliminary results, magnesio-wüstite surrounded by perovskite annealed at 2000°C showed the shape with straight grain boundaries. On the other hand, magnesio-wüstite surrounded by perovskite annealed at 1700°C showed the convex grain boundary. This observation suggests that interfacial energy between perovskite and magnesio-wüstite depends on the temperature and/or Mg/Fe ratio.

High frequency resonant ultrasound spectroscopy for sub-millimeter specimens of high pressure phases

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Resonant ultrasound spectroscopy (RUS) is one of the typical techniques to measure elastic moduli of relatively small sample; it is based on natural vibration mode analysis on detected peaks in the frequency domain. However we have been unable to detect peaks of natural frequencies higher than 10MHz frequency by conventional RUS method. In other words the size of sample must be larger than 1 mm. Therefore it is significant for us to develop high frequency RUS up to 100 MHz for measurement for a few hundred microns sample.

We examined the performance of the high frequency RUS apparatus up to 50 MHz by using a ZrO₂ sphere of 200 μ m diameters. We succeeded in detecting 8 resonance peaks between 15 MHz and 50MHz. We calculated the P wave and S wave velocities from those resonance frequencies; V_p=8470 m/s, and V_s=4839 m/s, respectively. The reference values supplied from the manufacturer (Tosoh, Japan) are V_p=8858 m/s and V_s=4870 m/s, respectively. Both the velocities are consistent within 5 %. The difference of these velocities may be cause by in homogeneity of sample and imperfection of sphere shape.

Measurements of the thermal properties of mantle minerals under pressure

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We present determination of the thermal properties of mantle candidate minerals under pressure, employing a pulse-heating method of one-dimensional heat flow. Thermal diffusivity and thermal conductivity are measured simultaneously and heat capacity is obtained by comparing these quantities. This study demonstrates a novel aspect of mineral physics: that the heat capacity of mantle materials under pressure could be determined experimentally. As a significant discrepancy in heat capacity is recognized between observed and theoretical values under even ambient conditions, the determination of the heat capacity and pressure derivatives of mantle materials will set an effective constraint on the equations of state of the mantle.

We have conducted measurements into thermal conductivity and diffusivity for garnet, olivine and pyroxene (jadeite) at pressures up to 8-10 GPa and temperatures to 1100 K in a Kawai-type apparatus at ISEI. The results show that the thermal conductivity or diffusivity of these major mantle minerals increases 3-4 % per 1 GPa, and that olivine likely preserves anisotropy in thermal diffusivity or conductivity throughout its stability in the mantle, i.e. down to 410 km depth. Heat capacities of olivine and garnet, from thermal conductivity and diffusivity at room temperature are within 5 % of previously reported values. Moreover, the heat capacities for the three crystallographic directions in olivine are consistent within 6 %, which shows the adequacy of our method for thermal diffusivity and conductivity. Under high pressures, heat capacities have slightly lower values to those at zero pressure. This is consistent with the identity of thermodynamics for changes in heat capacity under pressure. At present the experimental data of heat capacities under pressure are not sufficiently accurate to discuss the equations of state of the mantle. Experimental errors probably come from unexpected deformations of samples during compression. We are continuing with our experiments by improving the assembly of samples as well as designing appropriate data-acquisition and -analysis techniques for measurements that will provide useful information on the thermal state of the mantle.

Stability and transition of methane hydrate up to 86 GPa

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High-pressure experiments of methane hydrate with a composition of full-occupancy of structure I were performed in a pressure range from 0.2 GPa to 86 GPa. X-ray diffractometry and Raman spectroscopy revealed that methane hydrate transformed from a known high-pressure structure, filled-ice-Ih structure, to a new high-pressure structure at approximately 40 GPa. The volume change at the transition was very small. Also, the relative intensity ratio of the high pressure structure to the ice VII was almost the same as that of the filled-ice-Ih structure to ice VII. Thus, the molecular ratio of methane to water is suggested to be unchanged between the two structures. Considering the molecular ratio and the small volume change, the fundamental structure of the new high pressure structure might be not largely different from that of the FIhS, although the true symmetry of the structure cannot be determined at present because of the limited diffraction lines. The reason for the outstanding retention of the filled-ice-Ih structure up to 40 GPa was examined, because the filled-ice-Ih structures for other gas hydrates decompose below 6.5 GPa. In the Raman spectra, new intramolecular vibration modes softer than the original ones appeared at 14 to 17 GPa. The appearance of the softer vibration modes indicates that the methane molecules began to receive an additional intermolecular interaction. The excellent stability of the FIhS under very high pressures could be substantiated by the increased intermolecular interactions between the methane molecules and the framework water molecules, as well as between the methane molecules. The new high-pressure structure survived at least to 86 GPa.

Surface physics of micro- and nanominerals under (P, T) – conditions

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During the past few years, the attention spent on researching micro- and nanominerals has increased dramatically. Micro- and nanominerals outperform their conventional counterparts due to their superior physical, chemical and mechanical properties. So surface physics is now an important branch of research especially for micro- and nanoobjects. Processes on a surface are less power-intensive. The surface of minerals is accessible for different outer processes; this opens wide scientific and technical possibilities of the application of surface phenomena. A parameter is determined which controls the mechanism of dispergation and aggregation of micro- and nanoparticles. It is Qs (surface non-compensated charge), which is resulted from the disturbance of adsorption-desorption equilibrium. It is determined that the value and sign of the charge depend on (P, T) conditions. The investigations of this kind can help to regenerate geological history of the Earth. It is determined that the processes depend on the quantity and relation of surface active centers.

For example, for photosorption activity two types of minerals are determined: with the deficit of surface electron centers (rutile, baddeleyite, kassiterite, periclase etc.) and minerals characterized by long-term electron centers (zinkite).

The efficiency of crystal-chemical transformations of carbon structures is studied on corundum and kassiterite. It is observed that the efficiency of carbon structure transformations depend on the value of deficit of surface active electron centers, which does not depend on the sample structure and depend on 1) the presence of long-term electron centers (zinkite) due to rich spectrum of deep perisurface levels trapping electrons; 2) on the spectral area of excitation of fine disperse mineral systems. During short wave irradiation electrons are likely to come to surface, while during long wave irradiation the presence of high perisurface barrier on oxidized samples prevents electrons from coming to the surface; 3) on the condition of the surface, e.g. under low pressures in the system oxygen-sample photosorption is observed, under high pressures photodesorption is observed (it correlates to negative or positive charge of the sample surface)

Shocked quartz and Corona texture at Takamatsu buried craterO. G. Iancu¹ and Y. Miura²¹Department of Geology and Geochemistry, Faculty of Geography and Geology, University "Al. I. Cuza" of Iasi, B-dul Carol I 20A, Iasi, 700505, Romania. ogiancu@yahoo.com²Department of Earth Sciences, Yamaguchi University, Yoshida, Yamaguchi, 753-8512, Japan. yasmiura@yamaguchi-u.ac.jp

1. Introduction: There are no reports of quartz minerals related to an impact event in the volcanic islands of Japan due to the hidden crater structure. The purpose of this paper is to elucidate the presence of shocked quartz and coronas (necklaces) textures in the granite basement rock found as drilled samples at Takamatsu buried crater near Takamatsu, Kagawa-Prefecture.

2. Shocked quartz: Bulk XRF data of the drilled samples are very different from bottom to surface compared to the magmatic crystallization trend. Shocked quartz with planar deformation features (PDFs) can be found in the granites from the basement of the surface rims (8 km in size), and in drilled melted breccias (450 m to 1120 m in depth). Typically shocked quartz with PDFs (one to three directions) is found in the granitic basement, though there are many cracks after formation of the PDFs texture.

3. Corona texture: Samples of grey - dark dotted breccias are found from 450 m to 1125 m in depth. In fact, the TK610 sample used in this study drilled from 610 m shows a granitic composition. There are various flow-shapes of elongated corona (necklaces) textures inside major corona textures of K-feldspar (clasts as rim) and quartz (matrix as core) with various elongated sizes between 0.1 mm and 0.4 mm. They are formed by the less evaporation of silica-coated components and more evaporated compounds of K-feldspar after impact reaction. These grains from the corona texture are considered to be of impact origin, because there are no large volcanic elements (S, Mg etc.) but considerable contents of meteoritic elements as Fe, Ni and Co.

4. Summary: The present results are summarized as follows:

1) Shocked quartz is found in Takamatsu buried crater structure from Japan.

2) Complicated "corona-in-corona texture" of quartz and K-feldspar derived from the granitic basement are found in the drilled breccias of the Takamatsu buried crater from Japan.

3) The data presented in this paper indicate that breccia samples have been originally created from an impact event produced in the granitic basement.

Structural change of sanidine crystal by shock compressionT. Kitatani¹, M. Okuno¹, T. Atou², K. Fukuoka², M. Kikuchi², M. Kawasaki², T. Araki³, B. Reynard⁴, M. Koyano⁵, and S. Katayama⁶¹Department of Earth Sciences, Kanazawa University, Kanazawa, 920-1192, Japan.²IMR, Tohoku University, Sendai, 980-8577, Japan ³MST, Tokyo, 157-0067, Japan ⁴ENS, 69364 Lyon cedex 07, France ⁵JAIST, Nomi, Ishikawa, 923-1292, Japan

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Sanidine is an important rock forming mineral of Earth crust. So, the study for shock deformation of sanidine is important to understand the meteorite impact phenomena on the Earth. The vitrification of sanidine by shock compression was already observed in experimentally and naturally compressed samples. However, the vitrification processes and the nano-structures of shock induced glass phases are not clear yet. In this study, the structural change of sanidine crystal by shock compression and the nano-structure of the shock induced glasses were investigated by X-ray diffraction measurements, infrared and Raman spectroscopy's.

Natural sanidine crystals (An₅Ab₇Or₉₈, Eifel, Germany) were compressed up to about 41 GPa. X-ray diffraction measurements reveal that amorphization by shock compression start at about 30 GPa and the total vitrification observed 41 GPa. However, the shock compression of 22 GPa gives some structure changes to sanidine. Increasing shock pressure, a decrease of peak intensity, an increase of peak width and background intensity were observed in X-ray diffraction data. The absorption of $\nu=580\text{cm}^{-1}$ band in IR spectrum with increasing shock pressure also observed. These facts may indicate that the distortion of crystal structure for sanidine increase gradually increase before abrupt vitrification at high pressure. On the other hand, the peak positions in X-ray diffraction profiles of 22 GPa and 26 GPa samples shift toward small 2θ angles. This structural change suggests that cell volume of sanidine expand by shock compression before vitrification. This kind of expansion was reported in the previous work on shock deformed quartz.

The detailed structure of totally vitrified sample at about 38 GPa was investigated by X-ray radial distribution (RDF) analysis and Raman spectroscopy. The result of RDF analysis shows shock induced sanidine glass structure has small difference with fused sanidine glass structure. The intensity of $\nu=580\text{cm}^{-1}$ Raman band of this sample is stronger a little than that of unshocked sanidine. This band is assigned to breathing mode of 3-membered ring of TO_4 tetrahedra (T=Si/Al). Therefore, the structure of shock induced sanidine glass has larger number of 3-membered ring of TO_4 tetrahedra than fused sanidine glass.

Phase relations and equation of state of ZrO_2 to 1 MbarO. Ohtaka^{1,2}, D. Andrault², P. Bouvier³, E. Schultz³, and M. Mezouar⁴¹Department of Earth and Space Science, Osaka University, Osaka 560-0043, Japan ohtaka@ess.sci.osaka-u.ac.jp²Laboratoire des Geomateriaux, IGP, Université Paris 7, 75252 Paris, France³LEPMI, INPG-CNRS, 38402 St. Martin d'Heres Cedex, France⁴ESRF, BP220, 38043 Grenoble Cedex, France

The phase relations and equation of state of ZrO_2 were investigated up to 100 GPa by means of *in situ* observation using laser heating in a diamond anvil cell and synchrotron radiation. A cotunnite (PbCl_2)-type phase, which appears above 12.5 GPa, is stable to a pressure of 100 GPa and a temperature of 2500 K. No post-cotunnite phase was observed within the present experimental conditions. The unit-cell parameters and the volumes of the cotunnite-type ZrO_2 were determined as a function of pressure at room temperature using a laser-annealing technique. The bulk modulus calculated using Birch-Murnaghan's equations of state is 278 GPa, which suggests that the high-density ZrO_2 is a candidate for potentially very hard materials. *In situ* high temperature experiments made below 12.5 GPa revealed that a tetragonal fluorite-type phase is stable up to 3000 K although a cubic fluorite-type phase has been assumed to exist at this high-temperature regime.

Local structure of noble gas in terrestrial and planetary materialsM. Okube¹, A. Yoshiasa², E. Ito³, T. Matsumoto⁴, Y. Terada⁵, H. Arima⁴, J. Matsuda⁴, S. Sasaki¹¹Materials and Structures laboratory, Tokyo Institute of technology, 4259, Nagatsuta, Yokohama, 226-8503, Japan.

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Noble gases have inert character and various radiogenic isotopes. The isotope ratio and abundance are sensitive to physical process of minerals and provide important information about the evolution of the earth and planets. It is still unknown where and how noble gas exists in the crystal structure of terrestrial and planetary materials. Since their concentration is limited, in the order of ppb level, the detection of such gases is very difficult. In this study, microanalysis with long-exposure measurement has been applied to investigate the local structures around noble gases by using fluorescence XAFS spectroscopy.

Kr-contained high-pressure mineral samples were synthesized in Kr atmosphere by using the Kawai-type high-pressure apparatus. Kr-doped silica gels and MgO were used as starting materials and sealed into Pt capsule to prevent an escape of Kr under high pressure. The concentration of Kr in coesite, stishovite, forsterite, wadsleyite and ringwoodite was measured by a mass spectrometer. Degassing of Kr for all samples was obtained as a function of temperature up to 1850°C. The concentration of Kr is about 2 ppm for each of most high-pressure mineral samples.

XAFS experiments were carried out for (1) the above synthetic mineral samples, (2) Kr-rich part of meteorites and (3) reference samples at BL01B1 in SPring-8 and BL12C in Photon Factory. The measurements at the Kr edge were made in fluorescence mode using either Lytle-type or 19-elements SSD detectors. We have succeeded to obtain XAFS spectra even in lower concentration than 2 ppm of Kr in minerals. Our XAFS results show that there are significant differences in Kr coordination such as atomic distances and coordination number among our samples of terrestrial and planetary materials.

Pressure-induced slip-system transition in olivine: high-pressure rheological measurements, microstructures and flow laws

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Seismic-velocity anisotropies are commonly used to characterize convective flows in the Earth's upper mantle. They are interpreted from the lattice preferred orientations (LPO) produced experimentally in olivine. A change in the dominant dislocation slip changes the resulting LPO. Olivine dominant slip systems have thus been extensively studied at pressure $P < 3$ GPa, showing that [100] dislocation slip dominates at mantle temperature $T > 900^\circ\text{C}$, which results in aligning olivine fast-velocity a-axis with the shear direction. Yet, recent experimental and computational reports suggest that olivine LPO is sensitive to P , and that olivine [001] slip may be dominant in the deep upper mantle where P reaches 14 GPa, thus promoting a shear-parallel slow-velocity c-axis.

In order to quantify the effect of P on olivine dislocation slip-system activities, deformation experiments were carried out in a Deformation-DIA high-pressure apparatus (D-DIA) on oriented single crystals of Mg_2SiO_4 forsterite (olivine Mg end-member, Fo100), at P ranging from 2.1 to 7.5 GPa and T ranging from 1373 to 1677 K. Two compression directions were tested, promoting either [100] slip alone or [001] slip alone, in (010) crystallographic plane. Constant applied stress (σ) and sample strain rates were monitored in situ using x-ray synchrotron radiation. Deformation microstructures were investigated in the run products by transmission electron microscopy (TEM), which reveals that dislocation creep assisted by dislocation climb and cross slipping was responsible for sample deformation at high pressure. X-ray diffraction and imaging data are interpreted in terms of rheological laws. An increase with pressure of [001]-slip activity in (010) plane, relative to that of [100] slip, is documented.

Extrapolation to natural P , T , and σ conditions shows that the activities of both slip systems are comparable in the deep upper mantle at the transition zone boundary, while [001] slip dominates deformation in subduction zones. These results provide an alternative explanation for the seismic anisotropy attenuation with depth observed in the upper mantle, interpreted so far as due to olivine diffusion creep, as well as for the "puzzling" seismic-anisotropy anomalies commonly observed in subduction zones interpreted so far as resulting from the presence of water.

Crystal growth of MgSiO_3 perovskite in $2\text{KHCO}_3\text{-Mg(OH)}_2$ solvent

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Magnesium silicate perovskite are believed to be dominant in the lower mantle. Investigation of its physical properties, such as diffusion and elasticity, is important for an understanding of the lower mantle dynamics and to constrain of the chemical composition and temperature profile in the deep mantle. In order to determine perovskite physical properties with high reliability using of large single crystals (0.5-1.0 mm) as sample is necessary.

Perovskite crystal growth experiments were performed using the uniaxial split-sphere Kawai-type apparatus (USSA-5000) installed in HACTO laboratory of ISEI of Okayama University. Recently we modified this apparatus for larger WC anvils in order to increase size of high pressure cell and so crystallization volume. In view of a perovskite refractoriness ($T_{\text{melting}} > 2800^\circ\text{C}$) the crystal growth from solution was applied. High solubility of a silicate in water-bearing alkali carbonate melts, their low viscosity and fusion temperature were motivated us to use a $\text{K}_2\text{Mg}(\text{CO}_3)_2$ water bearing melt as solvent. At 1500°C and 25 GPa crystallization of perovskite+slishovite and perovskite+periclase was detected in the case MgSiO_3 and Mg_2SiO_4 silicate source, respectively. The using of an intermediate composition ($\text{MgSiO}_3+\text{Mg}_2\text{SiO}_4$) allowed avoiding an appearance of additional phases.

Single crystals of MgSiO_3 perovskite up to 1 mm in size have been grown by the temperature gradient (TG) method from MgO-SiO_2 solution in $\text{K}_2\text{Mg}(\text{CO}_3)_2$ water bearing melt at 25 GPa, 1500°C . At this parameters size of crystals mostly depends on the quantity of crystal nuclei, which are formed in abundance in a lower temperature part and prevent overgrowth one another. Reduction of the temperature difference in the sample from 100°C/mm (natural) to 20°C/mm provides a decrease of solution supersaturation and so a reduction of a number of crystal nuclei from $2 \times 10^1 \text{ cm}^{-2}$ to $20\text{-}50 \text{ cm}^{-2}$. Growth of relatively large perovskite crystals was realized at the lowest TG on spontaneous nuclei and seed crystal. The morphology of perovskite crystals mostly formed by faces of {110} prism and {001} pinacoid, with subordinate development of {011} bipyramid.

O03-01

Near field spectroscopy for nano and bio-materials

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Microspectroscopy is widely used for physical, chemical and biological microanalysis of various materials. A focused spot that is formed with objective lens probes electronic or vibrational states of sample by measuring light response as a function of frequency or wavelength. However, a size of the focused spot, which determines spatial resolution of microanalysis, is limited to a half of wavelength due to diffraction phenomenon of lightwave. Near field optics is one of key technologies to overwhelm the barrier of wavelength and bring optical measurement to nano-world.

We have proposed a metallic needle having a nano-tip for near field optical microscopy in 1994. Light or photons are confined around the nano-tip by coupling with collectively oscillating electrons in metal, e.g. local plasmon polaritons. Hence the confined photons work as nano-light source for nanospectroscopy or nanoanalysis. Moreover, light field is enhanced due to the resonant effect of plasmon. Then, we have realized near field nano-Raman spectroscopy and imaging by inducing Raman scattering with the nano-light source generated at a silver nano-tip in 1999.

Our designed near field Raman nanoscope consists of an atomic force microscope (AFM), inverted optical microscope, and a dispersive spectrometer equipped with a liquid-nitrogen-cooled CCD camera and an avalanche photodiode. An AFM cantilever that is coated with silver thin film is used as a metallic nano-tip. The AFM controls position of the metallic nano-tip with nanometric accuracy. The inverted microscope is employed for launching local plasmon at the nano-tip and gathering Raman scattering from sample located under the nano-tip.

We have measured tip-enhanced near field Raman spectra and molecular nano-imaging of nanomaterials and biomolecules, such as adenine nanocrystal, carbon nanotube, C_{60} , double stranded DNA network, and so on. Enhancement factor of tip-enhanced Raman scattering reached to several thousands and 30 nm spatial resolution was achieved. Furthermore, we combined the tip-enhanced effect with nonlinear Raman scattering (e.g., coherent anti-Stokes Raman scattering: CARS) in order to improve spatial resolution, then adenine molecules in double stranded DNA networks were imaged with 15 nm resolution. Synthetic oligo-DNA containing 30 guanine bases and that containing 100 adenine bases were successfully detected. We found specific Raman band variations (shift, intensity, appearance) that are induced by forming a complex of molecule and metallic atom and by giving perturbative force to molecules via the nano-tip. Vibrational calculation for complex of a molecule and silver atom cluster supports these phenomena.

O03-02

New visible and infrared spectroscopies for water-rock interactions

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In order to study speciation of geochemical components and its change with time during various water-rock interactions, several new spectroscopic methods have been developed. Most of the water-rock interactions are occurring in the presence of water from around 4 to 200 °C. Conventionally, the hydrothermal reactions have been investigated by "batch methods" in reaction vessels placed in electric furnaces and by analyzing products after their quenching to room temperature. However, the batch methods have only limited data points and might have modifications of product species. Therefore, in-situ hydrothermal monitoring system is required for detailed mechanistic and kinetic studies of aqueous reactions.

An in-situ heating ultraviolet-visible (UV-Vis) cell up to 200 °C and 4 MPa was developed for studying hydrothermal transformation of aqueous compounds. By using this in-situ measurement, detailed kinetic behavior of dissolved organics has been elucidated. A heatable Attenuated Total Reflection (ATR)-Infrared (IR) cell was also developed here to monitor kinetics of various water-rock interactions. A pressure line was attached to this ATR-IR cell to enable regulation of gaseous pressure environments.

Heating-cooling stages were used under Visible and IR microspectrometers to investigate color change and dehydration kinetics of earth and planetary materials including water. A new high temperature cell with regulated gaseous pressure is being developed to study physicochemical changes of aqueous solutions.

Physicochemical forms of materials in microscale have been conventionally studied by FT-IR microspectroscopy with a spatial resolution of the order of 10 μ m. In order to develop a new type of IR microspectroscopy that is capable of performing both IR spectral and topographical mapping with a spatial resolution of sub-micron scale, we combined an FT-IR spectrometer with a near-field (NF) microscope. By using this NF-IR microspectrometer, IR spectra can be measured in the 4000-1000 cm^{-1} with a typical wavenumber resolution of 16 cm^{-1} . Mapping area of sample surface is 1 $\mu\text{m} \times 1 \mu\text{m}$ to 20 $\mu\text{m} \times 20 \mu\text{m}$, with a minimum step size of 50 nm. The spatial resolution of this instrument is on the order of 300 nm from the mapping results on polystyrene particles deposited on an Al mirror. We applied this NF-IR microspectroscopy to some natural geomaterials. Mapping results on an agate sample, polycrystalline hydrous silica, showed a heterogeneous distribution of different states of water with different degrees of hydrogen bonding. The NF-IR microspectroscopy is thus expected to be a powerful tool for submicron characterization of complex earth and planetary materials.

O03-03

Development of a "Built-in" Scanning Near Field Microscope Head for an Atomic Force Microscope System and its Applications to Natural Polycrystalline Diamonds (carbonado) and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Eutectic Composites

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We constructed a scanning near-field optical microscope (SNOM) on a commercially available atomic force microscopy (AFM) apparatus (SPM-9500J2; Shimadzu Corp.) to measure the stress distribution in minerals and ceramic composite materials. Features of our SNOM system are: (1) a compact SNOM head substituted for the original AFM head; (2) a wide scanning range (125 $\times$ 125 μm) inherited from the original scanner; (3) use of conventional shear-force regulation; (4) an optical system for the illumination-collection (I-C) mode; (5) excitation by a 488 nm line of an Ar-ion laser; (6) and light detection by photon counting or a polychromator equipped with an electronically cooled charge coupled device (CCD).

This SNOM system was used to measure the surface structure and photoluminescence (PL) distributions of natural polycrystalline diamonds (carbonado) and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic composites. We simultaneously measured topographic images and PL spectra of the sample surfaces with high spatial resolution (< 1 μm). Peak intensity, peak position and peak width from the PL spectra were measured during scanning. PL intensity of carbonados was weaker at grain boundaries, the region of radiation halo showed very low intensity of PL and a small pore of 7-8 μm diameter located at the halo center. This result suggests that a radioactive inclusion existed in the pore and that a radiation halo formed around the pore. Mapping images of a $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic composite showed that the stress and its anisotropy were weaker in the center of the Al_2O_3 grain than its boundary between Al_2O_3 and ZrO_2 . That observation suggests that Al_2O_3 underwent intense anisotropic stress induced by volume expansion in the phase transition of ZrO_2 from the cubic phase to the monoclinic phase during preparation.

O03-04

SR-XRF analysis of mineralogical samples using X-ray microbeam

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Currently, the 3rd generation synchrotron radiation light source is bringing the progress to various applications. The primary characteristics of the third-generation light sources are their extremely high brilliance and the availability of high-energy X-rays. The former characteristic gives nanometer order X-rays at SPring-8. Some X-ray microbeam optical systems in hard X-ray region are developed by using various focusing elements such as Kirkpatrick-Baez (K-B) mirror, Fresnel zone plate (FZP) and refractive lens. X-ray optical system with K-B mirror consists of combination of two total reflective mirrors, and the system is energy tunable. The system achieved beam size less than 500nm in hard X-ray region. FZP is X-ray focusing element applying the Fresnel diffraction. It is required that the optical system is used at fixed energy because the focal length changes at each energy. The FZP optics enabled to achieve microfocusing at high energy region, and its beam size was 1 μm at 82 keV.

The advantages of high-energy X-ray fluorescence (XRF) over conventional analytical techniques used in mineralogy and geochemistry are summarized as follows. The identification of the XRF peaks is more straightforward and measurement is easy compared with secondary ion mass spectroscopy (SIMS), and enables us to analyze trace heavy elements with two-dimensional resolution. For example, in geochemistry, rare earth element (REE) pattern is an important indication of the origin of a sample. The high-energy XRF technique enables direct measurement of the REE pattern as stated above. Another advantage of the high-energy SR-XRF technique is the nondestructive two-dimensional chemical imaging of the trace heavy elements. We measured the distribution of each rare earth element and other heavy elements in idiomorphic garnet. The results showed that the zoning position of each element shifts outside the garnet crystal with an increase in the atomic number.

In this talk, the current status of X-ray microprobe at SPring-8 and some experimental results of XRF analysis will be presented.

Anomalous elastic behaviour of (Ca, Sr)TiO₃ PerovskiteJ.N. Walsh¹, M.A. Carpenter¹, J. Schreuer², T.W. Darling³¹Department of Earth Sciences, University of Cambridge, Downing St, Cambridge CB2 3EQ, United Kingdom.

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Resonant ultrasound spectroscopy (RUS) has been used to characterise the bulk and shear moduli of calcium strontium titanate perovskite (CST), Ca_{1-x}Sr_xTiO₃, as a function of both temperature and composition through the cubic-tetragonal and tetragonal-orthorhombic phase transitions. This system has been chosen because it undergoes analogous phase transitions to those expected to occur in silicate perovskites under the conditions of the lower mantle.

Samples were prepared as polycrystalline pellets with around five percent porosity by cold pressing synthetic powders and then firing them at 1600°C. The pellets produced were cut into rectangular parallelepipeds with edge lengths between two and three millimetres. Four key compositions ($x = 0$, $x = 0.5$, $x = 0.7$ and $x = 0.95$) were studied as a function of temperature. Calcium rich samples were studied at high temperatures (275 K -1474 K and 275 K -775 K, respectively) and strontium rich samples were studied from 275 K down to 110 K. The frequency range of all the RUS experiments was between 300 kHz and 1500 kHz.

The bulk modulus was relatively poorly constrained and showed a degree of scatter greater than changes expected to occur as a consequence of the phase transitions. The shear modulus was more tightly constrained and showed several interesting features. In both the compositional and temperature dependent study softening of the shear modulus was observed in the tetragonal phase field accompanied by strong dissipation. With increasing temperature the resonance peaks disappear abruptly at the transition from the orthorhombic to the tetragonal phase and reappear on transformation to the cubic phase indicating strong attenuation in the stability field of the tetragonal phase. This phenomenon might be caused by anelastic processes due to the mobility of twin walls.

NMR studies of high-pressure minerals and glasses: pushing the limits of sensitivity

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Solid-state NMR has often been described as a method with "low sensitivity," which is justified relative to others that involve much higher energies, such as visible and x-ray spectroscopies. However, recent technological developments have greatly improved the range of applicability and the types of structural questions that can be addressed by NMR in the small samples that typically produced in high pressure experiments, or for concentration ranges of some elements of interest to trace element geochemists. I will discuss several recent examples of applications to problems in mineral physics and high-pressure petrology.

Al is one example of a "favorable" NMR nuclide, especially with the high resolution provided by newer, high-field systems (e.g. 14.1 to 18.8 Tesla), and NMR probes with small, very fast-spinning sample rotors. We have shown in several recent studies that low concentrations of Al₂O₃ (5 to 10%) in MgSiO₃ perovskite can be accurately characterized even in products of single 26 GPa runs in multi-anvil apparatus (1-3 mg of sample, < 100 micrograms of Al), demonstrating that both Mg/Si coupled substitution and vacancy mechanisms can operate in at least some range of P/T/X. Similarly, the Al environment in stishovite can be shown to be almost entirely octahedral, in samples of only a few mg and only 1% Al₂O₃. In contrast, Al in ambient P experimental samples (1000-1500 C) of rutile (TiO₂) has a complex range of environments (4- and 5-fold coordination and multiple octahedral sites) that can readily be characterized in samples down to < 0.1% Al.

In somewhat larger samples from "medium" high pressures (e.g. 10-20 mg, 10 GPa), Si-29 NMR on samples of natural isotopic abundance can reliably characterize structure in glasses and detect 5- and 6-coordinated Si at the several % level; isotopic enrichment remains useful for smaller samples or more subtle pressure effects. Al-27 NMR has proven to be very revealing of the effects of pressure, temperature, and composition on Al coordination in glasses quenched from high P melts. For example, Al coordination increases are strongly enhanced by high field strength modifier cations, and will thus be especially important in Mg-rich mantle melts; recovered glass density changes are also systematically linked to Al coordination. Through the application of two-dimensional, triple-quantum magic-angle spinning NMR on O-17 enriched samples, changes in the oxygen network can also be directly linked to network cation coordination shifts.

²⁹Si MAS NMR study of synthetic Scandium-pyroxenes: NaScSi₂O₆, LiScSi₂O₆, and Ca-Tschermak partial solid solutions CaScAlSiO₆-CaAlAlSiO₆ and CaScAlSiO₆-CaTiAl₂O₆.R.L. Flemming¹ and H. Ohashi²¹ Department of Earth Sciences, The University of Western Ontario, 1151 Richmond Street, London, Ontario, Canada, N5Y 3R5.

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²⁹Si magic angle spinning nuclear magnetic resonance spectroscopy (²⁹Si MAS NMR) has been used to examine the local cation arrangements in several Sc-substituted synthetic clinopyroxenes. Within the Ca-Tschermak pyroxene group, four samples across the CaScAlSiO₆-CaAlAlSiO₆ partial solid solution and four samples across the CaScAlSiO₆-CaTiAl₂O₆ partial solid solution have been examined by ²⁹Si MAS NMR at 9.4 T (79.36 MHz). Two non-Tschermak Sc-substituted clinopyroxenes, NaScSi₂O₆ and LiScSi₂O₆, have also been examined.

²⁹Si MAS NMR spectra for NaScSi₂O₆ and LiScSi₂O₆ each exhibit a single narrow peak, at -93.7 and -94.9 ppm, respectively. This indicates long-range order, where M2 is fully occupied by M²⁺, and M1 and T are fully occupied by Sc and Si, respectively.

End member CaScAlSiO₆ exhibits three peaks, at -82.9, -86.3 and -90.6 ppm, having intensities of ~55%, ~43% and ~2%, respectively. These peaks are assigned to Si with two, one and zero tetrahedral Al nearest neighbours, respectively (i.e. Si(2Al)[M³⁺], Si(1Al)[M³⁺] and Si(0Al)[M³⁺], where M³⁺ indicates trivalent cation in M1. Peaks are broadened relative to NaScSi₂O₆ and LiScSi₂O₆ due to Al-Si disorder on the tetrahedral chain.

Compositions along the CaScAlSiO₆-CaAlAlSiO₆ partial solid solution represent substitution of Al³⁺ for Sc³⁺ in M1. All spectra exhibit three peaks, similar to CaScAlSiO₆. Peak position and intensity changes little upon substitution of Al³⁺ in CaAlAlSiO₆ for Sc³⁺ in CaScAlSiO₆, suggesting that tetrahedral cation ordering is affected little by exchange of trivalent octahedral cation.

Compositions along the CaScAlSiO₆-CaTiAl₂O₆ partial solid solution represent coupled substitution on both the tetrahedral and octahedral sublattices, as (Si⁴⁺) + [Sc³⁺] = (Al³⁺) + [Ti⁴⁺], where () and [] represent tetrahedral (T) and octahedral (M1) sites, respectively. As above, the peaks at ~-83 ppm and ~-86 ppm are assigned to Si(2Al)[M³⁺] and Si(1Al)[M³⁺] (+/- Si(2Al)[M⁴⁺]), respectively. There is no peak at -91 ppm (Si(0Al)[M³⁺]), suggesting a paucity of Si-O-Si-O-Si linkages. Relative peak areas change systematically across the solid solution. From CaScAlSiO₆ to CaSc_{0.70}Ti_{0.30}Si_{0.70}Al_{1.30}O₆, peak intensity at -83 ppm (Si(2Al)[M³⁺]) increases from 55% to 81%, with a corresponding decrease in peak intensity at -86 ppm (Si(1Al)[M³⁺]). This suggests an increase in tetrahedral Si-Al ordering as a function of CaTiAl₂O₆ component, where Si form alternating Si-O-Al-O-Si linkages.

In both solid solutions, peak broadening increases with increasing Tschermak component (CaAlAlSiO₆ or CaTiAl₂O₆) due to cation disorder on both the octahedral and tetrahedral sublattices. Chemical shifts for the Sc-substituted clinopyroxenes also correlate with structural parameters such as Si-O-Si angle.

Spectroscopic investigation of transition elements in minerals: a comparative approach

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Transition elements are important trace components of minerals, which impart them characteristic colorations and are widely used to understand the formation conditions of minerals and rocks. Various spectroscopic methods may help understand their location in the mineral structure, and the combination of these approaches gives an improved understanding of the mechanisms governing trace element incorporation in minerals. We will present several examples of application of spectroscopic techniques to the understanding of crystal chemistry of substituted transition elements in minerals, with relevance to mineralogy, geochemistry and environmental sciences. Trivalent Cr imparts minerals and gems a broad range of colors, among which the red color of ruby and spinel and the green color of emerald or uvarovite have been the most described. We will present the application of several spectroscopic techniques to understanding the origin of the differences in the color of Cr-containing minerals, including electron paramagnetic resonance, UV-visible spectroscopy and synchrotron x-ray absorption spectroscopy. A major finding is the presence of a structural relaxation around Cr impurities in minerals, which implies that the size of the substituted site is not at the origin of the differences in the crystal field magnitude. Another kind of structural problem, which can be solved using spectroscopic methods, concerns the inter-site and the intracrystalline distribution of transition elements in minerals: Ni in olivines and Fe in kaolinite will illustrate examples taken from minerals formed under different conditions. In some cases, the high sensitivity of spectroscopic techniques such as EPR may be used to determine the mineral hosting a particular element: we will take the example of the structural location of Cd in phosphates. Though not strictly a transition element, Cd is a major issue in environmental sciences. Eventually, we will present an application of spectroscopic methods to determine the redox state of transition elements substituted in minerals. The oxidation state of V in Ti-magnetites, the major vanadium ore, has been recently determined using high-resolution x-ray absorption spectroscopy. By considering the mineral/melt partition coefficients of the different oxidation states of vanadium, it is possible to get information on the redox formation conditions during the emplacement of large basic intrusions.

Electronic structure calculations for Mössbauer spectroscopy of disordered materials

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Fe is abundant, redox active, and magnetic. It plays major roles in geology, planetary science, and the life sciences. One of the most powerful tools for studying Fe-bearing solids and substances is ⁵⁷Fe Mössbauer spectroscopy (MBS). The main difficulty with this technique, however, is the indirect relation between the local structural and chemical environments of the probe and the hyperfine parameters that determine the measured spectrum. Much insight about this relation can be obtained from modern ab initio electronic structure calculations. Whereas previous work has mainly only looked at calculated electronic structures for specific mineral structures using refined structures from X-ray diffraction for specific samples, we have examined the direct effects of local distortions and local chemical differences. Using cell average atomic positions from refinements cannot provide information about the multitude of different local probe environments in a given mineral sample. We have also performed simulations with sets of distorted local environments characterized by both a starting coordination and the standard deviation of atomic displacements about this starting configuration. Such sets represent the local environments in given chemically or structurally disordered samples and the corresponding sets of hyperfine parameters are used to simulate the Mössbauer spectra that would be observed. We thereby establish the first direct relations between the degree of atomic positional disorder and the widths of the hyperfine parameter distributions. We also establish the first relationships between the different hyperfine parameters [quadrupole shift(ϵ)/splitting(QS), isomer shift (IS), hyperfine field (HF)] in disordered materials, as functions of the degree of atomic positional disorder. These relationships provide needed constraints in fitting real Mössbauer spectra. Some of our main and most surprising first results are as follows. (1) The correlations between IS and QS in doublets and between ϵ and HF in sextets are complex, highly non-linear, and inconsistent with single-valued functions. (2) The contributions to spectral broadening from IS spreads are much more significant than generally assumed. (3) HF distribution broadening directly arising from local atomic positional disorder, without spin or magnetic moment disorder, is much greater than generally assumed and is a challenge to the notion of dominant spin disorder and transferred HF broadening. Whereas Debye-Waller factors from X-ray diffraction give convoluted static and thermal contributions, the new Mössbauer evaluation method directly give the static disorder contribution alone, because of the larger characteristic time of the Mössbauer method compared to thermal vibration frequencies.

In situ high temperature visible microspectroscopy under controlled atmosphere for studying color change processes of volcanic materials

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Volcanic eruptive materials often show red coloring such as Takatsukayama scoria, North-east Izu, Japan and olivine was found to be one of its origin (Yamanoi et al., 2004). We have investigated visible spectral change processes of olivine thin sections in high temperature oxidation under air by means of in situ high-temperature visible microspectroscopy (Yamanoi and Nakashima, 2005). Olivine thin sections put on a synthetic alumina plate are heated on a heating stage at 600 – 800 °C under a visible microspectroscope. Changes in visible absorption spectra are monitored every 60 seconds for 5 hours. The obtained high temperature visible spectra showed a gradual increase with time in absorbance in the shorter wavelength region (400 – 600 nm). The changes of 430 nm absorbance (ligand field transition of Fe³⁺) increased with time more at higher temperatures. In order to simulate different atmospheric conditions during volcanic eruptions such as oxygen fugacity and relative humidity, visible spectral changes of olivine at high temperatures are investigated by means of in situ high-temperature visible microspectroscopy under controlled atmospheric conditions. Olivine thin sections were put on a synthetic alumina plate in the sealed sample chamber with flowing nitrogen gas or dry/wet air. The olivine thin sections are heated on a heating stage at 700 °C and changes in visible absorption spectra are monitored every 60 seconds for 5 hours. The obtained high temperature visible spectra showed a gradual increase with time in absorbance in the shorter wavelength region (400 – 600 nm). The changes of 430 nm absorbance (ligand field transition of Fe³⁺) increased with time and showed different trends than those under ambient air conditions. Based on these experimental results, effects of oxygen fugacity and relative humidity on the visible spectral changes of olivine at high temperatures will be discussed.

High Temperatures and Pressures IR Spectroscopy of Water at Solid-Water Interface

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In order to investigate molecular behavior of water under sub- and supercritical conditions, a high temperature-pressure cell for IR and Raman spectroscopy was developed with optical microscopy. The cell was designed as reflected type for spectroscopic measurement to analyze structure of interfacial water on the specific rock and solid materials. The maximum temperature and pressure of the cell were 400 °C and 50 MPa, and artificial yellow diamond was installed as a window for light beam path. Water was pumped into the cell by a hand pressing pump, and then thin water was obtained between the diamond window and reflector in the cell. Pressure of the objective water was adjusted for a given temperature with heating. In case of microscopic IR spectroscopic measurement, infrared beam was illuminated to the cell through the Cassegrainian mirror, and reflected light was detected for FTIR spectroscopic measurement. In case of microscopic Raman spectroscopic measurement, an incident laser beam (Nd:YAG laser: 532 nm) was irradiated into the cell through standard optical lens, and Raman scattering was detected for Raman spectroscopic measurement. IR and Raman spectroscopic measurements were conducted independently for the same microscopic viewing field. A broad peak of IR spectrum, attributed to OH stretching vibration mode of water molecule, was observed at ca. 3360 cm⁻¹ under room temperature and pressure, and wavenumber of the peak shifted to higher values continuously with increasing temperature and shifted to lower values continuously with increasing pressure. Compared with the result of IR absorption properties of free water, IR spectra of the interfacial water on quartz exhibited different trend: wavenumber of OH stretching peak shifted higher values with increasing temperature but didn't shift with pressure. Molecular structure of interfacial water on the rock and rock-forming mineral at elevated temperatures and pressures were not only changes due to physical conditions such as temperature and pressure but also interaction between interfacial water and solid rock materials. Raman spectra were measurable under hydrothermal conditions using the newly developed high temperature-pressure cell.

Induction Heating Diamond Anvil Cell (IH-DAC) for Raman microspectroscopy

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A high temperature diamond anvil cell by high frequency induction heating (IH-DAC) was newly constructed for Raman microspectroscopy. DAC is widely used high pressure apparatus to investigate the depth of the Earth. Two heating methods are often chosen to heat a small sample in DAC. One is external heating DAC with electrical resistance heater surrounding diamonds. This is an easy way to heat sample, but not easy to avoid some experimental difficulties such as the breaking of the electrical wire. The other is internal heating method by laser. This is very refined way of heating sample in gasket. However, laser heating DAC costs a lot and may encounter unstable heated states of sample. In this study, we adopted a high frequency induction heating to elevate temperature of DAC. The IH-DAC will possibly be a modified external heating method to heat DAC stably. The IH-DAC was designed as modifying the Merrill-Bassett DAC as to apply pressure with a lever. The modified DAC was made by Engineering Workshop of Osaka City University. One turn of induction coil of Cu made for IH-DAC surrounds a pair of diamonds. The temperature of a sample in gasket can be directly measured by Raman spectra. The intensities of Stokes (I_s) and anti-Stokes (I_{as}) lines are related by the Boltzmann factor as I_{as}/I_s = exp(-hν/kT). Stokes and anti-Stokes lines of silicon were used for calibration of temperature.

As preliminary experiments, dummy plates of SUS, WC, Re were heated by IH. Temperature of dummies was measured by infrared thermometer. SUS was stably heated up to 1200°C in air. Surface of WC reacted in air over 800°C. Re evaporated over ca. 400°C. Based on the dummy heating, Two kinds of parts setting composing DAC were examined for IH. As first setting, Rockers supporting diamonds were made from WC. The WC rockers are directly heated by the induction coil. In this way, a sample in gasket can be easily heated up to 800°C. In the second, rockers were made from Si₃N₄ and hybrid gasket was made from Re plate sandwiched by welded SUS plates. In this way, whereas the hybrid gasket can be heated by IH, no heating effect for rockers. In this setting, high temperature was not attained as the former way. Therefore, heating directly rockers by IH is hopeful way to attain high temperature over 1000°C. IH-DAC is a workable method for HT-HP experiments. We will report some direct observation of high pressure phase transformation of minerals.

The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals

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The RRUFF project is an integrated study of the physical properties of minerals with freely accessible data that can be obtained from the Internet at RRUFF.geo.arizona.edu. The goal is to obtain representative samples of all known minerals from which X-ray diffraction patterns and chemical composition are obtained. These two sets of data are used to identify and characterize the samples. The samples are then oriented along crystallographic and optic directions, mounted and polished on pins. Polarized Raman and infrared spectra are then obtained in a number of orientations. The data is presented in a searchable format through a web interface. Algorithms and software are being developed to permit searching and identifying unknown samples from chemistry, diffraction profiles or vibrational spectra. A database of Raman spectra is being developed for use in remote sensing, such as on the Mars Rover, and for the new generation of compact, hand-held Raman instruments that are coming to the commercial market.

P03-01

Resonant ultrasound spectroscopy of natural polycrystalline samples

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The elastic properties of minerals have been determined largely using ultrasonic techniques on single crystals. Bulk moduli have also been obtained by fitting equations of state to single crystal diffraction data for unit cell volume as a function of pressure. These are then converted to bulk and shear moduli for polycrystalline samples using the Voigt/Reuss/Hill or Hashin-Shtrikman averaging schemes. We have started to use resonant ultrasound spectroscopy (RUS) to measure the bulk and shear moduli directly for natural monomineralic polycrystalline samples. Data from natural anorthosite samples show close agreement with known single crystal values for shear moduli, within the limits of the Voigt and Reuss averages. For pure anorthite, good agreement has also been obtained with known values for its bulk modulus. We have also used RUS to follow the evolution of the bulk and shear moduli and the quality factor (Q) through the high temperature phase transitions in quartz. These experiments show the same softening of the bulk and shear moduli on approaching the α - β phase transition at 573°C as determined from single crystal experiments. There is a slight discrepancy between the two data sets close to the transition; however this inaccuracy may be due to the significant decrease in Q in the vicinity of the transition, the evolution of which can be followed easily using this method. This approach will also allow the systematic variation of elastic properties as functions of composition and temperature across a solid solution series to be determined quickly and accurately using natural samples or synthetic polycrystalline pellets.

P03-02

XAS and structure refinement allied to understand site preference and local environment of major and trace elements in garnets

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Notwithstanding the many published studies undertaken with a plethora of experimental and theoretical approaches, some important details of the crystal chemistry and thermodynamics of garnets are still to be fully understood. XAS analysis is useful to clarify two important issues: (i) site preference and local environment of trace elements, to obtain a better interpretation of experimental partition coefficients; (ii) changes in the local coordination and possible clustering effects in non-ideal solid solutions (e.g. pyrope-grossular, prp-grs).

XAS measurements at different elemental absorption edges were done on natural and synthetic garnets of various composition, previously characterised by electron and ion microprobe and single-crystal structure refinement.

Combining all the available information, we obtained the following conclusions:

1. REE enter the X site. In the loose structure of melanites, their local environment (in terms of X-O distances) varies linearly with their ionic radii; however, site distortion, expressed as $\Delta X-O = X-O_{\text{long}} - X-O_{\text{short}}$, tends to decrease as a function of the ionic radius.

2. The local coordination of REE and Ca changes in distinct garnet compositions (e.g., melanites, pyrope, grossular). Moreover, the trends obtained for Ca and REE have different slopes in different garnet compositions, suggesting a failure of the ionic model at least in the prp-grs join.

3. Measurements done at the Ca K-edge along the prp-grs join show that Ca local environment depends on the overall composition of the sample, and that $\Delta X-O$ tends to decrease passing from grossular to pyrope. At prp60grs40, the two distances are indistinguishable by EXAFS analysis, whose resolution is however limited by the presence of oxygen as back-scatterer species.

4. Measurements done at the Sc K-edge show that Sc may enter all the available structural sites depending on the overall composition and the relative dimension of the sites. In the very compact structure of pyrope, Sc enters the X site, and local charge balance is achieved by Mg at the adjacent T site.

5. Sc is generally considered an octahedral cation in garnets. We found that Sc at Y does not exceed 0.20 apfu when the dominant cation is Al, whereas the Sc vs. Fe²⁺ exchange is almost ideal.

Given the complexity of the problem, the intrinsic limits of each technique, and the implications of these results, we are presently comparing our data with those obtained with other spectroscopic techniques, such as NMR, and with potential-based computations done by other groups.

P03-03

Chemical state of Fe in igneous rocks using high resolution X-ray fluorescence, HRXRF

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The Moessbauer spectroscopy is only method for practical use, when someone wishes to analyze the chemical state of Fe without destruction of the sample. However, the method is not so high sensitivity, and possible utilizing place has been limited due to the necessity of radioisotope.

On the contrary, X-ray fluorescence spectroscopy (XRF) is so wide use method for qualitative and quantitative analysis as well known. And, it was already reported on several fields that the spectrum profile of characteristic X-ray obtained by high resolution measurement shows the change in proportion to the chemical state. Using this phenomenon, the chemical state of any element can be decided.

In this report, the application result of this high-resolution X-ray fluorescence spectroscopy (HRXRF) for the chemical state analysis of Fe in the typical volcanic rock samples was presented. The method is not necessary of ultra vacuum around the sample. And it is available for insulators, solutions, materials containing water. HRXRF is only method for correct chemical state information for bulk. The HRXRF spectra were measured by the double crystal type spectrometer whose crystals are the ++ alignment. The standard samples for assignment of chemical state were Fe₂O₃ for Fe(III) and FeTiO₄ for Fe(II). In the following report, we would like to mainly discuss the result of the volcanic rocks of Asama Volcano.

From the comparison between the of Fe K α spectra of two standard samples, the peak position of FeTiO₄ (Fe(II)) was 0.10eV higher than that of Fe₂O₃ (Fe(III)). On the other hand, the peak position Fe K α of the lava sample obtained from Onioshidashi lava in Asama volcano appeared between the positions of these two standards, 0.07eV higher than Fe₂O₃, and the width of the peak was also broader than Fe₂O₃. Then, the peak separation technique with measured spectra for components spectra were adopted to this spectrum, and it was found that Fe(II) : Fe(III) was 64:36 with the sufficient precision of the calculation. In addition, two pyroclastic fall samples obtained at Asama B' were also analyzed with same process, and it was also found that the amount of Fe(II) existed further than Fe(II). Additionally we could discuss the results about the other igneous rocks. Finally, we would like to suggest this method, HRXRF could be contributed for the progress of mineralogy, petrology and volcanology.

ESR study on methane hydrateA. Tani¹, K. Ishikawa¹, K. Takeya², T. Otsuka¹ and S. Nakashima¹¹Department of Earth and Space Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan.
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Gas hydrate is a clathrate compound of water molecules surrounding a gas molecule like methane, ethane and carbon dioxide. Methane hydrate is naturally formed in permafrost and deep-sea sediments and attractive as a future energy resource. For example, methane hydrate in Nankai trough located off southwest Japan appears in sand layers, especially in turbidite. Those marine sediments usually contain natural radioisotopes like ⁴⁰K, U-series, and Th-series as sources of α -, β -, and γ -rays. We have investigated radiation effects on synthetic methane hydrate by γ -rays with the electron spin resonance (ESR) spectrometer. Additionally, chemical products induced by radiation were investigated using the IR spectrometer accompanied with a cylindrical gas cell.

Methyl radicals and hydrogen atoms were observed at 77 K in methane hydrate irradiated by γ -rays at 77 K. Although the hydrogen atoms disappeared at 120 K, the methyl radicals decayed around 200 K at 0.1 MPa, close to dissociation temperature of methane hydrate at atmospheric pressure. Radiation-induced methyl radicals in water ice (*I_h*) are much less stable. This means that the methyl radicals in hydrate may be trapped and stabilized in clathrate cages.

Isothermal annealing of γ -ray irradiated methane hydrate reveals that activation energies of the methyl radical decay were estimated as 20.0 ± 1.6 kJ/mol for 210-230 K and 54.8 ± 5.7 kJ/mol for 235-260 K. They are concordant with the enthalpy changes in dissociation of methane hydrate into water ice and methane gas (18.13-23.37 kJ/mol) and liquid water and methane gas (54.19-67.85 kJ/mol), respectively. The dissociation of methane hydrate over 235 K may occur through metastable state (liquid water and gas) to stable state (water ice and gas).

The stability of the methyl radicals at higher pressure has different features. The radicals decayed at 210 K even in methane atmosphere of 10 MPa, though methane hydrate is stable at that condition. This implies that the radicals diffuse and encounter each other without any dissociation of methane hydrate at 10 MPa.

Only ethane was observed in fingerprint region of 1000-700 cm^{-1} after dissociation of the sample irradiated at 77 K, even though ethylene, acetylene and methanol should be observed in the same region. The methyl radicals will be dimerized into ethane in the decay process.

Radiospectroscopy of vein quartz of the Subpolar Ural deposits

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The vein quartz and mountain crystal used as raw material for synthesis of monocrytals and melting of glass is characterized by a wide variety of the constitution and properties. The main task of the research is estimation of the contents of the structural impurity-related paramagnetic centers in basic industrial and potentially industrial quartz types of some Subpolar Ural deposits. This investigation is of interest as for the analysis of minerogenesis conditions as for an estimation of quality of quartz raw materials. Researches were made using electron spin resonance (ESR) data on defects connected with isomorphous incorporation of Al- and Ge- ions into the lattice of vein quartz. ESR spectra of Al- and Ge-centres of the powder preparations of quartz were recorded with the radiospectrometer SE/X 2547 (RadioPAN, Poland) at 77 K and 300 K.

The carried out research has shown variety of the basic industrial types of vein quartz and mountain crystal under the contents paramagnetic aluminum and germanium centers. The increase of average values and of variations ranges of these centers concentrations from earlier primarily fine-grained vein quartz generation to later smoky and smoky-citrine quartz generations is stated. The positive correlation between the Al- and Ge- centers contents in quartz of various types was established. The received data on the contents of structural impurity in quartz characterize the quality of the Subpolar Ural quartz as raw material for melting of glass. Primarily fine-grained and granulated vein quartz, which widely advanced in the Subpolar Ural provinces, is regarded as less structural impured and potentially perspective.

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Effect of sample temperature on cathodoluminescence of tridymite and cristobalite

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Although CL of quartz has been extensively studied, there have been few investigations about CL of other silica minerals such as tridymite and cristobalite. Since tridymite and cristobalite have several polymorphs corresponding to heating or cooling processes, CL spectral data of these minerals at various temperatures should be useful for a study of polymorphism of silica minerals. We have measured CL spectra using SEM-CL in wide temperature range, and quantitatively discuss temperature quenching effect and short-lived luminescence here.

Natural tridymite and cristobalite were selected for CL measurements. A cathodoluminescence scanning microscopy (SEM-CL), SEM (JEOL: JSM-5410) combined with a grating monochromator (OXFORD: Mono CL2), was used to measure CL spectra ranging from 300 to 800 nm, where the sample temperature was controlled from -192 to 300 °C with a cryo- and heating-stage.

CL image of tridymite and cristobalite show homogenous blue or violet emission. CL spectra of both minerals have a broad peak at approximate 480 nm at room temperature. This blue emission is attributed to recombination of self-trapped exciton (STE) and/or E' center caused by oxygen deficient defects. CL intensities of tridymite and cristobalite decrease with an increase of electron irradiation duration. The rate of these reductions is a remarkably high by comparing other minerals such as quartz, which indicates a decrease of CL emission during electron irradiation as a short-lived luminescence. Such behavior might be related to a diffusion of impurity elements or an effect of the beam-induced electric field.

Tridymite and cristobalite exhibit a rapid decrease of CL spectral intensity in blue color region on heating. This phenomenon can be construed in terms of a temperature quenching theory based on an increase in the probability of non-radiative transition with rising of temperature. A least-square fitting of the Arrhenius plot by assuming Mott-Seitz model provides activation energies of 0.025 eV from -192 to -70 °C and 0.129 eV from -70 to 50 °C in temperature quenching process for tridymite. These activation energies are equivalent to the order of Si-O stretching vibration energy. Activation energies for cristobalite are 0.032 eV from -192 to -70 °C and 0.182 eV from -70 to 120 °C. The former value corresponds to O-Si-O bending vibration energy, and the latter to Si-O stretching vibration energy. It implies that the energy of non-radiative transition in heating process might be transferred to lattice vibration as phonon.

Temperature quenching mechanism of cathodoluminescence of Mn activated calcite

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The effect of sample temperature on the CL of calcite, however, has scarcely been investigated so far. This study provides quantitative estimates of the temperature effect on CL emission of the calcites having various concentrations of Mn²⁺ activator.

Six natural calcites with Mn content of 13, 129, 1260, 3520, 9170 and 66500 ppm, were used for CL measurements, labeled as CM13-CM66500. Scanning electron microscope combined with a grating monochromator was used to measure CL spectra ranging from 300 to 800 nm. The sample temperature was controlled in the range from -192 to 300 °C with a cryo- and heating-stage.

CL spectra of all samples exhibit almost similar pattern with a single broad peak at 620-650 nm, of which variation might be attributable to crystal field (Mn-ligands distance). The emission peak can be assigned to the electronic transition from the excited ⁴G to the ground state ⁶S. Only CM13 with a low Mn content gives a broad band peak at 370 nm in blue region, resulted from lattice defects. Gaussian curve fitting of CL spectral peak gives a luminescent efficiency, which is employed for the derivation of activation energy in temperature quenching process.

CL intensities of CM13 and CM129 with a low Mn content shows an increase with rising temperature up to -50 °C, but unchangeable at higher temperature. This sensitized effect may be caused by an energy transfer from defect center to Mn²⁺ center. CM1260 and CM3520 with Mn content of several thousand ppm exhibit a similar behavior of their intensities on heating, where the intensities has not so much change over a wide range of temperature. This fact suggests that CL emission process has not any non-radiative transition for these samples. On the other hand CM9170 and CM66500 with a high Mn content are characterized by rapid decrease of their intensities with increasing temperature. Such behavior is explained on the basis of a temperature quenching theory based on an increase in the probability of non-radiative transition with the rise of temperature. Activation energy of 0.03 eV for CM9170 and 0.053 eV for CM66500 in temperature quenching process correspond to lattice vibration energy. It implies that the energy of non-radiative transition might be transferred to lattice as phonon.

The result leads that activator (Mn²⁺) concentration considerably affects temperature quenching effect on CL of calcite. There are no other precedents except such calcite.

Cathodoluminescence and 3D Raman spectroscopy of shocked quartz from impact craters

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In this study we discuss an effect of shock-metamorphism on quartz from impact craters by means of CL and 3D Raman spectrometry. Samples used for this study were twenty quartz at various shock stages from impact craters, Ries Crater and Barringer Meteor Crater. They were prepared as polished thin section using nonluminescent epoxy resin and coated with 20 nm thickness carbon. The planar microstructures (PDFs: planar deformation features and PF: planar fractures) were observed in several quartz grains under a petrographic microscope. Raman spectra were obtained with an Almega: confocal micro-Raman spectrometer with a 20 mW at 532 nm with Nd:YAG laser excitation system. CL spectral measurements were carried out using a SEM combined with a grating monochromator in wavelength range of 300 to 800 nm, where operated condition was at 15 kV and 0.05 nA beam current. The sample temperature was controlled in the range from -192 to 25 °C using a cryostage. CL observations were performed with a CL imaging system (MiniCL). Raman spectra of shocked quartz exhibit a pronounced peak at around 455 cm⁻¹, which can be assigned to Si-O stretching vibration, whereas typical low-quartz has a sharp and intense peak at 464 cm⁻¹. This frequency shift might be related to a distortion of structural configuration caused by shock-metamorphism. 3D Raman imaging analysis using this Raman peak reveals a striped image comprised of high and low crystalline parts. This 3D Raman image corresponds to the optical image of PDFs. Furthermore, MiniCL imaging of some shocked quartz gives apparent features related to PDFs, which can be clearly observed under polarized microscope. CL spectra of shocked quartz exhibit a doublet peak in the range from 450 to 500 nm. Upon heating the CL intensity rapidly decreased. The decay of CL intensity in low-quartz is well known as a temperature quenching effect. Activation energy in temperature quenching process was evaluated by assuming Mott-Seitz model. Arrhenius plot leads to activation energy (E) of 0.85 eV in the range from -180 to -30 °C for shocked quartz. Usual quartz exhibits two temperature quenching processes, where the E is 0.03 eV up to -110 °C and 0.235 eV above -110 °C. Therefore, the effect of shocked-metamorphism might affect to electronic transition process in defect centers correlated to CL emission. A combination of CL and 3D Raman spectroscopy is a powerful technique for appreciating an effect of impact shock on minerals.

Infrared Spectroscopy of Aqueous Solutions - Effects of Dissolved Ionic Species -

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In order to study natures of fluids in earth and planetary materials in the form of fluid inclusions trapped in minerals by infrared spectroscopy, it is necessary to understand changes in infrared spectra by solutes, temperature and pressure. In this study IR spectra of synthetic salt solutions (NaCl, KCl) were measured by attenuated total reflection infrared (ATR-IR) spectroscopy to study effects of dissolved ionic species. The apparent peak position of OH stretching absorption band shifted from 3330 cm⁻¹ to higher wavenumber with the salt concentration. The peak shift was similar for NaCl and KCl solutions. By taking difference spectra from the pure water, the absorption intensity of the higher wavenumber component (3430 cm⁻¹) increases, while that of the lower wavenumber component (3170 cm⁻¹) decreases. The increase rate of 3430 cm⁻¹ component with the salt concentration was larger for NaCl (0.040/M) than for KCl (0.031/M), while the decrease rate of 3170 cm⁻¹ component was smaller for NaCl (-0.062/M) than for KCl (-0.072/M). These results suggest that the long H-bond distance character increases, and the short H-bond distance character decreases due to addition of NaCl or KCl to pure water. These changes can be explained tentatively by the following ionic hydration theory. The "positive" hydration region just around an ion might be composed of H₂O molecules with shorter H-bond distance. This region is surrounded by the "negative" hydration region composed possibly of H₂O molecules with longer H-bond distance. The difference of OH bands between NaCl and KCl solutions might be due to the difference in relative volumes of these hydration layers.

Direct observation of the quartz-coesite phase transformation by using IH-DAC

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Induction heating diamond anvil cell (IH-DAC) installed Raman micro-spectroscopy is a proper method for the kinetic study of phase transformation in minerals at high temperature and high pressure, because of following two advantages. First, the induction heating, which is a new method for heating a DAC, keeps the sample chamber to be heated uniformly and stably for long time. Second, Raman micro-spectroscopy enables to identify polymorph at short time with the spatial resolution of about 2 micrometers.

Direct observations and kinetic studies of the quartz-coesite phase transformation have been performed with the instruments at 400-700 °C, 3.0-5.5 GPa. High pressure experiments were performed under a dry and quasi-hydrostatic conditions by using NaCl as pressure medium. Oriented thin sections of 30-50 micrometers thickness and powdered sample of about 20 micrometer of synthetic quartz were prepared as starting material. The sequence of reaction from quartz to coesite under HT and HP was directly observed under a polarizing microscope. The interference color of the thin section gradually changed from the rim to the inside. The area of changed interference color was identified as coesite by micro-Raman in situ measurement. In the experiment of powdered sample, relative intensity of intense Raman band of coesite to that of quartz was monitored every 3-10 minutes. The measurement of aggregate of randomly oriented particles permits ignoring the polarizations of the Raman intensity due to the orientation of single crystal. The raw relative intensities were converted the transformed volume fraction as a function of time by the calibration curve which shows a relation between the relative intensities of Raman peaks of coesite to quartz and the volume fraction of coesite. The calibration curve was determined by the micro-Raman spectra of well mixed powders of quartz and coesite which previously weighted, which was collected with rotating the mixed powders. By the converted data fitting by the Avrami equation (Avrami, 1939, 1940, 1941), the value of exponent n was determined approximately as 1.0. These results suggest that the quartz-coesite phase transformation is controlled by phase boundary reactions.

Water Diffusion into Synthetic Beryl Channel at 500-700 °C, 50-150 MPa

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Beryl (Be₃Al₂Si₆O₁₈) is a typical cycrosilicate found in pegmatite. The crystal structure of beryl is characterized by rings of six SiO₄ tetrahedrons. The rings are connected with BeO₄ tetrahedron and AlO₆ octahedron. They stack along the c axis making long cavities. The cavity is often called a channel. In natural beryls, many experimental and theoretical studies show that extra molecules such as H₂O, CO₂ and alkali ions are located in the channel. Alkali ions are introduced to compensate charge balance by the replacement of Be²⁺ or Al³⁺ with other ions. Depending on temperature, pressure and H₂O fugacity during beryl growth, the number of H₂O molecules varies in beryl channel.

Two kinds of orientation of H₂O molecules in the channel have been recognized by IR and Raman spectroscopy. H₂O which locates its H-H direction parallel to the c axis and perpendicular to c axis in the channel is labelled as Type I and Type II, respectively. The rotation of the direction of H₂O molecules is attained by the attraction of alkali ion close to it.

To investigate the H₂O contents in beryl channel under various temperature and pressure, we observed diffusion of H₂O into the beryl channel. First, we synthesized anhydrous single crystal beryl of about 1 mm by flux method using MoO₃-Li₂CO₃ as a starting material. Several synthetic beryls and water about 5-15 micro liters enclosed in gold capsule were kept for 36-360 hrs, under 500-700 °C, 50-150 MPa in hydrothermal reactor. The recovered samples were made into polished thin sections parallel to the c axis. Two peaks around 3700 cm⁻¹ and 3603 cm⁻¹ were observed in the recovered samples. They are assigned to Type I and Type II H₂O respectively. Type II H₂O results from alkali ion in the channel. Li⁺ is a candidate of alkali ion in the channel because Li₂CO₃ was used as flux for synthesizing beryl. Polarized IR spectra were measured along c axis from rim to core every 100 micro meters. Along the c axis from rim to core, line profiles of absorption due to the H₂O molecular vibration in 3000-4000 cm⁻¹ were measured. Total amounts of H₂O molecules diffused into beryl channel were estimated from normalized absorbance due to Type I and II. Diffusion coefficient and activation energy, under some temperature and pressure were calculated from the line profiles.

O04-01

Ab initio investigation of post-perovskite phase change

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High-pressure phase transition in orthorhombic MgSiO_3 perovskite to CaIrO_3 type post-perovskite structure was discovered and reported in 2003-2004. Several properties suggesting importance of this phase change in the lowermost mantle such as PT condition of the transition, Clapeyron slope, seismic velocity, etc. have been revealed by density functional investigations. This type of phase transition has now been found in several other perovskite compounds. Also effect of impurity and the transition in more geophysically relevant compositions have been extensively investigated. Here, we summarize systematic properties of the post-perovskite phase change based on our theoretical studies of MgSiO_3 and other relating materials. Also present structural, elastic and energetic properties of iron-bearing phases will be presented.

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O04-03

Computational study of mineral structures and properties

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Computation of equations of state, phase transitions, thermoelasticity, and magnetic properties of minerals at high pressures will be reviewed. Elastic properties and vibrational spectra of silicate perovskite (pv) and post-perovskite (ppv) studies have been computed with linear response lattice dynamics as functions of composition, in order to understand compositional effects on the perovskite to post-perovskite phase transition. We found that ferrous iron stabilizes the ppv phase over pv, so that pure FeSiO_3 would prefer the ppv structure over pv even at zero pressure. Aluminum stabilizes pv over ppv. We find that Fe increases, and Al decreases the bulk modulus K at a given pressure, and both Fe and Al decrease the shear modulus G. Both Fe and Al decrease V_p and V_s . We predicted the Raman intensities for ppv before they have been measured, and find only one strong peak in MgSiO_3 at 850 cm^{-1} at 60 GPa, increasing to 950 cm^{-1} at 120 GPa. The large difference from the pv spectrum should make Raman a good tool for quick identification of ppv. To obtain thermal properties there are three main methods: quasi-harmonic lattice dynamics (QHL), molecular dynamics, and the particle-in-a-cell model (PIC), the latter being suitable to Fe under core conditions. We have applied QHL to mantle minerals using first-principles linear response theory with ABINIT, and PIC and QHL to Fe in the bcc, fcc, and hcp phases using FLMTO to obtain the thermoelastic properties. We find that PIC works very well for the equation of state, and can give reasonable elastic properties when converged. The agreement between QHL, most valid at low temperatures, and PIC, more valid at high temperatures, gives support to both. We find a small change in c/a with temperature in hcp iron, but still find the elastic constants to behave with increasing temperature under core conditions as previously predicted, giving an estimate by comparison with seismology of the temperature of the inner core of about 6500K. Self-consistent calculations robustly show hcp-Fe to be antiferromagnetic (AFM) up to 50 GPa. Computations of hyperfine fields show cancellation between valence and semicore contributions, consistent with the absence of hyperfine fields in experiments. Frozen phonon calculations for the AFM structure show a split Raman mode that agrees with experiment. We have also developed a multiscale model for non-collinear, magnetic fluctuations in iron to obtain the magnetic contributions to thermal properties.

O04-02

Aluminum-bearing Post-perovskite in the Earth's D'' Layer

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The effects of Al on the physical properties of the newly found MgSiO_3 post-perovskite (PPv) [e.g. Murakami et al., 2004; Oganov & Ono, 2004], which is the major mineral of the Earth D'' layer, are not well known. As our previous work [e.g. Zhang & Oganov, 2006] has shown the substitutions of Al^{3+} and Fe^{3+} are independent of each other in PPv, in contrast with the case of MgSiO_3 perovskite (Pv). Therefore, the effects of these impurities on PPv can be decoupled and studied separately. Here, using large-scale ab initio simulations, we investigated the substitution mechanism of Al^{3+} into PPv through all the lower mantle pressures. We examined three types of Al substitution in PPv: model with 6.25 mol % Al charge-coupled mechanism (CCM) substitution, 6.25 mol % Al oxygen-vacancy mechanism (OVM), and Si-free oxygen-vacancy end member $\text{Mg}_2\text{Al}_2\text{O}_5\text{PPv}$ [e.g. Brodholt, 2000]. At pressures from 10 to 150 GPa, we have simulated five models of CCMs and five models of OVMs where Al atoms were put in different positions. Our calculations show that Al^{3+} replaces (by CCM) the next-nearest-neighbor cation pairs in PPv at pressures of the Earth's D'' layer. Incorporation of 6.25 mol.% Al^{3+} increases the zero-pressure compressibility of PPv by 3.15%. In agreement with previous works [e.g. Ono & Oganov, 2005; Caracas & Cohen, 2005; Akber-Knutson et al., 2005], we find that the incorporation of Al_2O_3 slightly increases the Pv-PPv phase transition pressure and the Al partition coefficient K equals 2.67 between Mg-Pv and PPv at 120 GPa and 3000 K.

O04-04

Ab initio calculations of the elasticity of deep mantle and core phases

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There are many unresolved problems concerning our understanding of the Earth's deep interior; even fundamental properties, such as its internal structure and exact composition, are poorly known. If we had sufficiently well constrained seismological data, together with accurate high-pressure, high-temperature elastic properties of the candidate materials, we could, in principle, fully determine the structure and composition of the deep mantle and core. Unfortunately, the extreme conditions of pressure and temperature required make results from laboratory experiments unavoidably inconclusive. However, computer simulations of materials at inner core conditions are now achievable. We have used ab initio molecular dynamics simulations to calculate the elasticity of hcp-Fe, bcc-Fe, FeS and FeSi at core conditions, and we use calculated shear wave to help constrain core composition. In addition, recent work on the structural and thermal properties of the lowermost mantle (D'') will be discussed. A number of theories have been proposed to explain the origin of the variety of characteristics of this seismically observed layer, including core-mantle interaction, the presence of remnants of subducted material, and that D'' is the site of a mineral phase transformation. This final possibility has been rejuvenated by recent evidence for a phase change in MgSiO_3 perovskite (thought to be the most prevalent phase in the lower mantle) at near core-mantle boundary temperature and pressure conditions. We have explored the efficacy of this 'post-perovskite' phase to explain the seismic properties of the lowermost mantle through coupled ab initio molecular dynamics and seismic modelling of perovskite and post-perovskite polymorphs of MgSiO_3 , performed at lowermost mantle temperatures and pressures. We have found that a post-perovskite model can explain the topography and location of the D'' discontinuity, apparent differences in compressional- and shear wave models and the observation of a deeper, weaker discontinuity. Our calculations show that the regional variations in lower-mantle shear-wave anisotropy are consistent with the proposed phase change in MgSiO_3 perovskite.

A Molecular Dynamics Study of the Equations of State of CaSiO₃ Perovskite

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The molar volumes and bulk moduli of CaSiO₃ perovskite are calculated in the temperature range from 300 to 2800 K and the pressure range from 0 to 143 GPa using molecular dynamics simulations that employ the breathing shell model for oxygen and the quantum correction in addition to the conventional pairwise interatomic potential models. The performance of five equations of state, i.e., the Keane, the generalized-Rydborg, the Holzapfel, the Stacey-Rydborg, and the third-order Birch-Murnaghan equations of state are examined using these data. The third-order Birch-Murnaghan equation of state is found to have a clear tendency to overestimate the bulk modulus at very high pressures. The Stacey-Rydborg equation of state degrades slightly at very high pressures along the low-temperature isotherms. In comparison, the Keane and the Holzapfel equations of state remain accurate in the whole temperature and pressure range considered in the present study. K_0' derived from the Holzapfel equation of state also agrees best with that calculated independently from molecular dynamics simulations. The adiabatic bulk moduli of CaSiO₃ perovskite along lower mantle geotherms are further calculated using the Keane and the Mie-Grüneisen-Debye equations of state. They are found to be constantly higher than those of the PREM by ~5%, and also very similar to those of the MgSiO₃ perovskite. Our results support the view that CaSiO₃ perovskite remains invisible in the Earth's lower mantle.

Atomistic simulation of minerals and melts using advanced interatomic potentials derived from first-principles DFT calculations

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Minerals and geologically relevant melts often contain three or more components and generally possess a rather complex structure. For a better understanding of processes in the Earth's interior, their physical properties need to be known in a wide range of pressures and temperatures. Atomic coordination often changes during the variation of the thermodynamic conditions. These requirements demand a great deal of atomistic computer simulations of such materials. First principles electronic structure calculations, e. g. in the framework of density functional theory (DFT), provide the most accurate and most general of the practicable simulation methods currently available. However, their use is still limited to rather small systems of a few hundred atoms and timescales in the range of a few picoseconds. Therefore, simpler models, such as classical interatomic potentials, are still needed. The general problem of empirical potentials is the limited transferability that restricts their range of applicability. Rigid ion models are usually optimized to reproduce a specific property in a narrow range of thermodynamic conditions. A more transferable description may be obtained if all relevant contributions to the atomic interactions are taken into account explicitly. This includes Coulomb interactions, polarization, ionic size and shape variations, and dispersion. The increased number of potential parameters is justified if they can be optimized in a controlled way, e. g. by reference to well-directed electronic structure calculations. Here, a first set of such advanced interaction potentials is presented. It is applied to minerals and melts of the CMAS (Ca-Mg-Al-Si-O) system. Transferability is demonstrated in a wide range of pressures and temperatures by comparison of model predictions to experimental and DFT results. Strengths and limitations of the present model are discussed.

Atomistic Simulations of Mineral Surface Structure and Stability

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The aim of this presentation is to highlight recent work using atom-based simulation methods to model the structure, stability and reactivity of mineral surfaces. Initially, the ways in which the surface structures are generated will be reviewed and then how we model the adsorption of a range of molecular species. We will then describe two approaches for increasing the scope and reliability of the simulations, either by including the dynamical contribution to the surface stability, or by increasing the reliability of the description of the interactions, using electronic structure simulations. The dynamical simulations based on molecular dynamics simulations give a further advantage of allowing us to evaluate the free energy profiles of adsorption and dissolution from flat and stepped surfaces. The results show that the type of surface has a profound affect on the free energies of desorption and dissolution. These dynamical simulations also require sensible starting compositions. The application of ab initio electronic structure methods based on DFT allows us to model the variation of surface composition in equilibrium with a vapour consisting of different gases. Thus, the stable structures and compositions can be evaluated at specific experimental conditions. The application of these approaches to several minerals will be discussed, including Al₂O₃, Fe₂O₃ and CaCO₃, which examine how the stability of the interfaces are modified by the presence of impurities and water. The results demonstrate that atomistic simulation techniques can provide a useful complementary tool for modelling oxide and mineral interfaces.

MgSiO₃ at conditions of the giants' cores and exoplanets

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We will present a comprehensive theoretical study of the thermodynamics and conductive properties of CaIrO₃-type MgSiO₃, the major planet forming silicate stable at pressures and temperatures (PTs) beyond those of Earth's core mantle boundary. We will address PTs typical of the cores of the giants and exoplanets.

First-Principles Calculation Studies on Mechanical Properties and Pressure-Induced Phase Transformations of Kaolin-polytypes

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The mechanical behavior of minerals under high pressure has attracted considerable interest in recent years. Clay minerals, including the kaolin group, are commonly found in sedimentary environments and their behavior under pressure is an important factor in understanding seismogenic zones. Kaolinite is a ubiquitous member of the kaolin group that has been found recently to undergo a structural phase transition between 2.0 and 2.5 GPa. In this study, the bulk modulus and elastic constants of kaolinite have been calculated from the first principles within density functional theory (DFT). The bulk modulus is predicted to be 23 GPa for kaolinite. The calculated elastic constant tensors indicate that the a-direction is slightly more flexible than the b-direction. The calculated elastic constant tensor along the c-direction is much lower than those calculated along the a- and b- directions, which is consistent with the crystal structure of kaolinite. The structural transformation of dickite, another polytype in the kaolin group, under high pressure has been modeled by extending the above results. Recent experimental evidence using Raman and X-ray diffraction methods revealed that dickite undergoes a structural transformation under hydrostatic compression above 2.0 GPa. In agreement with the experimental data, the first principle results predict that a structural phase transition occurs in the pressure range to 2.0 to 2.5 GPa. The phase transition involves a change in the interlayer hydrogen bonding between the aluminum octahedral layers and the opposing siloxane surface in the adjacent layer.

Dehydroxylation of Pyrophyllite by means of ab initio Molecular Dynamics and metadynamics

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Pyrophyllite is an important mineral for material design and other industrial applications that require thermal treatments, dehydration, dehydroxylations, and transformation processes, losing the hydroxyl groups of this mineral. The dehydroxylation of pyrophyllite involves the reaction of OH groups and elimination of water molecules throughout two possible mechanisms: that evolving the bridging hydroxyl groups of an octahedral pair (on-site mechanism), or that where two hydroxyl groups participate across a dioctahedral vacancy (cross mechanism). However, there are some discrepancies and no clear information is known about the dehydroxylation mechanism.

First principles calculations at DFT-BLYP-GGA level and Troullier-Martin pseudopotentials are used in the Car-Parrinello Molecular Dynamics (CPMD) code and the metadynamics algorithm is applied at 900K and 1500K. Unit cells and supercells of Pyrophyllite are used for the calculations. We explore the potential energy surface (PES) and the first step of the dehydroxylation reaction, where an intermediate was found in previous calculations in agreement with experiments.

Different reaction paths of this process and the critical points of the PES are found for both mechanisms. Similar activation energies reveal that both mechanisms are competitive with one another. Following the evolution of the system we detect that the apical tetrahedral oxygen can be implicated in the dehydroxylation mechanism forming silanol groups.

Crystal structure prediction: new methodology and geologically important results

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It is well known that structural transformations of minerals under pressure play a crucial role in determining the internal structure and dynamics of the Earth [1-4]. For instance, recent (almost accidental) finding of the post-perovskite phase of MgSiO₃ [2,3] has explained many anomalies of the Earth's D'' layer and may have major geodynamical and geochemical impact. This has motivated us to develop a theoretical methodology that could predict the stable crystal structure at given pressure-temperature conditions just from the chemical composition and using no experimental information. Crystal structure prediction on the basis of just the chemical formula has long been considered a formidable problem. Solving this problem would open the possibilities to find new phases of planetary materials, to solve structures where experimental data are insufficient, and to design new technologically useful materials entirely on the computer.

We have devised a powerful new method based on an ab initio evolutionary algorithm and featuring local optimization and spatial heredity, as well as further operators such as mutation and permutation. This method uses ab initio free energy as the evaluation function and turns out to be extremely efficient and reliable for predicting crystal structures with very different geometrical features and types of chemical bonding. It has been implemented in the USPEX code (Universal Structure Predictor: Evolutionary Xtallography, [5-7]). This method has been widely tested and applied to solve a number of important problems. In this talk I will discuss some of the applications of this method to a number of geologically or planetologically interesting materials (MgSiO₃, CaCO₃, MgCO₃, Al₂O₃, C, O, H₂O). Future developments of the method will be outlined.

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Structure and freezing of MgSiO₃ liquid in Earth's interior

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Silicates liquids are primary agents of mass and heat transport, yet little is known of their physical properties or structure over most of the mantle pressure regime. We have applied density functional theory to the study of silicate liquids via first principles molecular dynamics. The electronic structure, total energy, stress tensor, and forces acting on the atoms are computed self-consistently at each time step and atomic positions advanced according to Newton's equations of motion. The simulations are performed in the NVT ensemble with a Nose thermostat. We find that over the pressure regime of Earth's mantle the mean Si-O coordination number increases nearly linearly with compression from four-fold to six-fold. The Grüneisen parameter of the liquid increases markedly on compression, in contrast to the behavior of mantle crystalline phases, and in accord with expectations based on the pressure-induced change in structure of the liquid. The density contrast between liquid and crystal decreases nearly five-fold over the mantle pressure regime and is 4 % at the core-mantle boundary. The melting curve, obtained via integration of the Clausius-Clapeyron equation yields a melting temperature of 5400 ± 600 K at the base of the mantle. Our results support the notion of buoyantly stable silicate melts at the core-mantle boundary.

The electronic and magnetic structure of Fe-bearing silicates

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Silicates are the main constituents of the Earth's crust and mantle and the most important rock-forming minerals. Iron is the most common transition element and many important silicates contain iron as a major or minor ion. Iron can carry a magnetic moment because of its partly-filled d shell and since the abundance of any other magnetic ion is more than an order of magnitude smaller than that of iron, the discussion of the magnetic properties of minerals must necessarily focus on iron oxides and iron silicates. Whereas the magnetic properties of most iron oxide minerals are rather well known, the magnetic behaviour of iron-bearing silicates is far less well understood. The obvious reason is the complexity of their structure so that (i) the interpretation of the experimental results is more difficult and (ii) reliable theoretical calculations are hardly to find. Nevertheless, the occurrence of magnetic ordering at low temperatures can still have significant influence on the thermodynamic properties at elevated temperatures since crystal-field effects and magnetic ordering can contribute up to 10 % and more to the specific heat, and thus to the enthalpy and entropy at room temperature.

The basic aim of our study is to understand the relationship between the magnetic structure on the one hand and the electronic and geometrical structure on the other hand of some important rock-forming Fe-silicates, such as garnets, olivines, pyroxenes, amphiboles, micas, and their solid solutions with their isotypic Mg- and Al-silicates, because this relation is not yet thoroughly understood. Therefore, systematic ab initio electronic structure calculations on the basis of experimentally determined crystal structures were performed from which spin density distributions, magnetic moments, and magnetic coupling constants can be derived. The most appropriate theoretical basis for electronic structure calculations on transition metal compounds, such as Fe-silicates, is provided by the density functional theory applied here in form of the local spin density approximation. On the one hand, the reliability of the calculations was proofed by comparison with the experimental data. On the other hand, the experimental data can be explained in more detail by the theoretical results. Because the magnetic effects contribute to a certain extent to the thermodynamic properties of Fe-bearing silicates, these aspects will also be discussed.

Geometrical Analysis of Mineral Structures under Compression Using the Centroid Approach

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Centroid, or the point with the minimum variation of distances to a set of points, can be used to characterize various aspects of coordination polyhedra, like their sphericity or eccentricity (Balic-Zunic & Makovicky, *Acta Cryst.*, B52, 78, 1996). A simple and unique parameter of polyhedral distortion which is related to the centroid parameters, the volume distortion (Makovicky & Balic-Zunic, *Acta Cryst.*, B54, 766, 1998) is especially useful and directly expresses the volume capacity of a coordination polyhedron. The calculations of centroid, sphericity, eccentricity and volume distortion of coordination polyhedra are available in the software IVTON (Balic-Zunic & Vickovic, *J. Appl. Cryst.*, 29, 305, 1996) together with calculations of volumes of coordination polyhedra and standard calculations of bond-distances and bond-angles.

In this work the behaviour of the centroid parameters of coordination polyhedra under the high pressures are investigated. At the same time the approach to the compressibility of both the coordination polyhedra and interpolyhedral voids is developed and applied for the full characterisation of compressional behaviour of crystal structures.

The analysis is applied to compressional behaviour of feldspars, fluoride- and oxide-garnets, and sulfosalts.

MD simulated equations of state of sodium chloride and argon

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In high-temperature and high-pressure experiments, it is essential to have reliable pressure calibration standards over wide temperature and pressure ranges. Known equations of state of standard materials, such as NaCl, MgO, Au, and Pt, have been often used to measure pressure in multi-anvil or diamond-anvil-cell high-pressure experiments. However, severe discrepancies are found between proposed pressure scales especially at high temperatures, and thus critical crosschecks on these pressure scales are strongly required. We have shown that by combining the molecular dynamics (MD) method with quantum corrections, it is possible to simulate accurately the structural and thermodynamic properties of crystals over wide temperature and pressure ranges. The MD method is particularly useful and powerful for the simulation at high temperatures where anharmonicity of atomic vibrations is important. Here we propose to use the MD simulated T-P-V equations of state of sodium chloride and argon as reliable pressure scales at high temperatures and high pressures.

The interatomic potential includes pairwise additive Coulomb, van der Waals, and repulsive interactions. In addition, to take into account non-central forces in crystals, the breathing shell model (BSM) is used for the MD simulation, in which the repulsive radii of Cl ions or Ar atoms are allowed to deform isotropically under the effects of other ions. Quantum corrections to the MD results are made using the Wigner-Kirkwood expansion of free energy. Required energy parameters, including Cl or Ar breathing parameters, were derived empirically to reproduce the observed volume, volume thermal expansivity, volume compression, and elasticity data for sodium chloride or argon as accurately as possible. Some properties are calculated also using the lattice dynamics technique with the quasi-harmonic approximation to see the effects of anharmonicity at high temperatures. The MD simulations with BSM are found to be very successful in reproducing accurately the measured T-P-V relations and elastic constants of both NaCl and Ar over wide temperature and pressure ranges.

Molecular dynamics simulations of MgSiO₃ enstatite and seismic discontinuity in the upper mantle

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The seismic velocities for three kinds of enstatite (MgSiO₃: low clinoenstatite, L-CEn; orthoenstatite, OEn; and high-pressure clinoenstatite, HP-CEn), which is a major component in the upper mantle, were estimated using molecular dynamics simulations based on the a two-body interatomic potential model. The calculated seismic velocities, V_p and V_s, for OEn are slower than those of L-OEn up to 6 GPa and 1000 K. This result means that seismic velocities become sharply and distinctly slower if the transition from L-CEn to OEn occurs with increasing depth. Clearly, additional experimental data are required, but it is tempting to speculate that the phase transition between OEn and L-CEn might contribute to a factor of the seismic low-velocity zone, if this phase transition exists. Both velocities in HP-CEn are faster than those of OEn at the transition pressure, and the velocity gaps give $\Delta V_p \approx 1.9\%$ and $\Delta V_s \approx 13.6\%$ at 7 GPa and 1000 K and $\Delta V_p \approx 2.4\%$ and $\Delta V_s \approx 7.6\%$ at 9 GPa and 1700 K. Although it is difficult to determine that this phase transition corresponds to the specific seismic discontinuity, we hypothesize that this transition between OEn and HP-CEn is the origin of one seismic discontinuity observed at less than 410 km depth, e.g., the X-discontinuity. Furthermore, anisotropy of the seismic velocity, in particular V_p parallel to [100] > [001] > [010], is observed. We conclude that the transitions in enstatites are related to the seismic discontinuity observed at depths less than 410 km and that enstatite is as an important a mineral as olivine for the mineralogical model and for the anisotropic propagation of seismic waves in the Earth's upper mantle.

Molecular dynamics simulation of CH₄-CO₂ mixed hydratesT. Akamatsu¹ and K. Kawamura²¹Faculty of Education, Kochi University, 2-5-1 Akebono-cho, Kochi, 780-8520, Japan.

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The molecular dynamics method was applied to CH₄-CO₂ mixed hydrates with the structures sI (cubic), sII (cubic), and filled ice (orthorhombic), in order to reproduce and predict the compositional dependence of crystallographic and thermodynamic properties.

The following three patterns of sI and sII mixed hydrate crystals were prepared for the simulation:

1) The CH₄ is completely partitioned into smaller S-cage, and CO₂ into larger cage (M-cage for sI structure, L-cage for sII structure).

2) The CH₄ and CO₂ are evenly distributed to smaller and larger cages (Disordered structure).

3) The CO₂ is completely partitioned into smaller cage, and CH₄ into larger cage.

The system with sI structure contains 216 gas molecules (= 54 in S-cage + 162 in M-cage) and 1242 H₂O molecules, whereas sII structure 192 gas molecules (= 128 in S-cage + 64 in L-cage) and 1088 H₂O molecules. The interatomic potential model employed is an empirical one, which can reproduce the dielectric constant, diffusion coefficient, and density for H₂O, the vibration spectrum, density, and structure for CH₄ and CO₂. The MD calculation was carried out under constant temperature and pressure conditions.

The lattice parameter varies systematically with the CO₂ concentration [= CO₂ / (CH₄ + CO₂)] in smaller and larger cages. The concentration of CO₂ in smaller cage largely affects the lattice parameter. Under low temperatures, a preferred orientation of CO₂ molecules occurs in sII structure crystals, and it lowers the symmetry of the crystal from cubic to tetragonal. The structure with the enrichment of CO₂ into larger cage is more stable than the disordered structure, where CH₄ and CO₂ are evenly distributed to both cages.

The system with filled ice structure employed in this study contains 64 gas molecules and 128 H₂O molecules. The MD calculation was carried out under constant temperature and pressure conditions, with the same potential model as mentioned above.

This filled ice structure is maintained only with the CO₂ concentration less than 20 %. In this range, the lattice parameters a, b, and c vary systematically with the CO₂ concentration.

Molecular dynamics simulation of twin boundaries in quartz

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Twin boundaries in quartz were studied by molecular dynamics (MD) simulation. Twins on Japan Law are the most abundant among inclined-axis twin laws of α -quartz, where as twins on Esterel Law are known to be most common in β -quartz. This difference in relative frequency of occurrence is analyzed from a viewpoint of energy and interface stress of twin boundaries.

The Ewald method was used to calculate long-range interaction between atoms. To achieve the periodic boundary condition required in the Ewald method, twin boundaries were placed parallel to one of MD cell planes by rotation of crystal lattice. Initial structures used in MD simulations are known to strongly affect on topology of relaxed structure. Then, the most stable structure of boundary was searched by scanning initial positions of two crystals parallel to twin boundaries.

There are six types of twin boundaries between {112} or {-1-12} composition plane in four subtypes of Japan twin. From the simulation results, topology of these boundaries can be grouped into two types. One is a boundary between left-handed and right-handed quartz, and the other is a boundary where both crystals have same handedness. Several types of stable structures are obtained for Esterel twin boundaries. Twin boundary energies of Japan twin and Esterel twin decrease with increasing temperature under α - β transition temperature, and they are almost constant above the transition temperature. At atmospheric pressure, twin boundary energy of Japan twin is smaller than that of Esterel twin at any temperature. With increasing pressure, one type of Esterel twin becomes more stable than any types of Japan twin.

Atomistic calculations of structural and elastic properties of serpentine (lizardite and antigorite) minerals

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Atomistic simulation is a powerful tool to investigate the physical properties of minerals. Using the Gulp code (J. Gale, Molecular Simulation, 2003), energy minimization has been performed on lizardite, a hydrous magnesian 1:1 layer-silicate which belongs to the serpentine family. This mineral is of large geological interest, as this is the main serpentine variety occurring in hydrated oceanic peridotites. Its own stability field is still not clearly established, mainly because of the lack of reliable thermodynamic data concerning the serpentine minerals in general. Modeling lizardite during a structural relaxation including variations of pressure and temperature should provide insights on its behaviour along a geotherm as well as on a better understanding of its spectroscopic behavior. Evolution of the total energy as a function of the lizardite unit-cell volume along with constant volume relaxations of all atomic degrees of freedom, converges to an energy that corresponds to the unit-cell dimensions and symmetry consistent with that of the experimental structure. These calculations also provide a cohesion energy between the layers of 0.32 eV (ie. 13 kJ per interlayer O-H... O bond). This is consistent with the accepted value for hydrogen bonding and also not so far from the energy obtained by *ab initio* calculations on the same mineral (19 kJ per bond). Finally, bulk shear and Young moduli along with transversal and longitudinal acoustic velocities are deduced from the elastic matrix analysis and the fit of the energy potential well using the Birch-Murnaghan equation. The effect of pressure and temperature was also investigated. Remaining in serpentine stability conditions, we evidenced that structural variations are mainly pressure-induced, temperature only playing a minor role which vanishes with increasing pressure. Pressure is mainly accommodated by a decrease of c-lattice parameter up to 10 GPa. These results are consistent with experimental data from Mellini & Zanazzi who investigated the structural modifications of lizardite up to 1.2 GPa. Lizardite density strongly increases with pressure. The bond length and angle analysis are compared to the results obtained in a high pressure Raman spectroscopic study and are in good agreement with the observed shifts of the Raman modes. This study also shows that the chosen set of interatomic potentials provides a reasonable description of lizardite. Preliminary results on antigorite, the higher pressure, modulated variety of serpentine, will be also presented.

Deformation and fracture of NaAlSi₃O₈ glass with regular arrangement of Al and Si ions using molecular dynamics simulationT. Taniguchi¹, S. Ito¹¹Research Center, Asahi Glass Co., Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama, 221-8755, Japan

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Dependence of network structure of almino-silicate glass on mechanical behavior was investigated. Two types of glasses, which have different network structure but the same composition, were made using molecular dynamics simulation method. One type was made by melting or pressing zeolite crystal, which has Al-Si ordered structure, and the other type was made by quenching melt with a random structure. The structures of the former glasses were fairly affected by the structure of zeolite, that is, the glass had a coarser network with a higher Al-Si ordering structure compared with the latter glass. Their mechanical behaviors were compared under stress. The glasses were fractured under tension of 5 GPa. However, the glasses with Al-Si ordering structure showed larger deformation than the quenched glass with less ordering structure before fracture. During the deformation, the former glasses deformed with decreasing Al-Si ordering, that is, forming the Si-O-Si and Al-O-Al bonds instead of the Si-O-Al bonds, while the latter glass deformed without changing Al-Si ordering. From these results, we considered that the larger deformation of the glass obtained from zeolite was caused by (1) coarse network and (2) decrease of Al-Si ordering.

O05-01

Deep seismicity triggered by the olivine-wadsleyite transformation: Multi-anvil acoustic-emissions results

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Despite many years of directed research the origin of deep-focus earthquakes remains enigmatic. We have developed a new 8-transducer technique for monitoring micro-seismic acoustic emissions (AE) during multi-anvil experiments. The technique is capable of locating AE sources and determining first-motions of failure surfaces.

Experiments in the pressure-temperature regime where $(\text{Mg}_{90}\text{Fe}_{10})_2\text{SiO}_4$ transforms from olivine to wadsleyite (14 GPa, 700–1400 K) show several important features pertinent to the deep-seismicity problem:

1) Olivine only shows brittle behaviour at the timescales of the experiment.

Faults can be induced in sintered olivine at room temperature at pressure up to 9 GPa. Pre-faulted samples show stick-slip behaviour on the fault-plane at all pressures and temperatures, with periodic bursts of associated AE. The fault gouge shows a range of grain-sizes to $<0.1\mu\text{m}$ and there is no lattice-preferred orientation detectable in the gouge.

2) Wadsleyite shows viscous behaviour.

Wadsleyite nucleates on the grain-boundaries of metastable olivine. Fine-grained olivine fault-gouge is rapidly replaced by wadsleyite. The wadsleyite has a constant grain-size of $\sim 1\mu\text{m}$. There is strong lattice-preferred orientation in wadsleyite, indicating dislocation creep deformation. There are no AE associated with this.

3) At high degrees of transformation large AE are observed away from the original fault zones.

We conclude from these data that wadsleyite generation in the subducting slab can cause remobilization of old fault-systems. Furthermore, although the observed deformation was plastic and free of AE, shear localisation onto these zones in the Earth can produce thermal run-away and seismogenesis. This is supported by the low observed seismic energy release in many deep-focus earthquakes. The volume change associated with transformation from olivine to wadsleyite within the metastable 'cold-finger' can induce sufficiently high stresses to initiate brittle-failure in the surrounding slab. However, transformation must be sufficiently fast that the 'transformational stresses' cannot be relaxed by plastic relaxation of the slab. Numerical models which include the thermodynamics and kinetics of the olivine-wadsleyite transformation suggest that this is possible.

O05-02

Lattice preferred orientation of akimotoite synthesized under deviatoric stress

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Akimotoite (ilmenite-structured MgSiO_3) is thought to be important to understand the seismic anisotropy in the deep part of the mantle transition zone (MTZ), particularly along a low-temperature geotherm. Recent molecular dynamics simulation demonstrated the anisotropic properties of akimotoite that P-wave velocity along the crystallographic c-axis is smaller than that in other directions and also that notable S-wave splitting (polarization) occurs in most of wave propagation directions except some specific ones (Zhang et al., 2005). This means that if lattice preferred orientation of akimotoite is provided by mantle flow, it will greatly influence the anisotropy of the lower MTZ. Thus, investigating the deformation property of akimotoite is significant for better understanding of mantle rheology. Here, we report the first application of electron backscatter diffraction (EBSD) techniques to characterize the nature of the crystallographic orientation of polycrystalline akimotoite, which was synthesized under quasi-hydrostatic pressure and under deviatoric stress.

Akimotoite was synthesized from MgSiO_3 enstatite at 21 GPa and at 1400°C using a Kawai-type multi-anvil high-pressure apparatus. For syntheses under quasi-hydrostatic pressure, the sample is enclosed in a platinum capsule, which is then loaded into MgO pressure medium. For deformation experiments, a pair of Al_2O_3 piston rods was placed just above and below the sample so that deviatoric stress was generated in the MgO pressure medium. Three types of samples were analyzed in detail by FE-SEM (JEOL) equipped with EBSD (Oxford): 1) Akimotoite synthesized under quasi-hydrostatic pressure, 2) that synthesized under deviatoric stress, and 3) that prepared by annealing sample 1) at 1200°C and 21 GPa under deviatoric stress. The EBSD analyses revealed that in sample 1) and 2) the crystallographic orientations of akimotoite appeared to be random, whereas in sample 3) akimotoite showed obvious lattice preferred orientations (LPOs) that many crystals locate their $\langle 001 \rangle$ directions (c-axis, i.e. elongation direction) perpendicular to the deviatoric stress direction. The LPOs of akimotoite are probably produced as a result of stress relaxations to attain the minimum energy configuration of the polycrystalline assemblage during annealing. Such LPOs were not observed clearly in sample 2). This may be because most of the deviatoric stress involved in the sample was released by the phase transformation from enstatite to akimotoite, resulting in the formation of randomly assembled crystals.

The results suggest that in the presence of considerable mantle flow (e.g. vertical flow generated by subducting slabs), lattice preferred orientation of akimotoite could be produced commonly and this may cause the seismic anisotropy observed in the lower part of the MTZ.

O05-03

Raman spectra of 10 Å phase at simultaneously HP-HT

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Recently high-pressure studies showed that the 10 Å phase, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{H}_2\text{O}$, a DHMS with a phlogopite-like stacking sequence and water molecules between the sheets, really supports high-pressure conditions and the water remained inside the structure by forming hydrogen bonds.

This study aims to examine the effect of temperature increase on the baric evolution and to check the water storage capacity of this phase under high P/T gradients. Raman spectra were collected from powder samples at simultaneously high-pressure (up to 27 GPa) and high-temperature (up to 707 K) by using an externally heated diamond anvil cell at the Bayerisches Geoinstitut (Bayreuth University, Germany). The results of isobaric runs show that at first approximation, temperature and pressure have opposite effects on the structure. The Raman frequencies of all lattice modes increase monotonically with pressure and slightly decrease when the temperature increase up to 700 K along different isobars. The intensities of the 359 and 679 cm^{-1} bands change in opposite direction with P and T: the differences in relative intensities increase with pressure, while temperature make them more equal in intensities.

The stretching bands of H_2O have as well an opposite behaviour with P and T: the mode with frequency 3597 cm^{-1} decreases with pressure ($\text{dv/dP} = -0.81 \text{ cm}^{-1} \text{ GPa}^{-1}$) and increases with temperature ($\text{dv/dT} = 0.025 \text{ cm}^{-1} \text{ K}^{-1}$), whereas the frequency of the 3672 cm^{-1} mode increase with P ($\text{dv/dP} = 1.38 \text{ cm}^{-1} \text{ GPa}^{-1}$) and decrease with T ($\text{dv/dT} = -0.011 \text{ cm}^{-1} \text{ K}^{-1}$). On the other hand, the hydroxyl stretching frequency at 3622 cm^{-1} , increases with P and T. This behaviour is similar to that observed in other DHMS (i.e. phase A, phase E) and may indicate a weakening of the bond that holds OH in the structure.

The 10 Å phase undergoes a reversible decrease of Raman signal, namely reaches its metastability limit, at P higher than 22 GPa (at 293 K). The very limited increase of the FWHM of all lattice modes with temperature along different isobars, indicate that the temperature does not affect the metastability limit. On the other hand the FWHMs of the OH stretching bands of the water molecules (especially that of 3597 cm^{-1}) result strongly affected by the temperature increase, a clear indication that the temperature favours both the hydrogen bond formation and the dynamic disorder of the water molecules. Following these data the 10 Å phase may be a competitive hydrous phase in the subducting zone beyond the stability field of antigorite.

O05-04

Equilibrium interface segregation in Earth's mantle

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We analyzed the equilibrium interface segregation of Ni, Mn, Sr, Al, Yb, Y, Nd, La and Ti at interfaces between diopside/diopside, diopside/forsterite and forsterite/forsterite by STEM/EDX (scanning transmission electron microscopy/energy dispersive X-ray spectrometry) to examine the effects of ionic size, valence state, co-segregation and interface type on interface chemistry. The segregation is quantified in terms of interface excess and segregation factor. The ionic size of the solutes affects their segregation via production of misfit lattice strain due to the difference between the size of a solute ion and that of the ideal strain-free lattice site. A difference in valence state between the host elements (i.e., Ca and Mg) and the solutes also drives segregation. Even when the ionic size of the solutes (e.g., Yb and Y) is almost identical to the size of the strain-free site, the concentration of solute at interfaces is >10 times that within the diopside grains. Segregation of rare-earth elements (REE) is coupled to the segregation of Al, indicating that the charge balance at the interfaces is likely maintained by the same reaction as in the diopside grain matrix. Segregation seems to be insensitive to interface type resulting in similar compositions at all interfaces within the same system. Overall, the segregation is comparable to element partitioning between crystals and melt. We analyzed the observed segregation behavior based on segregation thermodynamics by introducing the energetics of crystal-melt partitioning.

Based on the relationship between interface segregation and crystal-melt partitioning, we derive a segregation factor (solute concentration at an interface divided by the concentration in the grain matrixes). This approach is applicable to a wide range of elements, so that we can estimate solute concentration at interfaces simply from mineral compositions. The calculated segregation factor supports our previous proposal that interfaces are primary storage sites for highly incompatible elements in the mantle. With measurements of mineral modes and grain size in a polycrystalline rock, we can estimate equilibrium solute concentrations in the "whole rock" or "primary rock", whose composition has often been altered by secondary contamination due to processes such as metasomatism.

Nano domains of Ir-bearing rutile within a Cr-rich spinel from a mantle-derived harzburgite - First evidence and petrological implications

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Transmission and Analytical Electron Microscopy (TEM-AEM) analyses show the presence of sparse domains of Ir-bearing lamellar rutile within a matrix of Cr-rich spinel from a mantle-derived harzburgite (Lherz massif - Eastern French Pyrenees). The Ir-bearing rutile domains appear as isolated long strips that are about 100 nanometers in width and are coherently sandwiched between (111) planes of the host spinel, according to an orientation already reported in literature for a pyrope-spinel xenolith. The presence of iridium is confined to the rutile lamellae having composition: 0.52% of IrO₂, 94.87% TiO₂ plus minor amounts of Al₂O₃, Cr₂O₃, FeO, MgO and ZnO. The percent of IrO₂ is low but statistically significant according to the sensibility of the instrument (JEM-2100F equipped with JEOL EDS system) used for the analysis. At the state of the art there are no evidences showing if the Ir is in solid solution with rutile or if it is present as metallic precipitate within the rutile structure matrix. Taking into account that *i*) Ir and Ti have close ionic radii (0.625 and 0.605 Å, in the order) and *ii*) the two oxides have the same rutile-type crystal structure (*P4₂/mmm* tetragonal space group and close cell parameters: *a* = 4.50 vs. 4.59 Å, *c* = 3.15 vs. 2.96 Å for rutile and IrO₂ respectively) the hypothesis of a solid solution between IrO₂ and TiO₂ looks reasonable. On the other hand, because the existence of a (Ti, Ir)O₂ solid solution has, so far, never been reported, the possibility to have Ir-clusters within the rutile structure should be kept in mind. This hypothesis can be supported by recent results in materials science showing that Ir clusters have been successfully deposited on the surface of rutile grains.

The spinel composition from AEM analyses is about 57% spinel, 34% chromite, 7% hercynite plus minor magnetite and traces of franklinite, jacobsonite, and ulvöspinel. The lamellar aspect of the rutile domains seems in agreement with an exsolution origin, probably reflecting very high temperature conditions (> 1100 °C); at the same time, the absence of ilmenite, indicates very high values of oxygen fugacity.

Core-Mantle Interaction - The Formation, Elasticity, Rheology, and Dynamics of Iron-Rich Silicate in Core-Mantle Boundary Layer

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Earth's D'' layer represents the lowermost 130 to 300 km of the silicate mantle just above the core. At the base of D'' layer, the boundary layer between the crystalline, silicate lower mantle and the liquid, Fe-rich outer core contains regions with ultra-low seismic velocities. In experiments simulating the high pressure-temperature conditions of the core-mantle boundary, we observed that a large amount of Fe incorporated into the post-perovskite silicate phase can significantly change its properties relative to the pure Mg endmember. We determined the aggregate compressional and shear wave velocities of this Fe-rich silicate at high pressure and found that a silicate with up to 40 mol % Fe endmember can explain the observed seismic signatures of ultra-low velocities and high Poisson's ratio. Mantle dynamics may lead to accumulation of the Fe-rich silicate reaction veneer between the Fe-poor lower mantle and the Fe-rich outer core into ultralow velocity patches observable by seismology.

One particularly intriguing feature of the D'' layer is its seismic anisotropy, manifested in shear-wave splitting, the origin of which is an area of active, unresolved debate. Here we report experimental observation of a sizable elastic anisotropy in a polycrystalline sample of ferromagnesian silicate in post-perovskite (ppv) structure which was recently found to be stable at D'' conditions^{1,2}. We used a novel composite x-ray transparent gasket to contain and synthesize ppv in a panoramic diamond-anvil cell along with oblique x-ray diffraction geometry to observe the anisotropic lattice strain and [100] or [110] slip-plane texture in the sample at 140 GPa. We deduced the elasticity tensor (*c_{ij}*), orientation-dependent compressional wave velocities, polarization-dependent shear wave velocities, and the velocity anisotropy of the silicate ppv. The results indicate that with sufficient preferred orientation, the elastic anisotropy of this phase can account for the observed shear-wave splitting in Earth's D'' layer.

Phase relations of aegirine at high pressures and temperatures: Na behavior in the compounds bearing ferric iron

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The behavior of sodium and its host minerals in the lower mantle have not been clarified sufficiently. High-pressure laboratory experiments on constituent minerals in subducting slabs have indicated that the two Na-rich phases are possibly stable. In the main part of the mantle, Na₂O component must exist as main content in the Na-rich phases of the accessory mineral or as a minor content in dominant minerals. In most of above-mentioned studies, it was considered that iron in the mantle should be ferrous. However, it has been reported that the aluminous magnesio silicate perovskite has an Fe³⁺/(total Fe) ratio of at least 0.6. The incorporation of Na with Fe³⁺ to the MgSiO₃-perovskite can be described in terms of the substitution: 2Mg²⁺ → (Na¹⁺, Fe³⁺). This substitution leads to the NaFeSi₂O₆ composition. This is the chemical formula of the mineral "aegirine." Here, we have investigated that the phase relation of aegirine at high-pressure and high-temperature in order to find a perovskite containing Na and Fe³⁺ at the lower mantle conditions.

High-pressure X-ray diffraction experiments were performed using LHDAC high-pressure apparatus (BL13A, KEK-PF and BL10XU, SPring-8). TEM images, qualitative chemical compositions, and SAED patterns of the recovered samples were examined by using a JEOL JEM-2010 attached with EDS.

In the diffraction data obtained at 31 and 52 GPa quenching from 1300-1500K, the diffraction peaks of aegirine could not be observed but the SiO₂ stishovite peaks could be assigned, proving that aegirine was decomposed. However, it is curious that the peaks of some Na-rich and/or Fe-rich phases could not be observed. TEM observation and EDS analyses of these recovered samples confirmed that a NaFeO₂ phase coexists with stishovite. SAED patterns show that the NaFeO₂ phase has a cubic symmetry. This phase seems to be a new high-pressure phase of NaFeO₂. It is noted that the grain size of the observed NaFeO₂ phase is very small (less than 50nm) and this evidence can explain lack of diffraction peaks from Na-rich and/or Fe-rich phases in the x-ray diffraction patterns. ATEM analyses of another recovered sample from 30 GPa and 2000K indicated that aegirine was decomposed into stishovite, iron oxide and sodium oxide. These experimental results showed that NaFeSi₂O₆ perovskite is not stable even at high pressures at least 50 GPa. The observed new high-pressure form of NaFeO₂ is stable only at relatively lower temperature than 1500K and is decomposed into two simple oxides over the temperature.

Magnesiowüstite in the Earth's lower mantle

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Magnesiowüstite [(Mg,Fe)O] is the second most abundant mineral in the Earth's lower mantle. Measurements of the sound velocities and transport properties of magnesiowüstite under high pressures and high temperatures are essential to relate seismic observations in the Earth's lower mantle and to infer its mineralogy, chemistry, and geodynamics. Pressure-induced electronic spin-pairing transitions of iron in magnesiowüstite have been predicted by theoretical calculations and detected by X-ray emission spectroscopy, Mössbauer spectroscopy, nuclear resonant inelastic X-ray scattering, and X-ray diffraction. These studies indicate that an isosymmetric spin-pairing transition from a paramagnetic high-spin state to a diamagnetic low-spin state occurs in MgO-rich magnesiowüstite, and that addition of iron into MgO stabilizes the high-spin state to higher pressures. The electronic spin-pairing transition in (Mg,Fe)O may terminate at a critical temperature, widening the spin transition to a more gradual spin crossover over an extended pressure range at high temperatures. Since magnesiowüstite constitutes a considerable volume fraction of the lower mantle (~10-20%), an understanding of the effects of the electronic spin-pairing transition on the thermoelastic and transport properties of (Mg,Fe)O is crucial to modeling deep-Earth geodynamics and geochemistry. Here I will discuss recent studies on the spin states of iron in magnesiowüstite and the isolated effects of the electronic transitions on the elastic, thermodynamic, magnetic, and vibrational properties of magnesiowüstite in the lower mantle. In particular, recent high-pressure X-ray diffraction and nuclear resonant inelastic X-ray scattering measurements at room temperature have showed a dramatic increase in the isothermal bulk modulus and sound velocities across the electronic spin-pairing transition of iron in magnesiowüstite. Such observation could explain the mismatch between seismic observations and proposed compositional and mineralogical models for the lower mantle. The nature of the electronic spin-pairing transition and its effects on the physical properties of magnesiowüstite under high temperatures of the Earth's lower mantle will also be addressed. The emerging picture of the Earth's deeper mantle indicates that previous models of lower-mantle from mineral physics data using high-spin magnesiowüstite and silicate perovskite are insufficient to correctly model the geophysical and geochemical behavior in the lower mantle.

Valence and spin states of iron impurities in lower mantle silicates

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Earth's lower mantle is believed to contain ~75 vol.% (Mg,Fe)SiO₃ perovskite, 20 vol.% (Mg,Fe)O ferropericlase, 5 vol.% CaSiO₃ perovskite. In the lowermost ~200 km of the mantle, (Mg,Fe)SiO₃ adopts the post-perovskite structure [1,2]. While the properties and behaviour of pure MgSiO₃ phases are well understood (see e.g. ref. [2-5]), the effects of impurities – most importantly iron and aluminium, are poorly known and the existing experimental studies are contradictory.

Here, we perform *ab initio* simulations that address the valence and spin states of iron impurities in MgSiO₃ polymorphs. In agreement with [6] we find a valence disproportionation reaction: $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^0_{\text{metal}}$. This highly exothermic (and somewhat counterintuitive) reaction results in the predominance of Fe³⁺ impurities in lower mantle silicates and produces free metallic iron. It occurs both in perovskite and post-perovskite, Al-free and Al-rich, at all lower mantle pressures. In presence of Al³⁺, iron forms Fe²⁺-Al³⁺ coupled substitutions in perovskite, but separate Fe³⁺-Fe³⁺ and Al³⁺-Al³⁺ substitutions in post-perovskite. Only the high-spin state is found for Fe²⁺ impurities at all mantle pressures, while Fe³⁺ impurities on the Si-site are low-spin at all pressures in both phases. Fe³⁺ impurities on the Mg-site are in the high-spin state in post-perovskite at all mantle pressures, but in perovskite we predict a high-spin - low-spin transition. The pressure at which this transition occurs strongly depends on the Al³⁺ content and according to our calculations increases from 76 GPa for Al-free to 134 GPa for Al-bearing perovskites. This explains previous experimental results [e.g., 7,8], which were thought to contradict each other. These findings have important geophysical implications [9].

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Mineral Elasticity: Implications for the Temperature and Mineralogy of the Lower Mantle

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There has been considerable recent progress in measurements and calculations of the physical properties of materials and phase transitions under pressure and temperature conditions relevant to planetary interiors. Densities and elastic wave velocities of mineral phases can now be directly measured under pressures corresponding to the Earth's lower mantle. This new generation of data is providing us with the opportunity to assess the chemistry and thermal structure of the deep Earth. In this talk we review some of the important recent experimental results on the properties of lower mantle phases. We investigate how these results may be used to assess the mineralogy and thermal structure of the lower mantle, via a generalized inversion using observed 1-D radial profiles of density and seismic velocities. This procedure allows us to evaluate the uncertainties inherent in such modeling, and to identify the magnitudes of associated compositional and thermal tradeoffs. Inversions using only the density and bulk modulus (or bulk sound velocity) provide relatively loose constraints on lower mantle mineralogical models, and a broad range of models can fit the reference 1-D profiles. We find that inversions using the seismic velocities V_p and V_s reduce the range of mineralogical and thermal models that are compatible with the seismic models. We conclude that shear properties provide a much stronger constraint on the state of the lower mantle than the density and bulk modulus alone, and emphasize the importance of determining accurate values for shear properties of lower mantle phases. We evaluate the effect of experimental uncertainties on measured shear properties when assessing averaged lower mantle composition and discuss possibilities of a chemically layered versus homogeneous mantle.

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A number of experimental studies demonstrated that (Al,Fe)-bearing MgSiO₃ perovskite, a predominant mineral in the lower mantle, contains substantial amounts of Fe³⁺. The high Fe³⁺ content in perovskite has large effects on electrical conductivity, radiative thermal conductivity, elasticity, and Mg-Fe partitioning. Recently Murakami *et al.* [2004] discovered that the MgSiO₃ perovskite undergoes phase transition to a post-perovskite phase under the lowermost mantle conditions. Does the post-perovskite phase also include certain amount of Fe³⁺? Major element compositions of post-perovskite formed in natural peridotite mantle and MORB bulk compositions were reported [Murakami *et al.*, 2005; Hirose *et al.*, 2005], but the valence state of iron has never been measured yet. By analogy with perovskite, Fe³⁺ in post-perovskite possibly has significant effects on its physical and chemical properties. In addition, it may have large but opposite effect from that of Fe²⁺ on the stability of post-perovskite phase. Moreover, iron metal is likely present in the lower mantle together with Fe³⁺-rich perovskite. The Fe³⁺/ΣFe ratio in post-perovskite is also important for the fate of such metallic iron in the D'' region. Recently, the Fe³⁺/ΣFe ratio is quantitatively determined with a nm-scale spatial resolution by ELNES spectroscopy [van Aken *et al.*, 1998]. In this study, the Fe³⁺/ΣFe ratios in both (Al,Fe)-bearing MgSiO₃ post-perovskite phase and Ca-ferrite-type Al-phase, synthesized in a natural mid-oceanic ridge basalt (MORB) composition at 113 GPa and 2240 K, were determined by electron energy-loss near-edge structure (ELNES) spectroscopy. Results demonstrate that post-perovskite includes significant Fe³⁺ much more than Fe²⁺ with Fe³⁺/ΣFe ratio of 0.59-0.69. The high Fe³⁺ concentration in post-perovskite may have significant effects on its physical properties, phase stability, and iron partitioning. The Fe³⁺/ΣFe ratio in Mg-perovskite has been extensively studied, showing that the concentration of Fe³⁺ strongly correlates with the Al³⁺ content and is independent from the oxygen fugacity [e.g., Frost and Langenhorst, 2002]. Present study of (Al,Fe)-rich MgSiO₃ post-perovskite showed that it contains 0.254 Al³⁺ and 0.223 Fe³⁺ in two-cations formula. This relation between Al³⁺ and Fe³⁺ observed in post-perovskite is quite consistent with that of perovskite. Since Al³⁺ contents are similar in perovskite and post-perovskite in a given MORB bulk composition, both should include similar amounts of Fe³⁺. This suggests that the whole rock Fe³⁺/ΣFe ratio in a subducting MORB crust does not change remarkably at the post-perovskite phase transition in the lowermost mantle.

Depth and Sharpness of the Post-perovskite Phase Transition

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The first publication on the post-perovskite phase transition by Murakami *et al.* [2004 *Science*] showed that it occurs in MgSiO₃ approximately at 125 GPa and 2500 K, corresponding to the 2700-km depth in the mantle, based on the P-T pressure scale (P-V-T equation of state). However, there has been extensive debate on the accuracy of such P-V-T equation of state of internal pressure standard. The MgO pressure scale may be most practical, because it has been well studied and is least controversial. Indeed, experimentally determined post-spinel phase transition pressure based on the MgO scale matches the depth of 660-km boundary [Fei *et al.*, 2004 *JGR*]. We therefore reexamined the post-perovskite phase transition boundary in MgSiO₃ by using MgO pressure standard. Results demonstrate that phase transition occurs at 119 GPa and 2400 K that corresponds to 2600-km depth in the mantle [Hirose *et al.*, 2006 *GRL*]. The Clapeyron slope was determined to be +11 MPa/K consistently with the previous theoretical calculations. Compositional effect on the post-perovskite phase transition is also very important to understand the origin of complex topography of the D'' region. We determined this phase transition boundary in pure MgSiO₃, (Mg_{0.98}Fe_{0.02})₂SiO₄ olivine, natural pyrolytic mantle (KLB-1 peridotite), and MORB bulk compositions using identical pressure standard. Results show that the phase transition in all of these natural compositions occurs at pressures very similar to that in Mg-end-member [Hirose *et al.*, 2006 *GRL*]. This indicates that (1) perovskite to post-perovskite phase transition in natural compositions occurs at the D'' discontinuity and that (2) chemical heterogeneity in D'' has little effect on the post-perovskite phase transition pressure. The sharpness of the post-perovskite phase transition was also investigated in the KLB-1 peridotite composition. Experiments demonstrate that the transition occurred in a pressure range of about 5 GPa at a given temperature. This is closely consistent with the seismological observations of the D'' discontinuity that showed a velocity jump occurs in a width ranging from 50 to 70-km [Young and Lay, 1987 *PEPI*], corresponding to the pressure interval of 3 to 4 GPa.

High solubility of FeO in perovskite and the post-perovskite phase transition in $(\text{Mg}_{0.5}\text{Fe}_{0.5})\text{SiO}_3$

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Phase relations in $(\text{Mg}_{0.5}\text{Fe}_{0.5})\text{SiO}_3$ were investigated in a pressure range from 94 to 123 GPa on the basis of synchrotron X-ray diffraction measurements *in-situ* at high-pressure and -temperature in a laser-heated diamond-anvil cell (LHDAC). Results demonstrate that perovskite is formed as a single phase below 108 GPa at 2200 K, indicating a high solubility of FeO in $(\text{Mg,Fe})\text{SiO}_3$ perovskite at such high pressures. A post-perovskite phase appears coexisting with perovskite above 107 GPa at 1500 K, the condition very close to the post-perovskite phase transition boundary in pure MgSiO_3 . The coexistence of perovskite and post-perovskite was observed to 123 GPa. In contrast to earlier experimental and theoretical studies, these results show that incorporation of FeO stabilizes perovskite at higher pressures. This could be due to a larger ionic radius of Fe^{2+} ion, which is incompatible with a small Mg^{2+} site in the post-perovskite phase.

The effects of pressure and temperature on the solubility of oxygen in liquid iron and implications for the composition of the Earth's core

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Although oxygen has been proposed as a possible light element in the Earth's core, the effect of pressure on oxygen solubility in liquid iron has been controversial. From phase relations in the Fe-FeO system, it has been proposed that oxygen solubility in liquid Fe increases with increasing pressure. However, based on previous results on the partitioning of oxygen between magnesiowüstite and liquid iron, oxygen solubility in liquid iron appears to decrease with increasing pressure. Here we report new data on oxygen partitioning between magnesiowüstite and liquid iron in the Fe-FeO-MgO system obtained over a wide P - T range (3-25 GPa, 2273-3173 K), which resolve this issue. We have determined the distribution coefficient, K_d , for the partitioning of oxygen between magnesiowüstite and liquid Fe, which depends on P and T but is independent of oxygen fugacity. We observe that $\ln K_d$ initially decreases with increasing pressure, reaches a minimum at 10-15 GPa, and then increases at higher pressures. This behavior is caused by the volume change (ΔV) of the oxygen exchange reaction being pressure-dependent and changing from being negative at <10 GPa to positive at >15 GPa. The change in ΔV is the result of the difference in the compressibilities of the FeO component in magnesiowüstite and liquid Fe respectively. The new experimental data together with data from previous studies, obtained over a wide P - T range (2-97 GPa, 2273-3150 K) have been fitted by $R\ln K_d = -\Delta H + T\Delta S - \Delta VdP$. The refined thermodynamic parameters ΔH and ΔS and equation of state parameters (V_0 , K , K') for the FeO component in liquid Fe reproduce well the entire dataset. This new model resolves the earlier controversy over the effect of pressure on oxygen solubility in liquid Fe: solubility decreases with increasing pressure at low pressures but increases with increasing pressure above 15 GPa. The model is consistent with the incorporation of ~8 wt% oxygen into liquid Fe during core formation in a deep terrestrial magma ocean and therefore confirms the possibility that oxygen is the main light element in the Earth's core. Extrapolating the model to conditions of the core-mantle boundary suggests that the outer core is undersaturated with respect to oxygen content. This conclusion has important implications for reactions at the CMB and would imply that the base of the mantle may be strongly depleted in FeO.

Iron partitioning between $(\text{Mg, Fe})\text{SiO}_3$ post-perovskite, perovskite, and magnesiowüstite to core-mantle boundary

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$(\text{Mg,Fe})\text{SiO}_3$ perovskite(Pv) and magnesiowüstite(Mw) are widely believed to form the most abundant mineral assemblage in the Earth's interior. Clarifying partitioning behavior between these phases is important for understanding the physical and chemical properties of the Earth's lower mantle. Fe-Mg partitioning relation is described by the parameter called Fe-Mg partition coefficient between Pv and Mw, defined as $K^{\text{Pv/Mw}} = (X_{\text{FeO}}/X_{\text{MgO}})^{\text{Pv}}/(X_{\text{FeO}}/X_{\text{MgO}})^{\text{Mw}}$, where X is the $\text{FeO}/(\text{FeO} + \text{MgO})$ in molar ratio. In previous studies using laser heated diamond anvil cells, Fe-Mg compositions of phases were measured by either using the relationship between V_0 (unit cell volume at ambient condition) and X or by ATEM (analytical transmission electron microscopy). There is a disagreement in the pressure dependence of the partition coefficients determined using the two methods. Furthermore, the pressure induced spin transition of iron in Mw and Pv has been expected to have a profound effect on the Fe-Mg partitioning.

In this study, we reevaluated the pressure and temperature dependence of the Fe-Mg partition coefficients between Pv and Mw. $K^{\text{Pv/Mw}} = (\text{FeO}/\text{MgO})^{\text{Pv}}/(\text{FeO}/\text{MgO})^{\text{Mw}}$ (in molar ratio), and those of PPv and Mw, $K^{\text{PPv/Mw}} = (\text{FeO}/\text{MgO})^{\text{PPv}}/(\text{FeO}/\text{MgO})^{\text{Mw}}$, up to 123.6 GPa at 1600-2000 K using laser-heated diamond anvil cell combined with synchrotron X-ray diffraction method and ATEM in a simple Al-free system (San Carlos olivine) in order to avoid the complicated effect of trivalent cations. We observed a high FeO content in PPv coexisting with Mw [$K^{\text{PPv/Mw}} = (\text{FeO}/\text{MgO})_{\text{PPv}}/(\text{FeO}/\text{MgO})_{\text{Mw}} = 0.30$] compared to that in Pv [$K^{\text{Pv/Mw}} = (\text{FeO}/\text{MgO})_{\text{Pv}}/(\text{FeO}/\text{MgO})_{\text{Mw}} = 0.12$] observed from 23.0 to 95.4 GPa at around 1600 K. We also observed that $K^{\text{Pv/Mw}}$ keeps a constant value 0.12 up to the PPv phase boundary at around 1600 K and $K^{\text{Pv/Mw}}$ decreases with increasing pressure at around 2000 K. The assemblage of PPv and Mw is 1.5-1.7 % denser than the Pv bearing assemblage, which results in a gravitational stabilization of the lowermost mantle.

Partitioning of elements between liquid metal and liquid silicate under conditions of a giant impact

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We are conducting a series of shock loading (impact) experiments utilizing composite iron alloy and silicate samples to investigate the abundance pattern of siderophile elements in the Earth's mantle and the less-directly sampled, metallic core with its inferred complement of light elements. The composition of these reservoirs are believed to reflect processes occurring upon accretion of the Earth and formation of the core. Gravitational and shock-induced heating are major sources of heat in the early times of the Earth and provide conditions of extended melting which allow the redistribution of elements between silicate and iron-rich metal as it sequesters towards the centre of gravity. Such quasi-static partitioning of elements is superimposed on extended large-scale melting events during large and giant impacts which are short-lived but involve extreme temperatures and mobilize deep layers of Proto-Earth as well as the material of the impactor.

Here we present the first quantitative results on chemical partitioning of siderophile and light elements in shock experiments on olivine and chondrite. Both iron-rich metal and silicate were heated to super-Hugoniot temperatures in their liquidus fields at a pressure of 25 GPa and a temperature ~ 4000 K during our experiments. The two liquids were intimately mixed by physical instabilities, allowing extensive chemical reaction during the short-lived melting event. We find significant reduction of Si out of silicate and dissolution in iron-rich metal. Moreover, we observe enhanced lithophilic behaviour of Cr, V, and Mn relative to ambient conditions, while Mo and Ni remain siderophile. The observed partitioning agrees with extrapolations of previous high P - T partitioning results, suggesting that the observed high temperature reactions occurred, at least in part, at pressures possibly as high as 25 GPa.

We discuss time scales and P - T conditions of melt formation and partitioning, closure temperatures upon release, and the time scale of eventual thermal and chemical equilibration.

Immiscible two-liquid regions in the Fe-O-S melt up to 21 GPa and implications for the planetary cores

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Geophysical observations imply that the Earth's outer core contains about 10 % of the light elements. Investigations of the phase relations in iron-light element systems are essential for understanding the composition and dynamics in the Earth's core. Oxygen and sulfur are the major candidates of the light elements. We investigated immiscible two-liquid regions in the Fe-O-S system at 15 GPa–2030 °C, 15 GPa–2300 °C, 18 GPa–2120 °C, and 21 GPa–2300 °C using a Kawai-Type multianvil apparatus. Starting materials are mixtures of Fe, FeS, and Fe_{0.9}O powders, and they are enclosed using sintered Al₂O₃ capsule. Starting compositions include 8.0–11.9 wt.% O and 0–7.6 wt.% S. They were heated using LaCrO₃ heater. Recovered samples are analyzed using a SEM and an electron microprobe. Immiscible two-liquids are observed in the starting compositions with the sulfur content up to 2.6 wt.% at 15 GPa and 2030–2300 °C, up to 1.8 wt.% at 18 GPa and 2120 °C, and without sulfur at 21 GPa and 2300 °C, whereas miscible one liquid is observed in the starting compositions with the sulfur content of 7.5 wt.% at 15 GPa and 2030 °C, 6.0 wt.% at 15 GPa and 2300 °C, 2.6 wt.% at 18 GPa and 2120 °C, and 1.0 wt.% at 21 GPa and 2300 °C. Our experimental results indicate that an immiscible two-liquid region narrows with increasing pressure at constant temperature, and with increasing temperature at constant pressure, and it almost disappears at 21 GPa and 2300 °C. The present result on liquid miscibility is consistent with the geochemical model of the Earth's core composition with 5.8 wt.% oxygen and 1.9 wt.% sulfur proposed by McDonough and Sun (1995). No stratified layer is expected to exist in the Fe–O–S system in the Earth's liquid outer core.

Core mineralogy, concept, crystal chemistry and its example

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Core minerals mean that the materials from E layer or D" layer of earth were raised by plume to shallow and cooled down to crystal. According to geophysics and astrolithology, core minerals should be Fe-Ni metallic compounds, heavy metallic compounds, metallic carbides and metallic silicides etc.. The crystal structure in most this kind of minerals belong to equal-sphere closest packing. Therefore the crystal structures will preserve invariableness in different layers of earth. They might possess high melting point and refractory property. In metallic carbides and silicides, based on the radius ratio of nonmetallic atoms to metallic atoms the crystal structure can be divided into complex compounds phase and interstitial phase. The coordination polyhedron of carbon is trigonal prism and octahedron respectively. The increase of temperature and pressure is useful to more octahedral formation in owing to the shortening between metallic atoms and carbonic atoms. Since 1981 a special mineral group in Luobusa ophiolite chromitites, Tibet has been researched in detail. About 60-70 species of mineral which were discovered in this area can be included as following: 1. Fe-Ni metallic element minerals (taenite, iron, wairuite and awaruite) and a lot of intermetallic compounds (Fe-Cr-Ni, Fe-Cr-Ni-C, W-Cr-Co, W-Ti-C, Al-Fe-La, Fe-Ti-Si, Ag-Sn-Si, Ni-Ir-Fe, Fe-Pd-Pt); 2. A lot of natural elements (Si, Fe, Zn, Pb, Al, Cr, Sn, Ni, W, Ti, Os, Ir, Ru, Pd, C, Au, Ag); 3. Some high melting-point minerals (W-C, T-C and many platinum group element (Os, Ir, Ru, Pd and Pt) compounds); 4. Some metallic carbides and silicide (Fe₃C (cohenite), Cr₃C₂ (tongbaite), (Fe,Cr,Ni)-C compounds and (Fe,Ti)-Si compounds); 5. Some high pressure minerals (diamond, coesite, moissanite and wustite etc.). According to the chemical composition, crystal structure, refractory property, strong reducing and no equilibrium state with ophiolite and chromitite, it is possible that a part of mineral group of luobusa is from the core.

Phase relation in the hydrogen-helium system at high pressure

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Hydrogen and helium are the most abundant elements in the universe and the major components of giant planets. In order to consider the interior of those planets, it is important to determine the phase relation in the hydrogen-helium system at high pressure and high temperature. Hydrogen-helium binary phase diagram has been studied up to 12 GPa and 373 K (Van Den Bergh et al., 1987; Loubeyre et al., 1987; 1991) and was known to be of eutectic type with a phase separation in the fluids. In this study, we investigated the phase relation of the hydrogen-helium system up to 30 GPa at room temperature.

High-pressure experiments were performed using a diamond anvil cell. Pressures were measured with the ruby fluorescence method (Zha et al., 2000). Samples were two gas mixtures of which compositions were H₂:He=1:1 (He=51.5 mol%) and H₂:He=3:1 (He=25.5 mol%). The optical microscope was used for phase identification and observation. Raman spectra of hydrogen Q₁ vibron mode were also measured for each phase.

Helium-rich fluid phase (F₂) which exsolved from the hydrogen-rich solid phase (S₁) has been observed in the S₁ grain probably because of decreasing the solubility of helium in S₁ with pressure. In the case of H₂:He=1:1, coexistence of S₁ and helium-rich solid phase (S₂) has been confirmed up to 30 GPa. Each phase transition can be confirmed from both optical observation, and the change of intensity and full width at half-maximum of Raman spectra.

Helium concentration of a fluid phase has been estimated by frequency shift of Q₁ vibron in the fluid phase and a scale of the helium concentration calibrated by Loubeyre et al. (1991). However, there was a disagreement between the present study and that of Loubeyre et al. (1991). Therefore, the helium concentration was re-calibrated based on the initial composition of gas mixture.

Although there remain some differences in the calibrated composition, the phase relation of hydrogen-helium system determined in this study was generally consistent with Loubeyre et al. (1991). It is necessary for accurate estimation to conduct further experiments with different sample compositions.

Wetting property at the core-mantle boundary and core signature in plume source region

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Chemical reaction and textural relationship between core (iron) and mantle ((Mg,Fe)SiO₃ perovskite or post-perovskite) at the core-mantle boundary (CMB) condition is an important process for dissolution of the light elements in the core and the anomalous seismic structure at the CMB. We have conducted reaction experiments at pressure from 121 to 139 GPa 3,000(200) K using laser heated diamond anvil cell technique. Powdered natural (Mg_{0.99}Fe_{0.01})SiO₃ enstatite and iron powder (99.5 %) for the first experiment at 139 GPa, and (Mg_{0.92}Fe_{0.08})SiO₃ and iron foil (99.99%) for the second run at 121 GPa were used for the starting material. Metallic iron coexisted with perovskite at 121 GPa, and with post-perovskite at 139 GPa, were confirmed by in situ X-ray diffraction studies at Photon Factory (KEK) in Tsukuba. We made detailed TEM observations of the textures and compositions of the metallic iron and post-perovskite coexisting in the run products.

The dihedral angles between molten iron and post-perovskite from TEM images of the recovered sample from 139 GPa and 3,000(200) K was 67 degrees. The required melt fraction to form an interconnected network of liquid iron (critical melt fraction) is around 2 vol.%, suggesting a small amount of metallic iron can be trapped at the bottom of the mantle. The amount of core metal trapped by this mechanism can produce the core signature in the plume source at the lower most mantle.

In situ X-ray observation of eutectic temperatures and subsolidus phases in Fe-FeS-FeO system at 23-34 GPa

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Temperature of Martian core is important for generation of Martian magnetic field and mantle dynamics. The temperature of the Martian core can be constrained when its physical state and melting temperature of core material are known. Recent Martian mission and study on geodynamo of the Martian core revealed that the physical state of the Martian core is could be liquid. Pressure condition of the Martian core was estimated to be 19 to 42 GPa and the core is likely to be composed of Fe-Ni-S-O alloy. Here we report eutectic temperatures and solid phases in Fe-FeS-FeO system at 23-34 GPa. The eutectic temperatures and the solid phases have been investigated by means of in situ X-ray observation using a Kawai-type multi-anvil high-pressure apparatus SPEED-Mk.II installed at a beam-line BL04B1 of a synchrotron radiation facility SPring-8. The subsolidus phases were γ -Fe, Fe₃S and FeO at 23-33 GPa, whereas those were ϵ -Fe, Fe₃S and FeO at 34 GPa. The eutectic temperature was determined by disappearance of Fe₃S diffraction peaks in in situ X-ray diffraction pattern of the sample. An oscillation system of the press was employed to obtain high-quality X-ray diffraction patterns of the sample and a pressure marker of MgO even when the numbers of their grains were limited at high temperature due to their grain growth. The eutectic melting observed using the in situ X-ray diffraction was confirmed by observation of quench texture of the recovered samples. The eutectic temperatures were 1260 and 1330 K at 23 and 34 GPa, respectively. The temperature of the Martian core is estimated to be above 1330 K since the Martian core is liquid and the eutectic temperature of the Fe-FeS-FeO system was 1330 K at 34 GPa.

Post-hollandite phase in KAlSi₃O₈ as a possible host mineral of potassium in the Earth's lower mantle

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High-pressure behavior of potassium in the deep Earth is of great interest because potassium is one of the important heat sources in thermal evolution of the Earth and the abundance of its radiogenic isotope has been used to constrain the structure and evolution of the Earth's mantle. Alkali feldspars in the system KAlSi₃O₈-NaAlSi₃O₈ are abundant minerals in the Earth's crust and can act as a potential carrier of potassium and sodium from the Earth's surface down into the deeper Earth through the subduction. High-pressure polymorphs of alkali feldspars may be major host phases for potassium and sodium in the Earth's mantle. Earlier quench experiments on KAlSi₃O₈ hollandite phase show this phase is stable up to 95 GPa, corresponding to the depth of 2200 km in the Earth's lower mantle. Recently, a new high-pressure phase of KAlSi₃O₈, KAlSi₃O₈ hollandite II, was discovered at 22 GPa by in situ X-ray diffraction measurements at high pressures and high temperatures, and its phase with monoclinic symmetry has more distorter than the ideal KAlSi₃O₈-hollandite structure with tetragonal symmetry. Here we report high pressure and temperature experiments on KAlSi₃O₈ composition in laser-heated diamond-anvil cell up to 134 GPa and 3600 K, corresponding to the conditions in the Earth's core-mantle boundary (CMB). In situ synchrotron X-ray diffraction patterns at 300 K show that post-hollandite phase in KAlSi₃O₈, hollandite II, is stable at pressures up to 134 GPa, and no further phase transition and no evidence for the completed dissociation of KAlSi₃O₈ under the present experimental conditions are found. The observed diffraction peaks at high pressure are quite different from those of KAlSi₃O₈ hollandite phase with the tetragonal structure, and can be reasonably indexed by KAlSi₃O₈ post-hollandite phase with the monoclinic symmetry, as reported in previous works. The KAlSi₃O₈ post-hollandite phase has the same structure as original hollandite BaMn₈O₁₆. Pressure-induced structural distortion lowers the symmetry to the monoclinic space group, resulting in the splitting of the diffraction lines for the tetragonal phase into ones for the monoclinic phase. The structural distortion leads to small deformation of tunnel-cation site in which large monovalent or divalent cations, such as K, Rb, Sr and Ba, can be placed. However, these cations could be kept in the tunnel-cation sites because of their high compressibility. Therefore, the KAlSi₃O₈ post-hollandite phase would be one of the important host phases for potassium in the whole Earth's mantle.

The fate of carbonates with subducted slabs into the lower mantle and a possible formation of diamonds

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Carbonates delivered deep into the mantle by subduction have greatly affected the global recycling of carbon. Although several previous researches suggested that the carbonates can be significant hosts for subducted carbon in the Earth's lower mantle (e.g., Biellmann et al. 1993, Isshiki et al. 2004), little is known about the fate of the carbonates in the slabs under the lower mantle condition. Here, we report the results of high pressure and high temperature experiments on mid-oceanic ridge basalt (MORB) - CaCO₃ system.

A mixture of 80wt% MORB glass and 20wt% crystalline CaCO₃ was used as a starting material. The MORB glass was prepared by quenching molten oxides under control of a valence of Fe as 2+. High pressure and high temperature experiments were carried out using a laser-heated diamond anvil cell (LHDAC), and the run products were observed with an analytical transmission electron microscope (ATEM). At 30-70GPa and 1800-2400K, the reaction products consist of MgSiO₃-Perovskite (Mg-Pv), CaSiO₃-Perovskite (Ca-Pv), Stishovite (St), CaFe₂O₄ type aluminous phase (CF), Magnesite (Mgs), and Aragonite (Arg). Mg-Pv are not in contact with Arg. Accordingly, the following reaction seems to be dominant under the condition; MgSiO₃ + CaCO₃ → CaSiO₃ + MgCO₃. The stable carbonate in the MORB should be magnesite, rather than aragonite, under the average mantle condition.

Discontinuous changes of heating temperature were also observed; e.g. after slightly increasing laser power at 45GPa and 2300K, the temperature drastically increases up to 3000K or higher. The temperatures at which the drastic change occurs are slightly higher than the typical geotherms. At higher temperature after the drastic increase, the run products consist of Mg-Pv, Ca-Pv, St, CF, and diamond. No carbonates were observed in the reacted zones. The drastic changes of temperature result from carbonate-silicate reactions, because those changes are not observed in 100wt% MORB system at the same P-T condition. The temperature runaway phenomena are probably due to an onset of melting (Hirose et al. 1999). Our current interpretation is that the following reactions successively occur: (i) MgCO₃ + SiO₂ → MgSiO₃ + CO₂ and/or CaCO₃ + SiO₂ → CaSiO₃ + CO₂, and (ii) CO₂ → C (diamond) + O₂. The CO₂ release reaction (i) may cause the partial melting, and then change the laser absorbcency. The diamond formation process by the reaction (ii) after (i) is suggested in carbonated subducted slabs at moderately high temperature (e.g. the early Earth at the lower mantle).

Rietveld analysis of Al-containing MgSiO₃ perovskites

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Two types of Al³⁺ substitution mechanism in MgSiO₃ perovskite can be considered. One is Tschermakitic substitution, Mg²⁺ + Si⁴⁺ ↔ 2Al³⁺, and the other is oxygen vacancy substitution, 2Si⁴⁺ ↔ 2Al³⁺ + V_O. The existence of nonstoichiometric Al-MgSiO₃ perovskite, which may contain the latter substitution mechanism, has been indicated by Navrotsky et al. (2003). In this study, Rietveld refinement of both stoichiometric and nonstoichiometric Al-MgSiO₃ perovskites was performed to show direct evidence of oxygen vacancy in the nonstoichiometric perovskite by comparing their structures.

High-pressure syntheses of Al containing MgSiO₃ perovskites were made using a Kawai-type high-pressure apparatus. Starting materials were the mixture of MgO, Al₂O₃ and silicic acid with the compositions of MgSi_{1-x}Al_xO_{3-x/2} (x = 0.05, 0.1) for nonstoichiometric perovskites and of 0.9Mg_{1-x/2}Si_{1-x/2}Al_xO₃ + 0.1SiO₂ (x = 0.05, 0.1) for stoichiometric perovskites. The starting materials were kept at 26-27 GPa and at 1873 K for 3-4 hours. Recovered samples were crushed into powders using a die at liquid nitrogen temperature. Powder X-ray diffraction profiles of them were measured using a Rigaku RINT2500V diffractometer (Cr K α , 45 kV, 250 mA) with a 2 θ range of 20° to 140° and a step size of 0.02°. The Rietveld refinement was made by the RIETAN-2000 program.

Determined lattice parameters of both stoichiometric and nonstoichiometric perovskites indicate that a-axis decreases slightly and b- and c-axes increase with increasing Al content. Particularly, an increasing rate of c-axis for nonstoichiometric perovskite is obviously smaller than that for stoichiometric perovskites. Average SiO₆ octahedra in stoichiometric perovskite show that Si-O1 and Si-O2 distances increase linearly with increasing Al content. On the other hand, those of nonstoichiometric perovskites are kept constant up to Al content of x = 0.05 and increase with increasing Al content more than x = 0.05 where x is number of Al ions on the three oxygen basis. These results suggest that oxygen vacancy probably causes the constant size of average SiO₆ octahedra in nonstoichiometric perovskites and that the oxygen vacancy substitution is superior to the Tschermakitic substitution up to x = 0.05 in nonstoichiometric perovskites. No change in both Si-O1 and Si-O2 distances implies that oxygen vacancy distributes randomly.

Effect of iron on the stability of lower mantle phasesT. Tsuchiya¹, and J. Tsuchiya¹¹Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, 790-0903, Japan.

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Mg-Fe substitution is most commonly seen in natural solid solution minerals. Recent high-pressure experiments have shown high-to-low spin transition in iron in lower mantle phases at the lower mantle P,T conditions. Also it has been suggested iron significantly affects the stability of silicate post-perovskite. Understanding the behavior of iron is therefore substantial for understanding the thermal chemical properties of the lower mantle. The mechanisms of these phenomena however still remain unclear. Previous failures of standard ab initio approaches to describe the iron oxide bonding have hindered its investigation. Here we have investigated the effects of iron on the stability of lower mantle phases using a first principles formulation of LDA+U, where the effective Hubbard U parameter is optimized in an internally consistent way at each volume and at each iron concentration. Compression property and phase stability depend on the spin and oxidation state of iron. Those are quite different from the results obtained using traditional technique in some cases.

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TEM foil preparation technique by Focused Ion Beam (FIB) systemM. Miyahara¹, T. Sakai¹, Y. Kobayashi¹, J.-H. Yoo², T. Kondo¹ and E. Ohtani¹¹Institute of Mineralogy, Petrology and Economic geology,

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Focused Ion Beam (FIB) system is a novel technique because a micrometer-order material can be manufactured under Scanning Ion Microscope (SIM) image. Recently, FIB system is rapidly introducing to the earth science and is used to prepare a TEM foil. However, the TEM foil preparation by FIB system is still developing technique. FIB system has several disadvantages; 1) TEM foil prepared by FIB system is slightly thick; 2) Gallium contamination; 3) damaged or amorphous layer. The quality and accuracy of TEM images and quantitative analysis of chemical composition are reduced by these disadvantages. These points should be resolved to apply FIB system extensively. In this presentation, our TEM foil preparation technique by a JEOL JEM-9320FIB, a dedicated optical microscope with a manipulator and a TECHNOORG-LINDA GENTLE MILL is shown. Firstly, an area to be observed by TEM in a specimen is identified under SIM image. SEM and BSE images of the specimen aid us to look for the area. Secondly, the block of the area is made by Gallium ion beam. The block is approximately $10.0 \times 18.0 \times 1.0 \mu\text{m}$. When the block is manufactured, a carbon-deposition bridge is made to avoid the falling or fly loss of the block. Subsequently, the block is removed from the specimen and put on the stage of a Mo grid using a glass pipette under the dedicated optical microscope. The stage is previously manufactured by Gallium ion beam on the section of Mo grid. The block attached on the Mo grid is thinned by Gallium ion beam again and becomes a TEM foil 120-130 nm thick. Finally, the TEM foil is completed by Argon ion milling method to take out Gallium contamination, amorphous layer and damaged layer. GENTLE MILL is employed to clean the TEM foil. The TEM foil is milled by Argon ion beam at very low voltage (1.0 and 0.25 kV) for several minutes. These procedures allow us to prepare a high quality TEM foil.

Seismic anisotropy of Akimotoite MgSiO_3 and implications for the structure of the subducting slabRei Shiraiishi¹, Eiji Ohtani¹, Kyuichi Kanagawa², Akira Shimojyuku¹, Masaaki Miyahara¹¹Department of Mineralogy, Petrology and Economic Geology Faculty of Science, Tohoku University, Sendai, 980-8578, Japan

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Seismic anisotropy is significant to estimate the mantle convection patterns. It is often considered that seismic anisotropy in the upper mantle is caused by the strain-induced lattice preferred orientation of elastically anisotropic minerals. Some seismological studies suggested existence of an anisotropy in the mantle transition zone (e.g., reference). Akimotoite, the ilmenite structured MgSiO_3 which is the major constituent of the harzbergite layer of subducting slabs, is likely to be the most anisotropic mineral in the mantle transition zone. Therefore, it is important to investigate the deformation-induced lattice preferred orientation of akimotoite for discussing the relation between seismic anisotropy and the lattice preferred orientation. We might be able to image flow patterns in the deep Earth based of the observed seismic anisotropy and the results of the lattice preferred orientation.

High pressure deformation experiments were performed using a Kawai-type multi-anvil apparatus installed at Tohoku University. First we synthesized polycrystalline MgSiO_3 ilmenite from MgSiO_3 glass by heating at 21 GPa and 1573K for 1 hour. The synthesized MgSiO_3 ilmenite was used as a starting material for the high pressure deformation experiments. The sample assembly was composed of sintered ZrO_2 pressure medium and LaCrO_3 heater. The sample was sandwiched between alumina pistons inserted in the furnace assembly. This assembly induced high differential stresses during compression. After deformation experiments, the lattice preferred orientation was determined by EBSD (electron backscatter diffraction) installed at Chiba University. The deformation microstructure was observed by TEM (transmission electron microscopy) installed at Tohoku University. The present result provides important implications for understanding the structure and dynamics of the subducting slabs.

Session 06. Hydrogen, water and volatiles in the deep Earth

O06-01

Effect of water on dynamics in the upper mantle and transition zone

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Water plays important roles in geodynamic process in the Earth's interior. Transport properties of hydrogen in the mantle minerals are essential to clarify distribution and circulation of water in the earth. Wadsleyite is the most abundant mineral in the mantle transition zone between 410 and 520 km depth. Recent experimental results revealed that it can accommodate up to 33000 wt ppm H₂O suggesting that the transition zone is the major water reservoir of the mantle.

The hydrogen diffusivity in polycrystalline wadsleyite was measured by IR spectroscopy in order to determine the diffusion coefficient of hydrogen in wadsleyite with the composition of (Mg_{0.89}Fe_{0.11})₂SiO₄. The hydration experiments were conducted at 15-16 GPa and temperature range from 900 to 1200 °C with Mg(OH)₂ as the water. The temperature dependence of diffusion of hydrogen in polycrystalline wadsleyite was determined to be $D_H = 1.0 \times 10^{-5} \exp [-128 \text{ (kJ mol}^{-1}) / RT]$. Hydrogen diffusion rate in wadsleyite is roughly consistent with the average diffusivity of hydrogen in olivine. On the basis of the water-dependence of the electrical conductivity and the observed conductivity, the water content in the mantle transition zone was estimated by using the Nernst-Einstein relation. The experimental results obtained here show that the water content in the transition zone beneath Philippine trench is around 4000 wt. ppm, and distribution of water is heterogeneous throughout the mantle transition zone [1].

We also made measurement of the density of hydrous magma at high pressure by sink-float test using a diamond density marker in order to examine the stability of the melt above the 410 km discontinuity. The partial molar volume values at 16.8 and 20.0 GPa at 2,200 °C are determined to be 8.5±0.7 and 7.5±0.2 cm³/mol, respectively. We also estimated the density of the hydrous silicate melt formed by the partial melting above the 410 km discontinuity [2]. Therefore, hydrous magmas containing up to 6.7 wt. % of water are stable in the lowermost upper mantle. Our results strongly support the recent suggestion of existence of a partial melt based on the seismological observation of a low velocity and low Q region just above the mantle transition zone [3,4].

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O06-02

Water circulation in the Earth's mantle

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Using recent results from high-pressure experiments and thermodynamic calculations (Komabayashi and Omori, This meeting; in the session of Phase transitions and thermodynamic modeling of minerals and rocks), phase diagrams of simplified hydrous peridotite in the system MgO-SiO₂-H₂O have been constructed to lower mantle conditions up to 35 GPa, 1600°C. On the basis of constructed phase relations, I discuss possible water subduction and circulation processes in the deep mantle. For water transportation by subduction of peridotites, important phase relations are (1) of antigorite (serpentine) at lower pressures (< 10 GPa) and (2) of up to seven different high-pressure hydrous phases at higher pressures.

In cold subducting slabs, water in antigorite will be partially transferred to hydrous phase A at depths greater than 160-km. With further subduction, water in phase A may be transported to the bottom of the transition zone via solid-solid reactions among seven high-pressure hydrous phases. At around 660-km depth, in the stagnant slab heated from the surrounding mantle, the free fluid will be released by the dehydration of superhydrous phase B or phase D. The released fluid will be trapped by wadsleyite or ringwoodite in the surrounding mantle. If the slab temperature at 700-km depth is lower than 1000°C, hydrous phase D will carry water into the deep lower mantle. Along the cold slab geotherm, large fluid fluxes are predicted at shallower (~300-km depth) and deeper (~700-km depth) levels, depending on the slab temperature. The depth distributions of dehydration reactions suggest that observed subduction zone seismicity could be related to dehydration reactions in the slab. In the upwelling plume through water-bearing transition zone, the free fluid will be produced when the plume passes 410-km depth. The fluid generated in the plume will facilitate the movement of upwelling in the upper mantle. Finally water will be released to the Earth's surface by magmatism.

O06-03

High pressure behaviour of hydrates and carbonates and the generation of C-O-H fluids in subduction zones: experimental constraints in mafic systems up to 5 GPa

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Volatile recycling in subduction zones is mostly controlled by transformations in phase assemblages bearing hydrates, carbonates and/or graphite/diamond. Experiments were carried out on a MORB bulk composition using piston-cylinder and multi-anvil machines at P from 1 to 5 GPa and T from 650 °C to 800 °C, in the presence of a fluid at variable C-O-H ratios ranging from pure H₂O to mixtures of oxalic acid dihydrate and silver oxalate. fH₂ was buffered at NNO, OH (X, COH) and hematite-magnetite HM, OH (X, COH) buffers using a double capsule technique (notation after Eugster H.P. and Skippen G.B. 1967, *Researches in Geochemistry* 2, 492-526).

Experiments in the presence of a C-O-H fluid show a large amphibole-carbonate phase field up to P < 2 GPa at NNO hydrogen fugacities, with calcite or dolomite at low pressure and with dolomite and magnesite above 1.6 GPa. Amphibole breaks down at 2.5-2.6 GPa, epidote persists to 2.7 GPa, 730 °C and talc to 3.3 GPa 800 °C. Graphite is ubiquitous above 1.8 GPa at both hydrogen fugacities (NNO, OH (GX, COH) and HM, OH (GX, COH)). Graphite is the dominant carbon compound at fH₂ buffered by NNO above 2 GPa; carbonates form only when the amount of oxalic acid dihydrate exceed approx. 20 wt.%. On the contrary, at HM hydrogen fugacities (oxygen fugacities close to GCO buffer in the inner charge), carbonate phase fields get wider with pressure: aragonite and/or dolomite are stable up to 2.4 GPa and at higher pressure they are replaced by coexisting magnesite and dolomite. Mg-calcite forms at 5.0 GPa 800 °C. Unexpectedly, lawsonite was found to coexist with magnesite at temperatures as high as 730 °C at 4.2 GPa and 700 °C at 3.0 GPa, revealing a thermal stability in C-O-H bearing systems exceeding that found in mafic assemblages in the presence of hydrous species only.

In C-O-H bearing systems, complex mass-balance relations govern the partitioning of volatiles between fluid, hydrates, carbonates, and graphite/diamond at fixed fH₂. In natural high pressure rocks, the relative amounts of ferric/ferrous iron in garnet and clinopyroxene versus C/carbonate may impose internally buffered oxygen fugacities and therefore fluid speciation. Relatively CO₂-rich compositions are expected only at high fO₂ in the presence of graphite/diamond.

O06-04

Second critical endpoint and properties of aqueous fluid in a hydrous upper mantle

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Water affects the physical and chemical properties of the materials in the Earth's interior. Therefore, knowledge of the phase relations in silicate-H₂O systems is fundamental for understanding the evolution of the Earth. Recently, we have developed the new experimental technique for direct observation of aqueous fluid and hydrous silicate melt coexisting under high pressure and high temperature conditions using X-ray radiography technique together with Kawai-type multi-anvil high-pressure apparatus (SPEED-1500) installed at SPring-8, Japan. Using this technique, the second critical endpoint in the peridotite-H₂O system has been determined. In the experiments up to 3.6 GPa, two fluid phases (i.e., aqueous fluid and hydrous silicate melt) were observed. At 4.0 GPa, however, we could not distinguish these two phases in the radiographic images. These observations indicate the second critical endpoint occurs at around 3.8 GPa and 1000 °C (corresponding to a depth of ~ 110 km) in the peridotite-H₂O system. Our experimental results suggest that hydrous silicate melt and aqueous fluid in the Earth's mantle becomes indistinguishable from each other and that melting temperature of hydrous mantle peridotite can no longer be defined beyond this critical condition. This position of the second critical endpoint could explain the previously observed drastic changes in composition and connectivity of aqueous fluid in mantle peridotite at around 3-4 GPa and could play an important role in magmatism and chemical evolution of the Earth's interior.

Physical and chemical properties of subduction zone fluids – direct insights by experiments in the hydrothermal diamond anvil cell

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The development of the hydrothermal diamond anvil cell (HDAC) 14 years ago has started a new era in the study of fluids at high pressures and temperatures. Applications include: (1) determination of the extent of miscibility between aqueous fluids and silicate melts, (2) in-situ speciation studies on silicates dissolved in aqueous fluids (and vice versa), (3) viscosity measurements on low-viscosity liquids, and (4) mineral solubilities in aqueous fluids. In all these examples, the HDAC technique is either the only way to obtain the desired information, or provides more accurate results than alternative methods.

For example, falling-sphere experiments in the HDAC allowed for the first time to determine viscosities of aqueous fluids containing 10-80wt% dissolved silicates [1]. Measured viscosities are surprisingly low. The viscosity of a fluid containing 20 wt% dissolved silicate at 800°C, for example, is similar to that of pure water at room temperature (1.0×10^{-3} Pa s), and that of a fluid containing 50 wt% dissolved silicate at the same conditions is comparable to olive oil at room temperature (0.8×10^{-1} Pa s). Silicate-rich fluids therefore combine low viscosities with favorable wetting properties, making them highly mobile in the subarc mantle.

The advantage of being able to observe the sample during the experiment becomes particularly evident in mineral solubility studies. Rutile solubility measurements in the HDAC demonstrate that previous values determined by the weight loss technique were up to three orders of magnitude too high, due to rutile redistribution in the presence of small temperature gradients [2]. Similarly, the dissolution behavior of common silicates sheds doubts on the validity of results obtained by the diamond trap technique, as new mineral phases are observed to precipitate throughout the HDAC sample chamber during continuous increase in temperature and pressure. Not knowing their true origin, these minerals would be interpreted as quench crystals in a typical diamond trap experiment.

In summary, the use of HDAC in the field of high-pressure fluid research seems to have just started, and many more applications are likely to emerge in near future.

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Hydrogen diffusion in garnet: a summary

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Water-related defects in garnet have been an important subject of study for decades but it is only since 1996 that hydrogen diffusion experiments have been performed. All kinetics data have been collected between 700°C and 1050°C on pyrope-rich garnets ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and garnets of the grossular-andradite solid solution ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$).

Isotope diffusion studies (H-D exchange experiments) could successfully be accomplished for pyrope (Dora Maira) and in grossular-andradite single crystals, whereas such experiments could not be performed for mantle pyropes due to the faster extraction of hydrogen into these minerals. All data follows a single diffusion law with an activation energy of 130 ± 15 kJmol⁻¹.

The kinetics of H-extraction in mantle pyropes can be described by a single set of diffusion laws with an activation enthalpy of 253 kJmol⁻¹, which is only slightly higher than the hydrogen diffusivity obtained for deuterium diffusion. The activation energies for H-extraction in other garnets range also between 200 and 300 kJ/mol, but the extraction diffusivity are one to two orders of magnitude slower than for mantle pyropes. Hydrogen extraction in garnet shows two notable features: individual OH bands exhibit different kinetics and diffusivities depend on oxygen partial pressure. In calcium-rich garnets, the diffusivities of hydrogen extraction roughly increase with the ferric iron content. The kinetics dependence on iron concentration, suggests that a redox-exchange reaction controls the hydrogen extraction. The implication of a redox-reaction is also confirmed by the simultaneous decrease of the Fe^{2+} concentration in grossular during hydrogen extraction. However, the activation energies of hydrogen extraction in garnets are, with an average value of 260 kJmol⁻¹ (180 – 329 kJmol⁻¹), much higher than the energies measured for redox-exchange reactions in other mantle silicates such as olivine and diopside. These activation energies are closer to those observed for reactions involving the migration of metal vacancies in olivine and enstatite.

Hydration of nominally anhydrous minerals: Melt generation, physical properties, and dynamics of the upper mantle

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The solubility of hydrogen in the nominally anhydrous silicates of the upper mantle may control melt generation, tectonic processes, and geochemistry of the Earth's upper mantle. Solubility of H in olivine increases from a few hundred ppmw H₂O at shallow depths to nearly one percent H₂O by weight near the 410 km discontinuity. At 12 GPa H solubility increases with temperature to about 1250°C and decreases at higher temperatures with the onset of melting. The major H substitution mechanism in olivine appears to involve octahedral vacancies and we have quantified the hydration effects on molar volume, and compressibility.

At shallow depths, hydrogen incorporation in orthopyroxene may control the generation of melt and dominate the seismic properties at the base of the Earth's lithosphere. Orthopyroxene may incorporate nearly one percent H₂O by weight at 1.5 GPa and 900°C. The major H substitution mechanism in orthopyroxene appears to involve tetrahedral Al in excess of octahedral Al and M2 vacancies. Because of the tetrahedral Al, H solubility in orthopyroxene decreases with pressure so that there is a minimum in the H solubility in peridotite at about 100 km depth, which corresponds to the low velocity zone. At the base of the lithosphere H incorporation into orthopyroxene would retard melt generation and contribute to the stiffness of the lithospheric plates.

In the transition zone, H solubility in wadsleyite may exceed three percent and ringwoodite two percent by weight H₂O so that this region may incorporate up to ten times the current ocean volume before melting would occur. Deep reservoirs of water incorporated as hydroxyl into solid silicate minerals of the Earth's interior may thus contain the majority of the planet's hydrogen and have acted as buffers to maintain ocean volume and continental freeboard over geologic time. Further, H solubility in the upper mantle may control melting and dynamics of upper mantle processes.

Water partitioning between olivine and wadsleyite near 410-km seismic discontinuity

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We measured H₂O content and H₂O partition coefficients between olivine and wadsleyite in a hydrous Fo₉₀ composition and apply the results to mantle dynamics near 410 km discontinuity. The hydrous starting composition (15 wt.% H₂O) was prepared by adding Mg(OH)₂ to Fo₉₀ composition adjusting the proportion of MgO. Experiments were carried out using a 1000-tons Kawai-type multianvil apparatus installed at Tohoku University. Polarized infrared spectra were obtained using a micro-FTIR spectrometer in the University of Tokyo. The OH-concentration was estimated by integration the absorption bands using the calibrations by Paterson (1982) for wadsleyite and Bell et al. (2003) for olivine. The IR spectra of olivine are composed of several absorption peaks at 3530-3613 cm⁻¹. Additional weak peaks are observed at 3400-3477 cm⁻¹. The H₂O content measured in olivine is 0.14 wt.% H₂O at 1473 K and 9.5 GPa, whereas it is increases to 0.42-0.61 wt.% H₂O at 1373-1773 K and 12.5-14.0 GPa. The spectra of wadsleyite is composed of a strong peak at 3326 cm⁻¹ and weak peaks at 2500, 3584, 3611, 3643, and 3657 cm⁻¹. The H₂O content measured in wadsleyite is 1.6-2.1 wt.% H₂O at 1373-1673 K and 0.67 wt.% H₂O at 1773 K (at 13-15 GPa). The partition coefficients of H₂O between wadsleyite and olivine ($D_{\text{w/ol}}$) are 4.0 at 1473 K, 2.1 at 1673 K and 1.3 at 1773 K. These values are lower than those obtained in previous studies ($D_{\text{w/ol}}=5-40$).

Estimates for the width of 410-km discontinuity vary between 4 and 35 km, whereas most estimates suggest 4-6 km width. The presence of water has dramatic effect to broaden the discontinuity. Wood (1995) predicted that the 100 ppm H₂O in olivine (with assumed olivine/wadsleyite partitioning as 1:10) would broaden the discontinuity by approximately 3 km. We observed similar broadening in present experiments. Recent observations that 410-km discontinuity is between 20 and 35 km thick beneath Mediterranean (Van der Meijde et al., 2003) may be accounted for by high H₂O contents in this region. If the transformation is 35 km thick, the H₂O content of olivine and wadsleyite would be 0.21 and 0.84 wt.% respectively according to the model by Wood (1995) and partition coefficients, determined in this work. These estimations are supported by the measurements of electrical conductivity of the upper mantle in this region, which is consistent with 0.1-0.15 wt.% H₂O in olivine (Tarits et al., 2004).

Partitioning of H₂O in the mantleT. Inoue¹, M. Katsuta¹, T. Wada¹, R. Sasaki¹, T. Irifune¹, and H. Yurimoto²¹Geodynamics Research Center, Ehime University, Bunkyo-cho 2-5, Matsuyama, Ehime 790-8577, Japan

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Water is the most abundant volatile component on the Earth's surface, and it has been supplied to the Earth's interiors by subducting slab. Water influences the physical properties and melting temperature of minerals. Olivine is the most abundant mineral in the Earth's mantle, and it is clarified that the high-pressure polymorphs of olivine (Ol), wadsleyite (Wd) and ringwoodite (Rw), can contain ~3wt% of H₂O in their crystal structures (e.g. Inoue et al., 1995, 1998). However, the partitioning of H₂O among these minerals has not been clarified yet except for Ol-Wd transformation (Chen et al., 2003). We have determined the partitioning of H₂O between Wd and Rw and between Rw and perovskite (Pv) to clarify the distribution of H₂O among upper mantle, mantle transition zone and lower mantle. On the other hand, majorite garnet (Mj) is the second abundant mineral in MTZ, so we also clarified the water solubility in Mj and the partitioning of H₂O between Wd and Mj and between Rw and Mj.

High-pressure experiments were conducted by MA-8 type (Kawai-type) high-pressure apparatus in Ehime University, and the chemical compositions were determined by EPMA. The water contents of minerals were measured by SIMS in Hokkaido University.

We succeeded to synthesize large (~50 μm) coexisting crystals of Wd and Rw, Rw and Pv, Wd and Mj, and Rw and Mj, and we could clarify the partitioning of H₂O between those coexisting minerals. The partition coefficients between Wd and Rw, between Rw and Pv, between Wd and Mj, and between Rw and Mj were approximately 2, >15, 10 and 5, respectively. We (Chen et al., 2003) have already determined that the partition coefficient between Wd and Ol is about 5, so the partitioning of Ol, Wd, Rw and Pv are approximately 6:30:10:1. In addition, the partition coefficients between Wd and Mj and between Rw and Mj were about 10 and about 5, respectively. Thus the contributions for the water reservoir in MTZ are mainly the existence of Wd and Rw, and a few effect for the existence of Mj. Thus the mantle transition zone should be a strong water reservoir in the Earth's interiors.

First principles studies of hydrous wadsleyite under high pressure

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Wadsleyite is thought to be the primary constituent in the Earth's transition zone and has been pointed out that this phase can be significant water reservoir in the Earth. We investigate hydrous wadsleyite (β-Mg₁₄Si₈O₃₂H₄) using first principles computation methods. Several structural models for stable hydrogen positions in this mineral have been explored. It has been shown that hydrogen bonds play important role on structural stability and its compression mechanisms as in the case of other hydrous minerals (δ-AIOOH, phase D etc.) which is stable under high pressure. First principles lattice dynamics calculation demonstrated the relationships of strength of hydrogen bonds and vibrational properties of hydrous wadsleyite under high pressure.

Cation order and hydrogen bonding of δ-AIOOH, phase egg and aluminous stishovite: An NMR and Raman study

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Phase egg (AlSiO₃OH) and δ-AIOOH are both hydrous phases with inter-connected octahedral network structures that have been found to be stable at successively higher pressures up to those of the lower mantle, and thus may be important water carriers in the subducted slabs. Aluminous stishovite is also known to incorporate water and thus may be a potentially important water reservoir beyond the stability fields of hydrous minerals. We have applied ¹H, ²⁹Si and ²⁷Al NMR and micro-Raman spectroscopy to gain insights into the H positions and Al-Si order/disorder in these phases.

High-pressure samples were produced in a Kawai-type double-stage uniaxial split-sphere multi-anvil apparatus. δ-AIOOH was synthesized at about 21 GPa and 1000°C using Al(OH)₃ starting material. Phase egg was synthesized at about 17 GPa and 1000°C using a starting mixture of SiO₂, Al₂O₃ and Al(OH)₃ of nominal AlSiO₃OH composition. Water-bearing aluminous stishovite was synthesized from a similar starting material with a bulk composition of 0.95SiO₂-0.05AIOOH at about 18 GPa and 1800°C. The identities of phases were confirmed by powder XRD, EPMA and/or micro-Raman analyses.

The ¹H MAS NMR spectra of δ-AIOOH and phase egg each yield a broad, symmetric peak near 12.5 and 12.0 ppm, respectively, consistent with strong hydrogen bonding. Raman spectra of both show several broad bands in the 1800–3000 cm⁻¹ range, typical of strongly hydrogen-bonded OH groups, resulting from Fermi resonance. Aluminous stishovite yields a sharp ¹H MAS NMR peak near 9.3 ppm and a Raman band around 3120 cm⁻¹, both consistent with moderate hydrogen bonding.

The ²⁹Si cross-polarization (CP)-MAS NMR data of phase egg show three peaks near -183.4 ppm, -173.8 ppm and -158.2 ppm, with relative intensities of 21.1%, 71.8% and 7.1%. These peaks roughly fall within the range reported for octahedral Si. However, there is only one unique Si (and one Al) site in the reported crystal structure (Schmidt et al., 1998), suggesting Si-Al disorder. The degree of disorder is estimated to be about 10% from random mixing model. The ²⁷Al MAS NMR spectra of phase egg are also consistent with local structural disorder. Such a disorder is expected to have a significant effect on its physical and thermodynamic properties and stability field. For aluminous stishovite, the ¹H-²⁹Si CP-MAS NMR data show a sharp peak near -191.3 ppm, similar to anhydrous stishovite, and the ¹H-²⁷Al CP-MAS NMR spectra contain only a peak attributable to octahedral Al.

Water activities of aqueous fluid phases at upper mantle conditions

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Considerable amounts of silicate components dissolve in aqueous fluid phases at high pressures (Stalder et al., 2001; Mibe et al., 2002). Water activities (a(H₂O)) of aqueous fluid phases decrease with increasing solubility of silicate components. Thermodynamic data of phase A (Mg₂Si₂O₈(OH)₂), clinohumite (Mg₉Si₄O₁₆(OH)₂), and chondrodite (Mg₃Si₂O₈(OH)₂) are useful to evaluate a(H₂O) of aqueous fluid phases at upper mantle conditions. The evaluated a(H₂O) of the aqueous fluid phases enable us to estimate variety of solubility of silicate components. This study derives an internally consistent thermodynamic data set for these hydrous phases, and then evaluates a(H₂O) of aqueous fluid phases at upper mantle conditions.

Thermodynamic data of phase A, clinohumite, and chondrodite were determined by mathematical programming analysis of measured or estimated thermophysical data and reversal phase equilibrium data for solid-solid reactions. The water activities of clinohumite breakdown reaction; clinohumite = forsterite + periclase + fluid were evaluated from comparing the calculated equilibrium curves with various a(H₂O) and experimentally determined pressure and temperature conditions of the reaction (Pawley, 2000; Wunder, 1998; Yamamoto and Akimoto, 1977). Thermodynamic data of forsterite, periclase, and H₂O were taken from Holland and Powell (1998) and volume of pure H₂O was calculated from the CORK equation of state for fluid species after Holland and Powell (1991). The water activities of the reaction can be regarded as unity below 2 GPa and begin to decrease between 2 to 3 GPa. This suggests that solubility of silicate components in the fluid start increasing between 2 to 3 GPa. The water activities of the fluid decrease with increasing pressures and temperatures from a(H₂O)=0.8-0.85 at 3 GPa and 1105 °C to 0.4-0.45 at 8 GPa and 1190 °C. The decrease of a(H₂O) suggests that the solubility of silicate components increase with increasing pressures. This behavior is consistent with experimental data of Mibe et al. (2002). They determined the composition of aqueous fluid in the system MgO-SiO₂-H₂O at 1100 °C and showed that solubility of silicate components in aqueous fluid coexisting with forsterite and enstatite increase with increasing pressures from 30 wt% at 3 GPa to 70 wt% at 8 GPa.

Raman spectroscopy of LiCl solution: Implications for chemical and physical features of aqueous fluids in the mantle wedge beneath the volcanic arcs

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Recently we learned important chemical features of aqueous fluids in the upper mantle conditions. First, the chemical compositions of silicate components dissolved into aqueous fluids coexisting with mantle peridotite change from silica-rich (andesitic) at pressures lower than 3 GPa to magnesium rich (peridotitic) at pressures greater than 3 GPa (Stalder et al., CMP 2001, Mibe et al., GCA 2002, Kawamoto et al., 2004 Am Min). This means that the aqueous fluids from downgoing peridotite have peridotitic compositions beneath volcanic arcs. Second, dihedral angles formed between olivine and aqueous fluids change from > 60 degrees to < 60 degrees at 1000 degree C at 3 GPa (Mibe et al., 1998 GRL). These conditions can determine the locations of the volcanic arcs (Mibe et al., 1999 Nature). Kawamoto et al (2004 J Chem Phys) reported that the pressure dependence of Raman frequencies of water change at 0.4 GPa, 25 degree C, and suggested a possible structural change of water from low-pressure water to high-pressure water. Kawamoto et al suggested that this structural change of water might affect the chemistry of silicate components dissolved into aqueous fluids.

Since aqueous fluids dissolve a significant amount of silicate components, in the present study we measured Raman spectra of 16.4 weight % LiCl bearing solution at 23 degree C. We observed a constant pressure dependence of the LiCl solution from 0.2 to 1.9 GPa (supercooled), and found its pressure dependence is similar to that of the high-pressure water. The solution behaves as high-pressure water even at low pressures. So, a possible transition from low-pressure water to high-pressure water may not be responsible for the above-mentioned features of aqueous fluids.

Alternatively Mibe et al (2006 JGR) performed a series of high-pressure and high-temperature X-ray radiography experiments to understand a second critical endpoint between a peridotitic melt and aqueous fluids. Mibe et al suggested it to be located at 3.8 GPa, 1000 degree C. This finding can explain the first and the second observations; approaching to the second critical endpoint, the aqueous fluids drastically change their chemical and physical features.

High-pressure stability field of aluminous hydroxide delta-AIOOH

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Hydrogen has long been recognized as one of the important volatile to understand the chemical and thermal evolution of the earth because it has significant effect on the physical properties of minerals such as melting temperature and viscosity. Water is transported from surface of the earth to deep mantle by hydrous phase in subducting plate thus the stability field of hydrous minerals at high pressure and high temperature is important to discuss the water concentration in the mantle. Delta-AIOOH is a high-pressure polymorph of diaspore (alpha-AIOOH). Its stability field has been investigated using in-situ X-ray diffraction experiment and found to stable up to 32 GPa with positive pressure-temperature dehydration boundary around 1500 K, but high-pressure stability field has not yet clarified. Here we report the stability field of delta-AIOOH at the lower mantle condition.

High pressure and high temperature experiment was conducted using laser heated diamond anvil cell. Powdered gibbsite and natural diaspore was used as a starting material. It was mixed with platinum black as a laser absorber and pressure standard in in-situ experiments. Sample was loaded into the sample hole of Re gasket sandwiched by gibbsite or diaspore without platinum, which serve as thermal insulator. Pressure was determined by ruby-fluorescence method in quench runs, and calculated from the volume of unit cell based on the equation of state of platinum in in-situ experiment. Nd:YAG laser or YLF laser operated multimode was introduced into the sample from both sides to generate high temperature. Temperature was measured by spectroradiometric method. Angle-dispersive X-ray diffraction experiment was carried out at BL13A at Photon Factory and BL10XU at SPring-8. In the quench experiments, synthesized phase was determined by X-ray diffraction after recovering the sample to ambient temperature and pressure. Delta-AIOOH existed in all samples recovered from 49 - 130 GPa and 1270 - 1750 except one sample that was recovered from 50 GPa and 1770 K, which consisted of corundum (alpha-Al₂O₃). In-situ x-ray diffraction experiment at high pressure and high temperature was also conducted. We observed synthesis of delta-AIOOH at 63 GPa and 1300 K after the duration of 5 min. It was stable up to 1700K and there was no change in the diffraction pattern after the duration of 10 min at 1700 K. Delta-AIOOH has wide stability field at the lower mantle condition and could become important water reservoir in the mantle beyond the decomposition of other hydrous phases.

Behavior of 10Å phase at low temperature

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The 10Å phase, Mg₃Si₄O₁₀(OH)₂·H₂O, represents an important phase for storage, transport, and release of water in subducting slabs to depths exceeding the stability field of talc. Its crystal structure was recently solved by single-crystal X-ray diffraction [Comodi et al., *Am. Mineral.* 90, 1012-1016 (2005)]: it consists of a mica-like stacking sequence of tetrahedral and octahedral layers as in phlogopite, with one water molecule localized in the interlayer in the site occupied in mica by potassium. The high atomic displacement factor of water oxygen suggests disorder along the [0 0 1] direction.

The thermal evolution of 10Å phase structure was studied by X-ray single-crystal diffraction method in the temperature range 116K - 295K, measuring the lattice constants at several intervals both on cooling and reheating. Intensity data for the refinement of the structure were collected at 116K.

As expected for a layer silicate on cooling in this *T* range, the *a* and *b* lattice parameters undergo a small linear decrease, the greater variation is along the *c* axis; the monoclinic angle β slightly increases. All these variations are similar to those expected for a pressure increase, showing that *T* and *P* effects are approximately reverse, as found for phlogopite.

The cell negative expansion can be modeled with the polynomial $V_T = V_{293} (1 + 8.0 \cdot 10^{-5} K^{-1} \Delta T + 1.4 \cdot 10^{-7} K^{-2} (\Delta T)^2)$, where $\Delta T = T - 293$ is in K and *V* in Å³.

The least-squares refinement with intensity data measured at 116K shows that the volume of the SiO₄ tetrahedra does not change significantly, while the volume of the Mg octahedra decreases of about 3%. To release the increased misfit between tetrahedral and octahedral sheets, the tetrahedral rotation angle α changes from 0.60° to 1.42°, increasing the ditrigonalization of the silicate sheet. This deformation has implications on the H-bond system between the water molecule and the basal oxygens. Furthermore, the very eccentric thermal ellipsoid of the water oxygen shows that the water position is disordered, as found at room conditions. The low-temperature results support the hypothesis that the disorder is static. It can be modeled with a splitting of the oxygen with a statistical distribution of the water molecules into two positions 0.6Å apart.

The resulting shortest O_{bas}-O_w distances are 2.95Å. The low-temperature behavior of the H-bond system is consistent with that hypothesized at high pressure on the basis of the Raman spectra evolution with *P* [Comodi et al., *EPSL* (2006, submitted)]

High-pressure form of topaz-OH: Structure and characterization by NMR and Raman

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Recently we have studied Al/Si disorder in phase egg (AlSiO₃(OH)) and topaz-OH (Al₂SiO₄(OH)₂, topaz I hereafter) using NMR and Raman spectroscopy (Xue et al., 2006). During this study, we found new high-pressure phase of topaz I (topaz II hereafter). Here we report its structure and spectroscopic characteristics as studied by means of XRD, NMR and Raman.

For synthesis of samples, Kawai-type double-stage multi-anvil high-pressure apparatuses were employed. Experimental conditions were 900 - 1200 °C, and about 9 - 13 GPa. Recovered samples were studied using NMR and Raman spectroscopy, and selected samples were analyzed by EPMA. Powder XRD was also employed to study the structure.

EPMA analysis showed no difference in composition between topaz I and II. In one fragment of the sample, we observed zonal distribution of topaz II sandwiched between topaz I and an assemblage of phase egg, corundum plus fluid, by micro-Raman mapping. This distribution with previous phase relation studies suggests that topaz II is high-pressure form of topaz I, and it directly breakdowns to phase egg-containing assemblages at further pressures.

Powder XRD peaks of topaz II can be indexed with an orthorhombic cell. Compared to topaz I which is also orthorhombic, *a*- and *b*-axes are slightly shorter, and *c*-axis is 1/3 of topaz I, resulting 2.2 % higher density. The structure is modeled using powder XRD data and crystal chemical considerations. Resultant model is supported by a preliminary Rietveld analysis. In topaz I, edge-shared Al octahedral dimers are bounded by Si tetrahedron by corner sharing, and run parallel to *c*-axis. In topaz II, however, such three-polyhedral-layer unit is reduced to one layer by stacking disorder in *c*-axis. Structural relationship with diaspore (alpha-AIOOH) is noted.

²⁷H-²⁹Si CP MAS NMR of topaz II reveals that 1/3 of Si is in octahedral site. ²⁷Al MAS NMR shows some tetrahedral Al in the structure, although quantification was difficult. Raman spectra of topaz II lack sharp peaks observed in topaz I. These results indicate significant Al/Si disorder in tetrahedral and octahedral sites, in addition to stacking disorder in topaz II. Topaz II would be stabilized in subducted sediments, and could bring water into the mantle transition zone.

References: X. Xue et al. (2006) *Am. Mineral.*, in press.

Dehydration reactions in orthopyroxene

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Orthopyroxene is one of the many nominally anhydrous minerals that have been shown to contain low but significant amounts of water, structurally bound in the form of OH defects. As orthopyroxene is one of the major minerals in the upper mantle, and hence may act as a host for mantle water, the stability of these OH defects as well as possible dehydration mechanisms are of interest.

In this study, we have investigated the relation between hydrogen extraction and Fe valence states by step-wise heating experiments performed on synthetic orthopyroxene crystals. Samples doped with several wt-% ⁵⁷Fe, and also ⁵⁷Fe + Al, were synthesised at 25 kbar and 1400-1150 °C by the piston-cylinder technique, and were subsequently subjected to heating experiments in air or H₂ at 700-1000°C and 1 atmosphere pressure. The change in OH content and Fe valence state was traced by infrared and Mössbauer spectra obtained on the same single crystals after the heat treatments. After heating in air, the infrared spectra for Fe-doped samples show a progressive decrease in OH-band intensities coupled to a corresponding increase in the Fe³⁺ doublet in Mössbauer spectra, indicating that the dehydration follows the redox reaction $\text{OH}^- + \text{Fe}^{2+} = \text{O}^{2-} + \text{Fe}^{3+} + 1/2\text{H}_2$. However, the more OH-rich Fe + Al-doped sample shows a different behaviour, where the dehydration is coupled to a decrease in Fe²⁺ contents associated with hematite precipitation, as shown by Mössbauer spectra.

For samples annealed in H₂ atmosphere (800-1000°C) a correlation of the decrease of the amount of Fe³⁺ and the intensity of specific IR bands associated with Fe³⁺, that decrease faster than other bands, was observed. The results indicate that at least two different dehydration mechanisms, with different kinetic characteristics, are active in dehydration processes in orthopyroxene, and confirm the previous observation that dehydration kinetics in pyroxenes depend on Fe content.

Effect of chemical environments on hydrogen related defects in wadsleyite

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Recent observations and high-pressure experiments have suggested that the order of 0.1 wt% water is stored in the Earth's mantle transition zone. Therefore, for accurate understanding of material behavior in the mantle transition zone, it is important to clarify the state of hydrogen related defects in wadsleyite as a function of chemical environments. In this study, we have investigated the effects of chemical environments on state of hydrogen related defects in wadsleyite by FTIR analyses of samples annealed at wide range of hydrogen and oxygen fugacities.

Experiments were carried out using Kawai-type multi-anvil apparatus, KIW1, installed at Yale University. Starting materials for the subsequent annealing experiments were synthesized from San Carlos olivine powder. The synthesis conditions are P = 14-15 GPa, T = 1230-1573 K and t = 1-2 h. In the annealing experiments, we used three different types of capsule assembly depending on target water content. In order to address effect of oxygen fugacity, each sample was surrounded by Mo, Ni or Re foil. The conditions of annealing are P = 15-16 GPa, T = 1450-2173 K and t = 0.25-48 h. Water content of recovered samples ranges from below detectable limit (less than 50 ppm H/Si) to 240,000 ppm H/Si. FTIR measurements were carried out using doubly polished thin sections with thickness of 50-200 microns.

As a result, state of hydrogen in wadsleyite was found to highly depend on both water content and capsule material suggesting influences of water and oxygen fugacities (fH₂O and fO₂). In the case of Mo capsule experiments (with low fO₂), relative height of a peak at 3200 cm⁻¹ increases with decreasing water content, and, finally, only this peak survives at <200ppm H/Si. On the other hand, in the case of Re capsule experiments (with high fO₂), relative height of a peak at 3620 cm⁻¹ increases with decreasing water content, and only this peak survives at <1,000 ppm H/Si. In the case of Ni capsule experiments, the intermediate behavior (between Mo and Re experiments) was observed. Previous studies on crystal chemistry of water-rich wadsleyite revealed that majority of hydrogen is incorporated by substituting an Mg atom by 2 H atoms. In this study, we found that peaks at 3200 and 3620 cm⁻¹ show distinct behavior. These peaks may be related to hydrogen incorporated as other types of defect.

Electrical conductivity of single crystal hydrous olivine

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The oceanic asthenosphere has very high electrical conductivity with high anisotropy in some locations. In the directions of parallel and normal to the plate motion, respectively, the conductivity is orders of 10⁻¹ and 10⁻² S/m, which cannot be explained by conductivity of anhydrous olivine. Because hydrogen can be incorporated in olivine at mantle pressures, the observation has been usually interpreted by the olivine hydration, which would cause anisotropically high conductivity by proton migration. In order to examine this hypothesis, here we report effect of water on electrical conductivity and its anisotropy for hydrogen-undoped and -doped olivine at 500-1500 K and 3 GPa.

The starting materials were prepared from a single olivine crystal with a (Mg_{0.92}Fe_{0.08})₂SiO₄ composition from China. Two experimental series (hydrogen-doped and -undoped conditions) were conducted to assess the effect of hydrogen on the conductivity. Hydrous olivine single crystals were synthesized by doping hydrogen to the single crystal cores. The single crystals were surrounded by a talc+brucite mixture, which were kept at pressure P = 3GPa and temperature T = 1373K for 6-8 hours. The concentration of hydrogen in samples was determined by Fourier-transform infrared (FT-IR) spectroscopy both before and after each conductivity measurement. H₂O contents in the hydrogen-doped olivine are around 230 ppm except for the cylindrical core oriented to [010] (approximately 100 ppm).

The hydrous olivine has anisotropically much higher conductivity and lower activation energy than anhydrous olivine. The hydrogen-doped olivine has higher conductivity by 2 orders of magnitude than the hydrogen-undoped olivine. The activation energies of the hydrogen-undoped olivine in the high temperature region are around 1.4 eV. In this temperature region, small polaron should be the dominant conduction mechanism. The activation energies of the hydrogen-doped olivine in each crystallographic axis are found to be E[100] = 0.73, E[010] = 0.97, and E[001] = 0.87 eV. At higher temperature corresponding to the top of the oceanic asthenosphere, the small polaron conductivity of olivine could be masked by proton one due to difference of the activation energy between these two mechanisms.

Extrapolation of the experimental results to higher temperature suggests that conductivity of hydrous olivine at the top of the asthenosphere should be nearly isotropic and only order of 10⁻² S/m. Thus, the hydrous olivine cannot account for the geophysical observations. The observation could be attributed to presence of partial melt elongated in the direction of plate motion.

O07-01

Diamonds with multiple growth stages and variable fluid sources from the Quebrada Grande region of Guayama, Venezuela

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Diamonds from the ca. 700 Ma kimberlites and derivative modern alluvial deposits in the Quebrada Grande region of Venezuela overwhelmingly belong to the eclogitic suite. Previous studies of these diamonds recognized anomalously low carbon isotope ratios, interpreted as indicating an origin involving subduction of oceanic crust that contained biogenic carbon. In our study, the small analytical volumes and spatial resolution afforded by *in situ* study of polished diamonds and their mineral inclusions with microbeam methods has allowed for discernment of details of geochemical evolution during diamond growth that are not possible in conventional diamond cracking and inclusion release studies. Cathodoluminescence imaging indicates complex zonation and growth history in all stones. Variation in carbon isotope ratio, nitrogen abundance (both determined by SIMS) and major/minor element composition of silicate inclusions (electron microprobe) is also complex. The carbon isotope ratio ($\delta^{13}\text{C}$) of the diamonds falls in the range -23.2 to -6.2 per mil (PDB) and nitrogen abundance ranges from below 1 ppm to approximately 2660 ppm. Within single diamonds carbon isotope composition can vary by as much as 15 per mil, and nitrogen abundance by as much as 2600 ppm. Variations in these values are not regular or predictable. Rims can have higher or lower nitrogen contents and carbon isotope ratios than cores within individual stones, and reversals are common. The spatial variations that we have documented are distinct from the "limit sector" and "slow growth fractionation" models of igneous diamond growth. Instead we envision diamond growth from a fluid medium whose composition varied locally and changed unpredictably over the course of diamond growth. Oxygen isotope compositions of garnet and coesite inclusions have been determined by SIMS. The oxygen isotope values ($\delta^{18}\text{O}$, VSMOW) of coesites are in the range +10.2 to +16.7 per mil and those of garnet are in the range +5.5 to +12.9 per mil, with most above +7.0 per mil. The oxygen isotope data are compelling evidence for an origin for the diamond eclogite suite by subduction of ocean floor basalt that had undergone low-temperature hydrothermal alteration on or near the sea floor. The fact that all eclogitic diamonds with low carbon isotope values (less than -10 per mil) occur together with silicates with elevated oxygen isotope values (above +6 per mil), in this and all other documented occurrences, is strong support for a substantial biogenic component of the isotopically light carbon in the diamonds.

O07-02

Olivine inclusions in Siberian diamonds: high precision approach to trace elements

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The geochemistry of mineral inclusions in diamond is important source of information about the composition of the continental lithospheric mantle at depths exceeding 120-150 km. At these depths two main types of geological environment support diamond formation: they are ultramafic (or peridotitic) (U-type) and eclogitic (E-type) environments as shown by minerals that occur as inclusions in diamonds (Sobolev, 1974; Meyer, 1987). In primary, diamond-bearing kimberlite or lamproite rock the ratio of diamonds from these two geological environments varies widely between localities. However, U-type diamonds dominate in the overwhelming majority of diamond occurrences worldwide.

Olivine is the most typical inclusion in U-type diamonds and coexists both as touching or nontouching inclusions with enstatite, pyrope, chromite (harzburgitic or dunitic assemblage without enstatite) and chromediopside (lherzolitic assemblage). About 200 diamonds containing olivine inclusions sometimes associated with enstatite, pyrope and chromite were selected from major Siberian mines including Aykhal, Yubileynaya and Internationalnaya and prepared for analysis of inclusions in a single polished surface with diamond. Inclusions were analyzed for major and trace elements with a Jeol JXA 8200 electron probe at the Max Planck Institute of Chemistry. Special efforts were made to obtain high precision and accuracy in our electron microprobe analyses, especially for Ni, Ca, Mn, Cr, Co and Al (A.V. Sobolev et al, submitted to Science, 2006). These elements were analyzed by using long counting times and high beam currents yielding detection limits of around 10-15 ppm and errors of 20-30 ppm (2 standard errors). Trace-element abundances of overwhelming majority of analyzed olivines vary within the following ranges in wt.% (NiO=0.320-0.408; CaO=0.005-0.045; MnO=0.079-0.131; Cr₂O₃=0.013 - 0.115; CoO=0.009-0.022 and Al₂O₃= 0.007-0.039). About 70% of all studied olivines demonstrate very low CaO not exceeding 0.02 wt.% which reflect relatively low temperature of equilibrium. Some olivines of anomalous composition were detected. They contain relatively low Forsterite (Fo), along with very low MnO and unusually high NiO (86.6-90; 0.063-0.076 and 0.461-0.556 respectively). The grain of such composition located in the inner diamond growth zone associates with olivine grain of "normal" composition in the outer zone. Such a difference in olivine compositions may indicate an enrichment of diamond growing source in garnet at the initial stages of diamond growth. The high precision approach to trace elements by electron probe opens new possibilities in more accurate estimation of olivine assemblages and the temperature of diamond formation.

O07-03

Multiple events affecting highly chromian, garnet-rich peridotite xenoliths from South African kimberlites

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Newlands and Bobbejaan kimberlites, South Africa, contain a suite of highly chromian, garnet-rich peridotites amongst their xenolith population. A high proportion of garnets and chromites in these rocks plot in the diamond facies fields on Cr₂O₃-CaO (Gurney, 1984; Grutter et al., 2004) and Cr₂O₃-MgO wt. % (Fipke et al., 1995) plots respectively. Many samples have garnets with inclusions of serpentine ± chromite (+ clinopyroxene in lherzolitic samples) whose arrangement is sometimes indicative of exsolution or annealed exsolution textures. Modal reconstructions reveal that the original crystals were garnets of higher chromium content. A particularly strong chromite-clinopyroxene association is seen in the matrix and included within garnet in most lherzolitic samples; a feature not reported in other garnet lherzolites. Most of the garnets have strongly developed zonation patterns which are a result of diffusion towards the matrix (external zonation) followed by zonation towards inclusions (internal zonation). Cr-Al and Mg-Ca inter-diffuse in both types of zonation and Ti may also be strongly zoned. External zonation is modeled to have occurred on an order of magnitude greater timescale than internal zonation (~20 Ma using $D_{\text{Mg}} = 10^{-20} \text{ m}^2/\text{s}$, Ganguly et al., 1998). P-T estimates on clinopyroxene-garnet boundaries indicate 40-50 kb and 900-1100°C (Nimis and Taylor, 2000, Ryan et al. 1996), whereas core garnet compositions yield pressures and temperatures consistently a little higher. The samples plot on a relatively cool continental steady state geotherm (equivalent to 38 mW/m²).

In order to achieve the level of Cr-saturation in these rocks, repeated melt extraction is required in the spinel stability field. Since Cr stabilises spinel relative to garnet at high pressures (Wood, 1978), the rocks must have been buried to depths well in excess of 90 km (30 kb) for Al-garnet peridotite facies before the observed exsolution occurred. External zonation appears to have happened whilst garnet was in equilibrium with inclusions so any exsolution (forming the inclusions) represents relatively early decompression to > 50 kb (i.e. greater than the final pressure estimate - see above). External zonation in garnet is the result of equilibration with the matrix which is predominantly along predictable compositional trajectories. Few samples, however, display evidence for equilibration with non-equilibrium Ca-Ti-LREE-rich metasomatic fluid thought to have percolated through the matrix (Burgess and Harte, 1999 and 2004). Internal zonation is the result of late P-T re-equilibration with inclusions subsequent to any metasomatic effects from > 50 to 40-50 kb.

O07-04

Nanometre-sized mineral and fluid inclusions in cloudy Siberian diamonds: new insights on diamond formation

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Over 40 nanometre-sized isolated inclusions have been studied in four cloudy octahedral diamonds from Internationalnaya and Yubileynaya mines (Yakutia). Transmission electron microscopy (TEM) techniques such as electron diffraction, analytical electron microscopy (AEM) including line scan and elemental mapping electron energy-loss spectroscopy (EELS) and high-resolution electron microscopy (HREM) were applied. All crystals exhibit octahedral external habit with opaque central cuboid cores which contain numerous nanoinclusions. The nitrogen content is higher within the cuboid regions than in the surrounding octahedral part according IR-determination by FTIR. TEM foils have been prepared from the central cubic cloudy part of studied diamonds by using the focused ion beam (FIB) technique [Wirth, 2004]. All of the nanoinclusions ranging between 30 and 200 nm in diameter are reflecting the diamond habit. They are composed of multi-phase assemblages, which include solid phases (silicates, oxides, carbonates), brines (halides) and fluid bubbles. Frequently, we have observed non-crystalline melt material in the center of inclusions. Lattice dislocations are found around some inclusions. All inclusions are relatively homogenous in composition and contain the distinguishable crystalline and fluid phases.

Al-bearing high-Mg silicate, Ca,Mg-carbonates, Ba-carbonate, Sr-carbonate, biotite, ilmenite, apatite, magnetite, K,Fe-sulfides, native Fe and kyanite have been identified as crystalline mineral phases by electron diffraction patterns. Halide phase is KCl. No diffraction pattern of the halide phase could be retrieved because of the extreme sensitivity to electron irradiation damage, but the element maps show that K and Cl are present in all nanoinclusions. Still closed fluid bubbles were identified as moving absorption contrast due to density fluctuations caused by the electron beam. Bubbles contained high K, Cl, O, P and less S, Ba, Si, Ti components. Carbonates were identified in TEM foils from all studied diamonds. They occur in all fixed assemblages and show a general enrichment in incompatible elements such as Sr, Ba, K. Some elemental variations may be explained by fractional crystallization of such fluid/melt or mixing of fluids with different compositions [Navon, 1999].

Similar nanometre-sized fluid bubbles and some crystalline phases have been recently described in fibrous diamonds from Canadian kimberlites [Klein-BenDavid, 2006]. Thus, the coexisting different carbonates, K-rich phases, including halides, and different solid phases are detected for the first in cloudy diamonds from two main Siberian kimberlite mines. The general similarity of the inclusions reported here with those described from Canadian kimberlite mines testify the similar composition of diamond forming environment in upper mantle.

Growth and resorption of diamond by redox reactions in kimberlitic and carbonatitic melts

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Growth and resorption processes of diamond likely depend on thermal perturbation, mechanism of carbon influx, and redox state in the subcontinental upper mantle. These also depend on the solubility of carbon (or CO₂) in volatile- and alkali-rich mantle melts or fluids at various depths of the upper mantle. Analyses of fluid inclusions in natural diamonds indicate that carbonatitic melts or fluids were present during the formation of many natural diamonds (ex. Navon et al., 1988). Diamond can be synthesized from graphite in the presence of non-metallic solvent-catalysts such as carbonate melts, kimberlitic silicate melts, C-O-H fluids, and CO₂ fluids under high-pressure and high-temperature conditions in the diamond stable region suggesting a possible role of these compounds in diamond formation in the Earth's mantle (refs. in Arima et al., 2002). The recent experiments (Arima et al., 2002; Pal'yanov, et al., 2002, 2005) demonstrate that diamond grows spontaneously by reducing reactions from carbonate-bearing melts and that such melts actually supply the carbon for diamond formation. The extremely low viscosity of carbonate-bearing melts allows them to percolate easily through mantle rocks, to transport the carbon into more reduced host mantle regions and to crystallize diamond by reducing reactions.

Natural diamonds hosted by kimberlite or lamproite display variety of morphological forms and surface textures reflecting mantle source conditions during and following the growth of a diamond and also resulting from dissolution throughout the host magma. Evaluation of dissolution features of diamond crystals is important to assess the preservation of diamond. The experimental study by Kozai and Arima (2005) highlights that diamond reacts with, and dissolves in, kimberlitic and lamproitic melts in the form of carbonate ions by an oxidizing reaction in the graphite stability field. The degree of dissolution highly depends on temperature, oxidation state, and the compositional dependence of CO₂ solubility in the host melts. Diamond crystal with 5 mm diameter exposed to the oxidized host kimberlite magma (under HM buffer) could survive dissolution only for about 20 hr at 1300°C. At relatively reduced condition (under MW buffer), a diamond crystal in 5 mm diameter could be preserved for about 30 days in the host magma at 1300°C. The data suggest that the activation energy of diamond dissolution in kimberlite melt is 410 kJ/mol under 1W-buffer at 1 GPa.

Peculiarities of diamond formation in the mantle carbonate-silicate-sulphide melts by experimental evidence

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The question of chemical and phase compositions of parental diamond forming media is of prime importance for the problem of diamond genesis. The parental media for natural diamonds consist of major carbonate and silicate components as well as minor components like sulphides, phosphates, haloids, oxides, carbon dioxide, water, etc. High-pressure experiments demonstrate that both the major and minor components may be efficient in diamond nucleation. This demonstrates that experimental studies have to be focused on a revelation of parental compositions which are common as for diamonds and so for their syngenetic inclusions. The carbonatite model is consistent with as experimental results on diamond nucleation and growth in melts of this type chemistry and so the mineralogical data for syngenetic inclusions of minerals, melts and fluids in mantle-derived diamonds. It is experimentally found that sulphide melts with dissolved carbon are efficient for diamond nucleation and growth. But it is unclear their ability for syngenetic formation of diamonds and their growth inclusions. Under this approach, we have been studying phase relations of aragonite CaCO₃ – pyrope Mg₃Al₂Si₂O₁₂ – pyrrhotite FeS system which is related to the compositions of natural diamond forming media. Experiments at 7.0 GPa on melting relations of the model aragonite CaCO₃ – pyrope Mg₃Al₂Si₂O₁₂ – pyrrhotite FeS system and eclogite garnet – pyrrhotite join revealed a nearly complete immiscibility of sulphide and silicate melts, sulphide and carbonate melts, as well as sulphide and completely miscible carbonate-silicate melts. The lack of any solubility of silicate and carbonate components in sulphide melts is found. This experimental evidence points to the fact that sulphide melts, although provide diamond formation, are not efficient for syngenesis of diamonds and their silicate and carbonate inclusions, in contrast to the carbonate-silicate melts. The parental carbonate-silicate media are compositionally variable in the context of major and minor components. Sulphide melts can be included to essential value as immiscible drops in carbonate-silicate one. A scenario is plausible when diamond crystals formed in carbonatite melt can include silicate, carbonate and sulphide material. Diamonds grown from sulphide melt can form sulphide inclusions only. Supports: RAS program № P9-3 on research at extreme conditions, RFBR grants 05-05-64101, 05-02-17283, 04-05-64979, and 04-05-97220 (jointly with the Ind. Sci. Ministry / MD).

Growth of diamond in multicomponent carbonate-carbon melts: formation of the mixed C- and A-defects

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According to present experimental and mineralogical views, multicomponent carbonate-silicate-carbon melts are the basic parental media responsible for diamond origin in the Earth mantle conditions [Litvin, 2005]. It was found in experiments at pressures of 5.5-8.5 GPa that diamond effectively crystallizes in melt-solutions of the multicomponent carbonate-carbon system. By chemical mineralogy evidence, components of the system are among the compositions of the natural media for diamond formation. Carbonate melts of multicomponent composition of K₂CO₃ – 27.21, Na₂CO₃ – 2.89, CaCO₃ – 26.91, FeCO₃ – 25.63, MgCO₃ – 17.35 (as for typical carbonate constituent of carbonate-silicate substance of primary growth inclusions in natural diamonds from kimberlite pipe Botswana [Schrauder, Navon, 1994; Litvin, Zharikov, 1999]) were used as carbon solvents. Experimental study on diamond nucleation and growth in carbonate-carbon melts of this type chemistry is performed. High-pressure high-temperature "anvil-with-hole" cell with graphite resistive furnace was used. Spontaneous crystallization of diamond octahedral single crystals with a density of nucleation more than 300- 500 nuclea/mm³ and formation of diamondite (polycrystalline diamond, up to 10000 nuclea/mm³) were run at PT conditions of labile carbon oversaturation in the K, Na, Ca, Mg, Fe-carbonate melt (with graphite as the carbon source). Diamond seeded growth is associated with PT conditions of metastable carbon oversaturation in the melt. The peculiarities of the face growth mechanism, carbon transfer in carbonate melt-solution, kinetics of diamond crystallization, formation of structural nitrogen defects for the carbonate-synthetic diamonds are studied with the methods of SEM microscopy, FTIR- and RAMAN-microspectroscopy. Two characteristic IR absorption bands at 1132 cm⁻¹ (nitrogen structural C-defect, Ib diamond type) and 1282 cm⁻¹ (nitrogen structural A-defect, IaA diamond type) are determined in spectra of the diamonds. Both are growth defects. The mixed Ib-IaA type of IR-spectra and high nitrogen concentration (up to 854.0 at. ppm) of the carbonate-synthetic diamonds are found to be the specific features in comparison with metal-synthetic diamonds formed under high pressure in metal-carbon melt-solutions. Supports: RAS program № P9-3on research at extreme conditions, RFBR grants 05-02-17283 and 04-05-97220 (jointly with the Ind. Sci. Ministry / MD).

Photoluminescence, Raman, and infrared studies of carbonado

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Carbonado is a natural polycrystalline diamond found in alluvial deposits in the Central African Republic and Brazil. Carbonado diamonds look black and are highly porous. Unlike other natural polycrystalline diamonds, carbonado contains no mantle-derived inclusions and its carbon isotope value is very low (δ¹³C = -28 to -23 ‰). Additionally, carbonado exhibits intense luminescence (photoluminescence and cathodoluminescence) attributable to lattice defects including nitrogen impurity, interstitials, vacancies, etc. The origin of carbonado is controversial, but several hypotheses regarding the origin of carbonado have been proposed: static high-pressure origin in the mantle, shock impact origin, and radiation-induced diamond formation.

For clarifying the origin of carbonado, optical properties (photoluminescence, Raman, and infrared) were investigated in this study. The studied samples are from Central African Republic (CAR) and were polished to the optical grade. The photoluminescence images and spectra of carbonado were collected using a confocal laser microscope (spatial resolution: ~1 μm) and Scanning Near-field Optical Microscopy (SNOM; spatial resolution: ~300 nm) for studying the heterogeneity of photoluminescence. Raman spectra of carbonado were measured using confocal laser microscope. Residual stress in carbonado was estimated from the frequency shift of Raman spectra of diamond. Infrared spectra were obtained using micro FTIR spectrometer to obtain information of aggregation state of nitrogen.

Photoluminescence mapping showed that the emission intensity was lower at the grain boundaries, indicating that the degree of crystallinity is low at those regions. Photoluminescence spectra of carbonado observed using the confocal laser microscope and SNOM comprised three sharp bands at 504, 575 and 638 nm with their side bands. The color of photoluminescence was heterogeneous in the sample. The results of Raman spectra revealed that the remarkable residual stress exists underneath the sample surface and the maximum stress value observed in this study was 0.72 GPa. These results support that carbonado had been at a high-pressure condition. The full width at half maximum (FWHM) of Raman band was as much as a typical value (6.2 cm⁻¹). However, in a radiation halo that width increased up to 9.6 cm⁻¹, indicating the crystallinity is low in a halo region. Infrared spectra of carbonado showed the two nitrogen-induced absorption bands at 1344 and 1282 cm⁻¹. This result indicates that the aggregation state of nitrogen is between Type Ib and Type IaA. The aggregation of nitrogen is not matured and a young age of crystallization, or unusually cool conditions in the mantle, or both can be supposed.

O07-09

Microdiamond formation during intraslab UHP metasomatism: An example from the Kokchetav Massif

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Microdiamonds from the Kokchetav UHP terrane show diverse features in their characteristics, and might have formed under the UHPM with high-H₂O activity fluid conditions due to dehydrations and decarbonations in deeply subducted continental materials.

Microdiamond is highly abundant (max. ca. 2700 carat/ton) in dolomite marble that was stable at XCO₂=0.1. The microdiamonds in dolomite marble are classified into 3-types; S, R and T. The dominant type S grew at two stages, core and rim stages. R-type grew at the core stage, and T-type grew at the rim stage. A possible source of carbon for 2nd stage growth is a UHPM fluid.

No diamond occurs in dolomitic marble, a product of strong H₂O-rich fluid effect during UHPM; Ti-clinohumite-aragonite corresponds to extremely low-XCO₂ (= <0.01), and the TiO₂ carrier could be a H₂O-rich fluid. Hydroxyl in lamellar-free diopside was confirmed as > 850ppm. Extremely low-XCO₂ condition is unsuitable for diamond formation.

A small amount of microdiamond occurs in some layers of titanite-bearing calcite marble. Other diamond-free domains contain titanite with coesite exsolution and the precursor silica-excess composition of titanite gave the minimum pressure as 6 GPa. Titanite indicates very low-XCO₂ (<0.02). All grains of microdiamond are similar to R-type in morphology and no 2nd stage growth was observed.

Gneisses are the 2nd abundant diamond-bearing rock, and microdiamonds show the strong contrast with those in dolomite marble. Dominant morphology is rounded to cuboidal form with rugged surface; this corresponds to R-type. S-type is rare in gneisses. Morphology was controlled by growth and/or dissolution. Rounded grain with smooth surface might show the resorption after diamond growth. The rareness of S-type diamond is a great difference from dolomite marble, and indicates that H₂O-bearing fluids played different roles in both two diamond-bearing rocks; 1) carbon dissolved into fluid in gneisses, and 2) carbon precipitated from fluid at the 2nd stage in dolomite marble.

Kokchetav UHPM carbonate rocks suggest the strong metasomatism under UHPM conditions. Mineral assemblages can be explained by different fluid compositions (low to extremely low XCO₂) at UHP. Low-XCO₂ conditions in carbonate rocks could be formed by infiltration of H₂O derived from dehydrations in gneisses and eclogites. H₂O-bearing fluid also controlled the formation of diamond in Kokchetav carbonate rocks. Such process can be called as Intraslab UHP Metasomatism.

O07-10

Carbon and nitrogen effects during ITHP diamond crystallization

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The interplay of fractionation and kinetic controls on nitrogen content and both carbon and nitrogen isotope ratios during the crystallisation of diamonds is not fully understood. Two synthetic diamond crystals were examined for spatial variations in these compositional characteristics using ion microprobe techniques at NERC-EMMAC facility in Edinburgh University (UK). The crystals were grown in Ni-Fe-C system at P=5.5 GPa and T=1450°C using a split-sphere multi-anvil apparatus at the UIGGM (Russia) and both have complex cubo-octahedral habit.

Within the octahedral sectors the average nitrogen characteristics are 240 ppm and -47‰_{AIR} for crystal 150/3/5 and 520 ppm and -41‰_{AIR} for crystal 140/4/6. The cubic sector of crystal 150/3/5 contains 76 ppm of nitrogen and δ¹⁵N is -20‰_{AIR}; for crystal 140/4/6 those values are 140 ppm and -8‰_{AIR}. Trapezohedral sector in crystal 150/3/5 has the lowest nitrogen content (17 ppm) but a δ¹⁵N value close to the octahedral sector (-49‰). The carbon isotope ratio is not concerned with the crystal sector structure but largely depends upon kinetics of growth of individual sectors.

Crystal 150/3/5 shows 1.6‰ variation in δ¹³C value and 104 ppm variation of N abundance along the direction of growth of the octahedral sector. The variations along similar direction in crystal 140/4/6 are 3.3‰ for δ¹³C and 215 ppm for nitrogen. In both crystals a gradual decrease of δ¹³C value is accompanied by increase of nitrogen content at the start of growth. Records of further crystallization are different but with similar relationship of C and N.

Two parallel processes appear in controlling the distribution of carbon isotopes and nitrogen atoms: 1) partitioning between crystal and solution; 2) crystal growth features (growth rate, atomic structure of crystal surfaces, etc). Initially the linear crystal growth rate is high and the nitrogen incorporation into the diamond lattice is intensive. Simultaneously, the carbon isotope ratio of the growing diamond changes to that of the source material, because of isotope fractionation between the diamond and the carbon in solution and the continual dissolution of the source.

Later in the experiments the growth rate became significantly lower with a moderate downtrend as a function of increase of crystal surface against a background of uniform carbon input. The downtrend is responsible for a gradual decreasing of nitrogen abundance of the diamond due to drift of partitioning coefficient. A similar reason for the rising of δ¹³C values is postulated.

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O07-11

An EBSD study of majoritic garnet inclusions in diamonds

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The samples investigated occur as inclusions within diamonds from the alluvial deposits of the São Luiz river, Juina province, Brazil. The inclusions vary from 100µm to 200µm in maximum dimension and contain both garnet and clinopyroxene.

The samples fall into two major groups according to whether the garnets include majoritic ('high-Si') compositions with Si > 3 cations per 12 oxygens, or have total Si cations close to 3 ('normal-Si'). Si contents range up to 3.23 in high-Si garnets and increasing Si is accompanied by increasing Na+Ca+Fe+Mg cation contents and decreasing Al(+Cr+Ti). Samples with high-Si compositions also show variations in garnet composition within each sample. The clinopyroxene compositions are omphacitic and are similar in all samples. The overall (bulk) inclusion compositions are similar to those of eclogitic xenoliths from kimberlites. In polished section samples containing high-Si garnet show complex intergrowths of garnet and clinopyroxene, with the clinopyroxene occurring in irregularly shaped bodies varying from <5µm to >50µm in maximum dimension concentrated towards the margin of the inclusions. Overall, in three dimensions, the clinopyroxene in the high-Si garnets probably has irregular plate-like or discoid shapes. In contrast, the samples with normal-Si garnets show more regular equidimensional bodies (ca. 20-25µm) of clinopyroxene occurring mainly around the margin of the inclusions.

Electron Backscatter Diffraction (EBSD) studies have been undertaken to better understand the complex and variable textures. In all cases the garnet in each sample has been shown to be a single crystal. Each body of clinopyroxene has a constant crystallographic orientation and in the high-Si garnets many of the clinopyroxene bodies show similar orientations with clinopyroxene [001] directions lying close to the {110} lattice planes of garnet. Thus the SiO₄ chains of the clinopyroxene structure tend to lie in planes of the garnet structure where there is a high density of Si atoms. In the normal-Si garnets each discrete clinopyroxene body has a constant orientation, but [001] directions may be similar or quite distinct between different bodies in the same sample.

The data suggest that the original inclusions were single grains of majoritic garnet, with likely depths of formation in excess of 400 kms. The high-Si samples retain textures indicative of the exsolution of the clinopyroxene from the original majorite and still show partly majoritic compositions. The normal-Si samples are believed to reflect completion of the exsolution process and the development of textural equilibrium.

P07-01

Occurrence and characterization of UHPM microdiamonds from the Kokchetav Massif

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Abundant microdiamond occurs in dolomite marble and pelitic gneiss in the Kokchetav UHPM terrane. Extremely high concentration of microdiamond has been reported in dolomite marble (2700 carat/ton). In dolomite marble, microdiamonds have been classified into three types (S-, R-, and T-types) by its morphology with other characters. Dominant S-type (star-shaped grain consisting of the core and the rim) occupies over two thirds of microdiamond grains in dolomite marble. These microdiamonds grew at two different stages: 1st stage of R-type and the core of S-type, and 2nd stage of T-type and the rim of S-type. Strong broad bands of CL spectra at 514 to 537 nm were detected at the rim of S-type. The core has the same broad band but intensities are very weak. Intensity images of CL spectra at peak (514-537 nm) showed a clear difference between core (weak) and rim (strong). Carbon isotopic compositions of S-type microdiamond by SIMS show the heterogeneity in δ¹³C; the rims (δ¹³C: -26 to -15 ‰) are clearly lighter than the core (δ¹³C = -14 to -9 ‰). The value of δ¹³C of core were similar to R-type (δ¹³C: -15 to -8 ‰). These isotopic compositions indicate different geochemical environments for core and rim stage growths in dolomite marble.

The other representative diamond-bearing rock is a pelitic gneiss. The dominant morphology is rounded to cuboidal form with rugged surface; this corresponds to R-type. Rounded grain with smooth surface, cubo-octahedron, and trigonal plate (spinel twin) are also observed. S-type is rare in pelitic gneiss. Most of microdiamonds are translucent and yellowish with exception of spinel twin that is extremely transparent and colorless. Different forms are observed even in the same host grain. Morphology of microdiamond may had been controlled by growth and/or dissolution. The rareness of S-type is a great difference from dolomite marble, and indicates that aqueous fluid played different roles in both two diamond-bearing rocks in the Kokchetav Massif; 1) carbon dissolved into aqueous fluid in gneisses, and 2) carbon precipitated from fluid at the 2nd stage in dolomite marble.

Minor amounts of microdiamonds (several tens grains) occur in UHP calcite marble and in K-tourmaline-bearing quartzofeldspathic rock. In addition to the microdiamonds in dolomite marble and gneisses, these minor occurrences also contribute to consider the genesis of the Kokchetav microdiamonds in relation to aqueous fluid circulation in deeply subducted continental materials.

Solidus of carbonated peridotite to 20 GPa

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Carbon dioxide and water are the most important volatile constituents in the Earth and they produce drastic changes in the melting phase relations and partial melt compositions of the mantle peridotite. Study of the peridotite-CO₂ system is closely related to petrogenesis of kimberlite and diamond. There are a few high pressure mineral inclusions (i.e. majorite garnet and Ca & Mg perovskite) in diamond which suggest that kimberlites may be originated from the transition zone and lower mantle. Recently Dasgupta and Hirschmann (2006) published phase relations near the solidus of multicomponent carbonated peridotite to 10 GPa. In this work we report the results on the solidus temperature and melt compositions of a model peridotite + 5 wt.% CO₂ system determined at 10-20 GPa and temperature range from 1200 to 2100°C.

It was difficult to determine the solidus temperature, because small fraction of carbonatite partial melt exists over significant temperature interval. However, we observed that magnesite is stable phase no more than 20-30°C above the solidus, which is near uncertainty of temperature determination in the present experiments. Therefore, temperature of magnesite stability can be considered as the solidus temperature. Dasgupta and Hirschmann (2006) showed significant increase of solidus temperature from 1100°C at 3 GPa to 1475°C at 10 GPa whereas our data indicate significant bending of solidus at pressure above 10 GPa. In our experiments, solidus temperature is 1450°C at 10 GPa, whereas it is almost same at 15 and 20 GPa (1500 and 1520°C, respectively). This bending may be connected with stability limits of clinopyroxene and clinoenstatite in the system. The partial melt formed by 10-25% melting at 10-20 GPa has high MgO (26-34 wt.%) and FeO (7.0-10.4 wt.%) and low SiO₂ (18-36 wt.%) and Al₂O₃ (0.5-1.3 wt.%) contents. It also contains 6-12 wt.% CaO, 0.6-2.0 wt.% Na₂O and 0.1-0.3 wt.% K₂O. The CO₂ contents in the melts are 14-32 wt.%. The SiO₂-poor nature of the partial melts is different from the results for melting of anhydrous or water-bearing peridotite. Partial melting of hydrous peridotite produces the melts enriched in SiO₂ compared to those in carbonated peridotite, which can be related to komatiite magmas. The composition of low degree partial melts (10%) in present experiments is close to magnesiocarbonatites, whereas higher degree melting (20-25%) produce CO₂-rich silicate melts, which is close to kimberlite magmas.

Characterization of microdiamonds in "K-tourmaline"-rich UHP rock by Raman spectroscopy

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Diamond is an excellent indicator for ultrahigh-pressure (UHP) condition. Abundant microdiamond inclusions have been reported in gneisses and marbles from the Kokchetav Massif. Recently, we found a new type of diamond-bearing rock; tourmaline-rich quartzofeldspathic rock (Shimizu & Ogasawara, 2005). We carried out intensive Raman study on microdiamonds in this rock. The results were compared with those of other rocks (pelitic gneisses, dolomite marble and calcite marble).

This tourmaline-rich rock consists mainly of quartz (45-55%), K-feldspar (10-25%), and tourmaline (20%) with minor amounts of titanite, zircon, phengite and several secondary minerals. Tourmaline displays discontinuous chemical zonation. Core parts are potassium-analogue of dravite (containing 2.75 wt% K₂O in maximum). The K₂O contents of mantle and rim parts are 0.55 wt% and 0.15 wt%, respectively. Diamond occurs exclusively in the K-dominant core parts of tourmaline and in zircon. Almost all diamonds are very fine-grained (2-10 µm) and show rounded morphology, except for a grain which has octahedral faces.

Twenty seven grains of microdiamond are confirmed in K-tourmaline. The position of Raman band of these diamonds is around 1331.9 cm⁻¹ with small variations (data of 24 grains fall in range of 1331.7 to 1332.2 cm⁻¹). The full width of half maximum (FWHM; bandwidth) of the spectra ranges 2.4 to 3.7 cm⁻¹ (average 3.0 cm⁻¹). No correlation between peak position and FWHM was found. Microdiamonds in zircon are significantly different from those in tourmaline in shape of Raman spectra. The position of Raman band varies from 1329.2 to 1332.0 cm⁻¹ and the peaks are broader (FWHM: 3.1-9.3 cm⁻¹). We found negative correlation between peak position and FWHM. The baseline of the Raman spectra strongly goes up toward large wavenumber. This is not an effect from host zircon because other inclusions and zircon itself do not show such an upward spectrum. Thus, diamond in zircon may record different information.

Diamonds from the V. Grib pipe: internal structure and origin

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Morphology, physical properties, mineral inclusions and internal structure of the diamonds (700 samples) from the V Grib pipe (Arkhangelsk province, Russia) have been examined.

The diamonds are characterized with a high quality and high quantity. The prevailing size is -4+2 and -2+1 mm (73.8%). The diamonds have a good preservation (14% - fragments) and high transparency (80%). A lot of them have a blue color of luminescence. The colorless crystals prevail (64.6%). There are many morphological types of diamonds in the pipe. The polyhedral O-D crystals are the predominant shape (44%). The round rhombododecahedra are the second in frequency (29-38%). The proportion of octahedral crystals is high (27.6%). The amount of cubic crystals and round tetrahexahedra is low (11%). All crystals have specific surface features, of which the forms of growth occur most frequently. The degree of resorption evident in the suite is not high.

According to IR-spectroscopy data the studied diamonds contain essentially nitrogen defects (260-1300 at.ppm). Their spectrums contain characteristic series of lines which correspond to the A and B type defect existence. The content of the H-defects is low (0-2,7 sm⁻¹). According to EPR-spectroscopy data, the diamonds have spectrum stipulated for the lines, connected with plastic deformation of the crystals (N2) and existence of P1 and P2-centers. The content of the defects is lower (5*10¹⁷ center/gramm) then the concentration of such centers in diamonds from the M.V. Lomonosov deposit. Ni-centers is absent.

The following mineral inclusions were determined in diamonds with the micro-beam analyses: chromite, olivine (fresh and after saponitisation), sulphides (millerite and Fe-Ni monosulphides), pyroxenes (diopside and orthopyroxene).

The distinctions in quantitative and qualitative distribution of crystals of various morphological types in our collection and other fields and pipes were revealed. The quantity of cubic, tetrahexahedron and irregular crystals increases in poor pipes. The sculptures formed during the process of solution (pits, hills, channels and caveats of etching) and strikes of plastic deformation also increase in the Verkhotinskoye and the Kepinskoye fields. The characteristic features of these diamonds are an abundance of the anisotropic crystals with low transparency and numerous crystalline defects (N3, S1, S3 etc.). The established tendency can be connected with the variations in P-T conditions of growth environments during the kimberlite emplacement.

O08-01

Radii of Transition-Metal Ions at High Pressures and Temperatures

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Recent applications of x-ray nuclear resonant inelastic scattering and synchrotron Mössbauer spectroscopy to the study of high-spin/low-spin transitions of Fe in phases typical of the lower mantle has generated extensive new interest in how HS/LS phenomena affect the crystal chemistry of these minerals. Shannon and Prewitt (1) published a table of effective ionic radii that included radii values for Fe and other transition elements in both HS and LS states, but because these radii were derived using data obtained at ambient conditions, several questions arise as to how and/or whether they can be extrapolated for use under varying temperatures and pressures. Examples of phases for which high-pressure data are available are FeS and Fe₂O₃. Iron in FeS I (troilite) is in the high-spin state, but becomes low-spin at about 6 GPa in FeS III (2). Although the average Fe-S distance is shorter in FeS III than in FeS I, it is substantially longer than the Fe-S distance in pyrite at ambient pressure. This could be because the S₂ group in pyrite exerts greater influence on the Fe-S bond than does S in FeS or the substantial shortening of the Fe-Fe distances in FeS III may be relevant. For Fe₂O₃, Pasternak et al. (3) reported a phase change at 50 GPa from the hematite to the Rh₂O₃ II structure that involved an insulator to metallic transition along with a spin crossover of the Fe ions. Rozenberg et al. (4) performed a Rietveld refinement of this structure with data obtained at 76 GPa and room temperature that provides Fe-O interatomic distances. Ono and Ohishi (5) showed that at high temperatures this structure further transforms to the post-perovskite structure at about 60 GPa. However, the variation in interatomic distances and, consequently, the related effective ionic radii have not been explained adequately and it is the purpose of this work to illustrate the inconsistencies and provide reasonable explanations of the structural changes in these and other phases that take place at varying pressures and temperatures.

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O08-02

Structure change of Fe_{3-x}Ti_xO₄ spinel solid solution under high pressures. - post spinel and Jahn-Teller effect under compression -

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Titanomagnetites Fe_{3-x}Ti_xO₄ solid solutions have an inverse spinel structure. Many of spinels transform into high-pressure phase with orthorhombic symmetry of CaMn₂O₄ (Pbcm), CaTi₂O₄ (Bbmm), or CaFe₂O₄ (Pnma) structure.

Using synchrotron radiation we performed high-pressure powder diffraction experiments up to 60 GPa and single-crystal structure analyses with diamond anvil cell up to 15 GPa. With increasing Ti content, the transition pressure from cubic-to-tetragonal decreased. The second-order transition was induced from the tetragonal distortion due to the Jahn-Teller effect of Fe²⁺ at the A site and was not found for specimens with less than x=0.6. Structure refinements of Fe₂TiO₄ using single crystals were investigated under high pressures at ambient temperature and under the low-temperature condition down to -170°C at ambient pressure. All least-squares analyses have R-factor of 1.5–4.0% at low temperature and 3.0–9.0% at high pressure. The low-temperature phase-transition takes place at -110°C. The c/a ratio is 0.9982(4) at 11.43 GPa at room temperature and 0.9967(5) at -170°C at ambient pressure. Based on the high-spin state condition, e_g electron configuration at the A site occupied by ^{IV}Fe²⁺ defines a bonding orbit rather than t_{2g}. Degeneracy of e_g orbit under the high-pressure or low-temperature condition prefers electronic state on d_{xy} orbit to d_{xy}-d_{xy}, inducing the tetragonal distortion with c/a<1. Difference Fourier maps on (100) and (001) planes of Fe₂TiO₄ reveal the electron density of d_{xy} state in e_g electrons of ^{IV}Fe²⁺. At the B site occupied by ^{VI}Fe²⁺ and ^{VI}Ti⁴⁺ ion, the electron densities on the t_{2g} orbit were not clearly observed.

Orthorhombic structure of Fe₂TiO₄ at 30 GPa determined by Rietveld method was CaTi₂O₄-type structure.

In addition, we found another new higher-pressure polyform for specimens with x=0.8 and 1.0 at 59 GPa and 45 GPa, respectively. We could not confirm the phase for specimens with less than x=0.7.

O08-03

Structural chemistry of high pressure polymorphs of CaAl₂O₄

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Monocalcium aluminate has been the subject of many investigations related to field of materials science. This interest is mainly due to the fact that this compound has many technological applications in calcium aluminate cements or after glow pigments, for example. However, CaAl₂O₄ is also interesting from a crystal chemist's point of view: in several publications [1-3] related to the field of earth sciences it was reported that the material undergoes a number of structural phase transitions at elevated temperatures and pressures. However, for the majority of the different polymorphic forms no detailed structural investigations have been performed so far.

In the course of an ongoing research project on the high pressure crystal chemistry of alkaline earth aluminates we were able to synthesize four different high pressure polymorphs using piston cylinder as well as multi anvil presses. The quenched samples were subsequently characterized by X-ray single-crystal and/or powder diffraction as well as Raman spectroscopy. Concerning their structural chemistry the different forms cover a wide spectrum of structure types, including stuffed tetrahedral [AlO₄]-frameworks, calcium ferrite-type tunnel structures containing double rutile-type octahedral chains as well as layer structures. The layered CaAl₂O₄ phases are of special interest, since they are built up from sheets of edge-sharing octahedra, similar to those observed in boehmite (AlO(OH)) or lepidocrocite (FeO(OH)). Linkage between the layers is provided by Ca cations occupying the interstitial space between the sheets. Furthermore, twinning by pseudo-merohedry and indications for polytypism have been encountered in these materials.

The present contribution will provide the results of our crystallographic and spectroscopical studies on the different polymorphic forms and will describe relationships with other known double oxides.

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O08-04

Crystal structure of hydrous forsterite with 0.38 wt% H₂O

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Beran and Putnis (1983) proposed a model of the OH position assuming the vacancies on Si site and M2 site in olivine. Miller et al. (1987) reported the natural occurrence of H in kimberlitic olivine up to 6.64 wt ppm and reported that the majority of the OH bands in IR spectra are inclined toward [100]. Libowitzky and Beran (1995) reported the existence of sharp strongly pleochroic IR absorption attributing to OH dipoles parallel to [100]. Kohlstedt et al. (1996) reported the solubility of H₂O in olivine up to 1510 wt ppm. Chen et al. (2002) reported the solubility of H₂O in olivine up to 7600 wt ppm in water saturated condition.

The single crystal of hydrous forsterite investigated here was picked from the specimen synthesized by Chen et al. (2002) using a multi-anvil apparatus under conditions of 1300 °C and 13.5 GPa. The single crystal sample has a chemical composition of Mg_{1.985}Si_{0.993}H_{0.006}O₄, as determined by electron probe microanalysis. The H₂O content in the sample was 0.38 wt% measured by using secondary ion mass spectroscopy (Chen et al., 2002).

XRD intensities were measured up to sinθ/λ = 0.90 Å⁻¹ using a single crystal of dimensions 59 × 47 × 35 μm (MoKα radiation, 50 kV, 20 mA) with a four circle diffractometer (MXC3K). No undesirable features such as peak broadening or streaks were present in the XRD patterns. From the total of 4488 reflections measured in the sphere of sinθ/λ = 0.90 Å⁻¹, 1092 symmetry-independent reflections were obtained by averaging the symmetry equivalent intensities in Laue group mmm (R_{int} = 5.6%). Absorption correction was not applied because the value of μ (~0.05) was considered to be negligibly small.

The systematic absences and an N(Z) test for a center of symmetry indicated the centrosymmetric space group Pbnm which corresponds to the reported olivine space group and was confirmed by structural refinement.

The agreement factor for the 788 independent reflections (I_o ≥ 1.5σI_o) was R(F) = 3.2% and Rw(F) = 2.8%, with anisotropic temperature factors. The result of structure refinement showed the site occupancies of 99.3% on Si-site (fixed), 98.6(2)% on Mg1-site and 99.9(2)% on Mg2-site. Calculated bond distances Mg2-O2 and Mg2-O3 of hydrous forsterite showed significantly larger values than those of anhydrous forsterite, suggesting the coordination of H to O2 coupled with the vacancy on Si-site and the coordination of H to O3 coupled with the vacancy on Mg1-site.

Isomorphism: The implications of understanding structural changes at extreme physical conditions

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Structural behaviors of minerals at extreme physical conditions have been often discussed with reference to isomorphism. Although they may not show actual structural aspects necessarily, however, those observed at relatively lower pressures and/or temperatures, even at ambient conditions, will give us a significant implication to the interpretation of structural behaviors which will appear at difficult experimental conditions.

Minerals in the transition zone and/or the lower part of the earth's mantle have been also investigated by various isomorphic substances. Co_2SiO_4 is one of examples which showed the transformation from olivine- to spinel-type phase under high-pressure and also the presence of 'β-phase' between olivine- and spinel-type phases¹. The system of NiAl_2O_4 - Ni_2SiO_4 , in which each end-member phase of NiAl_2O_4 and Ni_2SiO_4 is spinel- and olivine-type, respectively, showed another interesting structural behavior at high-pressure and high-temperature. In this system, new spinel-related structures in addition to β-phase have been found and structurally systematized as 'spineloids'². A series of these phases may imply an intermediate stage of structural change at high pressures.

Perovskite-type phase is now considered as one of main constituent minerals in lower mantle of the Earth. However, crystal structures of perovskite-type phases are variously distorted depending on the chemical compositions, and also temperature and pressure conditions, resulting in various crystal structures with orthorhombic, tetragonal, rhombohedral, cubic lattices and so on. Remarkable thing is that their lattice distortions from an ideal cubic are very small to each other, so that their crystal system may sometimes tend to be erroneously designated. Expects of structural changes of perovskite-type ABO_3 at high-pressure have been experimentally made by appropriate selections of cation sizes of A or B. Trivalent or tetravalent lanthanoid ions of La through Lu and Zr^{4+} were applied to control the structures. Structural changes from orthorhombic to trigonal system has been found in $(\text{Nd}_x, \text{Sm}_{1-x})\text{AlO}_3$ by substituting Sm^{3+} for Nd^{3+} which are in 8- to 12-coordinations³ and those from orthorhombic to cubic through trigonal system were observed in $\text{Ba}(\text{Ln}1, \text{Ln}2)\text{O}_3$, where Ln are Ce^{4+} , Pr^{4+} , Tb^{4+} and Zr^{4+} which occur in octahedral coordinations⁴. It is interesting to note that structural diagram represented by temperatures against ionic radii implies a temperature-pressure phase diagram.

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Crystal structure and bonding in the new mineral AsSbO_3 .

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A new mineral with ideal chemistry AsSbO_3 , has been found with leucite, ludlockite, and quartz in a vug in massive tennantite from the Tsumeb mine, Namibia. The symmetry is monoclinic, $P2_1/n$, with $a = 4.5757(4)$ Å, $b = 13.1288(13)$ Å, $c = 5.4216(5)$ Å, $\beta = 95.039(4)^\circ$, $V = 324.44(5)$ Å³, $Z = 4$, and $d_{\text{calc}} = 5.009$ g/cm³. The new mineral forms adamantine, colorless bladed crystals to 6 mm, bound by {010}, {110}, {111}, and {-101}. The crystal structure consists of corrugated sheets of corner-sharing AsO_3 and SbO_3 trigonal pyramids with average $\langle R(\text{AsO}) \rangle$ and $\langle R(\text{SbO}) \rangle$ bond lengths 1.782 Å and 1.993 Å, respectively. We compare the crystal structure of AsSbO_3 with a new crystal structure refinement of the isostructural mineral claudetite, As_2O_3 . Claudetite also has monoclinic symmetry, $P2_1/n$, with $a = 4.5460(4)$ Å, $b = 13.0012(14)$ Å, $c = 5.3420(5)$ Å, $\beta = 95.329(2)^\circ$, and $V = 314.83(5)$ Å³ with $Z = 4$. Bader (1998) defines a bonded interaction if and only if there exists both a bond path and a saddle point in the electron density between a pair of atoms. A bond path is a line, not necessarily straight, of continuous local maxima in the perpendicular plane between the atoms. The saddle point, referred to as a bond critical point (bcp), is a local minimum along the bond path. The analysis of the electron density distributions from ab initio quantum calculations confirm the classical short range bonding of the AsO_3 and SbO_3 groups, and also shows several long-range interactions between As and O and Sb and O. The bonds are ranked into three separate groups by the electron density at the bond critical points. The strongest of these bonds are associated with close contacts between As and Sb with O. A distinctly weaker group of bonds stabilize the corrugation of the structural sheets. A yet distinctly weaker pair of bonds holds the sheets together and is associated with the observed cleavage plane (010). The analysis provides insight to the bonding and topology systematic of arsenite and antimonite minerals in general.

Crystal-chemical behaviour of Ge and Ga in Pb-Fe members of the alunite supergroup

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Jarosite-like Pb-Fe arsenates, phosphates, sulphates and their solid solutions exist widely in nature and form part of the $\text{AB}_3(\text{XO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$ alunite supergroup (space group R-3m). In this supergroup the A site can be occupied by monovalent Na, K, Ag, NH_4 or H_3O , divalent Pb, Ca, Sr or Ba, or trivalent (Bi, REE) ions; the octahedrally coordinated B site can be occupied by either Al, Fe^{3+} , V^{3+} or Ga, whilst the tetrahedrally coordinated X site is occupied by either P^{5+} , As^{5+} , S^{6+} or, reportedly, Ge. These minerals are commonly found in the oxidised zones of ore deposits, but can also occur in soil horizons and as precipitants from acid mine drainage. Galloebudantite, the Ga analogue of budantite, and Ge-bearing budantite from Tsumeb, Namibia, present novel variants of the well-established species in the Pb-Fe subgroup. This contribution reports the results of a crystal-chemical investigation into the roles of Ge and Ga in natural and synthetic Pb-Fe members.

Several AsO_4 -dominant Pb-Fe members were hydrothermally synthesised (Teflon vessels, 220°C, 7 days, pH 0.5 to 1.0) at the Institute for Mineralogy and Crystallography, University of Vienna. Several specimens of Ge-bearing budantite and segnitite in the collection of the Museum Victoria have been analysed and compared with the synthesised compounds.

The results of the single-crystal structure refinements show that the partitioning of Ge in the synthetic Pb-Fe members is not a straightforward substitution for As in the X site. Instead, in the absence of any other minor elements (e.g. Al), Ge prefers octahedral over tetrahedral coordination in Ge-rich members. This is in contrast to previous considerations that all the Ge sits on the X site. However, in natural samples, minor amounts of Al ± Cu or Zn commonly occupy the octahedral site, while Ge occupies the tetrahedral site.

The results for a synthetic Ge- and Ga-rich segnitite confirm that Ga substitutes for Fe in the octahedral site; however, this synthetic sample shows higher symmetry (R-3m) than that proposed for galloebudantite (R3m). The synthetic members also have the Pb atom on the origin — the first such example among Pb-Fe members. The unit-cell parameters for the synthetic Ge-rich segnitite and Ge- and Ga-rich segnitite are $a = 7.276$, $c = 17.058$ Å and $a = 7.240$, $c = 17.054$ Å, respectively, and are similar to those of the As-dominant members of the group.

Periodic Nets and Crystal Structures

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Non-molecular crystal structures consist of periodic arrays of atoms joined by bonds. The atoms and bonds correspond respectively to the vertices and edges of a special kind of graph (simple, connected, periodic) called a net. Increasingly, the language and methods of graph theory are being used to describe such structures and combined with the methods of combinatorial tiling theory. In this presentation I will describe recent developments in the taxonomy of nets and in the enumeration of possible structures using these new methods. Special attention will be given to the topics of regularity, transitivity, natural tilings, and dual structures. Illustrations will focus particularly on three-periodic, four-coordinated nets such as are the underlying topologies of important minerals such as quartz, feldspar and related framework aluminosilicates, and zeolites.

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Although arsenic has been classified at the top of the priority list of the most hazardous substances, the crystal structure of numerous arsenates remain poorly determined. This is an important handicap because an in-depth study of the arsenate behaviour in soils, sediments and natural waters that have been subjected to pollution requires a precise knowledge of the possible precipitating phases, their crystal chemistry, and their thermodynamic properties. With this focus extensive studies of the crystal chemistry of arsenates were performed during the last years. Two examples exhibiting complex order phenomena based on the hydrogen bonding scheme are presented here.

About 30 natural and synthetic compounds with the general formula $M_1M_2(XO_4)_2 \cdot (H_2O/OH)_2$ belong to the tsumcorite group. For each of the cation sites M_1 , M_2 and X at least two different valences are possible; the coupled exchange at these cation positions and adjusting the ratio $OH:H_2O$ ensures electro-neutrality. Most members are monoclinic forming H_2O_2 groups, i.e., a strong symmetry-restricted hydrogen bond between two OH groups ('tsumcorite type'). Two triclinic structure variants are known: Two H_2O molecules per formula unit require an avoidance of the symmetry-restricted hydrogen bond ('helmutwinklerite type'). Cu^{2+} besides Fe^{3+} ions cause individual environments at the M_2 sites ('gartrellite type'). $SrCo_2(AsO_4)(AsO_3OH)(OH) \cdot H_2O$ maintains monoclinic symmetry and represents the first proof of (partial) protonated arsenate groups: 'Sr-Co type'. The As-atom site splits into two crystallographically independent sites. The symmetry restriction of the hydrogen bond is given up. The formation of protonated arsenate groups is controlled by the pH and Eh condition during syntheses.

A further complex variation of a parental structure is verified in the triclinic $MHXO_4$ compounds (monetite, weilite, α - $NaHSO_4$, α - $SrHPO_4$, $HgHPO_4$, and $SrHAsO_4$). The location of the M atoms and XO_4 tetrahedra is roughly the same. There are three topologically distinct hydrogen bonds: (i) One hydrogen atom is located close to an inversion centre forming a symmetry-restricted hydrogen bond. (ii) A short hydrogen bond has the donor and acceptor atoms not related by (average) space-group symmetry. However, the direction of the hydrogen bond (OH dipole) may be inverted. (iii) In total four O atoms are involved into the formation of the third hydrogen bond: their interactions with respect to the H atom differ. The (bifurcated) hydrogen bond is either in or close to an edge in the MO_4 coordination polyhedron. In $Sr(AsO_3OH)$ a superstructure avoids symmetry centers in the vicinity of all the H atoms. Complete order of the H atoms cause mono-protonated anion groups. In the other cases $[XO_3(OH)]_2$ groups are necessarily formed besides $[XO_4(OH)]$ and $[XO_4]$ groups.

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Crystal structures of a natural norbergite, $Mg_{2.98}Fe_{0.01}Ti_{0.02}Si_{0.99}O_4(OH_{0.31}F_{1.69})$, from Sterling Hill, USA, at 0.0001, 4.7, 6.3 and 8.2 GPa conditions were refined using synchrotron radiation and FT-IR spectra of the norbergite under high-pressure conditions were observed up to 15.4 GPa every about 1 GPa.

From X-ray diffraction studies, the linear compressibilities of this specimen were determined as $\beta_a = 2.18(4)$, $\beta_b = 2.93(7)$ and $\beta_c = 2.77(7) \times 10^{-3} \text{ GPa}^{-1}$, respectively. The isothermal bulk modulus of this sample was 113 (2) GPa with a pressure derivative $K' = 4$. Systematic relationships between K and Filling Factor, K and Packing Index showed simply positive linear correlations. The R-value at each pressure was yielded from crystal structure analyses between 3.8 % and 5.3 % through this experience. Using the results, the polyhedral bulk moduli were calculated for each polyhedron in this structure using the Birch-Murnaghan equation of state assuming $K' = 4$. The tetrahedral and octahedral bulk moduli of norbergite were $K_{Te} = 293(15) \text{ GPa}$, $K_{M2} = 106(5) \text{ GPa}$ and $K_{M3} = 113(2) \text{ GPa}$. K_{tet} is significantly larger than that of olivine (1.9 Mbar, Kudoh and Takeuchi, 1985), but K_{M2} and K_{M3} were significantly smaller than those of olivine and chondrodite. From the results of the FT-IR observations, with increasing pressure, the peaks (3557, 3585 and 3667 cm^{-1}) shifted to the higher wavenumber ($dv/dP = 2.4$, 2.7 and 3.8 $\text{cm}^{-1}\text{GPa}^{-1}$, respectively) and the 3363 cm^{-1} peak shifted to the lower wavenumber ($dv/dP = -1.8 \text{ cm}^{-1}\text{GPa}^{-1}$). The lower shift indicated that the hydrogen bonding was strengthened with increasing pressure. The small peak jump was observed around 11.3 GPa in the lower shifting peak. This observation indicated that the hydrogen position was significantly changed at around this pressure.

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Pale green massive veins cutting the Yugoslavian serpentinites consist of 15- and 30-sectors polygonal serpentine (less and more common, respectively), having random textures but becoming stress-oriented close to the vein walls. [100] cross-sections show ordered one-layer and two-layer projected polytypic sequences, as well as disordered multilayer sequences. From sector to sector, these sections always show concerted polytypic alternances, that obey the O-L-R and O-R-L alternance rules in 15- and 30-sectors polygonal serpentine, respectively. Furthermore, [010] longitudinal sections systematically show a unique two-layer sequence. By combining the two projections, we reconstruct the 3D polytypic assemblage of the observed two-layer polygonal serpentine, that from sector to sector consists of alternating M5-M15-M15, or M5-M16-M16 polytypes (using the nomenclature of Dódy 1997).

The individual fibers may be described as cyclically twinned crystals, based upon continuous 1:1 layers, with possible octahedral rotation from one sector to the other. Continuous curved sector boundaries join adjacent sectors, with no tetrahedral sheet inversion; the curved boundaries behave as similar folds and have variable interplanar spacings.

Simulated electron diffraction patterns reproduce all the observed diffraction geometries, even for faulted stacking sequences, and quantitatively explain exotic features such as variable numbers of diffraction cusps and chords.

Additional XRPD reflections are indexed taking into account the different polytypes present in 15- and 30-sectors polygonal serpentines.

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Magnetic alignment is believed to occur only on solids with spontaneous magnetic moments. Ordinary crystals cause alignment by their anisotropy of diamagnetic susceptibility $(\Delta\chi)_{DIA}$, although its possibility has been neglected in both basic and applied science. Here we report that significant rotational oscillation are easily induced by weak field of 1000 G produced by a horseshoe magnet for popular diamagnetic minerals such as apatite, corundum, gypsum, α -quartz, phlogopite and orthoclase. Rotational oscillation of diamagnetic crystal at such low field intensity does not appear in previous literatures. Small $(\Delta\chi)_{DIA}$ above 10^{-8} emu/g is easily obtained from the period of oscillation. The origin of $(\Delta\chi)_{DIA}$ of oxide mineral is explained consistently by assuming that the individual bonding orbital composing the crystal possess constant amount of $(\Delta\chi)_{DIA}$; diamagnetic anisotropy originate from a spatial anisotropy of localized electrons. $(\Delta\chi)_{DIA}$ of a single bond was newly obtained as $3.7 \times 10^{-30} \text{ emu}$ for a hydrogen bond, $1.1 \times 10^{-30} \text{ emu}$ for a T-O bond of tetrahedral $[TO_4]$ unit, and $0.32 \times 10^{-30} \text{ emu}$ for M-O bond of octahedral $[MO_6]$ unit. The origin of the differences between these values is an open question; the spatial distribution of individual bonding orbital can be the cause of this differences. The $(\Delta\chi)_{DIA}$ values are not measured for most of the diamagnetic minerals at present. However, the above model indicate that $(\Delta\chi)_{DIA}$ exceed 10^{-8} emu/g for many of the oxide minerals. Hence $(\Delta\chi)_{DIA}$ can be newly detected for immense number of minerals in various facilities that are not equipped with an electromagnet. Magnetic alignment of grains due to $(\Delta\chi)_{DIA}$ is reported on some organic and inorganic materials. It is generally believed in these studies that the alignment requires a strong field produced by a superconducting magnet. However, almost full alignment is achieved for micron-sized particles at field below 10000 G at room temperature when $(\Delta\chi)_{DIA}$ is larger than 10^{-8} emu/g ; this is because a magnetically stable axes of grains dispersed in fluid at temperature T align almost parallel to field when field-induced energy $(1/2)M\Delta\chi B^2$ of the crystals are one order of magnitude larger compared to Brownian motion energy $(1/2)k_B T$ (M is the mass of the crystal). Hence grain alignment is easily achieved by a permanent magnet for many of the diamagnetic minerals. Attempts to investigate new magnetic effects due to $(\Delta\chi)_{DIA}$ may become popular in various field of magnetic science when magnetically active materials at low field are easily chosen from ordinary minerals.

Double wollastonite chains: topological/conformational varieties and polytypic forms

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Various natural and synthetic phases, mainly calcium silicate hydrates (CSH) compounds, display structures characterized by the presence of double wollastonite chains.

Topological varieties. A wollastonite chain presents three distinct tetrahedra in the repeat unit ('dreier' chains in Liebau's terminology). When the chains are connected to form double chains, the linkage may involve one, two or all three tetrahedra in each chain to give rise to distinct types of 'dreier' double chains in epididymite and elpidite (full condensation of the chains), in okenite (linking of two out of three tetrahedra), in xonolite (linking of one out of three tetrahedra).

Conformational varieties. Whereas the fully condensed double chains are rigid, the less condensed double chains may occur with various conformations: contracted shape and $[-2/m \cdot]$ symmetry (**b** axis is always taken along the chain) in xonolite; extended shape and $[-2/m \cdot]$ symmetry in clinotobermorite; extended shape and $[2m \cdot m]$ symmetry in tobermorite 11A.

Polytypic forms. The building modules in calcium silicate hydrates are the wollastonite chains, with the typical repeat of 7.3 Å and the calcium polyhedral ribbons or layers, with the typical repeat of 3.65 Å: the tetrahedral chains may be connected to the calcium polyhedral ribbons or layers in two distinct but equivalent positions, shifted by 3.65 Å in the **b** direction. This peculiar crystal chemical feature gives rise to various possible polytypic forms displayed by nearly all the CSH compounds.

OD theory presents a very effective way to deal with the polytypic aspects of those phases, in particular in the case of the members of the wide 'tobermorite' group of natural and synthetic compounds. It was just through the application of the OD approach that the real structures not only of clinotobermorite and tobermorite 11 Å (in both normal and anomalous forms), but also of the single-chain products obtained through double-chain disconnection (tobermorite 9 Å, 'clinotobermorite 9 Å', tobermorite 14 Å), have been fully defined.

On the structure of the low temperature phase of the incommensurate $\text{Ca}_2\text{CoSi}_2\text{O}_7$

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The incommensurate tetragonal phase of $\text{Ca}_2\text{CoSi}_2\text{O}_7$ was determined by the treatment of the structure in a (3+2)-dimensional space (Hagiya et al., Acta Cryst. B49, 172, 1993). The results revealed that the coordination number of Ca atoms varies from six to eight in the structure. The magnitude *q* of the primary wave vectors of the modulation waves ($q = 0.2913$ at 293K) in the incommensurate phase increases with fall of temperature and jumps to the magnitude of the low temperature phase. The phase transition is a reversible change with a remarkable hysteresis. Two different structures have so far been reported as the structure of the low temperature phase. One of them is a nearly commensurate structure ($q = 0.324$, $P4$) and stable below 160K (Riester et al., Z. Kristallogr. 212, 102, 2000). Another is a commensurate structure ($q = 1/3$, $P2_12_12_1$) stable below 242.3K (Hagiya et al., Acta Cryst. B57, 271, 2001). The diffraction symmetry of the latter is enhanced to tetragonal by twinning. These phenomena suggest that these two structures may be formed under different conditions.

Using a simulation method, the present investigations have been undertaken to clarify what the most probable structure of the low temperature phase is. By the simulation method we could generate not only the incommensurate structures with various *q*-values but also the structures of the low temperature phase.

Structures of the incommensurate phase are characterized by the formation of CaO_6 polyhedra (28.5% of Ca atoms have a six-coordination) and by the formation of the bundles composed of four arrays of CaO_6 polyhedra along the *c*-axis. More than 21% of Ca atoms participate with the formation of the bundles in incommensurate structures. In the $P4$ structure 22.2% of Ca atoms have the six-coordination, and 11.1% of them contribute to form bundles. However 44.4% of Ca atoms are six-coordinated in the $P2_12_12_1$ structure and all of them form bundles. This difference suggests that the $P2_12_12_1$ structure should be the most probable structure of the low temperature phase, because the number of the bundles in the incommensurate structure increases with temperature fall.

The simulation indicated also that the variation of the modulated structure including the transition to the low temperature phase is caused by systematic phase changes of the modulation waves induced by the change of the *q*-values.

Short-range order, non-linear chemical variation and phase transitions in scapolites

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The scapolite structure consists of two interpenetrating frameworks: $[(\text{Si,Al})_{12}\text{O}_{24}]$ and $[\{\text{Na,Ca}\}\{\text{Cl,CO}_3\}]$. The unstrained dimensions of each framework are significantly different (as determined by the valence-matching principle and distance-least-squares refinement), and there is an intrinsic steric stress between the two frameworks, the magnitude of which is a function of chemical composition. Evidence of the resulting structural strain is the large U_{eq} values for Cl at the A-site across the marialite-meionite series and the large U_{eq} values for (Na,Ca) at the M-site in marialite. Local bond-valence considerations indicate extensive SRO (Short-Range Order) about both Cl and (CO₃). The short-range bond-valence requirements of the (CO₃) group are satisfied by coordination Ca₄ at ~Me₁₀₀, NaCa₃ at ~Me₈₀, Na₂Ca₂ at ~Me₅₅, Na₃Ca at ~Me₄₀, and Na₄ at ~Me₂₀. The driving mechanism for the $I4/m \rightarrow P4/n$ phase-transitions is the coupling of SRO between the $[(\text{Si,Al})_{12}\text{O}_{24}]$ and $[\{\text{Na,Ca}\}\{\text{Cl,CO}_3\}]$ frameworks. At a composition of ~Me₅₀, local bond-valence requirements force the local clusters Na₂Ca₂ to occur in a trans configuration ($\{\text{NaCaNaCa}\}$ around the A-site). Anion bond-valence requirements also force these clusters to link to each other through Na-O-Na or Ca-O-Ca linkages, and hence the combination of SRO and bond-valence requirements gives rise to LRO (long-range order). In turn, Al and Si are constrained to order at different tetrahedra, an ordering that breaks the topological $I4/m$ symmetry and gives rise to two distinct tetrahedra, T(2) and T(3), dominated by Al and Si, respectively. The result is the $P4/n$ scapolite structure. As Na or Ca become dominant, the number of Na₂Ca₂ clusters decreases, the effectiveness of the symmetry-lowering mechanism lessens, and the degree of order of Al and Si over the T(2) and T(3) sites decreases toward both the marialite and meionite ends of the series. At the compositions ~Me₂₅ and Me₇₅, the clusters NaCa₃ and Na₂Ca dominate, the driving mechanism for lower symmetry vanishes and the structures revert to maximal $I4/m$ symmetry. The non-linear variations in bulk composition across the marialite-meionite series are also the result of SRO of M-site Na and Ca around the A-site [which is occupied by Cl in end-member marialite and (CO₃) in end-member meionite]. The local valence-sum rule shows that Cl cannot occur in I-centered meionite (except in the presence of K, where it occurs as $\{\text{K}_2\text{Ca}_2\}\text{Cl}$ clusters).

Distribution of Fe³⁺ and Ti⁴⁺ in $\text{CaFe}^{3+}_{0.8}\text{Ti}^{4+}_{0.2}\text{Al}_{1.2}\text{Si}_{0.8}\text{O}_6$ -pyroxene: X-ray and TOF neutron Rietveld study

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CaFeAlSiO_6 -pyroxene (Esseneite; Es) contains $\text{CaTiAl}_2\text{O}_6$ -component (Titanium pyroxene; Tp) as much as 23 mol% at 1 atm and 1200°C (Onuma and Akasaka 1980; Akasaka and Onuma 1980). In the pyroxene solid solutions on the join Es–Tp (Cpx_{ss}), Si is less than a half of the tetrahedral site. Although Onuma and Akasaka (1980) and Akasaka and Onuma (1980) considered that Al fills the deficiency of Si at the tetrahedral site by the $\text{Fe}^{3+}_{\text{VI}} + \text{Si}^{4+}_{\text{IV}} = \text{Ti}^{4+}_{\text{VI}} + \text{Al}^{3+}_{\text{IV}}$ substitution, the X-ray Rietveld and ⁵⁷Fe Mössbauer studies for the Cpx_{ss} by Akasaka et al. (1999) revealed the strong preference of Ti for the tetrahedral site. In this study, Es₈₀Tp₂₀-Cpx_{ss} have been investigated by using X-ray and TOF neutron Rietveld methods to determine site occupancies of Fe³⁺ and Ti⁴⁺ at the octahedral and tetrahedral sites.

Es₈₀Tp₂₀-Cpx_{ss} was synthesized from oxide mixture at 1240°C in air for 45 days. Although the Cpx_{ss} was associated with 1.2 % gehlenite, 1.2 % ilmenite and 3.1 % hibonite (mass fraction), its chemical composition was almost the same as that of Es₈₀Tp₂₀-starting material. X-ray powder data was taken between 10° and 130° in 2θ using a step interval of 0.02° (Cu Kα-radiation at 35 kV and 25 mA). A time-of-flight (TOF) powder diffractometer, VEGA, has been operated at the KENS pulsed spallation neutron source. The resulting X-ray and neutron diffraction data were analyzed by the Rietveld method with RIETAN-2000 (Izumi and Ikeda, 2000) and RIETAN-TN (Izumi et al., 1987).

The structural refinements are characterized by $R_{\text{wp}}=13.56\%$ and $S=1.56$ for X-ray diffraction pattern, and $R_{\text{wp}}=3.98\%$ and $S=1.998$ for neutron diffraction data. The unit-cell parameters are $a=9.8209(4)$, $b=8.7802(3)$, $c=5.3827(3)$ Å, $\beta=105.692(3)^\circ$ for X-ray data, and $a=9.823(3)$, $b=8.7866(3)$, $c=5.3846(1)$ Å, $\beta=105.731(1)^\circ$ for neutron data. By site-scattering refinement (Hawthorne et al. 1995), the site-scattering values of 20.67 and 6.106 epfu were given for the X-ray and the neutron diffraction data, respectively. On the basis of these site-scattering values, the site occupancies of Fe, Ti and Al at the M1 and T sites were determined, and atomic contents at the M1 and T sites were given as follows: $(\text{Fe}^{3+}_{0.53}\text{Ti}^{4+}_{0.08}\text{Al}_{0.39})_{\text{M1}}(\text{Fe}^{3+}_{0.26}\text{Ti}^{4+}_{0.12}\text{Al}_{0.81}\text{Si}_{0.81})_{\text{T}}$. Thus, M³⁺:M⁴⁺-ratio in the tetrahedral site is 1.07:0.93, indicating that the Al-avoidance rule is not hold for in the Es–Tp Cpx_{ss}.

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The stannite-kesterite join studied by neutron diffraction

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Stannite (Cu₂FeSnS₄, space group $I\bar{4}2m$) is one of the best-known sulfide mineral, not only because of its economical importance as a tin ore, but also because of its structural and physical characteristics. The Zn-analogue Kesterite, Cu₂ZnSnS₄, is closely related, but assigned to different space group ($I\bar{4}$), because of site exchange between half of the Cu and the Fe (Zn) atoms. The structures of both consist of a ccp array of sulfur atoms, with metal atoms occupying one half of the tetrahedral voids. They are topologically identical, but different in the distribution of Cu⁺, Zn²⁺ and Fe²⁺ among the positions (0,0,0), (0,½,¼) and (0,¼,¾).

The work presented here will clarify the symmetry problem along the Stannite-Kesterite join Cu₂Zn_{1-x}Fe_xSnS₄. This has been the object of considerable studies described in literature before, but always done by Rietveld refinement of X-ray diffraction data, notwithstanding that Zn²⁺ and Cu⁺ have equal atomic scattering factors. To solve that problem neutron powder diffraction (experiments at Berlin Neutron Scattering Center (BENSNC) with $\lambda=1.79$ Å) was applied, because of the different neutron scattering lengths of Zn²⁺, Cu⁺ and Fe²⁺. The samples used in this study were synthesized by solid state reaction from the elements. Cation site occupancies and structural parameters were determined by Rietveld analysis of the neutron diffraction data.

It was revealed that in Kesterite, Cu₂ZnSnS₄, the both cations Cu⁺ and Zn²⁺ not order in the way described in literature. Our results show Cu on (0,0,0) with the remaining Cu and Zn are statistically distributed on (0,½,¼) and (0,¼,¾). The way from Stannite to Kesterite was found to be a three stage cation re-ordering process involving Cu⁺, Zn²⁺ and Fe²⁺. Starting from Stannite, Cu₂FeSnS₄ with $I\bar{4}2m$, all substituted Zn occupies first the structural site (0,0,0) replacing Fe. In the region $0.35 \leq x \leq 0.7$ the re-ordering takes place: Cu starts to occupy (0,0,0) and forces Zn on the (0,½,¼) site, at $x \sim 0.7$ the (0,0,0) site is nearly random occupied by Cu, Zn and Fe. For $x > 0.7$ Cu occupies (0,0,0) more than Zn and Fe and the fraction of Cu and Zn on (0,½,¼) becomes more and more equal. This process results at $x=1$ (Kesterite) in a fully occupancy of (0,0,0) by Cu, the Zn and remaining Cu are disordered at (0,½,¼) and (0,¼,¾) assuming $I\bar{4}$ or (0,½,¼) assuming $I\bar{4}2m$ respectively.

Our studies present impressively the power of neutron diffraction in solving the symmetry problem along the Stannite-Kesterite join.

Tourmaline-fluid interactions: Fluorine monitor and the role of tourmaline crystallography

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Tourmaline effectively partitions F relative to many hydrous minerals and can be a monitor of the F in coexisting fluids. However, F contents in tourmaline are a function of external factors such as the F concentrations in the coexisting fluid and, probably, PT conditions and internal factors such as crystallographic surface energy constraints. The proper interpretation of the relation between tourmaline chemistry and fluid compositions depends on the relative influences of both factors.

The general formula of tourmaline is XY₃Z₆(T₆O₁₈)(BO₃)₃V₃W; with the most common site occupancies being: X = Ca, Na, K, ^X□ (vacancy); Y = Li, Mg, Fe²⁺, Mn²⁺, Al, Cr³⁺, Fe³⁺; Z = Al, Mg, Fe³⁺, Cr³⁺; T = Si, Al; B = B; V = OH, O; W = OH, F, O. Of particular importance is that F occurs at a single anion site, the W site. Incorporation of F in this site is influenced by the occupancy of the X site. The X-site is generally occupied by cations of variable charge (Na⁺ or Ca²⁺) and/or is vacant (zero charge). Because of local bonding of the W site anion to three neighboring Y-site cations and the X-site cation, the charge of the X-site cation affects the F occupancy in the W site. Infrared and Raman spectroscopy measurements and local charge balance considerations establish that F for OH substitution will be favorable where the Y site charge of 6+ such as where the X-site is occupied by Na⁺ or Ca²⁺. However, F substitution will be unfavorable where there is a 7+-charge (or more) environment such as proximal to the three Y sites in ^X□ tourmaline. Natural tourmaline data verifies the antipathetic relationship between the magnitude of ^X□ and concentration of F. A summary of >600 tourmaline analyses from different tourmaline varieties illustrates that in tourmalines not dominated by ^X□, F concentrations range from 0-1.0 apfu. However, tourmalines with more than 0.5 ^X□ there is little or no F present in the tourmaline. In addition to the crystallographic factors, F concentrations are also a function of the F concentrations in the coexisting fluid phase. This influence can be illustrated from a study of fibrous tourmaline replacing preexisting tourmaline in a pegmatite pocket that apparently has undergone rupture. Change in the tourmaline fiber compositions reflect that of a varying infiltrating fluid. Empirical calibrations of HF contents in the fluid are being correlated against fluid-biotite systematics.

The Atomic Arrangement of Lunar Merrillite

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The atomic arrangement of lunar merrillite, ideally (Na_{2-x})(Mg, Fe²⁺, Mn²⁺)₂[Ca_{18-x-y}(Y,REE)_{x-y}]₁₈(P_{14-z}Si_z)₁₄O₅₆, has been refined to R = 0.0452 using X-ray diffraction data recorded on a CCD detector; previous attempts at structure solution using a point detector were not successful because of the poorly-crystallized nature of the lunar material. The atomic arrangement of lunar merrillite has a structural unit of [(Mg,Fe)(PO₄)₆]₂¹⁶⁻ that forms a "bracelet-and-pinwheel" unit that is common in hexagonal-closest-packed layers. The individual structural units are not polymerized, and exist in layers at z = 1/6, 1/3, 1/2, 2/3, and 5/6. In lunar merrillite, the [(Mg,Fe)(PO₄)₆]₂¹⁶⁻ structural units are linked by a [(Ca,REE)₁₈Na₂(PO₄)₂]₂³²⁺ interstitial complex, formed of CaO₈, Ca₂O₈, Ca₃O₈, NaO₆, and P₁₀O₄ polyhedra. Ordering of the cations and substituents is discernable in the calcium and phosphorous sites. There has long been speculation regarding the relationship between merrillite and terrestrial whitlockite, and the solution of the Fra Mauro merrillite atomic arrangement allows distinction of the lunar and terrestrial phases. Lunar merrillite and terrestrial whitlockite are largely similar atomic arrangements, but differ due to the presence or absence of hydrogen. In whitlockite, H is an essential element, and used to balance charge. H is incorporated into the whitlockite atomic arrangement by disordering one of the phosphate tetrahedra, and forming a PO₃(OH) group. Lunar merrillite is devoid of hydrogen, and thus no disordered tetrahedral groups exist. Charge balance for substituent Y and REE (for Ca) and Si (for P) in merrillite is maintained by vacancies in a partially-occupied Na site, with charge balance yielding (Y,REE) + Na - Si = 2 in merrillite. The structure solution demonstrates the effectiveness of the CCD detector in unraveling previously-intractable diffraction data, and urges that the lunar material be reexamined using this new technology.

Plumbian Microcline and the Pb-dominant Analog of Celsian Included in Amazonitic K-feldspar, Mount Ploskaya, Kola Peninsula, Russia

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The NYF-type granitic pegmatites exposed at Mount Ploskaya, western Kevy, in the Kola Peninsula of Russia, of Paleoproterozoic age, contain at least two generations of perthitic amazonitic K-feldspar, one bluish (0.2 wt% PbO) and one greenish (1.2% PbO). Published reports pertain to the bulk properties only. We have characterized the specimens on the basis of X-ray diffraction, electron-microprobe and laser-ablation ICP-MS data. Back-scattered-electron images reveal two types of micrometric grains as inclusions in the amazonitic microcline, both with a notably greater intensity of luminescence than the host. The domains of the first type are non-uniformly disseminated within the matrix; they form strings of consistently aligned parallel films in two perpendicular directions and, to a lesser extent, irregular grains and veinlets, typically 10-30 : m across. The films propagate along cleavages, and presumably result from fluid-based replacement along microfissures and other discontinuities. The contact with the matrix is sharp. These tiny domains consist of Pb-enriched K-dominant feldspar containing from 6 up to 10.8% PbO. The maximum is equivalent to 20% PbAl₂Si₂O₈. In addition, we document the exceptional presence of even smaller (<10 : m) elongate grains of a second type, found in cracks in association with cerussite. The energy-dispersion spectra reveal the characteristic peaks of Pb, Si, and Al only. Quantitative analyses gave 39.2% PbO, 22.4 wt.% Al₂O₃ and 30.3% SiO₂, with traces of K, Fe and Ba, corresponding to the formula Pb_{0.8}Al_{1.8}Si_{2.2}O₈ calculated on the basis of eight atoms of oxygen. The low analytical total (93.3 wt.%) may reflect the presence of H₂O or missing light elements. The coexistence of this phase with cerussite along cracks indicates that it formed from a hydrothermal fluid during the cooling of the pegmatite. Insofar as part of the Pb in the plumbian microcline host accommodates Pb in a defect [2K⁺ = Pb + G], it seems likely that upon Al-Si ordering and exsolution reactions, the lead was progressively ejected from the host structure as it dissolved and reprecipitated. This is the first report of a Pb-dominant analogue of celsian in nature, but the phase is readily synthesized. We continue our search for coarser material of this new mineral species.

Major precision and accuracy benefits from direct least-squares extraction of crystal-chemical parameters in $P6_3/m$ eco-apatites

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The $P6_3/m$ apatite structure type is a flexible framework that is capable of trapping metals (Pb, Cd, As, V, Zn), rare-earth elements (La, Ce, Pr, etc.) and actinides (Pu, Cm) within densely packed "eco-apatites". With apatites being under consideration as safe storage materials for toxic elements from incinerator fly ash or high-level radioactive nuclear waste, solid-oxide fuel cell electrolytes, catalysts and environmental remediation applications, a predictive tool that can tailor apatite compositions with specific structural characteristics is of interest.

A crystal-chemical parameterization has been developed for $P6_3/m$ apatites. It involves 10 parameters and 4 constraints allowing prediction of unit-cell parameters and all atomic coordinates. It was shown to be equivalent to the regular crystallographic description with 14 parameters (a, c, 12 atomic coordinates). The crystal-chemical flexibility of the model was examined against both the published experimental data for 18 apatite end-members and ab initio modeling of those materials. Observed correlations between those 10 algebraically independent crystal-chemical parameters showed a degree of flexibility that allowed cations with diverse radii and valences to be accommodated within this flexible structure type. Results from ab initio modeling were shown to agree with only the very best single-crystal results, opening the way to modeling of $\text{Ca}_5(\text{VO}_4)_3\text{Cl}$, $\text{Cd}_5(\text{VO}_4)_3\text{Cl}$, $\text{Ca}_5(\text{CrO}_4)_3\text{Cl}$, $\text{Cd}_5(\text{CrO}_4)_3\text{Cl}$, and $\text{Pb}_5(\text{CrO}_4)_3\text{Cl}$ eco-apatites known to exist but awaiting experimental crystal-structure determinations.

The algebraic equivalence of crystallographic and crystal-chemical parameterizations invites direct least-squares Rietveld refinement on crystal-chemical parameters. A TOPAS script prepared for this purpose showed that precision increased by nearly an order of magnitude in the least-squares e.s.d.s for directly extracted versus indirectly extracted crystal-chemical parameters, i.e. those obtained indirectly by analysis of atom coordinates derived by regular Rietveld refinement. Addition of random noise to experimental data exposed the much greater spread of indirectly extracted crystal-chemical parameters. Directly and indirectly extracted results laid many e.s.d.s apart for all 10 crystal-chemical parameters. Accuracy, as judged by comparison of Rietveld results with single-crystal results, was in favor of directly extracted crystal-chemical parameters in all cases. A Singular-Value-Decomposition approach to the assessment of the numerical stability of the two least squares schemes showed their numerical stability to be similar. We are currently implementing this novel approach to the direct extraction of crystal-chemical parameters from actual Rietveld profiles of synthetic eco-apatites together with ab initio modeling with the goal of systematizing their crystal chemistry. This work was funded as a joint research program between NRC (Canada) and A*STAR (Singapore).

P08-01

High-index twins in minerals

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The classical reticular description of twins distinguishes four main types on the basis of the values of the twin index n and of the obliquity ω : merohedry ($n = 1$, $\omega = 0$), reticular merohedry ($n > 1$, $\omega = 0$), pseudo-merohedry ($n = 1$, $\omega > 0$) and reticular pseudo-merohedry ($n > 1$, $\omega > 0$). This classification makes use of only one sublattice of (quasi-)restored nodes; the twin index n being usually within the Friedelian's empirical limit of 6. High-index twins in minerals are not rare in the literature, e.g. pyrite and galena {052} twins ($n = 29$), but, as shown recently by the authors, they can often be explained by taking into account that, within the Friedelian limit of 6° on the obliquity, more than one sublattice may be quasi-restored. The fraction of quasi-restored nodes is then contributed by all these sublattices and not only by the one corresponding to the minimal obliquity: the result is a non-integral effective twin index n_E , whose value is normally within the Friedelian limit. Twins in which the quasi-restored nodes belong to more than one sublattice are termed hybrid twins: we have developed an algorithm for the systematic exploration of possible hybrid twins on the basis of the lattice plane/axes quasi-perpendicularity condition. Several examples of hybrid twins in minerals will be presented among which pyrite {052} ($n = 29$, $n_E = 4.8$), galena {052} ($n = 29$, $n_E = 7.2$), forsterite {012} ($n = 13$, $n_E = 2.6$), pyrrargyrite ($n = 7$, $n_E = 3.5$), and klockmannite {130} ($n = 13$, $n_E = 6.5$).

Some high-index twins remain that cannot be interpreted as hybrid twins – for example the $n = 12$ {231} twin in staurolite. In these cases the role of the structural match at the composition plane likely plays a major role.

P08-02

Crystal structure, Space Group, Phase Transition and Octahedral Tilting of the Calcium Titanate Perovskite

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Perovskite-structured compounds are promising materials in current science and technology, and are of fundamental importance in mineralogy, solid-state science and geoscience. The mineral perovskite CaTiO_3 is the parent compound of the perovskite-structured family. It is widely used in electronic ceramic materials and in immobilizing high-level radioactive waste. The structural phase transition of CaTiO_3 has been studied extensively. The present work has been undertaken to examine the structural phase transitions of CaTiO_3 in the temperature range of 296 K to 1720 K [1]. In particular we focus on the possibility of the $Cmcm$ phase between the $Pbmm$ and tetragonal $I4/mcm$ structures by using not only neutron but also X-ray powder diffraction data. With the help of higher angular resolution of the X-ray method, the present work reveals no possibility of the $Cmcm$ phase. The crystal structures of all existing phases are refined by the Rietveld analyses of neutron powder diffraction data with the help of the relatively large scattering length of oxygen in neutron diffraction.

The present work demonstrate that the compound exhibits two reversible phase transitions of orthorhombic $Pbmm$ -tetragonal $I4/mcm$ and of $I4/mcm$ -cubic $Pm\bar{3}m$ at 1498 ± 25 K and 1634 ± 13 K, respectively. No evidence of $Cmcm$ phase is observed between the $Pbmm$ and $I4/mcm$ structures. The structural phase transitions are characterized by the tilt of the TiO_6 octahedron. The tilt systems of the $Pbmm$, $I4/mcm$ and $Pm\bar{3}m$ CaTiO_3 are $\phi_x \phi_y \phi_z^+$ ($\phi_x = \phi_y$), $\phi_x \phi_y \phi_z^+$, and $\phi_x \phi_y \phi_z^0$, respectively. Here the ϕ_x^- , ϕ_z^- , and ϕ_x^0 stand for the out-of-phase tilt angle of TiO_6 octahedron along x axis, the in-phase octahedral tilt angle along z axis, and no octahedral tilting along x axis, respectively. All the tilt angles, ϕ_x^- , ϕ_z^- , and ϕ_x^0 , decreased with increasing of temperature where the critical exponents were about 0.25. The ϕ_x^- and ϕ_y^- of the orthorhombic structure decreased discontinuously to ϕ_z^- of the tetragonal structure or 0° through the $Pbmm$ - $I4/mcm$ transition. The tilt angle, the unit-cell parameters and unit-cell volume discontinuously changed at the $Pbmm$ - $I4/mcm$ transition temperature, indicating the first-order nature. The increase of the cell volume in the $Pbmm$ -to- $I4/mcm$ transition was 0.088 vol. %. In contrast, the unit-cell volume continuously increased and the tilt angle ϕ_z^- continuously decreased with temperature and became 0° at the $I4/mcm$ - $Pm\bar{3}m$ transition temperature, indicating a continuous nature of the transformation.

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P08-03

Incommensurate modulated crystal structure of Ankangite

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Ankangite, A hollandite-type titanate, has been found Shanxi Ankang, China and previous attempts to determine the structure of ankangite with conventional point detector diffractometers indicated an apparent tetragonal unit cell of approximate dimensions. This structure could not be successfully refined due to an incommensurate modulated structure. We have recently recollected single crystal data using a Bruker SMART APEX-CCD system and carried out integration and absorption correction calculations on the main reflections as well as the satellite reflections. Its average structure solved from main reflection data and incommensurate structure has also been found within a $(3 + 1)\text{D}$ formalism. The average structure of ankangite has tetragonal symmetry, space group $I4/m$ with the following cell parameters $a = 10.1408(10)$ Å, $b = 10.1408(10)$ Å, $c = 2.9572(6)$ Å, and $V = 304.108(6)$ Å³ ($Z = 1$). Its crystal refinement yielded the residual factor $R = 5.90\%$ for 23 parameters and 311 independent reflections at a $2\sigma(1)$ level. The crystal refinement of the true modulated structure within the $(3 + 1)\text{D}$ formalism (wavevector: $q^* = 0.444c^*$, superspace group: $I4/m(00\gamma)00$) based on the superspace Direct methods and refined by JANA2000, yielded the residual factor $R = 3.20\%$ for 1463 independent reflections (311 main reflections and 568 first order satellites and 584 second order satellites). In the aperiodic crystal, the modulation results from occupation and position of Ba in the crystal and it would also induce displacement parameter modulated. A displacive modulation wave, acting on only Ba atom, and a modulation wave governing the occupancy probability of Ba sites inside the tunnels are involved in the crystal. The modulated vectors period comes from the period of occupation modulation and modulated direction is the same as positional modulation's direction, and displacement parameter modulation relate to occupational and positional modulation.

Single-Crystal Maximum-Entropy Study on the Electron-Density Distribution of Orthoenstatite

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In X-ray diffraction, it is known that the atomic coordinates obtained from the Fourier series are the same as those given by minimizing the residual factors in the least-squares refinement, if the crystal structure is simple and the Fourier series are corrected for series-termination error. And, a difference-Fourier synthesis provides a mean for the location of hydrogen atoms or bonding electrons, by subtracting out the electron density of other atoms in the crystal structure.

On the other hand, the maximum entropy method (MEM) is a reconstruction technique and can be used in the sense of maximizing a given functional. The MEM in crystallography gives us the deduced electron-density distribution without the use of any structure model and yields an improvement to derive the distribution of bonding electrons from the accurate reflection data (Sakata and Sato, 1990). Since the model-free reconstruction technique requires the reliability of the reflection data, the application must be discussed with more intensity information using single-crystal diffraction data.

Having the Bragg reflection intensities collected with a single-crystal four-circle diffractometer, the MEM treatment generalized as routine work has been tried to produce accurate electron density for relatively complicated structures of orthoenstatite, MgSiO₃. The use of this sample is of great advantage of (1) small absorption and extinction effects with relatively lighter atoms, (2) a large number of independent reflections with orthorhombic large unit cell and (3) difference in electron density detected by different bonding characters of Si-O. The MEM maps derived from single-crystal X-ray diffraction data were compared with difference-Fourier maps (Sasaki et al., 1980; 1982), after optimizing MEM parameters such as resolution and constraint condition. Orthoenstatite has two types of one-dimensional Si-O chains. There is a clear difference between bridging and non-bridging bonds in SiO₄ tetrahedron. It is conclusive that electron-density distributions deduced by the MEM are well compared with those estimated from the difference-Fourier calculation.

Symmetry variations of vesuvianite formed by retrograde metamorphism of gehlenite in high-temperature skarn at Kushiro, Tojo, Hiroshima, Japan

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Vesuvianite is a well-known rock-forming mineral with complex crystal chemistry and structure. High-symmetry (P4/nnc) vesuvianite occurs in metamorphic calc-silicate rocks, mostly in skarn formed at high temperature. Low-symmetry (non-P4/nnc) vesuvianite occurs in rodingites, in veins found in mafic rocks and serpentinites and rarely in metamorphic calc-silicate rocks in which it formed at relatively low temperature during retrograde metamorphism. In low-symmetry vesuvianite, two types of possible ordered arrangements (P4/n and P4nc) exist. There are less research reports on vesuvianites with P4nc symmetry than on those of P4/n symmetry. A rare type of high-temperature skarn is developed in Kushiro, Tojo-cho, Hiroshima prefecture, Japan. The formation temperature of the skarn is estimated at about 800°C, although skarn forms generally at about 500°C. Primary minerals of the high-temperature skarn are gehlenite and spurrite. Vesuvianite formed by retrograde metamorphism of these minerals. The purpose of this study is to clarify the characteristic of the crystal structure of the vesuvianite from the high-temperature skarn. Special attention was paid on the structural and chemical differences among several structural types of the vesuvianite. It is expected that this study sheds light on the formation conditions of different ordering patterns in vesuvianite. 30 small single-crystals were picked up from one hand-specimen collected from the Hirata outcrop, Kushiro. 20 crystals were ground into spheres, but polygonal shapes of 10 crystals were retained without grinding. These crystals were mounted on fine glass capillaries and single-crystal X-ray intensity data were collected on a Siemens SMART three-circle diffractometer with a CCD detector using graphite-monochromatized MoK α radiation (50kV, 40mA). Data were corrected for Lorentz and polarization effects. Subsequent to the X-ray diffraction experiments, electron microprobe analyses were carried out on the same crystals. 30 structure data sets were refined using the SHELX program. The symmetry of vesuvianite was determined by precise analyses of the systematic absences of reflections. Tojo vesuvianites are classified into 3 symmetry types.

(1): P4/nnc high symmetry (2): Mixtures between P4/n and P4nc (3): Almost pure P4nc

Moreover (2) and (3) are both divided into two sub-groups by chemical composition.

(2)a: with hydrogarnet-like substitution for the orthosilicate group (2)b: without hydrogarnet-like substitution

(3)a: with boron and fluorine (3)b: without boron

These groups can also be distinguished by their cell parameters. An almost pure P4/n structure was not found in this study. It can be concluded that the crystals of the above structural types grew during several stages of retrograde metamorphism.

Some kinds of Superstructures of (Ge, Si) Wollastonite

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Three kinds of superstructures of wollastonite whose compositions were Ca(Ge_{0.15}, Si_{0.85})O₃, Ca(Ge_{0.55}, Si_{0.45})O₃ and Ca(Ge_{0.65}, Si_{0.35})O₃ were synthesized. In this abstract, they are called 0.15Wo, 0.55Wo and 0.65Wo. The lattice constants of 0.15Wo, 0.55Wo and 0.65Wo are: (angstrom, degree) a=4X7.949(5), 2X8.016(4), 2X8.038(5), b=7.352(1), 7.421(1), 7.451(1), c=7.093(1), 7.157(2), 7.194(1), alpha=90.06(2), 90.08(2), 89.93(1), beta=95.11(1), 94.86(2), 94.85(2), gamma=103.39(1), 103.44(2), 103.34(1), respectively.

Both of 0.55Wo and 0.65Wo are twice as large as the structure of the basic-wollastonite but their structures are different. Basically, 0.55Wo consists of the two units of the basic-wollastonite along a-axis. The stacking order of 0.55Wo is represented as AA, where A is the unit cell of the basic-wollastonite. The difference between the basic wollastonite and 0.55Wo is the fact that the basic-wollastonite has an inversion center but 0.55Wo has not it. Therefore, the basic-wollastonite includes only the 15 independent atoms but 0.55Wo includes the 60 atoms in the unit cell. As the results of the structure refinement of 0.55Wo, the final R-value was 6%.

0.65Wo consists of the two units of the basic-wollastonite along a-axis, too. However, the X-ray diffraction pattern of 0.65Wo was largely different from that of 0.55Wo and it showed the extinction rule of the pseudo-C lattice. The structure model having the stacking of the basic-wollastonite unit with b/2 displacement was tried and the final R-value was 9% after the structure refinement. Accordingly, the stacking order of 0.65Wo is represented as AB, where A is described above and B is the unit cell of the basic-wollastonite with b/2 displacement.

15Wo is four times as large as the structure of the basic-wollastonite. The possible stacking orders were considered. There were four possible stacking orders and they were shown as AAAA, ABAB, AABB and AAAB. According to their sequences, their characteristics on X-ray diffraction are predicted as the next. The structure having the sequence AAAA will show the strong intensity on the h=4n diffraction. The structure ABAB will show the strong intensity on the h=2n diffraction. The structure AABB will show the extinction rule of the pseudo-C lattice. The last structure AAAB will not show any characteristics on X-ray diffraction. As the result of the structure refinement, the structure having the sequence AAAA was most reasonable and the final R-value was 13% for the triclinic lattice with inversion center.

New monoclinic superstructure of mordenite with 2a x 2b x c cell

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The crystal structure of mordenite, both natural and synthetic, have been extensively investigated since the structure of the Na-exchanged form was first determined in 1961. Natural mordenite from Challis Valley (Idaho, U.S.A.) have been used in many structural studies, and orthorhombic space group Cmc₂, Cmc₂i, and additional space group Cmmm, Immm and Imcm have been proposed so far. The orthorhombic unit cell with a = 18.1, b = 20.5, c = 7.5 Å have been used in all the previous studies.

We report a new monoclinic superstructure of natural mordenite from Challis Valley. X-ray rotation photographs on a*, b* and c* axis were taken with a Nonius KappaCCD diffractometer. In addition to reflections originated from an usual orthorhombic cell, some weak reflections with indexes h = n + 0.5 or k = n + 0.5 (n: integer) were found in the photographs. These reflections clarify a presence of new superstructure with cell dimensions a' = 2a, b' = 2b and c' = c.

Reflections for cell parameters and symmetry were collected with a Nonius MACH3 diffractometer equipped with scintillation counter. They show that cell parameters are a = 18.099(2), b = 20.460(1), c = 7.523(1) Å, α = 90.003(5)°, β = 90.007(6)° and γ = 90.000(5)° for the basic structure and a' = 36.182(6), b' = 41.03(15), c' = 7.521(2) Å, α' = 90.069(34)°, β' = 89.931(17)° and γ' = 90.028(22)° for the superstructure. R_{int} obtained from eighty main reflections indicates an orthorhombic unit cell for the basic structure (R_{int} for mmm: 3.6%). On the other hand, R_{int} obtained from eighty superstructure reflections (R_{int} for mmm: 54.2% and 112/m: 5.3%) show a monoclinic cell (c-unique axis). Eight reflections equivalent in mmm are clearly classified to two sets of four reflections equivalent in 2/m, in the intensity of several indices hkl for superstructure, which demonstrates that the superstructure is monoclinic although the cell-angles are all 90°. The systematic absence of reflections clearly yields the primitive cell rather than A- or B- centered cell. But reflections originated from the superstructure are so weak that the possibility of different cell settings can not be rejected, and this is now under investigation.

Guanacoite, $\text{Mg}_2(\text{Mg,Cu})_3(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$, low-temperature crystal structure and revised chemical formula

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The crystal structure of guanacoite, ideally $\text{Mg}_2(\text{Mg,Cu})_3(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$, monoclinic, $a = 5.459(2)$, $b = 16.808(9)$, $c = 6.917(3)$ Å, $\beta = 100.44(1)^\circ$, $V = 624.1(5)$ Å³, $P2_1/c$, $Z = 2$, has been resolved by direct methods and refined to an R index of 3.09% for 1385 observed [$I_0 > 4\sigma(I_0)$] reflections measured with MoK α X-radiation. The structure contains one crystallographically distinct As site occupied by As⁵⁺ coordinated by four oxygen atoms in a tetrahedral arrangement. In addition, one M site [M(3) site] is occupied only by Mg²⁺ cation coordinated by six oxygen atoms in an anisotropically distorted arrangement and two M sites [M(1) and M(2) sites] are occupied by Cu²⁺ and Mg²⁺ cations coordinated by six oxygen atoms in approximately tetragonal elongated octahedral configurations. Therefore, the chemical formula of guanacoite should be revised to $\text{Mg}_2(\text{Mg,Cu})_3(\text{OH})_4(\text{H}_2\text{O})_4(\text{AsO}_4)_2$ according to these structural results because the chemical variability of guanacoite occurs mainly at the M(1) and M(2) sites. Guanacoite is structurally identical to akrochordite, which belongs to the general family of basic manganous arsenate minerals. The guanacoite structure consists of the edge-sharing octahedral polyhedra running along [100]. The edge-sharing octahedral sheets are held together by O(1), O(2) and O(3) of AsO₄ tetrahedra to form a sheet-like modular unit that is parallel to [001]. Concerning hydrogen bondings assigned to water molecules in this structure, H atoms form an extremely strong hydrogen bonding network between octahedral edge-sharing sheet and the oxygen atoms of the AsO₄ tetrahedron.

Structure and composition of Baltic Sea manganese nodules

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Studies on Baltic Sea manganese nodules are a subject of great interest of mineralogists. These shallow sea iron- manganese nodules are potentially a promising source of many useful metals such as manganese and iron and specially Ni, Co, Cu, etc. The chemical analysis of the major and trace elements reveal following percentage: MnO -28.99; Fe₂O₃ -36.74; P₂O₅ - 4.5; A₂O₃ -4.7; SiO₂ - 18.42; S - 0.51; K₂O -1.3; CaO -2.5; TiO₂ -0.29; ZnO -0.12; Sr -0.13; Ba -0.18, etc. Baltic Sea manganese nodules is characterized by the joint presence of both well crystallize modifications, and fine phases with the lowest order strength (with the contents of roentgen-amorphous component till 50 - 60% at significant concentration of ore component). This fact till now has no enough strict scientific explanation. We examined formation of roentgen-amorphous nano-dimensional manganese oxide from positions of biogenic mineral formation and used electronic-microscopic investigations, XRD, TG-DTA and Mössbauer study.

Electronic-microscopic investigations showed a great expansion of mineralized biofilms on the studied samples. The content of the bacterial mass make (%): MnO - 28.34; Fe₂O₃ - 17.14; SiO₂ - 7.11; CaO - 2.41; TiO₂ - 1.90; Na₂O - 1.74; Al₂O₃ - 1.73; MgO - 1.30; P₂O₅ - 1.25; SO₃ - 1.25; CoO - 0.68; CuO - 0.54; NiO - 0.53; K₂O - 0.50.

We determine that manganese is present in the crystal forms like asbolan, berneseite, δ -MnO₂ and Mn₂O₃. Also we discovered small amount of quartz, feldspar, phillipsite, barite and monazite. Iron mainly as roentgen-amorphous phases in Baltic Sea manganese nodules. Investigations of processes heating at different temperatures showed the phase transformations in nodules. The TG-DTA study indicate that at 600-700°C, iron phase is transformed into haematite. Mössbauer spectrum of the air-dried manganese nodules have a slightly asymmetrical doublet with isomer shift 0.35mm/s, quadrupole splitting 0.92 mm/s and width of the doublet 0.65 mm/s. This indicates that iron is in Fe³⁺ valence state. Mössbauer spectrum of the nodule heated more 600°C have a sextet structure which shows presence of haematite (α -Fe₂O₃) and bixbyite (Mn,Fe)₂O₃. More than 70% of iron fall on haematite.

Hydrogen deficiency in volcanic and plutonic biotite

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Volcanic and plutonic biotites from Yake andesite, Kamitakara rhyolite welded tuff, Unzen dacite and Oyama quartz syenite, vary in oxidation state. Ferrous (or Ferric) content was measured by Mössbauer spectroscopy and/or colorimetry, and hydrogen was by Karl Fischer moisture titrator. The biotite contains 0-2.8 apfu for Fe²⁺ and Fe²⁺/ΣFe ratio is approximately 1, 0.65 and 0. OH content is varying from 0.5 to 2.5 apfu. Although hydrogen is lost by dehydrogenation with ferric-ferrous oxidation, the biotites don't contain sufficient hydroxyl to compensate for lost of hydrogen. Deficient hydroxyl content in the biotites is strongly correlated with Fe³⁺ and also with Ti content. This relation implies that the volcanic and plutonic biotites include Ti-oxy component as well as Fe-oxy component. In spite of various Fe²⁺ content, the only settled ratio (0, 2/3, 1) of Fe²⁺/ΣFe were observed in the biotites. OH absorption peak of infrared spectra, 3550-3700cm⁻¹, has two fine bands (high and low bands), and decrease of high and low bands is dependent on the oxidation of Fe²⁺. The consistency between IR spectra and Ferric-Ferrous ratio suggests that Fe²⁺ oxidizes preferentially in the trans-M(1) site through hydrogenation process, and Fe²⁺ in the M(1) and cis-M(2) sites changes to Fe³⁺ under dehydrogenation-oxidation condition.

Hydrothermal synthesis and crystal structure analysis of RE(CO₃)OH with the hydroxyl-bastnäsite-type structure

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Two mineral species are known for rare earth hydroxycarbonate, RE(CO₃)OH, hexagonal hydroxyl-bastnäsites and orthorhombic kozoites. The major chemical constituents of both minerals are light rare earths with larger ionic radii. The structure of kozoite-(Nd) has already been refined by Rietveld analysis with synchrotron radiation powder diffraction data, whereas crystallographic investigation on hydroxyl-bastnäsite-(Ce) has been insufficient. Hydroxyl-bastnäsite-(Ce) occurs as fine powder, and the occurrence is very rare. Although, no direct determination of space group has been made yet, the same space group as bastnäsite-(Ce) (P6₂c) is proposed for hydroxyl-bastnäsite-(Ce). On the other hand, the crystal structures of the synthetic hexagonal RE(CO₃)OH phases were analyzed with a different space group, P6, for RE = Nd and Dy.

In the present study, a systematical hydrothermal syntheses of the hexagonal RE(CO₃)OH phases were carried out for a series of rare earth elements for the hexagonal RE(CO₃)OH phases to clarify the above problem. The hexagonal RE(CO₃)OH phases were synthesized from the rare earth hydroxides and aqueous solution of formic acid in platinum capsules under hydrothermal conditions of 300-500°C, 600-1000 kg/cm² for 4 days. Single crystals were grown for La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er, and were used for the subsequent XRD study. The single crystal XRD intensity data were obtained with a CCD detector. Full-matrix least-square refinement was done for each data set. All of the present crystal structure analyses gave the same space group and unit cell setting as those previously reported for synthesized materials. The basic structural scheme of the synthetic phases is the same as the literature data. However, it is found that the coordination mode of one of the carbonate anions to the rare earth atom in the structure of the present crystal is different from that reported for Nd(CO₃)OH. The crystal structure of synthesized RE(CO₃)OH (P6) is not isostructural with that of bastnäsite-(Ce), Ce(CO₃)F (P6₂c), though both structures are similar to each other. The present crystal structure analyses suggest that reconsideration on the space group is necessary for hydroxyl-bastnäsite-(Ce), a potential natural analogue of the synthesized RE(CO₃)OH.

Reexamination of yedinite, $\text{Pb}_6(\text{Cl},\text{OH})_8\text{Cr}^{3+}(\text{OH},\text{O})_8$, using single-crystal X-ray diffraction and Raman spectroscopy, and redetermination of the chemical formula

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The crystal structure of yedinite was determined by Wood et al. (1974) and refined to $R = 14\%$. They suggested several possible chemical compositions and the IMA adopted $\text{Pb}_6\text{Cl}_6\text{Cr}(\text{O},\text{OH},\text{H}_2\text{O})_8$. Wood et al. (1974) suggest that the Cr valence should be 6+ based on their short Cr–O bond length (1.82(10)Å). They state that yedinite is the first recognized mineral containing 6-coordinated Cr^{6+} . Due to the rarity of Cr^{6+} , its toxicity, and the high R-factor in the previous study, we undertook a reinvestigation of yedinite with single-crystal X-ray diffraction and Raman spectroscopy. Using 5310 X-ray diffraction intensity data collected on a Bruker X8 Apex CCD diffractometer, the crystal structure of yedinite has been refined to $R_1 = 1.5\%$ with 37 variables and 824 independent reflections. The space group is $R\bar{3}$; $a = 12.8762(2)$ Å and $c = 9.8367(3)$ Å.

Our refinement indicates that Cr is bonded to six OH groups with bond lengths of 1.973(3)Å, consistent with Cr^{3+} in 6-coordination with O^{2-} or OH^- , as observed in chromite and chlorite ($\text{Cr}^{3+}\text{--O}^{2-} = 1.995$ Å and $\text{Cr}^{3+}\text{--OH}^- = 2.008$ Å) (cf. Lenaz et al. 2004; Bailey 1986). Difference Fourier maps reveal the locations of H bonded to O^{2-} atoms in the structure. H atoms were not located in the previous study, and have rarely been found in structures with heavy atoms such as Pb. The refinement also indicates that O, OH, or H_2O substitutes for Cl in about 11% of the sites.

If Cr^{3+} is coordinated to six OH in an octahedral arrangement, then O–H...O groups are oriented subparallel to the c-axis of the crystal with an average O–O separation of ~2.9Å. Therefore we collected polarized Raman spectra, which shows a broad O–H...O stretching peak centered at 3515 cm^{-1} , consistent with an O–O distance of ~2.9Å (Nakamoto et al., 1955). The mode only appears when the laser polarization is subparallel to the c-axis of the crystal, indicating that OH is subparallel to this axis. This observation supports our conclusion that Cr is coordinated to OH.

To test our conclusions, bond valence calculations (Brown, 1981) were undertaken. These verify the valence of Cr^{3+} and show significant underbonding of both O1 and O2 sites. The underbonding can be explained by the presence of OH in both sites, with occupancies of ~0.75 and ~0.25, respectively. This study indicates that the formula of our yedinite is $\text{Pb}_6(\text{Cl}_{0.887}\text{OH}_{0.113})_8\text{Cr}^{3+}(\text{OH}_{0.63}\text{O}_{0.38})_8$.

Site distribution and structural state of Th in fluorapatite determined by single crystal XRD and EXAFS

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Thorium in apatite has been used extensively in geochronologic and petrogenetic studies for decades. Because of its high affinity for Th and other radionuclides and its thermal annealing behavior, there is also great interest in apatite as a solid nuclear-waste form and an engineered contaminant barrier. Fundamental to our understanding of thorium retention and release by apatite are crystal chemical parameters such as site occupancy and structural distortions created by this substituent. Despite the interest in Th in apatite, the basic crystal chemistry of its substitution in the structure is still unknown. There are two cation sites in the apatite structure that can accommodate Th. The Ca1 site has a coordination shell of nine oxygens, and six nearest neighbor oxygens and fluorine surround the Ca2 site. We present the first direct evidence of the site of incorporation and the response of the structure to Th. Single crystal X-ray diffraction data were used to refine the structure and site occupancies of a synthetic fluorapatite with approximately 2 wt% Th in the structure. Extended X-ray absorption fine structure (EXAFS) was used to probe the local structure of Th within the synthetic sample and a natural fluorapatite from Mineville, NY with a Th concentration of approximately 2000 ppm.

Structure refinements of three separate crystals of the synthetic Th doped fluorapatite ($R = 0.0167\text{--}0.02167$), including site occupancies, indicate that Th partitions almost exclusively into the Ca2 site. EXAFS results also indicate that Th substitutes into the Ca2 site and yield Th specific bond distances not obtainable from XRD data. Discrimination of the site of Th occupation

Crystal chemistry of the new asbestiform fluoro-edenite amphiboles of volcanic origin from Biancavilla (Sicily, Italy)

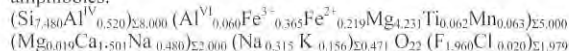
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Natural fluoro-edenite, $[\text{NaCa}_2\text{Mg}_3(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2]$, a new end-member of the Ca-amphibole group, belonging to the edenite→fluoro-edenite series, was found as both prismatic and asbestiform morphologies in the altered lavic products of the Monte Calvario locality, Biancavilla (Mt. Etna, Sicily, Italy). Environmental studies of the area allowed recognizing the fluoro-edenite asbestiform variety as the cause of the health disease in the local population. Crystal chemistry of the prismatic variety was first described by Gianfagna and Oberti (2001), whereas the asbestiform variety has never been studied so far.

Present work reports original crystal chemical data on these asbestiform amphiboles. Chemical investigations on the fibres from Biancavilla were performed through specific methodologies: SEM-EDS standardized microanalyses, and Mössbauer spectroscopy. The specific procedures adopted for material preparation are also reported. Prismatic fluoro-edenite was utilised as chemical reference standard for fibre microanalysis. Mössbauer investigation in the region from -10 to 10 mm/s showed no evidence of magnetic sextets due to Fe oxides or hydroxides. On these bases, both the sharp and the wide components were considered when quantifying the actual Fe^{3+} content, which turned out to be 67.2% of Fe_{tot} .

Combining Mössbauer $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios with microchemical data, the following averaged chemical formula was obtained for the asbestiform fluoro-edenite amphiboles:



Powder diffraction data were collected on a fully automated parallel-beam Siemens D5005 diffractometer, and were evaluated by the Rietveld method using the GSAS crystallographic suite of programs. Cell parameters, positional parameters for all the atoms, and site scattering for O3, M1, M2, M3, M4, A, and Am were refined. In agreement with cation site partition based on both XRPD and Mössbauer data, Fe^{3+} was assigned to M2 and M3 sites and all Fe^{2+} was assigned to M2 site. In particular, Fe^{3+} content of each M2 site is far larger (0.090 apfu) than the analogous content of M3 (0.039 apfu).

The results of this multi-analytical approach to the crystal chemistry of the asbestiform fluoro-edenite amphiboles, in addition to mineralogical interest, is also highly relevant for environmental and health aspects. In fact, detailed chemical and structural characterization of fibres revealed to be extremely useful to understand the reactivity mechanisms between mineral fibres and biological environment.

Architecture and physical properties of Cyndrite $\text{Fe}_{12}\text{mSn}_{42}\text{Pb}_{32}\text{Sb}_{22}\text{S}_{14}$

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For to find novel semiconducting materials promising application in micro- and nano-technology, we focused on cyndrite $\text{FeSn}_4\text{Pb}_3\text{Sb}_2\text{S}_{14}$, due to its narrow band gap, magnetic properties and the possibility to design the morphology. Natural cyndrite appears as lamellae and as cylinders. Its crystal structure is incommensurately modulated. Its band gap energy (E_g) cyndrite was found to be 0.65eV [1]. Paramagnetic behaviour and ferromagnetic effects were observed for $T < 30\text{ K}$ [2], which correlate to cylinder size and Fe(II) -content. For the first time, synthetic crystals of cyndrite, lamellae, cylinders, tubes and scrolls around glass rods, have been produced by CVT from 660° to 630°C with iodine as transporting agent. Depending on the chemical composition of the educt we influenced the morphology of the cyndrites. At excesses of Pb leads cylindrically shaped crystals occurred, while cylindric cyndrites appear for $(\text{Pb}+\text{Fe})/(\text{Sn}+\text{Sb})$ -ratios larger than 0.64 ± 0.02 . For ratios less than that value the growth of lamellar individuals are favoured. The crystal structure (SG P1) is formed by alternating T-slabs (pseudo-tetragonal, PbS-type) and H-slabs (pseudo-hexagonal, SnS_2 -type) with a misfit between them. According to Makovicky [3], subcells can be defined: T-slabs are characterized by $a_0=11.73\text{Å}$, $b_0=5.79\text{Å}$, $c_0=5.81\text{Å}$, $\alpha=90^\circ$, $\beta=92.38^\circ$, $\gamma=93.87^\circ$ and H-slabs show $a_0=23.42\text{Å}$, $b_0=3.67\text{Å}$, $c_0=6.32\text{Å}$, $\alpha=90^\circ$, $\beta=92.58^\circ$ and $\gamma=90.85^\circ$. In both cases there is a long-range incommensurability along the b-axis. Smaller mismatches along the c-direction are accommodated by a semicommensurate modulation of wavelength $6c_0^{||}$ or $6.5c_0^{||}$. For cylindric cylinders the c-direction lies parallel to the "rolling-axis", whereas the curvature follows the b-direction. The a-axis lies perpendicular to both slabs and to the cylinder. For natural cyndrite ($\varnothing > 1\text{ mm}$) the curvature is realized by intergrowth of wedge-shaped segments, inside of which the (100) layers are relaxed. Within the relatively sharp interfaces between adjacent wedge-shaped segments, they are appreciably bent or interrupted. TEM studies revealed a tilt angle of about 14° between adjacent segments. Superstructure models for the (001)-plane indicate an interfacial plane (120). Due to the above mentioned tilt angle, the (120) plane acts as symmetry plane and, therefore, the wedge-shaped segments are in twin-orientation. In contrast to natural cyndrites, the (100) planes inside the segments of synthetic cylinders ($\varnothing < 20\text{ }\mu\text{m}$) are elastically strained. They are continuously bent without a well-distinct interface between adjacent segments. The platelets and lamellae do not show any segmentation. U-I-measurements of natural and synthetic cyndrite cylinders confirm the semiconducting behaviour. Hall-measurements of a synthetic lamella of $\text{Fe}_{10}\text{Sn}_{42}\text{Pb}_{36}\text{Sb}_{15}\text{S}_{14}$ revealed n-type conductivity and an electrical resistance of $0.5\text{ }\Omega\cdot\text{m}$. Optical measurements of E_g ranged from 0.65eV for natural cyndrite cylinders to 1.15eV for synthetic platelets with decreasing $(\text{Pb}+\text{Fe})/(\text{Sn}+\text{Sb})$ -ratio from 0.71 to 0.53.

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XAFS characterization of REE adsorbed on ferrihydrite and manganese dioxides

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Extended X-ray absorption fine structure (EXAFS) spectroscopy has been applied to characterize the structural change effects inferred from the distribution coefficients of REE ($K_d(\text{REE})$) between ferrihydrite ($\text{Fe}(\text{OH})_3$) and Mn dioxides ($\delta\text{-MnO}_2$) and solution. $\delta\text{-MnO}_2$ uptakes light REE (LREE: La, Pr, and Nd) preferentially compared with $\text{Fe}(\text{OH})_3$ and the ratio of $K_d(\text{REE}: \delta\text{-MnO}_2/\text{sol.})$ to $K_d(\text{REE}: \text{Fe}(\text{OH})_3/\text{sol.})$ has the kinked trend at LREE. Each variation pattern of $\log K_d(\text{REE})$ has another irregularity in heavy REE (HREE) and shows the turnoff point between Yb and Lu. These irregular variations in experimental $\log K_d(\text{REE})$ suggest structural changes in REE(III) adsorbed on $\text{Fe}(\text{OH})_3$ and $\delta\text{-MnO}_2$. The local structure of REE(III)-adsorbed samples may be fairly disordered: its local structure is similar to the hydration structure of REE(III) in aqueous solutions. Therefore, EXAFS spectra of $\text{REE}^{3+}_{(\text{aq})}$ have been measured to check the validity of EXAFS analysis; their structural parameters have been compared to those of REE(III)-adsorbed samples. The EXAFS spectra around the L_{III} -edge of REE(III)-adsorbed samples and $\text{REE}^{3+}_{(\text{aq})}$ have been measured in the fluorescence mode at the BL12C of KEK-PF under the atmosphere and at room temperature. The EXAFS spectra indicate that REE(III) adsorbed on $\text{Fe}(\text{OH})_3$ has similar structural parameters to $\text{REE}^{3+}_{(\text{aq})}$. The coordination number of $\text{REE}^{3+}_{(\text{aq})}$ are 9 in LREE and decreases to 8 in HREE, but the REE-O distance of LREE(III) adsorbed on $\text{Fe}(\text{OH})_3$ systematically shorter (about 0.01-0.015 Å) than those of $\text{REE}^{3+}_{(\text{aq})}$. On the contrary, LREE(III) adsorbed on $\delta\text{-MnO}_2$ has a quite distorted nine coordination sphere different from LREE(III) adsorbed on $\text{Fe}(\text{OH})_3$ and $\text{LREE}^{3+}_{(\text{aq})}$. Preferential uptake of LREE(III) by $\delta\text{-MnO}_2$ is characterized by the change of coordination state of LREE(III) adsorbed on $\delta\text{-MnO}_2$. The HREE(III) (Yb and Lu) adsorbed on $\delta\text{-MnO}_2$ and $\text{Fe}(\text{OH})_3$ has the same structure to each other and are characterized by having a second shell of HREE-Mn or HREE-Fe different from $\text{HREE}^{3+}_{(\text{aq})}$. Structural change of HREE(III)-adsorbed samples is expected to be expressed by the decrease of REE-O distance from those of $\text{REE}^{3+}_{(\text{aq})}$. In fact, however, there are slight differences in structural parameters of REE-O shell between them. It is possibly hard to detect the structural change in HREE(III) adsorbed on $\delta\text{-MnO}_2$ and $\text{Fe}(\text{OH})_3$ only by the change of the REE-O distance or the coordination number.

Detailed Structure and Microchemistry of 15-sectored Polygonal Serpentine

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Serpentine has an ideal chemical composition of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and is found in three distinct forms with flat (lizardite), cylindrical (chrysotile) or wave-like (antigorite) layers. This structural variety is related to the degree of dimensional fit between the lateral dimensions of tetrahedral and octahedral sheets. Parachrysotile and Povlen-type chrysotile have also been reported. Polygonal serpentine (PS) is an ambiguous serpentine variety that has been revealed by transmission electron microscopy (TEM) to be structurally restricted to 15 or 30 sectors, and structure models explaining this phenomenon have been proposed by a number of researchers. To examine this structural constraint in more detail, the microstructure of a PS sample from the Bowman Mine in Ontario, Canada (ROM specimen No. M25510) is examined by TEM and scanning TEM (STEM) using an annular dark-field detector. These observations, in conjunction with selected area electron diffraction (SAED) measurements, reveal the specimen to be primarily composed of 15-sectored polygonal serpentine crystals, each of which consists of 2-layer and minor 4-layer and 1-layer polytypes. Most PS crystals in this sample are 50–400 nm in size, although crystals larger than 700 nm can be found. The SAED patterns reveal a five-fold repeated M-O-M structure, where O is an orthogonal sector and M is a monoclinic sector (i.e., b^* and c^* not perpendicular). This serpentine specimen is not a single phase, but is a mixture of two major phases; a 2-layer orthorhombic phase and a 2-layer monoclinic lizardite phase, corresponding to $2H_2$ and $6R$ polytypes, respectively. The two-dimensional elemental map obtained by combining STEM and energy dispersive x-ray spectroscopy analyses shows that the PS crystals exhibit a rim of elevated Fe and Al content, while the core retains the ideal serpentine composition. The substitution of Fe^{3+} or Al for Mg and Si reduces the lateral misfit between tetrahedral and octahedral sheets, giving rise to the unexpected stability of the flat layer in the relatively large PS crystals.

Single-crystal X-ray diffraction study of high-pressure and high-temperature phase of MgFe_2O_4 - post-spinel phase structure -

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[Introduction] Iron and magnesium elements are the major components in the mantle. Oxidation state of iron under high pressure and high temperature in subduction zone is one of the significant subjects for earth science. Andrault et al. reported the high-pressure phase of MgFe_2O_4 (Pbcm $Z=4$) by Rietveld analysis (Phys Chem Minerals 28, 2001). However their diffraction data at high pressure may propose other structures because of the very poor resolution of the powder pattern. In this study we clarified a high pressure and high temperature phase using single-crystal x-ray diffraction experiment.

[Synthesis of the single crystal] The single-crystal of MgFe_2O_4 high-pressure phase was synthesized under 23GPa and 1800°C condition with multi-anvil press (USSA-5000, ISEI). The crystals are black and platy with around 100µm in diameter. The spinel having ferrimagnetic property at ambient pressure was changed to antiferromagnetic of high-pressure phase.

[Experiments] X-ray diffraction experiments were conducted by using of precession camera to determine the space group symmetry that reveals different space group symmetry from the reported. Diffraction intensity measurement was also carried out at PF BL-10A in KEK ($\lambda=0.69028$ Å) and four-circle diffractometer. Rigaku AFC-5S (MoK α $\lambda=0.71069$ Å). The number of the observed reflections was 1136 ($5^\circ < 2\theta < 80^\circ$) at ambient conditions.

[Analysis and discussion] The absorption correction program ABSORB (R. J. Angel 2004) and the least-squares refinement program RADY89 (Sasaki 1989) were used for crystal structure analysis. The unit cell parameters were $a=9.710(2)$ Å, $b=10.154(2)$ Å, $c=2.980(3)$ Å, and the space group was Pbnm; $Z=4$. The variable parameters of the present analysis were scale factor, atomic coordinate (x and y), isotropic temperature factor and site occupancy (metal atom).

The possible atomic positions were arranged on the basis of space group symmetry. They were adopted as an initial model and refined them by full matrix least-squares method. The reliability of the refinement for each initial model was proved by differential Fourier synthesis. The most possible structure of high-pressure and high-temperature phase of MgFe_2O_4 was different from the data reported previously. Mg and Fe atoms occupy six or four coordination sites in four metal sites with disordered mode. At this moment the R factor was converged to 13%, because the peak profiles of X-ray diffraction were very broad, probably because of the disordering of the metal atoms.

Study of the site symmetry change of high-pressure phase of ZnFe_2O_4 by single-crystal structure analysis

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A high-pressure phase of ZnFe_2O_4 converted from spinel structure was reported for CaMn_2O_4 -type (Pbcm), CaFe_2O_4 -type (Pbnm) or CaTi_2O_4 -type (Cmcm) by in-situ X-ray powder diffraction study or in-situ Raman spectroscopic study. In the present study single-crystal structure refinement of ZnFe_2O_4 has been conducted with high accuracy. ZnFe_2O_4 spinel sample was synthesized by heating for 24 h at 1350 K at ambient pressure with a stoichiometric mixture of ZnO and Fe_2O_3 . This sample was confirmed by X-ray diffraction pattern and EPMA. The high-pressure phase of ZnFe_2O_4 was synthesized by using 1000-ton multi-anvil apparatus. The single-crystal samples recovered from about 20 GPa and 1600 K for 30 min were black and grainy with 30 ~ 200 µm in diameter. EPMA composition analysis proved to be $\text{Zn}_{0.92}\text{Fe}_{2.08}\text{O}_4$. We conducted single-crystal X-ray diffraction structure analysis at ambient condition. Precession photographs indicate that the space group was Pbam (No.55) or Pba2 (No.32) by extinction rules. Space group and structure were different from those reported previously. Moreover, remarkable diffuse streaks in the direction parallel to $\langle 100 \rangle$ were observed. The lattice parameters were $a=9.698(6)$ Å, $b=10.242(6)$ Å, $c=2.989(6)$ Å from peak refinements of 25 reflections by four-circle diffractometer. Total observed reflections were 1142 with $2\theta < 70^\circ$. The intensity data were corrected for absorption by profile approximation. Absorption correction program is ABSORB6.0 (R. J. ANGEL 2003). Because of unknown structure, a possible candidate of crystal structure of the high-pressure phase of ZnFe_2O_4 was obtained by direct methods (SIR-92). Using thus obtained structure for the initial structure parameters, least-squares refinement was executed by least-squares program is RADY89 (S. Sasaki 1989). The reliability factor of the refinement using 195 reflections was converged to $R=9.8\%$. The characteristics of the high-pressure phase of ZnFe_2O_4 are that a part of Zn occupies six coordination sites rather than four coordination site, and the large temperature factors of cations are caused by the remarkable diffuse streaks observed by precession camera.

Relics of samarskite structure in a metamict ABO₄ mineral and its high-temperature transformations

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A mineral predetermined as samarskite and originating from Beinmyr, Iveland, Norway, was found to be amorphous to X-rays. The chemical analysis yielded the empirical formula (REE_{0.381}Ca_{0.241}Fe_{0.207}U_{0.142})_{90.971}(Nb_{0.764}Ta_{0.236}Ti_{0.065})_{Σ1.091} that fits quite well to the one of the assumed structural models for samarskite. Due to the metamict nature of the mineral, the structure recovery was induced by annealing experiments in air at 400, 500, 650, 800 and 1000°C. The sample portions were also heated in N₂ and in slightly reductive Ar/H₂ atmosphere at 600, 1000 and 1300°C. The annealing experiments in air showed the start of recrystallization at 650°C with crystallization of a pyrochlore phase and the occurrence of a new phase at 1000°C, which can be characterized as a proposed high-temperature samarskite phase with wolframite-type structure (s.g. P2/c, a=5.63(1) Å, b=9.93(2) Å, c=5.19(1) Å, β=93.6(2)°). The results of the annealing experiments in N₂ and Ar/H₂ atmosphere show similar recrystallization sequences like the experiments in air for 600 and 1000°C. At 1300°C, the phases that crystallized at lower temperatures are still present and there is no indication of new phases or phase transitions. Different atmospheric conditions during recrystallization seem to influence the heating products since the high-temperature samarskite phase is observed only for the mineral heated in air. For N₂ and Ar/H₂ atmosphere beta-fergusonite seems to be the most probable high-temperature phase along with pyrochlore. The variability of recrystallization of samarskite should be attributed to complex chemical composition, stability of the original structure, annealing conditions and heavily metamictized crystal structure, thus imparting the identification of the original structure in the thermally untreated sample. TEM micrographs of the unheated samarskite reveal the preservation of the original structure fragments in a predominantly amorphous mineral matrix. These crystalline domains show lattice fringes with d-values which could be assigned to a presumed low-temperature samarskite phase. SAED patterns obtained for the unheated sample confirmed these indications of the samarskite structure, which can be considered as the original one. The patterns might be indexed on an orthorhombic cell with Pbcn space group and calculated unit cell parameters a=5.69(2) Å, b=4.91(2) Å, c=5.21(2) Å. The low-temperature samarskite phase could be envisaged as a columbite-related structure assuming octahedral coordination for B-cations and octahedral or higher coordination for A-cations.

First in situ X-ray identification of coesite and retrogressed quartz on a glass thin section of ultrahigh-pressure metamorphic rock and their crystal structure details

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To ensure the presence of coesite and its transformed polymorph, quartz, in UHP rocks and to examine the relic of the phase transformation, crystal structures were analyzed by single crystal X-ray diffraction directly using the rock thin section mounted on a slide glass. The rock sample used is a coesite-bearing eclogite in the Sulu UHP terrain, eastern China. The crystal structures were successfully determined by this new method and the presence of coesite and quartz in UHP rocks are identified for the first time by X-ray diffraction. The R(F) converged to 0.046 for coesite and 0.087 for quartz. The displacement ellipsoids for coesite and quartz are larger than that previously reported for these two phases, and is consistent with expected effects of trapped strain due to the phase transformation from coesite to quartz during exhumation from the Earth's mantle.

This paper is the first report of single crystal X-ray diffraction of a rock thin section on a glass slide and establishes the technique, and provides proof-of-concept of the method. Although the mineral species included in a thin section can often be identified by other methods, such as Raman spectroscopy, an advantage of the reported method is that it can be applied to any mineral in a thin section, and not just to the UHP minerals. Moreover, it is applicable to an unknown or new mineral in a thin section, discarding the spots of known minerals and constructing a lattice from the residual spots to find the structure of the unknown phase.

Reexamination of renegeite and strontio-orthojoaquinite from Ohmi-Itoigawa region, central Japan by TEM

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Varieties Sr-bearing minerals occur in tectonic block such as jadeite from serpentinite mélange exposed at Ohmi-Itoigawa region. Six Sr-bearing new minerals from this area have been reported. Crystal structure of renegeite and strontio-orthojoaquinite have been determined, however we carried out HRTEM observation and reexamined the structure. Renegeite crystals were very small, so HRTEM method is useful for these fine grained minerals.

Renegeite (Sr₄ZrTi₄(Si₂O₇)₂O₈) is Sr-Zr analogue of perrierite-(Ce)(Ce₄MgTi₃(Si₂O₇)₂O₈). We found orthorhombic polymorph of renegeite from mineral grain which was apparently renegeite-like. This mineral species has not been reported. The orthorhombic polymorph is over 5 μm in size and occur in parallel intergrowth with monoclinic renegeite.

Strontio-orthojoaquinite((Na,Fe)₄Ba₄Ti₄(Sr,Ba,Nb,REE)(O,OH)₄(Si₄O₁₂) · 2H₂O) belongs to the joaquinite group. Strontiojoaquinite (monoclinic) is another polymorph. Only strontio-orthojoaquinite in joaquinite group mineral had been found in Japan. In this study, monoclinic structure was found in HRTEM examination. Monoclinic structure area is in parallel intergrowth with orthorhombic structure. HRTEM image shows that orthorhombic unit cell is composed of two monoclinic unit cells with twinning relation on (001). This structural property is based on the fact that orthorhombic joaquinite structure has pseudo mirror plane (Cannillo et al., 1972). Furthermore, we found another orthorhombic polymorph of 4O by HRTEM image. The orthorhombic joaquinite (Strontio-orthojoaquinite) is composed of two monoclinic unit cells, but this 4O orthorhombic structure is composed of four monoclinic cells with twinning-like relations.

These two minerals occur in different conditions in the same Ohmi-Itoigawa region; renegeite occurs as secondary veins in jadeite. Strontio-orthojoaquinite is spotted aggregate or lens-like in albite. Formation conditions of structure varieties of renegeite and strontio-orthojoaquinite are related to mother rock formation processes. We will discuss these formation conditions. Thus, HRTEM method is powerful tool even for descriptive mineralogy.

In situ high temperature single crystal X-ray diffraction study of natural heulandite at 150 °C

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In situ high-temperature crystal structure analysis of heulandite from Moharastra, India was conducted at 150°C to study the mechanism of dehydration to heat collapse phase. Both room temperature and high-temperature X-ray diffraction intensities of a single crystal (400 x 280 x 160 μm) were measured using Rigaku R-axis IV⁺ diffractometer (MoKα radiation, 50kVx80mA) with imaging plate and the U-shaped furnace (Huber high temperature attachment:231).

The chemical composition of the specimen was determined by E.P.M.A. as (Na_{1.14}K_{0.40}Ca_{3.64}Sr_{0.21})(Al_{0.21}Si_{26.88})O₇₂·25.86H₂O (number of H₂O molecules is from the result of structural refinement). At room temperature, the specimen has monoclinic, C2/m symmetry [a=17.761(3) Å, b=17.838(2) Å, c=7.431(1) Å and β=116.45(1)°]. Structural refinement of the data at room temperature yields the final R value 0.049 and Rw 0.123 for 1832 independent reflections, applying the weight w=1/[σ²(Fo²)+(0.0351p)²+23.740101p] where p=[2Fc²+Max(Fo²,0)]/3 for each reflection with anisotropic temperature factors. At 150 °C, the crystal has still monoclinic C2/m symmetry [a=17.762(3) Å, b=17.586(2) Å, c=7.452(1) Å, β=116.81(1)°]. Result of the structural refinement of the data at 150°C yields the R value 0.077 and Rw 0.206 for 1672 independent reflections, applying the weight w=1/[σ²(Fo²)+(0.0913p)²+36.4561p] where p=[2Fc²+Max(Fo²,0)]/3 for each reflection with anisotropic temperature factors.

The result of structural refinement at 150 °C showed that the size of the channels were compressed and elongated with the unit cell volume decrease of 1.4% compared with the room temperature data. Three cation sites found at room temperature were Na1, Ca2 and K3. The result of the crystal structure analysis at 150°C revealed that cations move towards the channel wall. Cation occupancy at Na1 site decreases more than at Ca2 site at 150°C, while the occupancy of K3 site increases.

Anharmonic thermal vibrations and disorder of atoms in tourmaline

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Elbaite (space group R3m), a Li-bearing tourmaline with general formula of $XY_3Z_6(BO_3)_3Si_6O_{18}W_4$, has 5 kinds of cations and 8 kinds of O (including W). Of the structural studies of tourmaline, those of Gabrielle Donnay and her group were unique in focusing on the structural aspects of the primary pyroelectricity (Donnay, 1977¹) etc. Donnay (1977) refined the structure of elbaite, and found that the magnitudes of u values for O₁ and, to a lesser degree for X and O₂, point to abnormalities in the thermal vibrations. From the atomic coordinates at two different temperatures, she noticed that, while neither X nor O₂ has shifted significantly, O₁ has. In the present study, we attempted least-squares refinement with a generalized structure factor expression, based on the Gram-Charlier expansion of atomic probability density functions (PDF), to examine the anharmonic characters of atoms in elbaite at room temperature, suggested by Donnay (1977).

The chemical formula of a green prismatic crystal from Lahgman (Afghanistan) was $X = (Na_{0.52}Ca_{0.13}K_{0.01}O_{0.34})_{\Sigma=1}$, $Y = (Li_{1.26}Al_{0.95}Fe_{0.50}Mn_{0.20}Mg_{0.01}Ti_{0.08})_{\Sigma=3}$, $Z = Al_{6.00}$ and $W = ([O_1(OH)]_{3.97}F_{0.03})_{\Sigma=4}$. All the diffraction data were obtained at room temperature with a spherical specimen of diameter about 0.3 mm. The unit-cell dimensions are $a = 15.874(3)$ and $c = 7.116(3)$ Å. All the refinement cycles were performed using the 3061 F_o without omitting any reflection from the measured. The polarity of our spherical specimen was determined with respect to the structure of Donnay (1977).

The harmonic least-squares refinement with 88 variables, initiated with the positional parameters of Donnay (1977), converged at $R = 0.0337$, showing considerably large thermal parameters for X, Y, O₁ and O₂ atoms (First group) compared to the rest atoms (Second group). The further refinements with additional 63 variables for the third and fourth order coefficients for the first-group atoms converged at $R = 0.0294$, resulting in significantly anharmonic or multimodal PDFs for the first-group atoms. These PDFs are clearly asymmetric along c with the modes shifted toward the positive side for the O atoms and toward the negative side for the cation sites from the corresponding means. Our result of the single-temperature measurement, particularly for O₁, is just concordant with Donnay (1977)'s two-temperature measurement of atomic shift. The present study further indicated that O₁ was disordered over three potential energy minima in the plane perpendicular to the 3-fold axis.

1) Donnay G. Acta Cryst. A33, 927-932, 1977

Software For Identification and Refinement of Cell Parameters From Powder Diffraction Data of Minerals Using the RRUFF Project and American Mineralogist Crystal Structure Databases

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The RRUFF project is dedicated to the identification and characterization of all minerals through X-ray powder diffraction, single crystal diffraction, Raman spectroscopy, and chemical analysis. Crystal Sleuth software was developed as an analytical tool for the RRUFF project and shares the common goal of providing a worldwide resource for identification of minerals and general advancement of the mineral sciences by providing an interactive environment for X-ray powder refinement and mineral spectra identification using the RRUFF project database and American Mineralogy Crystal Structure Database (AMCSD). Among the many utilities that have proven to be invaluable in the reduction and analysis of diffraction patterns and Raman spectra, Crystal Sleuth gives the user the ability to remove cosmic rays, correct the spectral baseline, allows for the visualization and comparison of several spectra, and forms mathematical models of peaks. The true power of this software is illustrated when it works symbiotically with AMCSD to identify and refine X-ray powder diffraction patterns to high precisions, and when it houses the efforts of the RRUFF project database within a library to provide a rapid method of mineral identification through Raman spectroscopy.

This presentation will focus on the usefulness of Crystal Sleuth in the area of X-ray diffraction. In this arena, the software's ability to correct spectral baselines, auto-fit and index peaks, search and identify the mineral, and refine cell parameters plays the largest role. The program gives the user the versatility to fit and index Ka1 and Ka2 doublets and singlet peaks and has been tested on patterns both from traditional lab and synchrotron sources. Moreover, the technique which all these features are integrated into an analytical tool has proven time and again to be able to produce cell parameters in X-ray refinement with a precision of four or more decimal places through a nearly automated routine which can take under a minute. This quick automation and high accuracy produced by Crystal Sleuth is clearly a method adapted to unravel mineral data with minimal human intervention for use in such ventures as exploring our Solar System on a Mars Rover.

Continuous crystal chemical space for the dioctahedral iron-rich micas and related phases (celadonite, glauconite, Fe-illite)

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The dioctahedral iron-rich mica-related phases, the celadonite-glauconite group minerals (CGGM), have been defined and differentiated upon all of their possible crystal chemical positions, namely interlayer charge (IMA nomenclature, 1998), octahedral charge (AIPEA nomenclature, 1986) and tetrahedral charge (AIPEA nomenclature, 1980). The multitude of crystal chemistry based nomenclatures already forecasts that these minerals are difficult to distinguish on a crystal chemical basis. The routinely used formal identification methods (d_{060} and FTIR) do have strong limits. CGGM have also been separated, from the second half of the 19th century on, on formation environment: celadonite was supposed to have magmatic, while glauconite sedimentary origin. However, data accumulating in the literature suggest that minerals of magmatic and sedimentary origin may have overlapping chemical composition. For comparison the chemical data set (>350 analysis) we collected on CGGM we started by building up a second database on all chemical data on CGGM available in the literature, with some outlook on their iron containing aluminous counterparts, too. At the moment, that second database contains more than 700 entries. Chemical data were filtered on the presence/absence of measured Fe²⁺/Fe³⁺ ratios and some crystal chemical constraints. The filtering process outlawed more than half of the data, leaving about 310 entries in the database for iron-rich dioctahedral micaceous phases. The valid(ated) data were plotted into different graphical representation systems to check the crystal chemical range of these minerals. We found that the crystal chemical space occupied by these minerals is continuous. The celadonite field of the IMA nomenclature is more populated towards the Fe³⁺-rich side, while the glauconite field at lower interlayer charges is more populated on the Al-rich side. The transition towards the Al-rich regions is continuous in the low interlayer charge regions, pointing out the need for enlarging the IMA definition of illite. These findings agree well with the predicted trend of glauconitisation: an Al-Mg-rich smectitic material is gradually turning into an Fe³⁺-Mg-rich mica, where the charge consequence of the K uptake is compensated by the decrease of octahedral occupancy and by Al-Fe²⁺ substitution in the octahedral layer.

Graphical representation systems for TOT layer silicates: a case study for iron-rich dioctahedral phases (celadonite, glauconite)

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We compare numerous graphical representations for the chemistry of TOT layer silicates, with special emphasis on the iron-rich dioctahedral mica and the related interlayer-deficient micas (celadonite-glauconite group minerals, CGGM). These minerals have been differentiated upon all of their possible crystal chemical positions, namely interlayer (IMA, 1998), octahedral (AIPEA, 1986) and tetrahedral (AIPEA, 1980) charge. In literature both 2D and 3D plots were designed to visualise the chemical composition of micas, applying 2-4 or even more variables. Special coefficients were created from individual cation numbers to reduce the number of variables. Ternary plots are widespread, but can be misleading, if normalised; source data normally cannot be read from the plots. Plots designed for micas often have the starting condition $X_{IL} = 1$ (X_{IL} : interlayer cation charge), rendering them limited use for interlayer-deficient micas. In CGGM tetrahedral cation charge (X_T) is defined by Si a.p.f.u., X_{IL} by K (+Ca,Na) a.p.f.u. (note sample impurity/homogeneity and H₂O⁺). Octahedral cation charge (X_O) is defined by $X_O = 22 - (X_T + X_{IL})$. X_O can also be expressed as $X_O = {}^{VI}R^{3+} * 3 + {}^{VI}R^{2+} * 2$ (Li-free; ${}^{VI}R^{3+}$, ${}^{VI}R^{2+}$ is a.p.f.u. of trivalent (Fe³⁺, Al) and divalent (Mg, Fe²⁺) octahedral cations). An additional parameter, normally omitted, is octahedral site occupancy (SO_O): $SO_O = {}^{VI}R^{3+} + {}^{VI}R^{2+}$ (Li-free). SO_O gives a direct relationship between X_O and the ratio of the di- and trivalent octahedral cations (${}^{VI}R^{2+} / ({}^{VI}R^{2+} + {}^{VI}R^{3+})$). At the particular case of "ideal" dioctahedrality ($SO_O = 2.00$) ${}^{VI}R^{2+} / ({}^{VI}R^{2+} + {}^{VI}R^{3+}) = (6 - X_O) / 2$. SO_O is frequently, and arbitrarily, fixed at 2.00 when calculating formulae from analyses (e.g. EPMA) where iron valence state is not measured. However, as we showed elsewhere, for CGGM SO_O cannot be fixed, and especially cannot be fixed for 2.00 (may go up to 2.08-2.15). Because of that (1) even good chemical data may plot outside of the "definition boxes" (IMA, 1998); (2) phases differing chemically may plot close; (3) these plots are very sensitive to SO_O vs. Fe²⁺/Fe³⁺ calculations. Diagrams (e.g. IMA, 1998) using ${}^{VI}R^{2+} / ({}^{VI}R^{2+} + {}^{VI}R^{3+})$ type variables can be regarded not only chemical, but also crystal chemical (= where chemical formulae can be reconstructed from the plots = ${}^{VI}R^{2+}$ type cations still not distinguished), only if SO_O is added. Conclusion: the graphical representation of crystal chemistry of the CGGM needs four dimensions (quality of ${}^{VI}R^{2+}$ disregarded). Additionally a new, easy to use, combined plot is presented, where e.g. the glauconitisation process can be well visualised.

O09-01

Dissolution mechanisms of water in depolymerized aluminosilicate melts (glasses): a comprehensive one- and two-dimensional ^1H , ^{29}Si and ^{27}Al NMR study

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Water is among the most important volatile components that significantly affect the physical and thermodynamic properties of silicate melts and glasses. Understanding the dissolution mechanisms of water is important because the formation of different water species may have contrasting effects on melt properties. For Al-free silicate compositions, water speciation in the form of molecular H_2O and SiOH are well known. A third important species, free OH (OH bonded only to metal cations, such as Mg and Ca), was recently confirmed as well for depolymerized silicate melts (glasses), and was found to be favored by metal cations with large field strength, such as Ca and Mg (Xue and Kanzaki, 2004). Whereas the formation of SiOH reduces the melt polymerization and viscosity, free OH may have an opposite effect. For Al-bearing silicate melts (glasses), the dissolution mechanisms of water remained controversial, despite relevance to natural magmas.

In this study, we have taken a systematic and comprehensive approach to gain new insights into the dissolution mechanisms of water in aluminosilicate melts (glasses). Samples studied include quenched melts (glasses) with 0–2 wt% H_2O in both the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ system with a range of compositions (NBO/T, Ca/Mg ratio, Al/Si ratio). A variety of advanced NMR techniques, from one-dimensional (1D) NMR, such as ^1H MAS and Hahn-echo MAS NMR, ^{29}Si MAS and $^1\text{H}\rightarrow^{29}\text{Si}$ CP-MAS NMR, ^{27}Al MAS, $^1\text{H}\rightarrow^{27}\text{Al}$ and $^{27}\text{Al}\rightarrow^1\text{H}$ CP-MAS NMR, to 2D NMR, including ^1H NOESY and DQ MAS NMR, $^1\text{H}\rightarrow^{29}\text{Si}$ and $^{27}\text{Al}\rightarrow^1\text{H}$ HETCOR, and ^{27}Al 3Q MAS NMR have been applied. The ^{27}Al 3Q MAS NMR revealed that five-coordinate Al (Al^{V}) is present in both the hydrous and anhydrous aluminosilicate glasses, with the hydrous glasses showing less population for part of the tetrahedrally-coordinated Al (Al^{IV}) that have large quadrupolar coupling. The ^1H NOESY results suggest that all water species are present in a homogenous glass structure (without phase separation), but spin diffusion is negligible at short mixing times <2 ms. The combined ^1H MAS, Hahn-echo MAS NMR, and $^{27}\text{Al}\rightarrow^1\text{H}$ CP-MAS NMR data clearly revealed, for the first time, that in addition to free OH (δ^{H} around 1 ppm) and SiOH /molecular H_2O ($\delta^{\text{H}} \geq 4$ ppm) that remain major water species, OH species involving Al, most likely AlOH groups (δ^{H} around 2–3 ppm) are also developed in the Al-bearing glasses. The $^1\text{H}\rightarrow^{27}\text{Al}$ HETCOR NMR data suggest the presence of AlOH groups linked to Al^{V} , in addition to those linked to Al^{IV} .

O09-02

Structural environment and aluminum coordination in calcium and magnesium aluminosilicate glasses

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Calcium and magnesium aluminosilicate glasses are important systems for both earth science and technological applications. We have synthesized glasses in the CAS system using classical quenching and containerless (laser heating) methods. Viscosity experiments have been made on these samples. We have previously interpret anomalous behavior of thermodynamic properties in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (CAS), as resulting of preference for Al to be localized in more polymerized units.

The structure of these glasses was studied by neutron and X-ray diffraction associated with simulation methods (Molecular dynamics and Reverse Monte Carlo) and Raman spectroscopy, showing modifications in structure with stoichiometry in relation with changes in rheology. The specific environment of each atomic species was determined by X-ray absorption at the Al, Si and Ca K-edges (SA32 beamline, LURE-France) and allowed to better defined the Ca environment and the speciation of Al in polymerized units with glass compositions.

The proportion of the various Al coordination sites were carefully quantified by ^{27}Al high resolution MAS-NMR (17.6 T – 750 MHz). Al in five-fold sites, ^{15}Al , is found in all CAS and MAS glasses, with a significant amount (7 % in the anorthite glass). The proportion of ^{15}Al increases for the peraluminous glasses with the formation of six-fold coordination, ^{16}Al . The presence of ^{15}Al agrees with previous observations on the existence of non-bridging oxygens (NBO) in tectosilicate compositions. However, the proportion of ^{15}Al in the present study indicates that no major proportion of triclusters (oxygen coordinated to three $(\text{Si,Al})\text{O}_4$ tetrahedra) is required to explain these NBOS. The role of this high coordinated Al species on the physico-chemical properties and their structural role within the aluminosilicate network will be discussed.

O09-03

Densification of vitreous MgSiO_3 and formation of high-coordinated silicon

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The atomic structure of densified MgSiO_3 glasses has been studied using ^{29}Si MAS-NMR spectroscopy. Glasses were compressed in a multianvil apparatus to 10.4 GPa at room temperature, heated to 500°C for four hours, quenched, and decompressed at 10.4 GPa/min or 0.04 GPa/min. The ^{29}Si MAS-NMR spectrum of the glass at ambient pressure has one dominant peak with an isotropic chemical shift ($\delta\text{-iso}$) of -83.3 ppm and corresponds to tetrahedrally coordinated Si (Si^{IV}) present as Q^2 species. The $\delta\text{-iso}$ for this peak in the spectra of high-pressure samples is -81.5 ppm, regardless of decompression rate. The ^{29}Si NMR spectrum of the rapidly decompressed sample contains two additional peaks at -180 ppm and -124 ppm. The peak at -124 ppm is nearly absent from the spectrum when the glass is decompressed slowly. The peak centered at -180 ppm is assigned to octahedrally coordinated Si (Si^{VI}) consistent with that measured in the crystalline ilmenite- MgSiO_3 (Stebbins and Kanzaki, 1991). In contrast, the peak at -124 ppm cannot be readily assigned to any recognized Si coordination state in known crystalline MgSiO_3 polymorphs. We assign this peak to 5-fold coordinated Si (Si^{V}) based on its intermediate position between the Si^{IV} and Si^{VI} and the results of ab initio chemical shift calculations on MgSiO_3 glass structure generated using first principles molecular dynamics (FPMD) simulations. These calculations predict a chemical shift of -119 ppm for Si^{V} present as $\text{Q}^{3\text{v}}$ species, in good agreement with the experimental observation. Measurements of density were also made on compressed glasses by Archimedes' method in toluene and suggest the glass has experienced up to $\sim 10.2\%$ permanent densification. We conclude that the densification of MgSiO_3 glass at 10.4 GPa and 500°C is largely accommodated by the twisting of network chains to form Si^{IV} and Si^{VI} . Molecular dynamics simulations coupled with ab initio ^{29}Si NMR chemical shift calculations indicate that the reduction of Si-O-Si bond angle between adjacent Q^2 species is partially reversible in these pressure-quench experiments. This interpretation is consistent with the preservation of Si^{VI} and absence of measurable Si^{V} in slowly decompressed glass reflecting differences in the time scales for structural relaxation of high pressure Si coordination and possible coupling of densification mechanisms. Structural insights gained from vitreous MgSiO_3 , among other fragile, refractory silicate glasses, constrain the nature of coordination changes to network-forming cations accommodating the densification of silicate melts in the Earth's deep interior.

O09-04

Structural origins of transport properties of silicate melts at high-pressure: Solid-state NMR and synchrotron X-ray study

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Recent advances and progress in solid-state NMR, x-ray optics with diamond anvil cell, and quantum chemical calculations allow us to obtain the structural details of silicate glasses and yield better insights into microscopic origins of melt properties at high pressures (e.g. Lee et al. Geophys. Res. Letts. 2003, 30, 1845; Lee et al. Phys. Rev. Letts. 2005, 94, 165507; Lee et al. Nature Materials 2005). Here we report recent progress that we have made on pressure-induced structural changes in various amorphous oxide glasses and melt at high pressures using multi-nuclear solid state NMR, and synchrotron X-rays. From archetypal borates to complex multi-component aluminosilicate glasses and melts, the fractions of ^{16}Si , ^{15}Al , ^{10}B increase with increasing pressure. The multiple densification mechanism for those glasses may be described by the topological variation including ring size at lower pressure and then in changes in coordination at elevated pressures. The distribution of highly coordinated cations at high pressure favors formation of oxygen linking dissimilar Si pairs. The degree of polymerization in the melts, types and fractions of network modifying cations at isobaric conditions are among the important controls on detailed pressure-induced structural changes. Topological disorder due to Si-O bond length and Na-O distribution increases with pressure. These structural changes with pressure enable us to account for non-linear pressure dependence of transport properties of silicate melts.

Oxygen sites and germanium coordination in alkali germanate glasses: oxygen-17 triple-quantum MAS NMR

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Crystalline germanates have long been studied as analogs of high-pressure silicates, as they often contain six-coordinated Ge (^{60}Ge) even at ambient P. Germanate glasses and melts may serve as well as analogs for high P silicate melts, in which coordination changes as functions of composition and temperature could be deduced. Unlike silicates but as in borates, addition of modifier oxides to GeO_2 is thought not to begin to produce substantial fractions of non-bridging oxygens (NBO) until about 20 mol % of the oxide (e.g. Na_2O) is reached. In consequence, the added oxide ion must be accommodated by some increase in Ge coordination. However, despite many studies by various spectroscopies and scattering methods, the details of this process (i.e. how much ^{13}Ge and/or ^{60}Ge , fractions of NBO) remain uncertain.

High-resolution, triple-quantum magic-angle spinning NMR of ^{17}O has recently revolutionized our ability to measure populations of NBO and various types of bridging oxygens in aluminosilicate, borosilicate, and other oxide glasses, and is beginning to reveal details of connections among high-coordinated Si and Al and the tetrahedral networks of high pressure glasses. Here we apply this approach to Na germanates.

New data for crystalline phases (GeO_2 rutile and quartz, Na_2GeO_3 , $\text{Na}_2\text{Ge}_2\text{O}_6$, $\text{Na}_4\text{Ge}_3\text{O}_{10}$) show that various types of oxygen sites in GeO_2 and Na germanates fall into distinct ranges of chemical shift, including NBO, oxygen bonded to two ^{4}Ge (O44), oxygen with ^{4}Ge and ^{60}Ge neighbors (O46), and oxygen with three ^{60}Ge neighbors. In glasses with about 15, 20, and 30 mole% Na_2O , we see no evidence for the latter. In contrast, the glasses clearly display large, partially resolved peaks in the region for O46, which we attribute to O46 and/or O45 until more constraints on the latter can be obtained. NBO peaks are also partially resolved in the glasses with higher Na contents, and directly confirm long-standing models that at low Na_2O contents, few if any NBO form. From these results, we can calculate the expected proportions of O44 with various scenarios, e.g. assuming high-coordinated Ge is either all ^{50}Ge or ^{60}Ge . Comparison with NMR results show that in general, models with only ^{50}Ge cannot match the data, indicating that as in most other network oxide glasses (e.g. high P silicates and aluminosilicates, ambient P aluminoborates), substantial fractions of all three coordinations are likely to be present.

Ab initio calculation of ^{17}O NMR parameter of oxygen sites in borosilicate glasses

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Borosilicate glasses have a variety of different oxygen sites in bridging bonds such as Si-O-Si, Si-O-B, and B-O-B. In addition, boron atoms have 3-fold and 4-fold coordination structures in glass, and it makes the issue so complicated. ^{17}O NMR is probably the only experimental method to identify the oxygen sites in the complicated borosilicate glass structures. Recently, Du & Stebbins (2003) have successfully resolved the ^{17}O 3QMAS NMR spectra into various oxygen sites in borosilicate glasses. However, the spectral assignments have been done empirically, and no theoretical interpretation has been given. Then, in the present study, ^{17}O NMR parameters, isotropic chemical shift and quadrupole coupling constant of the bridging oxygen sites in Si-O-Si, Si-O-B, and B-O-B bonds were estimated by an ab initio calculation using the Gaussian03 program. According to the calculation, the isotropic chemical shift of the bridging oxygens was expected as Si-O-Si < Si-O-B[4] < Si-O-B[3] < B[4]-O-B[4] < B[3]-O-B[4] < B[3]-OB-[3] (B[n]: n-fold coordinated boron) in the ascending order, which was in accordance with the previous assignments. The quadrupole coupling constant showed a narrow distribution between 4 and 6 MHz, suggesting that it was difficult to differentiate between the oxygen sites from the quadrupole coupling constant.

Industrial application of multi nuclear solid state NMR (^{17}O , ^{25}Mg , ^{27}Al , ^{43}Ca) to glassy slags at high field (16.4T) and super high field (21.8T)

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Recent new development of a super conducting magnet can make a new application field for solid state NMR. Especially, NIMS in Tsukuba succeeded in the development of 930 MHz (21.8T) solid state NMR system. In this paper, we would like to show industrial topics, which have new finds in industrial application when this developed high field solid state NMR system is applied. A new approach to structural analysis of inorganic polymer, we called slag which is by products of steel making, has been proposed using multi-nuclear solid state NMR at high magnetic field that is capable of obtaining the structural information of each element composing the slag such as Si, Al, Mg, O, Ca and effective to both crystalline and non-crystalline solid materials. In this study, we applied mainly ^{27}Al and ^{25}Mg and ^{17}O and ^{43}Ca solid state NMR two types of steel-making slags. In ^{27}Al NMR measurements, drastic improvement of spectral resolution at high magnetic field (16.4T) 5QMAS experiment clarified the existence of at least 11 chemical sites of Al in slag. And, we successfully obtained ^{25}Mg 3QMAS spectra in slags, when special probe has been developed to overcome low sensitivity. Additionally, solid state ^{17}O NMR is very useful and powerful tools for the structural analysis of oxygen in various inorganic materials. However, quite low sensitivity on NMR is main difficulty point. And then, we tried to synthesize each ^{17}O -labeled stating materials such as $\text{Ca}(\text{OH})_2$, Al_2O_3 and SiO_2 in order to overcome low sensitivity. Using these materials, the formation of slag network was investigated at 1273 to 1673K by ^{17}O MQMAS. The process of network formation of oxygen in slag could be observed by means of ^{17}O full labeled materials at each temperature. Moreover, ^{17}O selective labeled materials became possible to assign each peak in spectra of full-labeled materials. ^{27}Al - ^{17}O CP/MAS methods were applied in order to make connectivity clearly. We first applied ^{43}Ca 3 and 5QMAS NMR spectroscopy for ^{43}Ca -enriched model slags. Local environments of Ca^{2+} ions in slow- and rapid-quench model slags were found to be different each other. The slow-quench slag has well-defined CaO_6 polyhedra in a crystalline form, although the rapid-quench slag is considered to have CaO_6 octahedral species as a main component. From above mentioned results, multi-nuclear solid state NMR is proved to be a very effective method in characterization of the slag.

Structure and properties of hydrous silicate melts

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The solubility of water in silicate melts at high pressure and temperature can exceed 50 mol %. There exists a pressure in the mantle above which the miscibility gap between silicate-rich aqueous fluid and water-rich silicate melts disappears. The pressure-temperature conditions of this closure depend on silicate composition and occurs in the 1-2 GPa range in felsic systems, but probably does not occur until pressures of 5 GPa or more in mafic systems such as basalt. The solubility dependence on melt composition is also seen in liquidus temperature depressions. The depression in silicic systems can be more than twice that in mafic systems such as basalt. Dissolved water has the well-known effect of enhancing the stability of depolymerized mantle phases on silicate melt liquidii, thus leading to more silicic melts. The extent of this effect does, however, depend on the melt composition, and probably also on pressure. Transport properties are very sensitive to the water content and may change by several orders of magnitude by dissolving only fractions of a percent of water.

The property behavior of hydrous silicate melts accords with spectroscopic data, where formation of OH-groups is a major water solution mechanism. Molecular H_2O is also formed. The proportion of H_2O and OH groups is sensitive to total water content and temperature. The diminishing effect of water on melt properties with increasing total water is consistent with increasing $\text{H}_2\text{O}/\text{OH}$ in the melt. Solution models based only on OH groups and molecular H_2O do not, however, account for the composition, pressure, and temperature effects of water on melt properties. This accords with recent NMR data indicating the formation of OH-complexes that involve only metal cations such as alkali metals and alkaline earths (M-OH complexes). These complexes become increasingly important the more depolymerized the melt. Formation of OH-complexes may be a dominant solution mechanism of water in ultramafic melts in the Earth's mantle, for example. Such a solution mechanism causes melt polymerization. Thus, it would not be surprising if the presence of water during deep Earth melting may result in melts that are more polymerized (silicic) than in the absence of water. It is likely that when water dissolves predominantly to form M-OH complexes, its effect on melt properties is much smaller than when water dissolves to disrupt the silicate melt network.

Local structure of sulfate ions in Na₂O-CaO-SiO₂ glasses and melts: High-temperature raman spectra

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Local structure of sulfate ions in molten Na₂O-CaO-SiO₂ glasses is investigated by high-temperature Raman spectroscopy. S-O stretching vibration band around 1000 cm⁻¹ is focused to analyze the interaction between sulfate ion and glass matrix. The measurements on various molten sulfates (Li₂SO₄, Na₂SO₄, K₂SO₄ and Na₂SO₄-CaSO₄) were carried out and showed the characteristic Raman shift depending on the counter cation and temperature. From the shifts in the molten Na₂SO₄-CaSO₄ mixtures, the characteristic scale to estimate the fraction of the surrounding cations around sulfate ions is derived. Temperature dependences of S-O vibration band in glasses and melts with various Na₂O/CaO ratio show that the fraction of cations surrounding sulfate ions changes with temperature; the interaction with Na⁺ ions increases with increasing temperature. The local structure of sulfate ions derived from Raman spectra are discussed from the points of view of the solubility of sulfate ions in the melts and the decomposition temperature of SO₄²⁻→SO₂+1/2O₂+O²⁻, combined with the previous results on Qⁿ distribution in the same glass system.

New experimental approach to determine Raman scattering profiles for Qⁿ species in silicate glasses and melts: preliminary results

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Raman spectroscopy has been used extensively to investigate the Qⁿ speciation in silicate glasses and melts. The conventional approach is to fit the high-frequency region of the spectra (900-1200 cm⁻¹) with a restricted number of highly overlapping Gaussian components and to calibrate the signal intensities with quantitative information from NMR. However, the shape, number and assignment of the various bands are still controversial and the effect of increasing temperature on the Raman scattering cross-section is poorly understood. To overcome this problem, we used Principal Component Analysis (PCA) and linear Programming (LP) to calculate both the speciation and the scattering profiles for the different species at various temperatures (see abstract by V.P. Zakaznova-Herzog et al.). This requires a large dataset to allow for an accurate determination of the Principle Components.

We collected a large set of Raman spectra of binary potassium silicate glasses and melts, at 44 different compositions and 5 different temperatures. The Raman spectra were collected using a wire-loop heating stage. For efficient data acquisition, the composition of the sample was varied in situ, i.e. inside the heating stage and under the Raman instrument. This was achieved by making use of the evaporation of potassium at high temperature (typically 1400K at high potassium content and 1674K at higher silica content). The potassium content decayed exponentially as a function of exposure time at high-temperature. Using this method, Raman spectra over a wide compositional range (50 to 13 mole % K₂O) with a high compositional resolution (more than one spectrum per mole % of K₂O) can be collected in a matter of hours. The composition was monitored by comparing the spectra of the intermediately quenched melt with the spectra of 14 conventionally prepared glasses with known compositions.

First results indicate that, for the high-frequency region, Q⁴ has a temperature dependent scattering profile that, in peak position but not in relative peak intensity, resembles the Raman spectrum of pure SiO₂ glass. The scattering profile of Q³ consists of one peak around 1100 cm⁻¹. The scattering profile of Q² shows two peaks; this could be related to the presence of two types of Q², consistent with NMR spectroscopy for potassium silicate glasses. The peak positions shift as a function of temperature and the degree of the shift for the different species increases in the order Q⁴-Q³-Q².

Quantitative raman spectroscopy: mathematical procedure for the treatment of spectral data in silicate glasses and melts.

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We developed an alternative approach that allows interpretation of the collected Raman spectra of binary silicate glasses and melts independently from other techniques and allows to derive equilibrium constants for the speciation reactions, e.g. $2Q_3 = Q_2 + Q_4$ (1). This approach is necessary to develop, since the quantitative interpretation of commonly used, in situ Raman spectroscopic measurements of silicate glasses and melts is dependent on ex-situ, ambient temperature NMR measurements and the interpretation is not accurate enough to analyze strongly overlapped signals from different species, especially, at higher temperatures. The reliable spectra interpretation allows acquiring knowledge of glass and melt speciation at high temperatures and, in turn, can be used to determine thermodynamic properties of silicate melt species over a wide compositional range.

The spectra of either glasses or melts of different compositions are computed at each temperature assuming that the shape of the spectrum of each species is independent of its concentration in the glass (or melt). Furthermore, we assume that the spectrum (*A*) is a linear superposition of the spectra of each species (*c*), following the formula $A = c \cdot \epsilon$ (2) (in matrix notation), where *c* is the abundance of the species. Since the spectrum of each species is not known, we use a mathematical optimization procedure to determine individual spectra and the concentration of each species from the measured glass (melt) spectra. By applying principle component analysis (PCA), we first determine the number of Raman active species (Qⁿ species) and then propose a chemical equilibrium model. This model is based on mass balance, charge balance, and mass action equations. Second, we use an optimization algorithm that minimizes the absolute value of the difference of the observed spectra and the theoretically calculated spectra, see (2). By using the absolute difference, instead of a quadratic difference, we can split the mathematical optimization of jointly determining *c* and *ε* into two separated steps: calculating the abundance of the species for a given equilibrium constant and solving for the spectra of the species by solving a large scale linear program (LP). The procedure finds the equilibrium constant for the speciation reactions, the abundance of the species, and the spectrum of each species. We applied the above approach to data from the binary K₂O-SiO₂ system (see abstract by Malfait et al.). Our results at ambient temperature show a good agreement with new and published NMR data.

O K-edge XANES: An indirect probe of cation coordination?

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Glasses are widely used as model for silicate melts. Furthermore, the role melt structure plays in determining physical properties and behaviour, remains an important issue in geological studies of silicate melt behaviour. Alkali-containing germanate glasses in particular exhibit large changes in physical properties with changing composition and this behaviour, known as the "germanate anomaly", makes them unique compared to alkali-containing silicate glasses. Consequently, alkali-containing germanate glasses are useful model compounds if one is interested in the influence of coordination changes on melt density and viscosity. The structural mechanism responsible for the germanate anomaly remains controversial. Two principal models have been proposed. The original and most widely accepted explanation invokes the formation of Ge in 6-fold coordination (⁶⁰Ge) while the second involves small ring formation without the need for the presence of ⁶⁰Ge. More recently, it has been suggested that 5-fold coordinated germanium (⁵⁵Ge) may play a role in the anomaly. Resolution of the controversy depends to a great extent on an ability to determine germanium coordination. Like many elements in amorphous materials, determination of coordination environment depends on whether or not a suitable experimental method is available that can discriminate the differing geometries. In many instances there are no techniques available or, for various reasons, they simply don't work i.e., ⁷³Ge NMR. Recently, O K-edge XANES has proven to be useful for indirectly determining the coordination environment of Ge. The spectral details of the O K-edge XANES spectrum are largely determined by the environment of the cation bonded to the oxygen. Consequently, O K-edge XANES is able to probe the Ge coordination environment in germanate glasses. Initial experimental results are supported by theoretical simulations of the O K-edge XANES which show that experimental spectra of crystalline GeO₂ polymorphs are sensitive to the presence of ⁴¹Ge and ⁶⁰Ge polyhedra.

Atomic structure and transport coefficients of Mg-Al-Si-O melts at high pressures and temperatures: A molecular dynamics simulation study

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The knowledge of properties of silicate melts at high pressures and temperatures is essential for a fundamental understanding of magmatic processes, such as volcanism or the chemical and physical evolution of the Earth during and after accretion. Melt density and viscosity are important parameters to model melt buoyancy or differentiation processes. Melt structure and atomic mobility may influence element partitioning between minerals and melts, or crystallization and melting processes. In situ experiments on melts under extreme conditions are still challenging. Results obtained so far already show that in many cases simple assumptions or extrapolations of ambient properties to high pressures and temperatures are not justified. The anomalous behavior of diffusion coefficients and viscosities observed in silicate melts at high pressure is usually discussed in terms of changes in the atomic structure of the melt upon compression. However, melt structures at high pressures and temperatures are widely unknown and so is the relation between the atomic structure of a melt and its transport properties. Atomistic computer simulations may help to interpret experimental results and predict melt properties that are difficult to study experimentally. Further, anomalous behavior of transport coefficients can directly be related to changes in the atomic structure. Here, results from molecular dynamics simulations of melts in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at high pressures and temperatures are presented. For the first time, a recently developed fully flexible interaction model that allows for ionic polarizability and shape deformations is applied to multicomponent melts. The accuracy of the model is demonstrated by comparison of model predictions to experimental data (static and dynamic structure factors, density, self-diffusion coefficients, viscosity). Anomalous behavior of the transport properties is observed both as a function of pressure and composition. The underlying atomistic mechanism is discussed in terms of changes in the melt structure and ionic coordination.

Structure and mixing properties in soda and alkaline-earth silicate melts

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The configurational properties of melts and glasses provide fundamental information needed to characterize magmatic processes. A principal difficulty, however is to link the "macroscopic" configurational entropy with the structure of melts. This has been done by combining viscometry with Raman spectroscopic structural studies. From the viscosity measurements at low and high temperatures, we have obtained the configurational entropy, S^{conf} ($\log \eta = Ae + Be/TS^{\text{conf}}$, where η is the viscosity, T the temperature and Ae , Be two constants).

We are using Raman spectroscopy at room temperature between the soda and alkaline-earth silicate melts. For these compositions, we establish some link between the variation of the viscosity, the configurational entropy as the function of chemical composition and the Q species obtained from the Raman spectroscopy. These structural variations are related to the changes in configurational entropy. It is possible, to understand this variation of viscosity and mixing between Na and (Ca, Sr, Mg, Ba) in silicate melts.

Viscosity and mixing in the system $\text{M}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ with $M = \text{Li, K, Na}$

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In order to modelling the thermodynamic properties of silicate melts, we have studied the influence of temperature and composition on the configurational properties. In a first time, we have interest on liquids in the simple system $\text{M}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ with $M = \text{Li, K, Na}$. With a creep apparatus, we have measured viscosities of supercooled silicate melts in the range 109-1014 poises with inaccuracies of less than 0.03 log poise. Using a relationship that derived to Adam and Gibbs theory of relaxation process. Viscosity data could be linked to the configurational entropy through :

$$\log \eta = A_e + B_e / TS^{\text{conf}}(T),$$

$$\text{with } S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T C_p^{\text{conf}} / T dT,$$

where A_e and B_e are two constants, T is the temperature. T_g , the glass transition temperature has been determined from viscosity measurements and C_p^{conf} by drop calorimetry.

Using these results along with available viscosity data above liquidus temperatures, we have interpreted these variations within the frame of the configurational entropy theory in terms of the composition dependence of the entropy of mixing. These results represent a first step towards a quantitative model of prediction of the viscosity of $\text{M}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ liquids, valid over 13 orders of magnitude. The structural implications of these results will also be presented.

Physical properties of molten slags and fluxes in steelmaking process

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It is important to have accurate and mutually consistent physical property data on slags for the modeling of steelmaking and casting processes. In this paper, an overview of thermophysical and mechanical property measurements carried out in our group are presented. These properties are of great interest even from a fundamental view point as they enable an understanding of the structure of complex slags. Inter property correlations also enable prediction one property from another as the slag properties are based on the structure. The present paper provides an insight into the thermophysical property measurements and some mechanical properties of slags carried out by the present research group over the years. The property that are focused upon are a) density, b) viscosity, c) surface tension, d) interfacial tension, e) thermal diffusivity, f) stress relaxation behavior and g) tensile strength. The thermophysical and mechanical property measurement results were discussed from the view point of structure of slags by using the structure information obtained by spectroscopic studies in order to establish the link between structure and properties. In order to investigate structure of silicate melts, Raman spectroscopic investigations have been carried out.

In addition to these measurements, modeling work of molar volume (density) on binary system has also been carried out in establishing a correlation between molar volumes and enthalpies of mixing. Excellent correlations were obtained in the case of a number of silicate systems. The molar volumes thus estimated agreed well with the reported experimental data. The integral molar enthalpies of mixing were evaluated from the earlier developed model for thermodynamic properties of slags in the present laboratory. The modeling of molar volume is currently being extended to multicomponent silicate melts.

Density measurement for MORB melts by X-ray absorption method

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Density of silicate melts at high pressure is one of the most important properties to understand magma migration in the planetary interior and the differentiation of the terrestrial planets. The density measurements of silicate melts have been carried out by several methods (shock compression experiments and sink-float method in static experiments, etc.). However, since these methods have difficulties in acquisition of data at a desired pressure and temperature, the density of the silicate melt has been measured only under the limited conditions of the density crossover with the density marker or along the Hugoniot. We have developed an X-ray absorption method, a new density measurement at high pressure and temperature. Advantage of this method is to measure the density of liquids at a desired pressure and temperature.

In the present study we measured the density of MORB melt by X-ray absorption method. Experiments were carried out at the BL22XU beamline at SPring-8. A DIA-type cubic anvil apparatus was used for generation of high pressure and temperature. We used tungsten carbide anvils with the edge-length of 6 mm. The energy of monochromatized X-ray beam was 23 keV. The size of the incident X-ray beam was reduced to 0.05x0.05 mm² by two slits. The intensities of incident and transmitted X-ray were measured by ion chambers. The density of the sample was calculated on the basis of the Beer-Lambert law. The starting material was a glass with the MORB composition.

Densities of the MORB glass, crystal and melt were successfully measured up to 4 GPa and to 1800 K. This method enables us to measure densities of the sample under the different pressure condition and therefore we can determine the bulk modulus of the sample.

Calorimetric enthalpy of multicomponent silicate melts

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Enthalpy of multicomponent silicate melt is essential for quantitative and precise understanding of igneous processes. Previous studies have attempted to formulate the enthalpy of silicate melts as function of temperature and composition based on the data of phase equilibria and element partitioning and thermodynamic data of end-members. However, these enthalpy obtained by the analyses depend always on the assumption of melt structure or method to calculate entropy of mixing of silicate melts. It should be emphasized that the real enthalpy of melts which can be used to discuss its physicochemical meaning must be determined by calorimetry.

At present, direct quantitative measurement of enthalpy of melts is difficult, because there is large error in the measured enthalpy ($\sim \pm 15$ kJ/mol) or compositional limitation in high temperature calorimetries (e.g. transposed-temperature drop calorimetry, differential scanning calorimetry). On the other hand, the enthalpy of melts can be obtained by a combination of solution calorimetry of glass and drop calorimetry of silicate liquid. Although the combination technique is an indirect method, more precise determination is possible because of small errors in solution calorimetry and drop calorimetry.

In this study, 158 calorimetric data are compiled from 12 papers previously published, and the enthalpy of silicate melts is determined by the combination technique. The obtained heats of mixing of 14 pseudobinary silicate melts composed of 9 end-members (CaAl₂Si₂O₈, CaMgSi₂O₆, NaAlSi₃O₈, KAlSi₃O₈, SiO₂, Mg₂SiO₄, CaSiO₃, MgSiO₃, Ca₂MgSi₂O₇) are generally within ± 20 kJ/mol and mostly $+5 \sim -10$ kJ/mol at intermediate composition. It is revealed that the size of the heats of mixing is related to the interactions of components. When the silicate melt is divided into three components, network-forming oxides (NF, SiO₂, NaAlO₂, KAlO₂), network-modifying oxides (NM, CaO, MgO) and intermediate oxide (IM, CaAl₂O₄), (1) interactions of NF-NM and NF-NF bring a endothermic heats of mixing, and (2) interactions of NM-NM and that involving the IM is exothermic reactions. The size of enthalpy of silicate melts likely depends on a combination of interactions among NF, NM and IM. The largest mixing enthalpy is observed in the system NaAlSi₃O₈-CaMgSi₂O₆ (+9.2 $\pm$ 1.4 kJ/mol). Calorimetric data suggests that the large heats of mixing can be rationalized by a positive excess heat capacity in this system.

The behavior of basaltic glasses during DSC experiments across the glass transition: evidence for hyperquenching

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Differential scanning calorimetry (DSC) has been performed on a wide variety of basaltic glasses. These include bubble wall fragments (limu-o Pele) and Pele's hair from layered volcanoclastic deposits erupted explosively at water depths of several kilometers on Loihi seamount, Hawaii; Pele's hair produced during subaerial eruptions at Kilauea volcano, Hawaii; and glass from the pillow rims and matrices and clasts of hyaloclastite sequences in the Hawaii Scientific Drilling Project (HSDP) drill core. After initial heating at either 5 or 10 K.min⁻¹ the glasses were cooled and heated again at matched rates of 25, 20, 15, 10 and 5 K.min⁻¹ to provide a series of C_p -temperature paths across the glass transition. Notably on initial heating for each sample the transient C_p forms a trough before the glass transition peak. The trough is absent in subsequent cooling-heating paths, with the C_p values observed for the glassy state within analytical error. This trough makes it impossible to apply the relaxation geospeedometer. Such a trough has also been observed in our laboratory and by other workers in DSC experiments on compositionally similar glasses created synthetically by fiber-spinning, splat- or drop-quenching. These can generate quench rates up to 10⁶ K.s⁻¹. The trough represents the total enthalpy released during the heating process and is believed to be, at least partly, a result of these extremely rapid quench rates. Therefore we believe that the troughs we have measured in the natural basaltic glasses indicate that these glasses also quenched very rapidly. The bubble wall fragments release by far the most energy, comparable to that released by fiber-spun synthetic glasses, suggesting that these glasses were hyperquenched. They start to release the energy at far lower temperatures and the troughs are deeper. The Pele's hair samples release about half as much energy, comparable to that released by glasses synthesized by drop-quenching and slightly less than the energy released by splat-quenched glasses. The glasses from the HSDP drill core release the smallest amount of energy, suggesting they have the slowest quench rates of all the glasses analyzed. However, the fact that they release energy suggests that they were quenched faster than other hyaloclastites on which DSC experiments have been performed, which have had cooling rates of 2.5 K.s⁻¹ defined by relaxation geospeedometry.

Viscosity measurement of subliquidus magmas: Alkali olivine basalt from Higashi-Matsuura district, Southwest Japan

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Subliquidus viscosities of alkali olivine basalt from Matsuura district, SW Japan were obtained at temperature from 1230°C to 1140°C at 1 atm and NNO oxygen buffer, using a concentric cylinder viscometer. The measured viscosity increased more than 40 times from 1230°C to 1140°C (0-30 vol% crystallization) for shear rotational rate at 5 rpm. Liquidus olivine appeared at 1210°C followed by plagioclase below 1170°C. In the presence of tabular plagioclase, non-Newtonian behaviors including thixotropy and shear thinning were pronounced. After each measurement, the basalt was sampled and its phase chemistry and textures were analyzed to determine the effect of crystals on the rheological properties of the basalt. Textural analyses showed that plagioclase crystals were tabular with the most frequent axial ratio around 4, and were aligned their longest axis along the flow direction. The thixotropic behavior was most likely caused by the time-dependent alignment of tabular plagioclase crystals. The shear thinning behavior is explained by the shear strain rate dependent decrease of the solid phase contiguity and/or increase of the orientation order of plagioclase. The relative viscosity η_r ($= \eta_{\text{magma}}/\eta_{\text{melt}}$) measured in this study was consistent with that of the Einstein-Roscoe relation whereas the basalt contained tabular plagioclase with large dispersion of crystal size. This is attributed to that both effects of crystal shape and of crystal size distribution were offset each other. This indicates that the Einstein-Roscoe relation is applicable for magma containing tabular crystals at least up to axial ratio around 4 with large dispersion of crystal size. However when the axial ratio is larger than 6.5, the relative viscosity deviates from the Einstein-Roscoe equation because the effect of crystal shape on the relative viscosity become too large to be offset by that of crystal size distribution.

Viscosity of andesite melts – implication for magma mixing prior to Unzen 1991-1995 eruption

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The viscosity of an iron-bearing melt with composition similar to Unzen andesite was determined experimentally in the high (109-1010.5 Pa·s) and low (5-103 Pa·s) viscosity range. At high temperatures (1323 to 1573 K) and pressures from 200 MPa to 2000 MPa falling sphere experiments were carried out in internally heated argon pressure vessels and in a piston cylinder apparatus. To enlarge the temperature range for the viscosity data, creep experiments were performed at 747 - 845 K at 300 MPa using the high pressure parallel-plate viscometer of Schulze et al. (1999). The water content of the melt varies from nominally dry to 6.2 wt% H₂O. The Fe²⁺/Fe^{tot} ratio in quenched glasses before and after viscosity experiments was measured colorimetrically using a microanalytical method modified after Wilson (1960). Pressure has minor influence on the viscosity compared with temperature, water content (main compositional parameter controlling the viscosity) and redox state of the melt (especially important at low water content of the melt). The combination of our new viscosity data with literature data allows us to model the viscosity η of andesitic melts (in Pa·s) as a function of temperature T (in K), water content w (in wt%) and Fe²⁺/Fe^{tot} ratio with the empirical equation

$$\log \eta = -5.72 + \frac{8530.8}{(T - 59.8)} + \frac{1845.1}{(T - 650.6)} * \exp \left[\frac{196.1}{\left(\frac{Fe^{2+}}{Fe^{tot}} * T \right)} \right] * \exp \left(-452.5 * \frac{w}{T} \right)$$

This expression reproduces the experimental data (87 in total) in the viscosity range from 100.5 to 1013 Pa·s with a 1 σ standard deviation of 0.21 log units. The viscosity data are used to interpret mixing processes in the Unzen magma chamber prior to 1991-1995 eruption. We demonstrate that the viscosities of the rhyolite and andesite melts from the two end-member magmas are nearly identical prior and during mixing, enabling efficient magma mixing.

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The effect of sulphur content on the liquid Fe-S density at high pressure

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Density of liquid Fe-alloys is a fundamental property to estimate the composition and dynamics of the core of the Earth and other planets. We have measured the density of liquid Fe-S at 4 GPa and 1923 K and determined the effect of sulphur content on the density using a newly developed sink/float method. In this method, we used composite density marker consists of Pt rod core and Al₂O₃ tube surroundings. Since the uncertainties of density of the composite marker is much smaller than the composite sphere which has been previously used, the density of liquid Fe-S can be precisely determined. The measured density of liquid Fe-S decreases with increasing sulphur content in Fe-alloy at 4 GPa and 1923 K. This tendency is consistent with the results measured at ambient pressure. The effect of sulphur content on the density become to be larger in the sulphur-rich composition ($S > 40$ at.%). Therefore, this result is applicable to discuss the density and the amount of light elements in the core. Furthermore, this new method is also applicable to density measurement of the other liquid Fe-alloy at high pressure.

Vitrification of opal by shock compression

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Opal is made of low crystalline or non-crystalline SiO₂ with OH and H₂O. Usually, opal is classified to 3 types; opal-A (amorphous phase), opal-CT (mixture of low crystalline tridymite and cristobalite), and opal-C (low crystalline cristobalite). Therefore, a study for shock compression of opal will give important information on vitrification and deformation of hydrated materials.

In this study, structural change in opal up to 38 GPa by shock compression was investigated by X-ray diffraction measurements, Raman and infrared spectroscopies. Opal from Hosaka, Japan was shock compressed by single stage power gun of IMR up to 38 GPa and recovered specimens were analyzed to understand its structural change.

By shock compression of 16 GPa, the crystallinity of opal was increased a little. This fact may be explained by the formation of ordered six-membered rings of SiO₄ tetrahedra with cristobalite like structure. Because silanol groups and molecular water of specimen decreased by shock compression and moderate residual temperature.

Increasing of shock pressure up to 27 GPa, a grate number of surface silanol were dehydrated and polymerized to form the three-membered rings of SiO₄ tetrahedra and promote density increase of the specimen.

By shock compression of 30-38 GPa, the average structure of opal closed to silica glass structure and its density decreased again. This is consistent with vitrification process of quartz by shock compression. High residual temperature with high shock pressure probably relaxed the three-membered rings of SiO₄ tetrahedra to four-membered rings. This four-membered rings is responsible of D1 band in observed Raman spectra. However, the density of opal compressed at 38 GPa is lower than that of silica glass. This low density may be due to remaining of silanol in the glass structure.

P-V-T equation of state of refractory silicate glasses and melts by X-ray microtomography and absorption

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A new high-pressure x-ray tomographic microscope on 13-BM-D at GSECARS-APS/ANL is being used to determine the equation of state of glasses and melts. Bulk moduli are constrained through direct measurement of changes in volume of glass microspheres isothermally compressed to 6 GPa. The pressure generation system consists of two opposing Drickamer anvils compressed within an X-ray-transparent Al containment ring supported by thrust bearings and driven by a 250-ton hydraulic press. This system permits the pressure cell to rotate under load, while collecting radiographs through 180 degrees of rotation. Individual radiographs are recorded by a CCD camera after conversion to visible light by a YAG scintillator and combined to render the volume using a back-projection algorithm and standard flat/dark field corrections with minimal filtering, following by image processing. The configuration of the beamline for 13-BM-D permits switching between a monochromatic beam to produce high-quality radiographs and a white beam to measure pressure through energy dispersive diffraction of a standard. Results are reported for two refractory magnesium silicate glasses (33 mol % and 38 mol % SiO₂) synthesized by levitation-laser heating. Vitreous forsterite (33 mol % SiO₂) compressed to 4.8 GPa shows a 5% reduction in volume, while 38 mol % SiO₂ glass compressed to 6 GPa shows a 9% decrease in volume - corresponding to bulk moduli of ~75 and ~55 GPa, respectively, for K' of 4. The contrast in the compressibility of these magnesium silicate glasses is linked to structural differences accommodating densification. Density is also derived from the Beer-Lambert law from X-ray absorption data coupled with 3D constraints on ray path length. Further developments include the use of a toroidal anvil cell that allows for sample heating under more hydrostatic conditions, enabling P-V-T equation of state determinations for molten materials.

Structural investigation on Mg local environments by high field ^{25}Mg MQMAS NMR spectroscopy

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The structural information on divalent cations such as Mg^{2+} , Ca^{2+} , and Fe^{2+} should have important aspects in magmatic liquids and its quenched glasses because of their abundance in the Earth's interior. The local structure around Mg^{2+} in silicate melts and glasses has been investigated by several researchers, nevertheless little is confirmed on its coordination state. Nuclear magnetic resonance (NMR) spectroscopy is an advantageous method to analyze a specific element in multi-components system. In the present study, we applied ^{25}Mg MQMAS NMR to investigate the Mg local environments in $\text{CaMgSi}_2\text{O}_6$ glass in comparison with its crystalline counterpart, diopside.

$\text{CaMgSi}_2\text{O}_6$ glass was synthesized from a mixture of CaCO_3 , 99 % ^{25}Mg -enriched MgO , and SiO_2 reagents. The mixture was melted at 1500 °C and quenched in air. ^{25}Mg single pulse MAS NMR spectra were accumulated on JNM-ECA920 spectrometer (21.6 T) working at 56.3 MHz, and MQMAS ($M = 3$) spectra were on JNM-ECA700 (16.4 T) working at 42.1 MHz. ^{25}Mg chemical shifts were externally referenced to MgSO_4 solution (0.0 ppm).

The single pulse MAS spectrum of $\text{CaMgSi}_2\text{O}_6$ glass at 21.6 T shows a single broad peak ($\delta_{\text{MAS}} \approx 15.0$ ppm, FWHM ≈ 60 ppm) with a lower-frequency tail, as reported by Kroeker & Stebbins (2000). On the other hand, 3QMAS spectrum presents the first evidence of distinct multiple sites in the amorphous structure. The estimated *true* chemical shifts δ_{CS} range from -10 ppm to 10 ppm, suggesting six-coordinated Mg-O species. Significant distortions of the coordination polyhedra were also indicated by large quadrupolar coupling constant C_Q values. We will further discuss the detailed site information on Mg^{2+} in $\text{CaMgSi}_2\text{O}_6$ glass and diopside.

In situ X-ray experiment on the structure of melt in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ under high-pressure and temperature

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Recent studies on melting of $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system have revealed that the liquidus phases change from olivine to pyroxene, and further stishovite with increasing pressure under hydrous condition, and the compositions of the liquid generated in the deep mantle become enriched in MgO component (e.g. Inoue, 1994, Yamada et al., 2004). These phenomena imply the structural changes of the hydrous silicate melts in the vicinity of the pressure at which liquidus phases are changed, because the liquidus phases and the melting relations should be strongly affected by the melt structures. We have conducted in-situ X-ray diffraction experiments of hydrous Mg-silicate melts under high-pressure conditions up to 10 GPa in order to clarify the structures. Experiments were conducted at AR-NE5C in Photon Factory (PF-AR) and BL04B1 in SPring-8, using cubic-type and Kawai-type high-pressure apparatus respectively. Starting materials were prepared by mixing of $\text{Mg}(\text{OH})_2$ and SiO_2 to make the systems of $\text{MgO-SiO}_2\text{-H}_2\text{O}$ ($\text{Mg/Si}=1.0, 1.5$ and 2.0). Special attentions were made to obtain the diffraction by introducing new diamond capsule system. We could succeed to get good quality diffraction data of hydrous silicate melt by using diamond capsule, and could 8 times reduce the exposure time comparing with the use of Ag-Pd capsule, in which we have done experiments previously. In the derived structure factors $S(Q)$ s, first sharp diffraction peaks (FSDP), which is related to the size of intermediate range ordering such as SiO_4 tetrahedral network in silicate melts, shift to higher Q (where Q is the scattering vector which dimension is $\text{\AA}^{-1}$) with increasing MgO content. On the other hand, the pressure dependence of the peak shift to high- Q was significant in the melt with lower Mg/Si. Moreover, in the comparison with the dry melt with $\text{Mg/Si}=1.0$ (Funamori et al., 2004), the FSDP in the hydrous melt with $\text{Mg/Si}=1.0$ shifts to higher Q side than those in dry melt under high pressure. This indicates that H_2O should be dissolvable into silicate melt by dividing the network structure of SiO_4 tetrahedron to form Si-OH. This interpretation of one of dissolution mechanism in hydrous silicate melt is consistent with previous spectroscopic and NMR studies (e.g. Mysen and Virgo, 1986, Kohn et al., 1989). Further details about the local structures of the hydrous melts from radial distribution functions which are derived by Fourier transform of structure factors will be presented.

O10-01

Pressure-induced sequential transformations of oxides and silicates with electron-lattice interactions

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Much attention has been given to the structure transformations of oxide and silicate spinel, ilmenite and perovskite bearing transition elements for geophysical interests. The electron density distribution has been investigated as functions of pressure and temperature by X-ray single-crystal and powder diffraction study at high pressures and temperatures. The diffraction intensity measurements of powder sample and single crystal have been made at high pressures up to 100 GPa using short wavelength of synchrotron radiation with DAC. Investigations of pressure-induced transformations have been attracted for not only for reconstructive structure changes but also atomic displacement with electron-lattice interaction such as change of density of electronic state, charge disproportion, band overlapping, high-low spin configuration, Jahn-Teller effect and spin-Peierls dimerization. Ferroelectric, ferromagnetic and ferroelastic compounds with perovskite structures change their physical properties under compression due to dipole moment, cooperative spin ordering and electron spin ordering. Structure transformation also related to elastic stability based on Born criteria. Structures composed of more than two cation sites indicate anisotropic compression. Perovskite ABO_3 structures having $t > 1$ (t indicates a tolerance factor) increase their crystal symmetry with pressure. On the other hand, those having $t < 1$ decrease their symmetry.

The maximum entropy method (MEM) analysis reveals the electron density distributions around cations, which are not spherical but elongated or deformed due to the electron orbital. The compression affects the Coulomb potential in the M-O bonds and the repulsive force is enhanced under high-pressure conditions. The electron densities on the M-O bonds are more increased with pressure. The localization of the valence electron around the cation is enhanced under higher pressure. The pressure dependence of the electron radial distribution obviously shows the more localization of electrons around cations with increasing pressure. The electron density between cations across the shared face becomes smaller with increasing pressure. This is because the repulsion of electrons between two cations is enlarged with the external compression. The electron conductivity measurement using a polycrystalline reveals increasing conductivity at higher pressure. Hence charge transfer or electron hopping is possible under pressure.

Thermal transformation is caused by the anharmonic thermal vibration of atoms, which can be proved by the difference-Fourier electron density based on the diffraction intensities as a function of temperature.

O10-02

Symmetry considerations in structural phase transitions

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The vast majority of structural phase transitions involve a change in symmetry. The analysis of phase transitions according to symmetry changes (e.g. Landau theory) is by no means new. It has however been facilitated in recent years by the availability of computer programs - such as ISOTROPY, from Hatch and Stokes at Brigham Young University - that assist such analyses.

The methods have proved particularly useful in studies of the different variants of perovskite, ABX_3 , and the phase transitions that might occur between them (C.J. Howard & H.T. Stokes, *Acta Crystallographica A* **61**, 93-111, 2005). Effects of cation displacement, cation ordering, the distortion and/or tilting of the BX_6 octahedra have been considered. In most cases, the results can be summarised on a schematic ('tree'), showing the different possible variants, group-subgroup connections between them and, where such connections exist, whether the corresponding phase transitions are allowed (in Landau theory) to be continuous. Such trees have proved useful in determining perovskite structures - for example the observation of a continuous transition from a higher temperature, higher symmetry structure to a lower symmetry structure, leads to quite tight constraints on the structural solutions. For group-subgroup transitions, it may be possible to identify the symmetry of the driving order parameter and then to monitor physical distortions of the corresponding symmetry. Regarding first order transitions, for example when there is no group-subgroup relation between the variants involved, it may be possible to use the trees to identify common subgroups and so to suggest a transition pathway. The methodology will be illustrated through examples, such as $SrZrO_3$, Nd_2TiO_5 , and $PrAlO_3$.

Computer assisted analysis is also being applied in systematic studies of other families of structures derived from a high symmetry parent. Currently under investigation are families based on layered perovskite, rutile, and fluorite.

O10-03

High pressure phase transformations of $CaSiO_3$, $FeSiO_3$ and $MnSiO_3$ in relation to the perovskite structure

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Studies on high pressure phase transformations of $MSiO_3$ (M = divalent cation) compounds are very important to understand the chemical and physical properties of the lower mantle. Compared to the studies on $MgSiO_3$, however, those on other $MSiO_3$ compounds are very limited. Here, we report the results of our recent studies on high pressure phase transformations of $CaSiO_3$, $FeSiO_3$ and $MnSiO_3$ in relation to the perovskite structure, using a laser-heated diamond anvil cell.

High pressure and temperature experiments on the $CaSiO_3$ - $FeSiO_3$ system were carried out at around 30-137 GPa and 2000 K, using mostly gel as starting materials. Analyses of the product phases by synchrotron X-ray diffraction and analytical electron microscopy revealed that $CaSiO_3$ cubic perovskite is stable up to 137 GPa at 2000 K and has Fe solubility of around 0.1 - 0.17 per formula unit, while for $FeSiO_3$ a mixture of FeO with a B1 structure and a high pressure polymorph of SiO_2 is stable up to 137 GPa. In the intermediate composition in $CaSiO_3$ - $FeSiO_3$, three phases of $CaSiO_3$ perovskite, FeO with a B1 structure and a high pressure polymorph of SiO_2 are stable up to 137 GPa. All the Fe bearing $CaSiO_3$ perovskite phases showed tetragonal symmetry at high pressure and room temperature after heating and the distortion from cubic seems to be enhanced by Fe incorporation and increasing pressure.

High pressure and temperature experiments on $MnSiO_3$ were performed at 30-60 GPa and 1800-2000 K, using $MnSiO_3$ rhodonite as starting material. X-ray diffractions at high pressure and temperature and at ambient conditions revealed that $MnSiO_3$ orthorhombic perovskite is stable at 30 GPa and 1800 K and at 60 GPa and 2000 K. But at higher temperatures it seems to decompose into MnO with a rhombohedral structure and stishovite, indicating the positive phase boundary between them in the pressure-temperature diagram. The orthorhombic distortion of $MnSiO_3$ perovskite decreases with increasing pressure. $MnSiO_3$ perovskite becomes amorphous after decompression.

The fairly large tolerance factor of $CaSiO_3$ perovskite and the decrease of the distortion of $MnSiO_3$ perovskite with increasing pressure indicate that $CaSiO_3$ and $MnSiO_3$ perovskites do not transform to the post-perovskite phase even at higher pressure. The reason why $FeSiO_3$ does not have a perovskite structure even at very high pressure, seems to be due to the energetic advantage of FeO with a B1 structure by the crystal-field stabilization energy of the octahedral Fe.

O10-04

Disorder and structural transitions in melanophlogite and tridymite

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The phase transition mechanisms in melanophlogite (MEP) ($23SiO_2 \cdot M^{12} \cdot 3M^{14}$; M^{12} denotes pentagondodecahedral and M^{14} tetrakaidecahedral voids) and tridymite (SiO_2) are reviewed based on recently published structural data^{1,2}. The unit-cell parameters and mean-square displacements (MSD) of O atoms of monoclinic tridymite (MC) show only weak temperature dependences, but abruptly change to those of an orthorhombic phase, OP¹. On the other hand, the c -dimension and MSDs of O atoms in the low-temperature tetragonal phase (α) of MEP more steeply increase at higher temperatures up to those of the cubic high-temperature phase (β)².

The extremely large MSDs of O atoms in OP tridymite and β -MEP, tetrahedrally coordinated to Si atoms with ordinary magnitudes of MSDs, arise from its disorder, probably orientational disorder of the corner-linked SiO_4 units. However, the different temperature dependences noted above reflect the difference in the mechanisms of the respective transformations for $MC \rightarrow OP$ and $\alpha \rightarrow \beta$. The disorder in β -MEP is considered to occur involving 12 domains of α -MEP, and a similar, but partial disorder already occurs in α -MEP and becomes increasingly significant with increasing temperature. On the other hand, the O atom disorder in OP may occur between two energy minima, corresponding to two orientations of SiO_4 . It is important to note that the distortion of such SiO_4 frameworks is not identified with that of MC, and no sign of disorder was indicated at all temperatures for MC. In conclusion, the $\alpha \rightarrow \beta$ transformation in MEP, appeared to be of the second order or tricritical one, is driven by increasing disorder of multiple domains of α -MEP with increasing temperature, whereas, in the $MC \rightarrow OP$ transformation, ordered MC suddenly changes to a disordered state over two orientations; the probable domain structures are of other than MC. In the present study, it is also argued that the near-to-second order or tricritical nature of phase transition in some minerals is resulted from temperature-dependent effects of disordering motions over multi-wells, that is boosted by low-frequency phonon modes through coupling, if both the motions are symmetrically compatible with each other.

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An in-situ X-ray diffraction study on kinetics of plagioclase breakdown at high pressure

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High-pressure transformations in plagioclase occur in subducting oceanic crust associated with the gabbro-eclogite transformation and in parent bodies of heavily shocked chondritic meteorites. Although equilibrium phase relations for these transformations have been well studied, the processes of plagioclase breakdown are poorly known, which makes it difficult to constrain the depth of eclogitisation in subducting plates and P-T conditions during shock events in parent bodies. Here we report experimental results on mechanisms and kinetics of plagioclase breakdown examined by in-situ X-ray observations.

Two kinds of starting material were used in this study, sodic (natural albite, Ab98.0An0.4Or1.6) and calcic (natural labradorite, Ab45.0An51.8Or3.2) plagioclases. These plagioclases decompose into jadeite + quartz (coecite), and jadeite + grossular + kyanite + quartz (coecite), respectively, at around 1-2 GPa. In-situ X-ray diffraction experiments were carried out using multi-anvil high-pressure apparatuses MAX-80 and MAX-III installed at KEK, Japan. Kinetics of plagioclase breakdown was observed at 2.2-18.8 GPa and 273-973K by taking time-resolved X-ray diffraction profiles every 10-300 seconds. Transformation microstructures and water contents of recovered samples were investigated using SEM and FTIR, respectively.

SEM observations show that the breakdown of sodic plagioclase occurs by grain-boundary nucleation and growth processes. Kinetic data obtained suggests that the growth distance is proportional to $t^{0.5}$ (t : time), which implies the diffusion-controlled growth mechanisms. In case of the grain size of about 20 micron in the present study, the reaction proceeds rapidly under both hydrous (about 0.5 wt.% H₂O) and nominally anhydrous conditions at temperatures of 673-773K and dP of more than 2 GPa from the equilibrium boundary. Extrapolations of obtained growth kinetics suggest that the breakdown of albite with the grain size of 5 mm can complete in 10000 years at 573K. We observed that the albite breakdown becomes very slow near the equilibrium boundary (dP of about 0.5 GPa) even at higher temperature of 923K probably due to difficulties of nucleation processes. On the other hand, decomposition of calcic plagioclase was much slower than that of sodic plagioclase, which is almost identical to the effect associated with a 400-500K difference in temperature. This is probably because of the very complex reaction (dissociation into 4 phases) and the slow diffusion rate of Ca. We also observed broadening of diffraction peaks in calcic plagioclase during cold compression to 18.8 GPa and amorphization when heating to 473K. High-pressure assemblages of calcic plagioclase appeared at around 1273K.

Mechanism of the olivine-ringwoodite transformation in the presence of aqueous fluid

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The mechanism of the high pressure transformation of olivine in the presence of aqueous fluid was investigated by high pressure experiments conducted nominally at the wadsleyite-ringwoodite stability field at 14.5 GPa and 700 °C and 800 °C. The microstructures of recovered samples were observed using a transmission electron microscope (TEM) and an analytical transmission electron microscope (ATEM) for which foils were prepared using a focused ion beam technique. The starting material was a mantle-derived deformed dunite collected from Uenzaru ultramafic complex in the Hidaka metamorphic belt of central Hokkaido, Japan. This dunite contained hydrous minerals, such as amphibole, chlorite, and serpentine which dehydrated at the experimental conditions. The dehydrated fluid influenced the transformation mechanism of coexisted olivine. Olivines began to transform to hydrous ringwoodites from their rims and along cracks, and, in general, were wholly replaced by ringwoodites. Subsequently, wadsleyites grew within the ringwoodites matrix and eventually coexisted with ringwoodites. Numerous micro-voids less than 1 µm in diameter were present in the area of these ringwoodites and had not been observed in the starting olivine. TEM observations showed that these micro-voids were filled with a glass substance and that glass films approximately 1 micrometer in width always occupied the interface between olivine and hydrous ringwoodite. ATEM measurements showed that the chemical compositions of the glass films had approximately the same Mg/Fe ratio as that of olivine, but a higher Si content. Micro-structural and -chemical observations suggest that these glass films formed as quenched glass from the aqueous fluid dissolving olivine and that hydrous ringwoodite was crystallized from the fluid. This indicates that the transformation of olivine to hydrous ringwoodite was prompted by the dissolution-reprecipitation process. A key aspect of this process is that replacement may result in a high density of voids in the product phase (Putnis 2002; Putnis and Mezger 2004) and that the mechanism is characterized by a sharp interface between the host and precipitated phases, which may also contain a fluid film (O'Neil 1977). Both of these characteristics were observed in our samples. This implies that dissolution-reprecipitation is likely an important mechanism in transforming olivine to its high pressure polymorphs in the Earth's deep interior where aqueous fluid is present.

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Mechanical properties of minerals: the role of transformation microstructures.

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Transformation twinning and inherited microstructures are common features of crustal minerals, and may be important throughout the deep Earth. Here, I shall present new results on the influence of such microstructures on the mechanical properties of minerals. Using low-frequency mechanical spectroscopy of samples held at high temperature and subjected to dynamic stress it is possible to identify modes of microstructural response that arise as a consequence of phase transitions. Results from a range of perovskite microstructures will be reviewed, alongside data from other silicates including leucite and enstatite.

New experimental constraints on nanodiamond formation mechanisms from carbon nanoparticles at high pressure

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During the last decade, several carbon forms (amorphous carbon, nanotubes, fullerenes, graphite ...) have been used as precursors in order to reduce the minimum pressure/temperature conditions of diamond formation with implications for producing ultra-hard aggregates of industrial interest. To better understand the mechanisms leading to diamond at high pressure, we chose five precursors covering the whole range of carbon structural organization, e.g. a quasi-amorphous soot (QAS), a raw carbon black (CB), the same CB but heat treated at 2600°C (HTCB), a high-purity polycrystalline graphite (PCG) and a highly oriented pyrolytic-graphite (HOPG). Those products were run at 15 GPa in the 1500 - 1900°C range between 15 and 60 minutes. The recovered products were then characterized by X-ray powder diffraction (XRPD) and Raman micro-spectroscopy in order to follow the evolution of the reactants and using high-resolution transmission electron-microscopy (HRTEM) to image textural relationships at the nanometre scale.

Within amorphous carbon, the small graphitic fringes are directly transformed into diamond, without any prior graphitization. The concentric microtexture of the CB yields interesting features. Indeed, the spherical particles are preserved almost until the end of the transformation but diamond nucleates in the middle of them. Within graphitized products (HTCB and PCG), Raman spectrometry indicates that the sp² carbon organization decreases while diamond nucleates. This is consistent with HRTEM images showing graphite delamination. These precursors mostly evolve according to a reconstructive mechanism with limited diffusion. A small amount of lonsdaleite is observed by XRPD. With respect to HOPG, a very high amount of lonsdaleite is obtained, probably through a martensitic-type mechanism. These transformations mechanisms are characterized by different kinetics, it appeared that disordered materials react faster than crystalline ones. They achieve higher transformation rates and become transparent more easily than crystalline precursors.

We show that the combined use of HRTEM (on FIB slices), micro-Raman and XRPD offers a powerful tool for characterizing samples which are only partly transformed into diamond. This study tends to show that diamond preferentially nucleates (and grows) from structural defects (pentagons, sp³ bonds). In highly crystalline precursors, as HOPG, this nucleation (and growth) mode cannot be dominant and is taken over by a martensitic-like transformation process.

Gismondine under HP: deformation mechanism and re-organization of the extra-framework species

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The response to compression of the zeolite gismondine ($\text{Ca}_4\text{Al}_8\text{Si}_8\text{O}_{32} \cdot 18 \text{H}_2\text{O}$) was explored by X-ray powder diffraction (XRPD) experiments and computer simulation studies via *ab initio* (Car-Parrinello) molecular dynamics techniques (CPMD). This approach is particularly useful for predicting the behaviour of systems at conditions different from the ambient ones because it allows to derive information on the deformation mechanism at an atomistic level. The high-pressure (HP) XRPD experiments were performed at SNBL1 beam-line at ESRF (Grenoble), using a wavelength of 0.7 Å, a MAR 345 detector, and silicon oil as non-penetrating pressure-transmitting media. The accessed P range was 0–36 GPa. With this experimental set up, a series of diffraction profiles were collected in the pressure range 0–8 GPa. Reversibility was checked, working upon decompression, at 6.7 and 4.3 GPa. Due to well known experimental difficulties, only the cell parameter values were obtained from Rietveld refinements of the XRPD data. In the studied P -range, the cell volume decreases approximately by 8% with respect to the ambient conditions and the corresponding bulk modulus is $K_0 = 63.8(2)$ GPa. The HP-induced cell modifications are found to be reversible upon decompression, at least up to about 4 GPa. Calculations were performed adopting gismondine cell parameters obtained from the XRPD experiments at room pressure and at about 2, 4 and 7 GPa. For each chosen set of cell parameters, atomic positions of all atoms in the unit cell were obtained by room temperature CPMD runs, thus providing atomic resolution information on the structure at 300 K. The P -induced framework modifications mainly occur *via* deformation of the four-membered rings of tetrahedra forming the “double crankshafts” which characterize gismondine structure. Consequently, the extra-framework channels squash and become more elliptic. This deformation mechanism can explain why gismondine is much more compressible along a and c with respect to b : the former two directions are those along which the flexible doubly connected 4-ring chains develop; on the contrary, b axis corresponds to the direction along which gismondine presents its dense layers. It is worth noting that this HP deformation mechanism is similar to that adopted by gismondine upon dehydration under vacuum. Concerning the extra-framework species, under HP Ca coordination number increases and the water molecules tend to organize themselves in a supra-molecular arrangement different from that present under ambient conditions.

Kinetics of cation distribution in synthetic $\text{Mg}(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$ spinels

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Two spinel samples, synthesised by flux-growth method were studied by means of single-crystal X-ray diffraction and a quenched-in method, in order to achieve the time and temperature evolution of intracrystalline cation exchange between T and M sites. The two samples have composition $\text{Mg}(\text{Al}_{1-z}\text{Fe}^{3+}_z)_2\text{O}_4$, with $2z=0.39$ and 0.61, respectively.

After annealing at 1000°C for 24 hours, the samples were isothermally ordered at 650 and 750°C in several time-steps in order to check the ordering rate before the achievement of equilibrium. Cation ordering was monitored following the variations of the oxygen positional parameter u , which is strictly related to the inversion parameter x , whereas the cation distribution was calculated using the bond-length method with ionic radii from Lavina et al (PCM, 2002).

The inversion parameter decreases with the decrease of equilibration temperature and reaches the values pertinent to 750 and 650°C in different times for the two samples. In particular the ordering is faster for the sample with higher Fe^{3+} content at both the investigated temperatures. The comparison with the synthetic MgAl_2O_4 spinel and with natural spinels with low Cr content indicates that the Mg-Al exchange reaction between T and M sites is faster for the samples here studied.

The Muller kinetic model, allowed the calculation of the kinetic constant K , linearly related to temperature by means of Arrhenius equations. The kinetics of ordering processes are influenced by Fe^{3+} content and the activation energy (preliminary data) is rather similar to that of Harrison and Putnis for pure magnesioferrite (PCM, 1999).

At least, isothermal runs at temperature lower than those yet performed are in progress in order to better calculate the kinetic constant.

Silicon diffusivity in ringwoodite at the transition zone conditions

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Ringwoodite is thought to be major constituent mineral in the mantle transition zone. Therefore the diffusion data in ringwoodite provide important constraints on rheology, electrical conductivity, and re-homogenization of chemical heterogeneities in the mantle transition zone. Because silicon is usually found to be the slowest diffusing element, silicon is possibly the rate-controlling species in silicate minerals. In this study, we conducted the silicon diffusion experiments in ringwoodite phase in order to constrain the rheology of the mantle transition zone. High-pressure experiments were carried out using a kawai-type multi-anvil apparatus installed at Tohoku University. Water contents in the samples were measured by a Fourier transform infrared spectroscopy (FTIR). Grain size of ringwoodite was investigated using a Scanning electron microscopy (SEM). Starting materials of polycrystalline ringwoodite have been synthesized at 20 GPa, and 1473–1773K from San Carlos olivine. The surface of the polycrystalline ringwoodite was polished with diamond paste and then coated with a ^{29}Si enriched SiO_2 thin film using a high-vacuum thermal evaporation. Oxygen fugacity was controlled by the Ni–NiO buffer. Diffusion annealing experiments were conducted at 20 GPa and 1473–1673K. After the diffusion annealing, concentration profiles of ^{29}Si were measured by the depth profiling method using Secondary ion mass spectrometer (SIMS) installed at Kyusyu University.

SIMS and ATEM measurement revealed that ilmenite phase possibly existed in a region between ringwoodite and SiO_2 thin film. Therefore diffusion coefficient of silicon in ringwoodite couldn't be measured in these experiments. We are planning to evaporate ^{29}Si and ^{18}O enriched $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ on the ringwoodite surface using the pulsed laser deposition system in order to overcome above problem.

Structure transitions of calcium metal under high pressure

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Calcium (Ca) forms a fcc lattice at ambient conditions and transforms to bcc lattice at 20 GPa and to simple cubic structure (sc) at 32 GPa [1]. And it has been reported that this sc structure is stable up to 85 GPa. Recently we reported that sc phase is stable in the wide region from 32 GPa to 117 GPa and a high-pressure phase, Ca-IV, existences above 113 GPa at room temperature [2]. The superconducting transition temperature T_c of Ca increases with pressure and reaches 15 K at 150 GPa [3]. In the case of Ba and Sr, the same alkaline earth elements as Ca, the maximum values of T_c are obtained at the state of the completion of the s - d electron transfer, where the crystal forms Ba-IV type structure. The higher-pressure phase of Ca than the sc phase could be expected to be such as Ba-IV type phase. Here we have investigated X-ray diffraction study on Ca up to 154 GPa. The polycrystalline sample was loaded into the diamond-anvil cell without any pressure transmitting medium. Pressures up to 70 GPa were determined on the basis of the ruby pressure scale. The pressure determinations above 70 GPa were conducted from the d values by the equation of state of Pt. The diffraction patterns were collected on BL-13A at Photon Factory (PF - KEK). We found that a new high-pressure phase V above 148 GPa. And we obtained the clear patterns of single-phase IV and V, respectively. However, these two phases are not same as Ba-IV structure. Those structures are remained to be analyzed. In order to clarify electrical conduction according to the phase transitions, the electrical resistance was also measured up to 160 GPa at room temperature by the AC quasi-four-probe method. The sample was placed on the alumina insulator. Thin foils of platinum have been used as electrodes. The electrical resistances of sc, Ca-IV and Ca-V phases formed by s - d transition are much larger than bcc and fcc. The electrical property and the crystal structure of some alkaline earth metals at high pressure are governed by the pressure-induced s - d electron transfer. Their electron-lattice interaction will be discussed.

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Convergent beam electron diffraction study on Si-Al ordering of albite by energy filtered transmission electron microscopy.

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The fine variations in crystal structures during the transformation from low to high albite was successfully documented in this study through the observations of convergent beam electron diffraction (CBED) patterns using an energy filtered transmission electron microscope (EF-TEM). Seven Amelia albites were heated at 1100 °C for 7 days and seven heated samples taken at one day interval were examined by X-ray diffraction (XRD) to confirm the transformation into the high albite. The angular distance between the diffraction positions of (131) and (1-31) peaks, $\Delta(131)$ was monitored to confirm the transformation in XRD and selected area diffraction patterns (SADP) in TEM. The changes in crystal structures in the transformation of low-to-high albite are visible in γ^* angle and it is most apparent in the TEM SADP patterns in the [001] and [10-2] directions.

The optimum condition for the most effective observation of ultra-structural variation in the CBED investigation was also documented in this study. An energy filtered TEM equipped with a cooling specimen holder, and a slow-scan CCD camera is essential for an optimum CBED observation in a research for minerals, and better results were obtained in this study with the accelerating voltage of 120 keV, the C3 aperture of 37 μm , the probe size of 25 μm , and the exposure time of 3 seconds. These conditions are calibrated to obtain the best photographs minimizing specimen damage by the irradiation of electron beam.

The CBED pattern from the [-418] direction which is obtained by tilting of 6.7° from the [10-2] direction is useful to identify the structural variations by observing the changes in HOLZ lines of albite. Many of the HOLZ lines in the CBED patterns of albite can not be indexed because the computer programs developed up to date are not accurate enough for the low symmetry crystal structure of albite.

XRD patterns of intermediate albite do not show the changes in $\Delta(131)$. However, the HOLZ line in the CBED observation demonstrates continuous changes in the crystal structures of low, intermediate and high albite according to the heating time. The systematic characterization of the detailed changes in crystal structures of albite that occur during the transformation from low to high albite became possible through the observation of HOLZ lines in CBED. The result of this study can be applied in the study on the formation and transition of the most rocks in geological environment.

Spinodal crystallization from impact glasses of labradorite feldspars

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1. Introduction: Solid-state crystallization on spinodal decomposition of plagioclase feldspar minerals has been considered to be formed by plutonic magma on the Earth. The purpose of the present study is to elucidate of origin of glassy state to form iridescent labradorite feldspar minerals (Miura et al, 2005; Miura and Tomisaka, 1978; Miura and Rucklidge, 1979). 2. Textures and NiCoFe-bearing phases of iridescent labradorite feldspars: The following evidences for textures and anomalous meteoritic elements can be found from labradorites from Nain, Canada. 1) The sample contains labradorite plagioclase, pyroxenes and minor minerals of ilmenites, TiO_2 , Fe-rich, NiCoFeS-rich, and carbon-rich phases. 2) NiCoFeS-rich phase of 10 μm in size shows round spherule shape with mixture of Ni, Co, Fe and S; which is considered to be mixed phases of NiS_2 , CoS_2 and FeS_2 . 3) The sample has relict texture of irregular patterns as shock-type within each block which shows exsolved and lamellar submicron-texture finally during later crystallization. 3. Crystallization of glassy phases by magmatic heating: The sample can be considered to be crystallized at the margins of the primordial continents of Canada and probably Finland and Madagascar Africa, where were moved by later continental movements. The above data indicate that original glassy state formed probably by large impacts on the primordial Earth cannot be eliminated due to spinodal decomposition under solid-solid state with keeping of original irregular texture and phases during crystallization from plutonic magmas. 4. Diaplectic plagioclases with and without reheating: Glassy diaplectic plagioclases with labradorite feldspar composition can be found on the surface of the Earth as in Manicouagan impact crater, Canada. Glassy maskelynites with labradorite feldspar composition are reported from Martian meteorites derived from Martian surface by impacts. The present data of iridescent labradorite with irregular textures and NiCoFe-rich phases indicate that global impacts on the primordial Earth form diaplectic labradorite phases to crystallize plagioclases with exsolved lamellar texture under solid-solid nucleation. 5. Summary: Irregular shock-type texture and NiCoFe-bearing spherules of labradorite feldspars indicate that glassy phases to form the exsolved micro-texture are formed by global impacts to survive on primordial continental margins and heating from plutonic magma during solid-solid crystallization to form multi-layers of labradorite feldspars finally.

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O11-01

Revisiting basic concepts of crystal growth to meet in situ AFM data – Gibbs-Thomson law, BCF theory, stoichiometry

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The 1951 Burton-Cabrera-Frank (BCF) theory includes major crystal growth concepts of the 20-th century and brought about solid physical background to understand and diagnose the growth kinetics. However, recent in situ AFM experiments on layer-by-layer growth of sparingly soluble salts (calcite, brushite, oxalates) and the protein lysozyme from aqueous solutions suggest failure of some basic assumptions requiring the theory expansion:

1. Equilibrium thermodynamic fluctuations seems to occur not fast enough to assure maximal kink density on steps. Therefore propagation of steps polygonized along simple crystallographic directions is limited by kink generation, not only by kink rate [1].

2. The Gibbs-Thomson Law (GTL) providing supersaturation decrease over a short step segment (in 2D) or over a small crystal (in 3D) is not applicable except for very close to equilibrium: $\Delta\mu/kT < 10^{-2} - 10^{-3}$ for objects of $10^2 - 10^3$ lattice spacings $\approx 10^2 - 10^3$ nm. This is because in crystals the GTL is implemented only by the (supersaturation dependent) kink exchange between step corners (2D) or crystal edges (3D). Unlike with a liquid droplet, where the information on the droplet size and local shape change is spread by fast capillary waves [2].

3. Dependence of the step segment velocity v on the segment length L on calcite and potassium biphthalate was found to be much steeper than that in the commonly used form $v = v_s(1 - L_c/L)$ where L_c is the critical nucleus linear size. As a result, a screw dislocation should generate steps several times faster than that predicted by the BCF theory [1,2].

4. Non-Kossel crystal has several types of kinks on their surfaces, unlike the Kossel crystal with only one type. This is for the latter for which major theory is developed. To the non-Kossel crystals belong those which molecules dissociate during dissolution, evaporation or melting or those that include several molecules in non equivalent positions per unit cell, or the both. The non-Kossel model for binary ionic lattice describes major features discovered when we have measured by AFM step rate v on faces of Ca and Mg oxalates. Namely, we found v to be about invariant with respect to the anion $\leftrightarrow$ cation replacement, $r \leftrightarrow 1/r$, and to be linear function of $r^{1/2} + r^{-1/2}$. Here $r \equiv [Me^{2+}]/[C_2O_4^{2-}]$ with $Me = Ca, Mg$ [3].

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O11-02

Stabilities of Crystal Faces of Calcite and Aragonite Compared by Atomic Force Microscopic Observation of Dissolution Processes in Aqueous Acetic Acid

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Dissolution processes in aqueous acetic acid or water at various crystal faces of calcite and aragonite, the two most important polymorphs of $CaCO_3$, were observed *in situ* with Atomic Force Microscopy (AFM). The relative stabilities of the crystal faces were reflected upon the formation of facet patterns in submicron-scale.

In the case of calcite, the polar (0001) face was faceted into electrically neutral {10-14} faces in the acid. The same face, however, was stabilized in the presence of Mg ion which is smaller in size than Ca ion, and can be buried among the anions. Prismatic {01-10} face was faceted into {1010}, {11-20} and {10-14} faces. At the (11-20) surface, the formation of {11-26} facets was observed. Partial cancellation of negative charges of carbonate ions by proton addition stabilizes some of the crystal faces. Planar arrangements of positive and negative charges in the outermost level of the surfaces are important for the stability of ionic crystals in aqueous solutions.

Natural aragonite crystals are strangely covered with polar faces such as (001), (110) and (010). In the dissolution processes of these faces in aqueous acetic acid, neutral faces such as (100), (130) and (112) were stabilized [1,2]. The polarity of the crystal faces are strongly affected by the protonation. The natural forms of aragonite most probably grew in alkaline environments.

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O11-03

Vertical Scanning Interferometry – A Review of Applications and Future Possibilities

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Over the last decade vertical scanning interferometry (VSI) has been successfully applied to the study of surface processes such as dissolution, corrosion, and crystal growth. During this time, it has been demonstrated that the VSI technique can be used not only to quantify surface topography with nanoscale vertical resolution but can be used to measure rates of processes that physically alter the solid surface. By measuring surface-normal retreat or advance in a spatially resolved way, kinetics of even slow processes, e.g., 10^{-11} moles/m²/sec can be studied in a quantitative fashion. Of particular interest is the fact that the technique circumvents the surface normalization problem, i.e., no external surface area measurement is required. Therefore, questions of reactive surface area versus total or geometric surface area can be addressed directly.

Recent studies involving direct observations of crystal and glass dissolution have led to an improved understanding of the kinetics of diverse materials, including minerals such as feldspars, carbonates, sulfides, and sulfates, as well as different types of glass. In concert with other experimental and analytical techniques such as atomic force microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS), interferometry has yielded new and fundamental insights into a range of complex problems, ranging from the interaction of metal impurities with carbonate mineral surfaces, the hydration and setting time of cement particles, and stress/strain relationships on metal surfaces. In addition, VSI brings a unique capability to the quantification of microbial attachment and interaction with solid surfaces. The non-destructive nature of the light-optical technique has led to a range of exciting applications in geobiology, microbiology, and biological engineering.

In addition, technical advances such as resolution enhancement (super-resolution) have already led to a significant improvement of lateral resolution. For the future, in situ and even in vivo applications are likely. Integration of interferometry, confocal and fluorescence microscopy at the instrument level will open new strategies and applications towards a quantitative understanding of fluid – microbe – solid interactions and their relevance in the geo- and life-sciences.

O11-04

Impurity induced defect and its effect on protein crystal perfection

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The impurity effect on protein crystal growth and perfection was studied by X-ray diffraction, rocking curve measurement, X-ray topography and etching technique. 5 % impurity (lysozyme dimer) addition degraded the B-factor (a factor used to evaluate the crystal quality in the field of protein crystal growth and is obtained from the Wilson Plot) value. Typical full width half maximum (FWHM) of the rocking curve of crystals grown from a pure lysozyme solution were $0.004 - 0.006^\circ$, while those crystals containing 5 % lysozyme dimer were $0.006 - 0.010^\circ$. X-ray topography experiments revealed that dislocations existed in crystals containing the lysozyme dimer. These dislocations are one of the causes of rocking curve width broadening. Many deep etch pits were observed in contaminated crystals, but few, if any pits were observed in either face of the pure crystals.

The positive effects of microgravity experiments will also be briefly introduced.

Metastable Phase Formation from Undercooled Melt in Containerless Processing

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Undercooling melts facilitates the preferential nucleation of metastable phases. In the present study, the formation of metastable phases from undercooled melts was considered from the viewpoint of the competitive nucleation criterion. The classical nucleation theory shows us that the most critical factor for forming a critical nucleus is the interface free energy σ . Furthermore, in the simple system such as mono-atomic metals, the negentropic model on σ shows that the scaling factor α on the polyhedral order in the liquid and solid phases is the controlling factor on the value of σ . In ionic materials such as oxides, however, in which oxygen polyhedrons including a cation at their center are the structural units both in the solid and liquid phases, the entropy of fusion, rather than α , can be expected to become dominant in the determination of σ . In the present study, based on this idea, the entropy-undercooling regime criterion on the formation of metastable phases is proposed and verified using REFeO₃ (RE: rare-earth element) as the model material.

Microscopic visualization of solid/liquid interface in crystal growth at high temperature under reduced convection condition

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Solution growth methods at high temperature, e.g., liquid phase epitaxy and a traveling heater method, have attracted considerable attention to reduce contamination from a crucible due to its lower temperature process than melt growth. Its growth mechanism is also interesting from a viewpoint of heat and material transport phenomena in liquid, because the solutal effect on the stability of the convection mode is conspicuous. However, characteristic defects are often observed on surface and in grown layer of an as-grown crystal in semiconductor solution growth. It is also known that the growth thickness and the compositional distribution in the grown crystal obviously depend on surface orientation of the substrate even using solvent with same initial composition.

Up to now there are mainly two types of dynamic methods for visualizing crystal growth at high temperature: X-ray imaging and near-infrared microscopic interferometry (NIR-MI). In the present study morphological changes in semiconductor solution growths were revealed by NIR-MI under a reduced convection condition such as a uniform static magnetic field and a low-gravity environment.

In-situ observation of structure and properties of undercooled melts by using high energy x-ray diffraction combined with containerless levitation technique

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The structure of undercooled melts is important to understand the nucleation mechanism in undercooled melts. However, the structure of undercooled melts has not been well understood because it is difficult to keep deep undercooled states long time for measurements. Recently, study of structural properties of undercooled metallic melt and molten semiconductors has been progressed by using the levitation technique, which can provide stable undercooled states on contamination-free conditions by containerless melting. We have studied structure of undercooled molten silicon and liquid state of metallic glass forming zirconium based alloys using by synchrotron radiation x-rays combined with the electromagnetic levitation technique. At BL11XU and BL04B2 beamlines of SPring-8, high energy monochromatic x-ray beams with energy of 50-113keV illuminated at the center of levitated molten samples, and the diffracted x-rays were detected by using the imaging plate (IP) and x-ray image amplifier with CCD camera. Using these x-ray detection devices with several Hz time intervals, we have been able to obtain the diffracted x-rays at just solidification from undercooled melt. From structural analysis of undercooled molten silicon, first nearest neighbor coordination numbers and interatomic distances were 5.6 and 2.48Å with small temperature change in the temperature range of 1900-1550K. From these results we conclude that the short-range order based on tetrahedral bonds of undercooled molten silicon was not change with the degree of undercoolings but medium-range order was changed by the degree of undercoolings. The medium-range ordered structure in undercooled melt would act as a nucleation center for crystallization of silicon. On the other hand, the total structure factor extracted for the liquid zirconium based alloys near its melting temperature shows a particular shoulder at high-q side on the second peak. This feature of structure factor is similar to those of structure factors observed in deeply undercooled metallic liquids. This means that icosahedral short-range ordered clusters exist even in the equilibrium liquid state of zirconium based alloys. From these experiments, the relationship between structure of undercooled melts and the mechanism of nucleation was discussed.

The Use of Computed X-Ray Micro-Tomography In Deciphering Growth Kinetics

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X-ray micro tomography (μ CT) has proven to be a powerful tool to investigate the mechanisms of crystallization of metamorphic minerals. The 3-D forms of crystals can now be routinely visualized in composite materials and mineral size as well as the location of the center of the crystal within the 3-D object can be readily determined. These quantities in turn are necessary to identify the mechanisms that dominate crystal nucleation and growth in metamorphic rocks. Acquisition of μ CT images is rapid and accurate due to recent technical developments and the availability of high quality commercial instruments. In contrast, image processing is challenging because of the large data sets (1GB size) obtained as well as the noise and artifacts encountered in many images. A cubic, 1GB sized 3-D image has roughly 1'000 pixels in each of the three directions. Size and volume measurements of mineral grains which have a linear size of only a few pixels result in large uncertainties due to the discrete nature of the images. Grains of a few hundred of pixels diameter on the other hand often intersect the boarder of the image domain. In either case significant errors are introduced. Hence the dynamic range of grain diameter size which can be statistically investigated in one image is limited to a factor of about ten to twenty. Advances in computer capacity will certainly significantly improve this in the near future.

The reminder of the talk presents data obtained from several μ CT investigations of our group on regional and contact metamorphic terrains. Investigations of the chemical composition, crystallographic orientation, and the three dimensional shape of snowball garnets collected from the Lukmanier Pass area in the central part of the Swiss Alps reveal that a) their nucleation centers are commonly located on a line which corresponds to the crenulation lineation; b) each corresponds to a linear cluster of different crystals; and c) two distinct mechanisms govern the growth of these snowball garnets. A first stage of simultaneous growth and rotation of the crystal was likely responsible for the onset of the development of the spiral-shape geometry while subsequent static crystallization is indicated by the geometry of the Mn-zoning. In a second example data on grain sizes and distributions of crystals for a periclase skarn is presented to illustrate the use of quantitative μ CT analysis in crystal growth and nucleation investigations.

Molecular level in-situ observations of elementary growth processes of protein crystals by advanced optical microscopy

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To elucidate the growth mechanisms of mineral crystals, direct observation of the elementary growth processes of crystals is crucial. One of the most promising model systems is protein because of their very large molecular size (<3 nm). Advanced optical microscopy enables us to observe the following elementary processes of protein crystals: 1) the behaviors of the solute and impurity protein molecules in the vicinity of a crystal surface, 2) the response of elementary growth steps to the behaviors of 1). In addition, it is also possible to observe 3) the kinds and distribution of defects inside protein crystals.

The behaviors of 1), such as diffusion and adsorption processes of protein molecules in the vicinity of a crystal surface, are observed using fluorescent-labeled protein molecules and a single molecule imaging technique. The diffusion process of protein molecules in the vicinity of a crystal surface shows significant anisotropy, which can be explained by anisotropy of charge distribution on a crystal surface. The observation of 2) is also achieved satisfactorily by laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM) [1]. The combination of the observations of 1) and 2) enable us to elucidate the correlation between the inhibition of the advancement of growth steps and the adsorption mechanisms of impurity proteins on a crystal surface. In the conference, we will also demonstrate that 3) dislocations and inclusions are also observed in situ during the growth by LCM-DIM and phase contrast microscopy [2]. We believe that the results obtained from the observations of protein crystals will provide significant contribution to the field of mineralogy.

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Surface mechanisms that control the dissolution and oxidation of sulphides

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Sulphide disintegration in the context of acid mine drainage (AMD) is currently studied with a variety of experimental techniques. Environmental variables such as pH, dissolved oxygen (DO) availability, iron and sulfate content, temperature, etc. affect the aqueous oxidation process of sulphides in different ways. We observed for example that under highly acidic conditions (1 < pH < 3) the kinetics of sulphide aqueous dissolution is significantly different among different sulphide phases, e.g., PbS, ZnS, CuFeS₂, AsFeS, and FeS₂. Dissolution of most of these sulphides does not lead to stoichiometric metal/sulphur ratios in solution, at least not with respect to the bulk mineral stoichiometry. In general, but particularly at very acidic pH values, solutions are enriched in the metal or metalloid in relation to sulphur. Consequently, aqueous dissolution of sulphides should be greatly dominated by the formation of a sulphur-rich layer that would form at the reacting surface.

At temperatures between 25 and 75°C, it was observed that sulphide dissolution kinetics is generally controlled by the diffusion of reactants and products through a porous polysulphide layer. Whereas some sulphides such as pyrite, galena, and arsenopyrite dissolve remarkably slower in the absence of DO, dissolution rates of, e.g., sphalerite and chalcopyrite are practically DO independent.

Different types of experiments (flow-through with sulphide powders and fragments, in situ AFM and ex situ VSI) as well as different surface analytical techniques (XPS, HR-TEM) are currently conducted to further elucidate the mechanisms that control the dissolution reactions between sulphides aqueous solutions.

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Phase shift interferometry on macro-particles of smectite in alkaline solutions

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Smectite dissolution in the engineered barrier system is one of the central issues for validation of long-term endurance of underground repository for radioactive wastes. Many studies have been repeated to determine the dissolution rates of smectite (e.g., Cama et al., 2000). We employed in-situ measurement on macro-particles (~100 µm) under various pH, ionic strength (IS), and solution-flow conditions, using newly developed phase-shift interference microscope (PSI-M). PSI-M can measure the topograph and dissolution velocity for long-period (~24 hrs). Obtained normal velocities (V_n) were calculated to be step velocities ($V_s = V_n/\text{slope}$) at the interface's slopes.

Dissolution experiments were conducted at 22 °C, 105 µm/s flow, and adjusted pH. The measured smectite consistently drew a plot of interstep distance ($l_s = d_{001}/\text{slope}$; $d_{001} = 1.0$ nm) vs. step velocity (V_s) as a function of $V_s = V_{\text{tanh}}(l_s/2X_s)$ with BCF theory (V_s = isolated step velocity). For runs at IS = 0.5 M (Na-Cl-OH), smectite showed mostly constant surface-diffusion distance ($X_s = 2-3$ nm). Dissolution rate as flux over the whole surface was obtained by integrating the step velocities at every interface to be $8.52\text{E}-9$ to $2.85\text{E}-8$ mol/m²/s at pH 8.7-13.4, showing a positive correlation between pH and log rate with a reaction order, $n = 0.11$ ($R^2 = 0.83$). For another runs at IS = 0.03 M Ca-Cl-OH, pH = 7.0 to 12.6, smectite showed slightly shorter length $X_s = 0.6-1.4$ nm than that at IS = 0.5 M. One result on 1.0 M NaOH showed a longer $X_s = 24$ nm. The integrated dissolution rate were calculated to be $3.62\text{E}-9$ to $8.15\text{E}-9$ mol/m²/s, showing less pH dependency ($n = 0.06$, $R^2 = 0.87$). This step-dynamics approach implies that ionic strength is important for step interaction and global dissolution of smectite. Compared with previous data, our observed results all showed 10² times much faster rate than the AFM for whole surface of flatten smectite (Yokoyama et al., 2005; Kuwahara, 2006) and also other flow-through data for suspended smectite (Sato et al., 2003). Such a significant discrepancy may be explained by effects of (1) interfacial undersaturation and (2) particle dimension (step density and distortion). We confirmed that reduced flow rate and presence of coexisting analcime effectively reduce the dissolution rate of smectite. Since the barrier system is comprised of compacted smectite, interstitial flow and grain-by-grain distortion may complicatedly reduce or accelerate the dissolution.

Self-Oscillatory Growth of Ice Crystals in Antifreeze Glycoprotein Solutions

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Antifreeze proteins (AFPs) and Glycoproteins (AFGPs) allow many organisms including fish, plants and insects to survive sub-freezing environments. They occur in a wide range of compositions and structures, but to some extent they all accomplish the same functions: They suppress the freezing temperature, inhibit recrystallization, and modify ice crystal growth. A complete description of the AFGP/AFP interface mechanism as well as other ice interface phenomenon has eluded scientists primarily due to a lack of direct interface studies. We study ice crystal growth in AFGP and AFP solutions with phase contrast microscopy combined with fluorescent optical system during free growth and one-directional growth. Free growth experiments show an anisotropic self-oscillatory growth mode of the steps and interfaces near the freezing temperature and enhancement of the growth rates in the c-axis. These results contradict the previous 'tight-binding' mechanism of protein molecules thought to be responsible for antifreeze function. One-directional growth experiments of ice crystals were also carried out to observe the diffusion and incorporation of protein molecules using AFGP labeled with fluorescent markers. Even though the protein concentration was extremely low (less than 0.5mg/ml=0.05wt%), the AFGP concentration distribution both in front of ice/water interface and inside ice crystal was clearly observed. Self-oscillation of the growth rates was also observed during the one-directional growth and the incorporation of AFGP molecules into the crystal was also changed in dependence upon the growth rates. This result strongly indicates that the striation structures frequently observed inside the mineral crystals are originated from the self-oscillatory growth coupled with the variation of impurity diffusion field in front of growing interface. Furthermore, to study the effects of temperature driven convective flows on the interface kinetics, microgravity experiments were performed in a jet airplane during a parabolic flight path. Step propagation on the basal plane slows down considerably when entering the microgravity condition and reaches a critical condition just below 0.2g.

In-situ high resolution transmission electron microscopy study of aggregation and coalescence of TiO₂ nanocrystals

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Although classic crystal growth theory can explain many growth phenomena, recent findings show that it has shortages when applying to sub-micro and nanometer-sized crystals. As the rapid development of nanotechnology, detailed study of nanocrystal growth becomes essential. In-situ method is efficient for this purpose since it can give more information concerning growth process than ex-situ microstructural analysis. Because of its atomic-level resolution, high resolution transmission electron microscopy (HRTEM) is an important technique for microstructure study. Recently, it shows that HRTEM can also be powerful for observation of dynamic process. For example, some novel behaviors of nanocrystals have been visualized by HRTEM, such as structural instability and surface atom migration. Moreover, surface reconstructions, breakdown of nanowires, and crystal growth have been recorded in-situ by HRTEM. Here we present an in-situ HRTEM observation and explanation of aggregation and coalescence of TiO₂ nanocrystals.

Spherical TiO₂ nanocrystals were prepared by the micro-emulsion method. Under intense electron beam illumination, structural fluctuations were observed. That is, a nanocrystal could undergo random phase transition between single crystalline, twinned crystalline, amorphous, and other sophisticated phases. The crystals were found to have the memory effect of their orientations during structural fluctuation. The most interesting phenomenon observed was the motion of the crystals in some cases. Motion path analysis indicates that the crystals intend to go to closer to their neighbors, so as to aggregate to the center of the distribution. As two crystals getting closer enough, atoms on the adjacent surfaces will form a bridge that connects them. The connection part of this dumbbell-like structure rapidly grows up and at the same time the two crystals come further closer. Finally, a new larger spherical crystal forms. There are cases that the aggregating and coalescing crystals do not fluctuate, thus orientations of the crystals can be precisely tracked. The result shows that adjacent nanocrystals rotate oppositely during aggregation, so that their misorientation reduces. Rotation continues even when the dumbbell forms and the connection part grows as long as misorientation exists. Based on a simple model, we suggest that diffusion of the mobile surface atoms induced by intense electron beam on amorphous carbon substrate lead to effective motion of the nanocrystals. When the distance between two crystals reduces to ~5 nm, an atom connection forms and grows because of the negative curvature. Meanwhile, in order to lower the free energy adjacent nanocrystals tend to adjust to similar orientation through opposite rotation.

Phase transformation in Titanium observed in-situ using Electron Backscatter Diffraction

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Metals transform faster than ceramics and minerals, but being crystalline they can provide insights into reaction kinetics and mechanisms that may assist in interpreting mineral reactions. At Liverpool we have a scanning electron microscope (Camscan X500), designed by David Prior in collaboration with Camscan) with heating stage which can gather Electron Backscatter Diffraction (EBSD) data live and in-situ during experiments. We have used this to observe phase transformations in metals and are beginning to investigate slower processes in ionic solids and minerals.

We made in situ observations of the hexagonal close packed (alpha) to body centred cubic (beta) phase transformation in commercially pure titanium at 882 degrees C using SEM imaging concurrent with crystal orientation determination using EBSD. Direct observations of the onset of the phase transformation show the early stages of the growth of beta plates within alpha grains and allotriomorphic beta along alpha-alpha grain boundaries. Intragranular beta plates have a Burgers orientation relationship (OR) with the parent alpha grain and are lenticular in shape. These plates also have a tent surface relief and surface-traces consistent with habit planes predicted by the phenomenological theory of martensitic crystallography for pure titanium. These features suggest a military component to the growth mechanism. The beta allotriomorphs have a Burgers OR with one of the alpha grains abutting at the boundary, but do not have surface relief characteristic of a military transformation. These are likely to grow by a civilian mechanism. The two beta forms compete to engulf the alpha, with the allotriomorphic beta dominating by virtue of its faster moving alpha-beta interfaces.

The study highlights the possibility that even in a simple polymorphic transformation transient reaction products may form which are later obliterated (in this case the beta plate morphology). Microstructures observed at a particular stage of a transformation may, consequently, not necessarily give a complete picture of reaction rate and mechanism. The study also illustrates the significant potential of in-situ EBSD studies of phase transformations.

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Crystallization of Cosmic Materials in Space

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Various levitation methods have been employed to simulate the crystallization of cosmic material as it was formed in the early solar nebula some 4.6 billions years ago. Since nucleation during levitation is known to be reduced considerably (the nucleation rate might be up to four orders of magnitude lower^[1]) because of the absence of heterogeneous nucleation, strongly supercooled melts can easily be obtained and thus the crystallization is quite different from that under gravity.

Two different sets of experiments have been performed; (1) crystallization of chondrules (small silicate spheres, ~1 mm in diameter, often included in meteorites) from levitated silicate droplets and (2) crystallization of cosmic dust (fine particles of olivine found in meteorites) from silicate vapor.

(1) Chondrule formation:

Levitated experiments showed that almost chondrule melts did not nucleate at all. The effect of heterogeneous nucleation was investigated by active seeding using small, micrometer sized particles. It is concluded from texture formation and nucleation experiments that the chondrules were formed in less than 10 s at a supercooling of $\Delta T = 500-1000$ K with seeding.

(2) Cosmic dusts:

FE-SEM and AFM observations showed that matrix olivines (cosmic dusts) in the Allende meteorite exhibit a variety of morphologies and surface pattern. In order to reproduce the natural matrix olivine, experimental results indicate that a large supercooling of 300-500 K is needed, in combination with a rapid cooling rate of several hundred K/s.

In both cases, by comparing morphology, texture and some other characteristics of natural cosmic material with the synthesized one, it is concluded that the cosmic material was formed from rapidly cooling melts (chondrules) or vapor (cosmic dusts), respectively. This conclusion gives us new and different ideas about the conditions in the early solar nebula and the formation of cosmic material.

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Characterization of alite crystal growth from high temperature solution by using in-situ observation

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Cement was manufactured in the kiln with temperatures of up to 1450 degrees from raw mixtures such as limestone and clay. These raw mixtures were partially melted, and cement clinker minerals were formed from molten and residual raw mixtures during the thermal process. The cement clinker minerals primarily consisted of alite (Ca₃SiO₅:C₃S), belite (Ca₂SiO₄:C₂S) and interstitial phases. In particular, alite is a crucial mineral in clinkers because its content is 50% in portland cement and relates to early hydraulic properties of cement lead to its hardening soon after mixing it with water. Alite crystals are known to grow from a high-temperature interstitial multi-component solution appearing in the kiln during the thermal process.

In this study, growing alite crystals from high-temperature solution appearing in the kiln have been successfully observed by means of in situ observation microscope. This observation reveals that alite does not nucleate and grow simultaneously in liquid according to phase diagram and that coexisting solid with liquid for alite crystal growth is required. The origin of this observation is discussed in associated with alite nucleation. Additionally, the growth behavior of alite in the actual cement manufacturing process is described.

In situ observation of crystal growth and dissolution in peritectic system

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From $\text{Sr}(\text{NO}_3)_2$ aqueous solutions, $\text{Sr}(\text{NO}_3)_2$ (α phase) and $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (β phase) can grow; the former and latter stably equilibrate with the solutions above and below peritectic temperature $T_p = 29.3^\circ\text{C}$, respectively. Since crystal growth and dissolution in aqueous solution are suitable for in situ observation, we used $\text{Sr}(\text{NO}_3)_2 - \text{H}_2\text{O}$ system to demonstrate the actual processes of incongruent melting and peritectic reaction. It was observed that α phase nucleated and grew around β phase dissolving in solutions above T_p . In the same way, β phase was found to form around α phase dissolving in solutions below T_p . The results indicate that both incongruent melting and peritectic reaction are solvent-mediated transformation in which the dissolution of metastable phases was followed by the growth of stable phases. The surface concentration of a growing or dissolving crystal in a solution is approximately the saturated concentration that is larger for metastable phases than stable phases in a peritectic system. Therefore, the dissolving metastable phases provide for the stable phases with higher supersaturation than that of the solution bulk and, thus, the stable phases favorably nucleate and grow around the metastable phases. Meanwhile, irrespective of temperature, the simultaneous growth of two phases was observed when the solutions were supersaturated for both phases. However, when the two phases grew to contact each other, the contacting portion of only the metastable phases dissolved and the stable phases continued to grow due to the difference in surface concentration; the solution in the vicinity of the growing stable phases are undersaturated for the metastable phases. We found two kinds of processes of crystal growth and dissolution at both sides of T_p , i.e. solvent-mediated transformation and simultaneous growth of two phases followed by the partly dissolution of metastable phases. However, the difference in the growth and dissolution kinetics of two phases led to the different micro-structural evolution depending on temperature. The kinetic measurements showed that both growth and dissolution rates were larger in β phase than α phase. Above T_p , either in incongruent melting or simultaneous growth, metastable β phase dissolved completely before stable α phase grew large. Consequently, only the α phase remained in the solutions without peritectic structure. On the contrary, below T_p , stable β phase grew fast and trapped metastable α phase as an inclusion before the α phase dissolved completely via both peritectic reaction and simultaneous growth, which resulted in peritectic structure.

Growth mechanism of synthetic quartz crystals

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The basal (Z) faces of synthetic quartz commonly show two types of cobble patterns; smaller type I shows cell pattern, whereas larger type II exhibits closed loop or spiral step pattern. Although it has been considered that type II cobbles were formed by ordinary spiral growth mechanism, the steps are not cliffs but grooves, which make a conflict with the hitherto believed mechanism. The groove nature has been re-confirmed by three-dimensional measuring system in the present study. Also AFM observations have demonstrated that the r, z, m faces on the same crystal show ordinary spiral steps, indicating the spiral growth mechanism, whereas Z face shows features suggesting adhesive type growth mechanism. Formation of cell pattern of type I cobble is clearly due to morphological instability of a rough Z interface. The morphological analyses of closed loop or spiral pattern of type II cobbles have demonstrated that these patterns appear similarly as cell patterns of type I cobbles, but in two-dimensional manner, due to morphological instability. Outcrops of mixed type dislocations trigger the morphological instability, which develops to closed loop or spiral like grooves as advancing two-dimensionally. This is the first evidence demonstrating that dislocations containing screw component can play a role not only as sources of spiral growth but also as triggers for morphological instability, forming apparent spiral like patterns.

Application of nano-scale mineralogical investigation to radioactive waste repository design

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Radioactive waste disposal repository is planned to be constructed in deep geological layer. Quantitative analysis with the coupled calculation of geochemical reaction and mass transport is applied to the evaluation of long-term performance of the disposal system in order to design the repository moderately. The PhreeqC-Trans code has been developed for the analysis. It is the improved code of USGS's PhreeqC. The analysis contains uncertainties resulting from present level of scientific knowledge. We will report the calculation process and the relation between the calculation and nano-scale investigation of mineralogy, especially dissolution mechanism of clay minerals. Clay mineral, for example bentonite, is candidate material placed around the waste as buffer preventing radionuclide transport to the environment. Cement materials are used together as structural materials in the repository. Porosity, hydraulic conductivity and contaminant diffusivity of the bentonite is influenced mainly by dissolution of smectite in the bentonite, which is accelerated by hyper alkaline leachate from cement materials. The dissolution rate of the smectite under the conditions from groundwater to hyper alkaline leachate is, therefore, one of the key input parameters in the analysis. To select moderate value of the dissolution rate of the smectite is usually very difficult because of the slow rate and complicated mechanism of the dissolution. Nano-scale and in-situ observation enable to measure refined displacement of the dissolution surface in short period. Recently developed nano-scale investigation techniques such as interferometry is useful to help the understanding of the in-situ dissolution style and to diminish the uncertainty of the analysis.

Geochemical monitoring of calcite precipitation and dissolution in Ca rich ground waters with a newly developed interferometer

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To examine the precipitation rates of calcite deposited from three types ground water, calcite thin sections were put into them flowing in the tunnels for 3 to 4 hours. Before the experiments, a part of the thin sections was covered with thin gold plate as a standard plane. The heights of calcite were measured by our newly developed interferometer. Only one Ca rich ground water is saturated with respect to calcite where calcite precipitation is observed. In contrast, dissolution of calcite is observed for ground waters undersaturated with respect to calcite. By these methods, we can expect the precipitation/dissolution rates of calcite in fractures and apply these results to control the water level of the tunnels.

Calcite step velocity in the presence of chiral amino acid

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Amino acid with chirality has been used as a modifier for calcite crystal growth and nucleation to understand the effect of D- and L-body molecules on the anisotropic growth and the dissolution rate of steps of calcite {10 $\bar{1}$ 4} faces.

We have employed newly developed phase-shift interferometer (PSI) to measure the very small step velocity of calcite as low as 10-3nm/s. The concentrations of calcite and amino acid were varied from 0 to 0.8 and from 0 to 0.01 mol/l, respectively. Normal growth rate and the slope of spiral hillocks in pure calcite solution were successfully measured by PSI. Normal growth rate ranges from 0 to 0.05 nm/sec. If surface diffusion model is assumed, ~17.9 nm of surface diffusion length could be calculated from BCF surface diffusion model. When 0.01M L-aspartic acid is added to the solution, the dependency of step velocity on supersaturation had non-linear with the maximum velocity at $\sigma=0.2$. Surprisingly enough, the step velocity at $\sigma=0.2$ was calculated to be 680% larger than that of pure solution. Aspartic acids act as promoter rather than inhibitor in such condition, and this is remarkable impurity effect which is not without example.

In order to obtain the interface free energy between solution and the crystal, which is the key parameter to determine the nucleation rate and dissolution rate, the incubation time vs supersaturation was successfully been measured. The reduction of interfacial free energy in the presence of aspartic acid was obtained from this experiment. Lowered interfacial would lead easier nucleation and the increase of step velocity due to the step roughing.

Application of phase-shift interference microscopy to the measurement of faint dissolution rate

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Although in-situ observation of growth and dissolution of crystals provides us a key to understand growth and dissolution mechanisms, it is very difficult to measure precisely the dissolution rate of less than 10⁻⁶ nm/sec., i.e., 1 μ m/year. However, we need to measure such faint dissolution rates of crystals such as smectite, because we must understand the assessment of high-level radioactive waste disposal in the soil.

So far, to make an accurate estimate of the dissolution in 100 or 1000 years, dissolution rates and the kinetics, generally, have been measured by a conventional batch method (chemical analysis of a solution), although it takes very long time to prepare a solution and there is no information on the dependence of the dissolution rate on the crystallographic orientation.

To overcome these difficulties, in this study, we developed Phase-Shift Interference Microscope (PSIM) with a highly sophisticated observation system for extremely faint dissolution. This method possesses much higher sensitivity than conventional interferometries. The lateral resolution corresponds to the optical resolution (sub-micron) and the vertical resolution is less than 1 nm. The phase data along one line selected on the monitor was calculated in real-time and lined up on the monitor (x-t diagram). The complete data processing was carried out after data collection. As a result, the normal dissolution (surface retreat) rate and surface topography were obtained. These are required to calculate the dissolution rate as flux (mol/m²/s).

To examine our in-situ measurement system, we measured dissolution rates of calcite etch pits. As a result, normal dissolution rates of calcite at every point on the x-axis were determined to be 0.1-0.01 nm/s from data obtained within 20 minutes from the x-t diagram. Then, this variation of the normal dissolution rates was explained by the dependence of the step velocity on the local surface slope on a basis of the classical BCF surface diffusion model.

In conclusion, by using our PSIM system, we successfully reduced the measurement time for the determination of the dissolution rate of calcite in water from 1day to 10-20 minutes. Therefore, dissolution rates 100 times smaller than that of calcite will be measured in one-day experiments. In addition, this will contribute to construct a new dissolution model based on step dynamics.

Development of laser confocal phase-shift interference microscopy for in situ observation

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To understand crystal growth and dissolution kinetics, it is essential to observe in situ crystal surface coexisting with ambient phase like a solution. When information on step dynamics is needed, the surface micro-topography and growth (dissolution) rates have to be measured at the same time. However, it is generally difficult to observe a crystal surface in a solution by reflection type optical microscopy, because reflection from the surface of the crystal decreases as the difference of refractive index between the crystal and the solution decreases. In case of transparent crystals, for example, ice crystal and protein crystal, high-resolution images could not be easily obtained so far.

Here, to overcome this problem, we employed laser confocal microscopy (LCM), which is widely used to measure 3-dimensional surface topography in sub-micron scale. This LCM employs the confocal optics, which picks up information only from a focused plane. Therefore, any reflected light coming from out of focus planes is blocked by the pinhole. This makes an image look sliced at the focal plane. Therefore, by using this optical sectioning function of LCM, the reflections from the back face and from the top-glass window, and the scattered light from inclusions in the crystal can be eliminated when we observe the surface of a transparent crystal in a growth cell.

However, the vertical resolution of LCM is not enough to measure the surface micro-topography in nano-meter scale. To increase vertical resolution up to 1 nm, LCM should be combined with Phase-Shift Interference Microscopy (PSIM). Namely, in this study, we newly developed laser confocal phase-shift interference microscopy (LC-PSIM) system for in situ observation. To examine this LC-PSIM, the surface topography of etch pits of calcite set in a glass cell with water was observed.

As a result, we successfully obtained phase-shift interferograms of high quality. Although He-Ne laser was used as a light source, no parasitic interference fringe from the top-glass window and from the backside was observed. Therefore, it was confirmed that LC-PSIM can be applied to in situ measurement in a solution as one of the most advanced phase-shift interference microscopy. LC-PSIM will be useful for measuring the dissolution/precipitation rates of transparent thin crystal like clay and the solid/liquid interface in a solution or melt.

Mass transport in a laminar boundary of oxide crystal growth

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Model experiments on oxide crystal growth and the mass transportation phenomenon were performed by Schlieren technique coupling with differential interference microscope which is especially designed to trace the "pure diffusive" mass flow. In experiments, KNbO₃ (40wt%) and Li₂B₄O₇ solution was used. The interfacial convection cells were formed around the KNbO₃ grains. Direct measurements of velocity and concentration of KNbO₃ solute near the solid-liquid interface of KNbO₃ grain have carried out. All these experimental facts can be neatly described by the calculation of two dimensional velocities $v_1(x,0)$ and $v_2(0,y)$ of KNbO₃ solute diffusion-induced bulk flow (convective flow). $v_1(x,0)$ and $v_2(0,y)$ are the velocities of transversal and normal to the solute grain surface respectively. The origin of coordinate axes is at the center of KNbO₃ grain face.

For drawing physically justifiable phenomena which is experimentally more readily accessible, a simpler analytical mass boundary layer equation was deduced to identify the dominant convective flow. The theoretical calculation shows the solute diffusion-induced bulk flow can be conveniently used for deductions of steady stable solutions for binary diffusion equation from existing solutions of $v_1(x,0)$ and $v_2(0,y)$. $v_1(x,0)$ and $v_2(0,y)$ are understood as interchange ability of diffusion-induced bulk flow and concentration boundary layer model. For the region inside the mass boundary layer, the magnitude of velocity of the total mass flow normal to the interface can be simplified with the average value $v_2(0,y)$ of the solute diffusion-induced bulk flow. In comparing $v_2(0,y)$, the magnitude of $v_1(x,0)$ can be expected as the morphology destabilizing factor.

Based on these results, we point out (a) physically justifiable applications of two-dimensional mass diffusional transfer model for solidified fluid and (b) the existence of mass diffusion-induced bulk flow, which flows around the solid-liquid inside the width of boundary layer.

Thermophysical property measurements of molten high temperature materials using an electrostatic levitator

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Thermophysical properties are fundamental and essential data for numerical simulations of solidification and crystal growth. However thermophysical property measurements of molten high temperature materials, whose melting temperatures are above 1500 degrees C, are very difficult and hardly conducted with conventional methods due to their high melting temperature and risk of reaction with container walls. Non-contact processing using an electrostatic levitation technique have solved above mentioned problem and enabled thermophysical property measurements up to 3500 degrees C. This presentation first briefly summarizes the procedures and methods adopted by the Japan Aerospace Exploration Agency in order to measure density, surface tension and viscosity. Typical data of superheated and undercooled liquids that would have been impossible to obtain without the use of these techniques are then reported.

Growth and Kinetics of Al-Tobermorite Under Hydrothermal Conditions: An In-situ Neutron Diffraction Study

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In aerated autoclaved concrete 1.13 nm tobermorite is the predominant CSH-phase with semi-crystalline CSH I as minor components. Tobermorite can substitute Al for Si up to 13 atom% at 175°C/Psat and 7.5 at 190°C/Psat. The kinetics of tobermorite formation under hydrothermal conditions within the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ have been studied by in-situ methods in order to determine reaction mechanism and kinetics for Al-bearing 1.13 nm tobermorite. Neutron diffraction has the capacity to collect data of the reaction progress under hydrothermal conditions in-situ. An autoclave cell has been designed for performing time-resolved neutron diffraction analyses (1 minute) of the dynamic processes during the hydrothermal reactions. Experiments were conducted at 190 to 210°C under saturation pressure and within a time-range of 8 hours. As initial materials for the mixtures $\text{CaO,C}_3\text{A}$ and natural quartz were used at $\text{Al}/(\text{Al}+\text{Si}) = 0.1$.

In the experiments the fraction of poorly crystallized CSH-phases rises to a maximum and decreases with the time by continuous crystallisation of 1.13 nm tobermorite in accordance to the Al-free system. In addition a hydrogarnet solid solution with 15% grossular-component occurs. This primary hydrogarnet disappears with increasing reaction time and is replaced by a pure hydrogrossular within 3 hours. Al-Tobermorite is not formed initially but by the reaction of poorly crystallized CSH-phases with quartz and the primary Si-rich hydrogrossular solid solution after 165 min. The precursor CSH-phases are more Ca-rich and vary in their Ca/Si in the range of 1.1 to 1.3 due to its disordered structure. The primarily crystallized Al-tobermorite display (hk0)-reflections only, implying the existence of ab-planes. With increasing time after 260 min. the ab-planes of Al-bearing 1.13 nm tobermorite are forming stacks along the c-axis, indicated by the existence of a (002)-reflection. The mechanism of the reaction can be described by the reaction conversion of quartz and display a non-isokinetic behaviour. In the early stage of the hydrothermal hardening process the reaction is determined by the solution of quartz and of Si-rich hydrogrossular solid solution up to 0.6 hours and subsequently followed by a diffusion controlled mechanism. After 2 hours the mechanism changed once more to a solution controlled process. The reaction kinetics can be described according to an Avrami equation.

O12-01

Grain size and mantle dynamics

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Grain size in planetary mantles is controlled by various processes including grain boundary migration, Ostwald ripening, phase transformations, and dynamic recrystallization. These processes are constrained by experiments on Earth materials, field observations, analysis of xenoliths and numerical simulations. Coupling between the grain size, rheology and convection drastically affects mantle dynamics and evolution. In particular, it changes the efficiency of heat transport and increases the rate of secular cooling of the planet, reduces the efficiency of convective mixing and results in formation of geochemical heterogeneities, suppresses convection on planets without spinel-perovskite phase transformation which is one of the key factors in grain size evolution, changes the dynamics of plume formation and sublithospheric instabilities and can cause shear localization.

O12-03

Local stresses and texture evolution during metamorphism

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It is undeniable that metamorphism involves volume change, even in the absence of fluids. These may induce local stresses as the reactions progress. Direct evidence is shown by, for example, the cracking of garnet when coesite inclusions transform to quartz, and by deformation in reaction rims of brucite. Usually, though, there is no such clear evidence but this does not mean that the stresses were not present, just that they were not high enough to induce brittle failure or plastic deformation. What effect can those induced stresses have on reaction progress and consequent textures? Any theory in this area should be consistent with that for stress-induced diffusion mass transfer (pressure solution) in which minerals respond to imposed stress by dissolving or precipitating. I see no reason why they should respond differently if stresses are internally generated as part of a reaction.

There is no definition of Gibbs free energy in a system under stress. Instead, there are strictly local equilibria between stressed solids and an adjacent interface. Chemical potential is controlled by the local normal stress at each point on the interface. Interfaces with different orientations sustain different normal stresses, so there are gradients along interfaces. At an interface between two different phases, the normal stress gradient will drive diffusion of all components and hence growth/dissolution rates are coupled. This "Relative Growth Rate Rule" (Wheeler 1987, 1992) predicts that there will be a lot of movement between grains during growth, rather than the apparent volume-for-volume replacement textures which are (apparently) exhibited by metamorphic rocks. Multiphase systems are predicted to be chemically open if interfaces are the sole diffusion pathway (Wheeler 1987; Ford & Wheeler 2004). That assumption is commonly made for moderate temperatures of metamorphism, but the prediction is challenging.

This is currently the only truly grain-scale theory for how stresses interact with reaction progress in rocks. Further theoretical development coupled to experiments in analogue systems is required.

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O12-02

Grain growth kinetics in the system forsterite-diopside-water

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Grain size of rocks is an important microstructural parameter for physical properties of rocks. Plastic flows of rocks by diffusion-creep and superplasticity strongly depend on grain size. As well as dynamic recrystallization, grain growth kinetics is the most important mechanism in controlling grain size.

Several grain growth experiments have been conducted for monomineralic rocks (e.g., Tullis and Yund, 1982). Grain growth kinetics is drastically enhanced by water in olivine aggregates (e.g., Karato, 1989). Most of natural rocks are composed of more than two major mineral phases. It has been known that grain growth kinetics in bimineralline rocks is known to be quite different from that in monomineralic ones (e.g., Ohuchi and Nakamura, 2006). The effects of water on monomineralic and bimineralline rocks are expected to be different. In this study, we have carried out grain growth experiments of synthetic wehrlites at 1200 °C and 1.2 GPa for 1.5–763 hours under aqueous fluid-saturated condition in order to understand the effects of water on grain growth kinetics in peridotites by comparing the results in dry condition (Ohuchi and Nakamura, 2006). The starting materials for dunite, clinopyroxenite and wehrlites were prepared from iron-free gel powder.

In forsterite-rich wehrlites (≥ 80 vol.% of forsterite), normal grain growth of diopside and abnormal grain growth of forsterite proceeded. Grain growth rate of forsterite and diopside was as fast as those under dry condition. In relatively forsterite-poor wehrlites (≤ 70 vol.% of forsterite), normal grain growth of both forsterite and diopside proceeded. The values of grain growth exponent n of forsterite and diopside in the wehrlites were 2.1–4.8 and 1.8–4.5, respectively. In contrast to the high n -values (≥ 3) reported for the wehrlites in dry condition, n -values of the dominant phase in wet wehrlites tend to show low values (ca. 2). Our experimental results suggest that fast grain growth of the dominant phase by normal grain growth with $n \sim 2$ proceeds in the aqueous fluid-saturated upper mantle, resulting in a large difference between wet and dry conditions. This is because grain growth rate with $n \sim 2$ is quite faster than that with n higher than 3. Relatively high effective viscosity would be maintained by the enhanced grain growth in wet upper mantle in the case of grain size sensitive creep.

O12-04

Transport and rheological controls on metamorphic crystallization

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In metamorphic petrology substantial progress has been made over the last two decades due to the extensive application of equilibrium thermodynamic methods. By definition, equilibrium thermodynamics deals with time invariant equilibrium states and neither takes time nor system geometry into consideration. In this contribution we address some of the kinetic aspects of metamorphic crystallization. In particular we explore the mutual feedback between chemical mass transfer associated with mineral reactions and reaction induced mechanical stress. With respect to transport control we focus on the role of grain- and inter-phase boundaries during chemical mass transfer. This is done by analysing microstructural features including nanometre scale chemical zoning patterns across individual grain- and inter-phase boundaries and the compositional zoning of minerals on a micrometer scale. With respect to rheological controls we address the magnitude of reaction induced stress and its potential to drive secondary mass transfer.

Reaction microstructures with a high degree of spatial organization such as reaction rims, symplectites, epitaxial relations, shape and/or lattice preferred orientation are commonly observed phenomena in metamorphic and magmatic rocks. Such microstructural and textural features reflect the interplay of a number of petrogenetic processes. If the microphysics of these processes e.g. nucleation, chemical diffusion, grain growth, generation of mechanical stress, grain boundary migration, ... can be unravelled, microstructures may provide crucial information on reaction kinetics. By this way, they may shed light on the dynamics of reacting rock systems.

We present petrographic observations made on natural and synthetic reaction rims and symplectites. We identify the mechanisms of chemical and self diffusion in polycrystals based on (isotope)geochemical data obtained from analytical techniques with high spatial resolution such as transmission electron microscopy and depth profiling with secondary ion mass spectrometry. We also explore textural relations within reaction rims by crystal orientation mapping using electron back scatter diffraction technique and discuss the driving forces for texture development in growing polycrystal layers. Finally we address the phenomenon of spontaneous nucleation and phase separation. We compare phenomena observed in natural and synthetic materials with numerical simulations.

Lattice preferred orientations of co-crystallizing igneous pyroxene and titanomagnetite at high degrees of undercooling

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The nature of phase associations in volcanic rocks raises fundamental questions about igneous crystallization processes. What is the importance of early-formed phases in the nucleation of later-formed phases? What are the magnitudes of crystal-crystal interfacial free energies, and how anisotropic are these energies? Under what conditions do gradients in the chemical potentials of crystal components in the melt control crystal growth kinetics? Two factors are recognized as important in co-crystallization: (1) diffusion-limited crystal growth leading to stabilization of phases that incorporate rejected components, i.e., constitutional supercooling (CS), and (2) interfacial energy reductions accommodated by coherent or semi-coherent lattice boundaries between two phases. In the latter case, nucleation may be heterogeneous, growth may be epitaxial, and a lattice preferred orientation (LPO) would develop. Interfacial energy controls are not expected to be important among minerals crystallizing from silicate melt at high undercooling.

Orientation mapping using electron backscatter diffraction (EBSD) reveals consistent textural characteristics in samples produced in 1-atm basalt cooling experiments. Clinopyroxene crystals are dendritic, with high surface area to volume ratios ($\geq 3 \times 10^3 \text{ mm}^{-1}$), indicating diffusion-controlled growth. Orientation maps of contiguous regions of individual pyroxene dendrites indicate incremental rotations during crystal growth—poles to the {010} planes are strongly aligned, whereas the {100} and {001} plane poles of describe great circles. Titanomagnetite crystals occur preferentially on the surfaces of feathery clinopyroxene dendrites. Poles of the six symmetrically equivalent {110} planes in titanomagnetite are weakly clustered. One of these poles is always coincident with the strongly oriented {010} pole of nearby clinopyroxene crystals. The presence of this LPO is being sought in volcanic samples.

Dendritic pyroxene morphologies indicate chemical potential gradients developing in a regime of CS. The high proportion of shared pyroxene-titanomagnetite boundaries is consistent with either CS or an interfacial energy advantage to co-crystallization. However, the LPO observed among crystals of pyroxene and titanomagnetite indicates a strong control of lattice interfacial energies in the formation of titanomagnetite. The same LPO we observe has been described in oxide-pyroxene intergrowths occurring by subsolidus exsolution, presumably at low degrees of undercooling (Okamura et al., 1976). It was interpreted to result from similarities in the oxygen frameworks of these minerals; i.e., the presence of a semi-coherent lattice boundary. The new results suggest that epitaxial growth and heterogeneous nucleation are also important in highly undercooled silicate melts in which CS provides the thermodynamic driving force for co-crystallization.

Intra-crystal textural and chemical reorganization during dissolution-reprecipitation reactions in alkali feldspars

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In the Klokken syenite intrusion, layers of impermeable granular syenite are interleaved with layers of permeable, cumulate, coarse grained laminated syenite, with modal layering. Aqueous fluids circulated in the laminated syenites from solidus temperatures ($\sim 850^\circ\text{C}$), causing along-strike cryptic variation within modal layers in the major element composition of Fe-rich clinopyroxenes, Fe-rich olivines, and alkali feldspars (bulk composition $\sim [\text{Ab}_{60}\text{Or}_{40}]\text{An}_{1.5}$). At T above the feldspar solvus chemical changes in alkali feldspars appear to have occurred by volume diffusion (Parsons and Becker 1986). The fluid continued to circulate to $<500^\circ\text{C}$, below the T of the beginning of coherent cryptoperthitic (sub- μm) exsolution, when it caused pervasive intracrystal dissolution-reprecipitation reactions in the alkali feldspars. The driving force for these 'unzipping' reactions was coherency strain energy in the cryptoperthites, which have a 'braided' configuration. A threshold level of strain was reached when the intrusion cooled into the microcline stability field. The unzipping reactions affect entire $>1 \text{ cm}$ crystals without modification of crystal shapes, leading to irregular patch perthites on scales up to 1 mm, although relics of braid microtexture persist. TEM shows that individual patches are mosaics of incoherent subgrains. These subgrains have 1–10 μm -scale, oscillatory CL zoning at blue-UV wavelengths. Adjacent albite or microcline subgrains sometimes display the same zoning pattern, with individual zones traceable over 100s of μm , implying the existence of connected fluid films, and cross-cutting dissolutional surfaces also occur, suggesting the arrival of batches of fluid temporarily out of equilibrium with the growing subgrains. Laser ICPMS shows that the ternary feldspar components in the Ab- and Or-rich patches partitioned on low- T tie-lines passing through the bulk composition of the braid cryptoperthite. Some trace elements partitioned isochemically in bulk during unzipping, but Fe, Ti, Ni, La, Ce, Pr and Nd were lost to the fluid. Irrespective of charge, trace elements likely to reside in the feldspar M-site (Rb, Ba, Pb, Eu, Sr, La, Ce) and the major cations (Na, K, Ca) plot on straight lines on plots of $\log D_{\text{Or/Ab}}$ against ionic radius, the slope of which must be strongly T sensitive. After unzipping, Or-rich patches underwent a further stage of strain-controlled exsolution leading to straight lamellar cryptoperthites with misfit dislocations. Solvus relationships show that this stage of exsolution occurred at $\leq 350^\circ\text{C}$. Fluid had either left the system by this T , or residual coherency strains were insufficient to trigger further dissolution reactions.

Consequences of thermal input on metamorphic textures in contact and regional-contact metamorphic terranes

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Metamorphic recrystallization is complex feedback among thermal energy input, rate of heating, cumulative residence time of the rock at elevated temperature (T), kinetic parameters, reaction mechanisms and infiltration of a fluid phase. The outcome of these interdependent processes is a rock texture that may contain information on the controlling mechanism(s).

Computational experiments of heat and mass transport combined with kinetic models of metamorphic textures and with field studies of metamorphic terranes, elucidate differences observed in crystal size distributions between rocks from contact and regional-contact terranes. Purely *conductive* heat transport from an 875°C intrusion results in a single, rapid heating pulse ($\sim 20,000$ yrs) that quickly dissipates followed by a long cooling cycle ($\sim 1\text{Ma}$). Rocks following this thermal path form many nuclei and grow a predominance of small grains. Near the intrusion, most nucleation and growth occur after the thermal maximum (T_{max}); the system ceases prior to $\sim 200,000$ yrs. Consequently, mineral growth during cooling, subsequent to T_{max} , dominates for diffusive heat transport. In contrast, *advective* heat transport results in a heating cycle(s) covering a much longer time span(s). The initial conductive pulse is of the same duration (for identical starting conditions), but as fluid circulation commences, warm fluids infiltrate resulting in an order of magnitude longer-lived heating cycle ($\sim 100,000$ yrs). Residence time of rocks at high T is significantly longer and mineral nucleation and growth continues to nearly 1Ma . A sustained and uniform heating pulse results in fewer nuclei forming and growth to larger grain sizes. Consequently, mineral growth during heating dominates for an advective system.

Textural differences in contact vs. regional-contact terranes can be explained by variations in the dominant heat transport mechanism. Heat transport by diffusion results in aureole textures consistent with contact terranes whereas advective heat transport results in textures consistent for regional-contact metamorphic terranes. These studies provide insights into the linkage among metamorphic heat transport, T , fluid-rock interactions and textures preserved in the rocks.

Metamorphic mineral growth and pattern transition from random distribution to cluster

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Diffusion of elements in heterogeneous medium plays important roles in textural evolution of metamorphic rocks. In other words, textural evolution of metamorphic rock itself will affect mass transport and progress of reactions. Research of metamorphic texture will contribute to understanding of universal picture of mass transport and reaction progress in composite silicate rocks at a certain depth of the Earth. To analyze metamorphic texture formed at different depths, I collected samples from two metamorphic complexes in Japan: metamudstone from oligoclase-biotite zone ($P = 1.0 \text{ GPa}$ and $T = 620^\circ\text{C}$; Enami, 1998) in the Cretaceous high-pressure Sanbagawa metamorphic complex, and metamudstone from sillimanite zone ($P = 0.3 \text{ GPa}$ and $T = 640^\circ\text{C}$; Miyazaki, 1999) in the Cretaceous low-pressure Tsukuba metamorphic complex. The Tsukuba metamorphic complex is an east extends of the Cretaceous low-pressure Ryoke metamorphic complex.

The collected samples were analyzed quantitatively with density correlation functions. Density correlation functions of 'Al-mineral', which groups Al-bearing minerals, show that 'Al-mineral' in the Sanbagawa metamudstone forms cluster. Formation of the cluster also affects to garnet-forming reaction at high pressure. Garnets formed at interfaces between muscovite in the cluster and inter-cluster quartz domain. Individual garnet crystal has euhedral form. On the other hands, density correlation functions show 'Al-mineral' in the Tsukuba metamudstone is distributed randomly. In addition, density correlation functions of cordierite formed at low pressure shows power-law relation. Cordierite crystals have highly branching form.

Origin of the cluster in the Sanbagawa metamudstone is not clear, however, progress of reaction and deformation play critical role for the formation of the cluster. One possible explanation for the textural discrepancy between the Sanbagawa and Tsukuba metamudstones is difference in dihedral angle of quartz-water system. Although metamorphic temperatures of both metamudstones are around 630°C , the dihedral angle at 1.0 GPa (Sanbagawa) is less than 60° and that at 0.3 GPa (Tsukuba) is larger than 60° (Holness, 1993). Therefore, metamorphic fluids in the Sanbagawa metamudstone can form 3-D network. Progress of reaction and deformation will be enhanced by mass transport through the network. Rapid transport of elements through the network also will reduce degree of supersaturation of mineral component. This prediction is consistent with progress of Ostwald ripening (Miyazaki, 1991, 1996) in high-pressure metamorphism and DLA growth (Miyazaki, 2001) in low-pressure metamorphism.

Texture development in coupled dissolution-reprecipitation replacement reactions

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The development of texture in minerals is always associated with mechanisms of phase changes in an attempt to reach a lower free energy state. When a mineral comes into contact with a fluid with which it is not in equilibrium, a reaction occurs in order to reach a new equilibrium. The generation of porosity is a key feature of a coupled dissolution-reprecipitation replacement process. Mineral replacement can occur if solubility differences between parent mineral and new product phase allow for more of the dissolving phase to remain in solution, i.e., a volume deficit reaction. If the dissolving mineral causes the fluid to become supersaturated with respect to any other phase, a new solid phase may precipitate. This initial step at a crystal surface is the start of a pseudomorphic replacement that may continue through a crystal at a moving interface until a new equilibrium is reached. The interfacial control, which dictates that the reaction interface is the original crystal surface, inevitably leads to the requirement of porosity in the product. Porosity also allows continuous fluid access to the reaction interface and so provides a pathway for mass transport. The interfacial fluid composition defines the local supersaturation relative to possible precipitating phases, while the surface crystal structure of the parent and degree of possible epitaxy control the kinetics of nucleation. Thus the mechanism described here is relevant, not only to the replacement of one single crystal by another, but also where a crystalline material is replaced by a polycrystalline or polyphase product. Textures resulting from reequilibration of a solid in a fluid typically include sharp compositional interfaces between parent and product, porous reaction rims seen as turbidity in the replaced zone, coarse porosity or channels, as well as fluid inclusion trails, all features reproduced in experiments in a simple solid solution-aqueous solution system, KCl-KBr H₂O. In natural pseudomorphic replacements the porosity may be an indication that a replacement process has taken place, e.g., cloudy feldspars as indicators of metasomatic processes. However, porosity may be a transient phenomenon, and textural reequilibration may result in a porosity-free product. Once an outer porosity closes, the internal porosity may be trapped and lead to the formation of fluid inclusions. Mineral intergrowths, such as symplectites, may also form by a similar mechanism when a mineral is in contact with a fluid which becomes supersaturated with respect to two new phases.

Computational modeling of mineral unmixing and growth

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Non-equilibrium textures contain valuable information regarding the history and properties of rocks. In order to understand the underlying processes in a quantitative sense it is therefore necessary to develop adequate numerical models. The specific example presented here is mineral exsolution and symplectite formation where initially homogeneous mixtures undergo phase separation, also called spinodal decomposition. The underlying process of phase separation requires uphill diffusion in which material moves against concentration gradients. This is modeled through a generalized diffusion equation originally developed by Cahn & Hilliard that also accounts for the surface energies of the newly formed interfaces. In order to tackle this rather cumbersome fourth order equation we split it into two coupled second order equations, which allows for solution by a standard finite element approach that has the usual advantages regarding complicated domains, locally increased resolution, and heterogeneous material properties. One key aspect of the developed model is the span of possible morphologies that result as a function of the free energy, composition in binary and ternary systems, and duration of the processes. We illustrate the formation and evolution of different morphologies with numerical examples and show how they can be interpreted and related to natural examples. We will pay particular attention to moving front systems, and the competition between diffusion and surface minimization which is especially important for anisotropic systems. Furthermore we investigate the effect of reaction-deformation coupling when there is a volume change involved. In this case the free energy must be augmented by the elastic strain contribution, stresses (and pressure) vary locally, deformation contributes to the texture arrangement, and the reaction can only progress if the driving force can overcome the matrix resistance. This latter point is of fundamental importance for natural systems that often show incomplete reactions.

An experimental study of plagioclase crystal size distribution during cooling of basalts

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An experimental study has been conducted to constrain how thermal history controls crystal size distribution (CSD) of plagioclase in cooling basalts. A ferrobasaltic glass powder was held above the liquidus (1180°C) for a minimum of 9 hours, then cooled at constant rate before quenching at temperatures from 1170 to 1110°C. At equilibrium the crystallization sequence is: plagioclase (~1180°C), olivine (~1170°C), clinopyroxene (~1130°C).

When the logarithm of the number of plagioclase crystals per unit volume is plotted as a function of crystal length, data from all experiments are dominated by a linear segment of decreasing number density with increasing crystal size. This linear trend does not extend to the smallest crystal sizes, where a down-turn in number density is typically observed. The decreasing log-linear form of the CSD can be explained by an exponential decrease of nucleation rate as a function of time at the beginning of the crystallization process. However, with decreasing temperature at fixed cooling rate the slope of the linear part of the CSD flattens significantly, implying that the growth rate of large crystals is higher than that of small crystals. Textural observations suggest that crystal agglomeration is the dominant process leading to this effect. Otherwise, at a given temperature, the slope of the log-linear part of the CSD is a function of cooling rate, faster cooling leading to greater slopes.

However, we also find that the thermal history above the liquidus has a major influence on crystallization. With increasing initial temperature of the experiments (and to a lesser extent increasing duration above the liquidus) phase appearances are shifted to lower temperature, with delays in nucleation reaching up to 100°C. This observation suggests that heterogeneous nucleation dominates in most experiments. This effect is also apparent in the CSD's, where, for example, a longer duration above the liquidus leads to a smaller total number of grains, of larger average size.

Our experimental data suggest that it will be extremely difficult to quantify the thermal history of a magmatic body based upon CSD's. Furthermore, processes such as convection or sedimentation may add additional complexity to the interpretation of CSD's in natural systems. Nevertheless, the evolution of the CSD observed during cooling (form of the CSD, flattening) is similar to that observed in the Makaopuhi lava-lake (Hawaii), implying that in a series of genetically related rocks, the CSD's may provide some qualitative insights into the cooling history.

Oscillatory zoning in a synthetic Fe-Mg olivine single crystal

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This paper reports an oscillatory zoning in a synthetic Fe-Mg olivine which is the largest single crystal ever synthesized (Ito et al, 2003) and proposes a new hypothesis on the genesis of the oscillatory zoning. The method of the synthesis was described in Ito et al. (Journal of Crystal Growth, 253, 557-561, 2003). Starting material was the melt of San Carlos olivine (Fo 89-91) with a seed crystal of a synthetic forsterite single crystal. Therefore the system is the MgO-FeO-SiO₂ ternary system. The synthetic conditions were 1900 °C, 1 atm, and N₂ atmosphere with the growth rate (the drawback rate) of 5 mm/hr (0.083 mm/min). The synthetic olivine contains 2 to 12 wt.% FeO and shows an oscillatory zoning with a wavelength of about 250 μm and a small compositional variation of 0.5 to 1.0 wt. % FeO.

We examined first whether the existing models can explain this oscillatory zoning. L'Heureux and Fowler (1994) employed a boundary layer model with a concentration dependent growth rate and showed an oscillatory behavior in a binary plagioclase system only if the partition coefficient between the melt and the crystal will take values reciprocal to those of natural case. Their assumption on the partition coefficient cannot be acceptable in our case. Because the observed compositional variation in our synthetic olivine is so small that the model of a concentration dependent growth rate in binary system cannot be applied to our case.

Nishiyama (PEPI, 107, 33-51, 1998) showed that uphill diffusion will take place in a ternary melt due to a coupling among diffusive fluxes under a constant volume reference frame. Similarly, we can expect uphill diffusion of SiO₂ in the MgO-FeO-SiO₂ ternary melt by the same mechanism if diffusivity of MgO is different from that of FeO. Suppose that a growth of crystal begin in a melt with the stoichiometric composition of olivine. When such uphill diffusion will occur in a boundary layer adjacent to the crystal surface, the melt composition in the layer will be different from the stoichiometric composition of olivine, resulting in prevention of further growth of the crystal. The growth of the crystal will take place again if the concentration gradient of SiO₂ will be relaxed by the progress of diffusion and as a result the composition of the boundary layer will become close to the stoichiometric composition of olivine again. This process will continue repeatedly and cause the oscillatory zoning.

Comparing growth microtopography and sector zoning in natural hydrothermal and synthetic magmatic clinopyroxenes

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Valuable information on the relationship between surface structure and element partitioning can be gained from investigating as-grown surfaces of natural and synthetic silicate minerals freed from a soluble carbonate matrix.

Hydrothermal diopside from Orford (Quebec) has a unusual morphology flattened on {100} and is sector zoned. A typical composition determined by electron microprobe analysis (EMP) is $\text{Na}_{0.007} \text{Ca}_{1.00} (\text{Mg}_{0.754} \text{Fe}_{0.22} \text{Mn}_{0.013} \text{Al}_{0.003}) \text{Si}_{2.00} \text{O}_6$. EMP analysis and back-scattered electron imaging show Fe and Mn to be sector zoned. Micrometer to nanometer-scale growth features resolvable by atomic force microscopy occur on their {100}, {010} and {110} as-grown surfaces. The faces of {100} and {110} are covered with growth hillocks. On {100}, hillocks are defined by four arrays of steps parallel to [010] and [001]. The [001]⁺ and [001]⁻ steps, related by symmetry, have similar affinities for Fe and Mn, but vicinal faces bearing [010]⁺ steps are enriched by 0.4 wt % FeO and 0.1 wt% MnO relative to other vicinal faces. AFM imaging also shows exsolution lamellae interrupted at the edge of some growth steps and continuing through others.

Fragments of this natural diopside were used to seed experiments in which synthetic clinopyroxenes of aegirite composition were grown at 800°C and 10 kbars for 24 hours, from alkaline melts modelled after the lavas of the Tanzanian volcano Oldoinyo Lengai. The melts were prepared from Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 and Fe_3O_4 reagents. One run was anhydrous and the others contained either 2.5 or 5 wt. % H_2O . The run products were disaggregated and clinopyroxene crystals were hand-picked. Euhedral clinopyroxenes were found in all three runs. The tabular crystals, freed from their carbonate matrix by overnight immersion in dilute acetic acid, consist dominantly of {110}, with minor {010} and {001}, and range in size from 100 to 300 µm across. AFM imaging show three contrasting surface growth topography: arrays of broad, straight macrosteps, lens-shaped islands and narrow fibers. EMP analyses of polished grain mounts show that non-equivalent growth sectors are either diopside-like or aegirite, around $\text{Ca}_{2+0.63} \text{Na}_{0.35} (\text{Mg}_{0.64} \text{Fe}_{0.36}) \text{Al}_{0.01} \text{Si}_{1.99} \text{O}_6$, in composition.

Our understanding of crystal growth mechanism at hydrothermal and magmatic conditions lags behind that of minerals that can be precipitated under controlled conditions at room temperature. This experimental approach can be applied to a wide range of silicate minerals and has the potential to put new constraints on current theories of element partitioning.

Morphogenesis of Quartz Crystals Twinned After Japan Law

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The logo mark of IMA2006 is designed based on quartz crystals twinned after Japan law. This twin law was explained as a contact twin, with {11-22} as composition and twin plane. The characteristic V shape was explained as representing upper half of an X shape, implying an interpenetration twin. So there was a confusion from the early times. The earlier explanation for the origin of characteristic V- or fan- shape was re-entrant corner effect at twin junction, but now it is understood that concentration of dislocations in twin junction is the real reason. In both mechanisms, however, evolution from prismatic, via V shape, to fan-shape is expected as growth proceeds. X-ray topography, however, indicated contrast image of fan shape within V shape. This is due to the difference in the activities of dislocations as growth centers on the faces meeting at twin junction, between earlier {10-11} or later {10-10}. When free growth occurs in an open space, V-shape transforms to Y shape, conclusively demonstrating that the twin is neither an interpenetration twin, nor contact twin on {11-22}. {11-22} is an apparent composition, and not real twin plane. It appears as an apparent composition plane, simply due to geometrical relation between two individuals conjugated on {10-11}. The relation poses a new question as to the classification of contact and interpenetration twins.

Crystallography and origin of colloform pyrite

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Pyrite with colloform texture is known from many sulphide deposits of different genetic type. For a long time, the specific colloform aggregates with characteristic sub-spherical outer surface and similar internal fine banding have been accepted as typical metacolloid formations ("crystallised gels"). Despite more recent debates, information about the real crystal nature of these aggregates is nearly absent, and so their genuine genesis remains problematic. Using appropriate techniques we have studied colloform pyrite aggregates from various localities, formed in open space and not affected by overprinted deformations.

Such a typical colloform aggregate of As-bearing pyrite from a vein Pb-Zn deposit represents millimetres thick crust overgrowing a rock fragment. The botryoidal pyrite surface consists of smaller rounded, close to spherical areas. The cross cleavages reveal fine-fibrous bundles with concentric zoning parallel to the outer surface. The precession X-ray photographs proved that the radiate fibres are elongated along [001], but the other two main axes are also nearly parallel, thus the whole bundle maintains the same 3D crystallographic orientation with only a small radial divergence. The extremely anisometric radial fibres, 2-3 to 20-30 µm wide, are bounded by longitudinal cubic and small pyritohedral side faces with cross and oblique striation. As seen by BSEI and microscopic observations on etched polished sections, the rounded concentric zones at high magnification show in fact, finely-jagged profile, outlining the fine primary growth zoning of the inclined terminals of the single needle-like fibres. TEM observations established well ordered pyrite structure without marcasite-like interlayers. The non-homogeneity of the zoned pyrite is due to variation in As-content in the 1.56-4.36 wt.% range, and is correlated with some Fe deficit. The thinnest radiate fibres are disposed in the As-richest zones. All data obtained prove that the colloform pyrite texture is of non-colloidal origin, a result of open space simultaneous crystallisation of multitude <001> needle-like individuals, formed by splitting of a restricted number of nuclei at the base of the aggregate.

Similar pyrite aggregates with low As content from other deposits have also concentric and radiate texture but consist of much thicker radial (100 µm and more) fibres. The outer botryoidal surfaces are formed by larger, equidimensional and equimorphic (e.g., {100} + {210}) crystal terminations in parallel position. All these aggregates possess rather high porosity determined by the radiate intergranular spaces, and are characterised by extremely high interface area. These features determine their very high reactivity, both in hypogene and supergene environment.

New radial dendritic oolites: constitution and crystallization evolution

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Two types of oolites and similar spherical mineral aggregates are known: concentrically drusy and spherulitic. In one of the excavations of Fluorite mine Palat in Bulgaria we have discovered a modern carbonate oolite field (cave pearls) which formed under intensive drip of highly mineralized subsurface waters. Their study resulted in determining principally new radial dendritic oolites. They are characterized by peculiar inner structure with nonrigorous linear radial rays and non-acicular skeletal subtypes confined by not induction but gran surfaces; by uneven lumpy or drusy surface; by considerably reduced aggregate density (2.26 and 2.64 g/cm³ accordingly) comparing to the density of composing skeletal mineral and high porosity (about 15%) comparing to 5.8% of other types; by the presence of two types of pores: small in separate subtypes and relatively interdendritic. The hydrochemical conditions of calcium carbonate crystallization are investigated and chemical and crystallization processes of forming radial dendritic oolites. The major factor, controlling their formation and crystallization evolution, is a very high supersaturation of mine or cave waters.

Striations and hollow channels in rounded beryl crystals by X-ray diffraction topography

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Two natural crystals of colourless beryl from Minas Gerais (Brazil) have been studied by X-Ray Diffraction Topography - XRDT and by Optical Microscopy - OM. The examined samples are elongated {1010} and {1120} strongly rounded prisms terminating in prominent {0001} pedio, exhibiting to OM vertical striations, on the crystal faces, and hollow channels parallel to the *c* axis, in the interior zones. The quoted internal channels, with diameters ranging from less than 1 µm to about 100 µm, manifest various morphologies, from conic-cylindrical to sharp hexagonal with edges parallel to the prism faces. Large irregular voids, crossing the samples from bottom to top, are also observed in the central inner cores. These last morphological features are visible by naked eyes and are often filled by minerals of the kaolinite group. Crystal slices were cut from the samples in order to investigate the structural defects by XRDT. Dislocations, growth bands, solid inclusions and precipitates were observed and permitted the growth-history reconstruction of the samples to be made. It was possible to conclude that the studied crystals share the following common features:

- vertical striations on the crystal faces were mainly caused by juxtaposition of a number of prism faces;
- selective dissolution, driven by the deformation fields of dislocations bundles, was responsible for the formation of channels, that gathered together formed irregular voids in the interior zones of the crystals;
- post-genetic alteration resulted in the formation of kaolinite minerals into larger channels and irregular voids.

On the other side, it was concluded that the two studied samples differ from each other by the manner in which they attained to their final rounded morphologies. In fact, in the first case, it is due to an abrupt increase of the growth rates of the first-order prism faces {1010} with respect to those of the other prism forms. In the second case, the sample consist of an aggregation of a small number of elongated crystalline individuals rotated of an angle of few seconds of arc about the *c* axis. Therefore the final morphology occurred by parallel intergrowth of different individual crystals growing parallel to the *c* axis with axial orientations deviating only slightly from the average orientation of the sample. In both cases, striations were observed at the intersection between faces of different prism forms. Post-genetic corrosion contributed only in low part to the rounded morphology of the samples.

P12-01

Magmatic differentiation processes in the Murotomisaki gabbroic complex – segregation of plagioclase-rich crystal mush from the crystallization boundary layer

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The Murotomisaki gabbroic complex is a sill-like layered intrusion of up to 220m thickness, located in Cape Muroto, Shikoku, Japan. The intrusion has a well-developed layered structure and there are at least three olivine-rich zones (basal, top and middle-level zones). We studied the detail of the layered structure by measuring modal composition, crystal size and crystal number density of olivine. We found out that the olivine-rich zones in the intrusion can be classified, according to the mode of its origin, into two categories: 'the crystal accumulation zone (AC zone)', which was formed by the crystal settling of olivine and 'the crystal growth zone (GR zone)', in which olivine crystals grew significantly (Hoshide, Obata and Akatsuka, 2005). The growth of olivine crystals in the GR zone was apparently accompanied with the increase of MgO, FeO and MnO contents from the initial value, which implies that the crystal growth has taken place in a chemically open system. That is, the increase of the MgO, FeO and MnO contents in the GR zone was brought about by material transfer between the crystallization boundary layer (the GR zone) and the overlying magma. From the examination of the whole rock composition and the mode of occurrence of the anorthositic veins that occur in the GR zone, it is suggested that the increase of MgO, FeO and MnO in the GR zone is caused by the segregation and upward transport of the anorthositic crystal mush that had generated from the boundary layer. Such segregation veins are common in many other localities of layered intrusions and sills such as the Skaergaard intrusion. The segregation and ascent of the crystal mush probably plays an important role in magmatic differentiation processes.

P12-02

Crystallization behavior of hydrous groundmass composition of the 1991-1995 dacite of Unzen volcano at 100 MPa

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We conducted isobaric cooling experiment to understand the crystallization behavior of the hydrous groundmass composition of Unzen dacite at 100 MPa. The starting material is quenched dry glass of fused groundmass separate of the 1992 dacite of Unzen volcano (SiO₂=68.2), which were sealed in Au70Pd30 capsules with 2 or 4 wt% of water. The charges were run in a gas-media high pressure apparatus (Dr.HIP; Kobe University), firstly melted at 1100°C for ca.50 hours, then cooled down to 900, 800, 700, 600°C within ca 4 minutes, and annealed at those temperatures for ca. 0.2, 2, and 20 hours and subsequently quenched. The crystallinity was estimated from the BSE image semi-quantitatively. Equilibrium liquidus temperatures are ca.1070°C and 970°C for water contents of 2 wt% and 4 wt%, respectively at 100 MPa (Sato et al. 1999JVGR). The TTT diagram thus constructed shows C-shaped curves with the shortest time scale of crystallization attained at ca. 750-800°C for the system with H₂O=2wt %, and at ca.700°C for the system with H₂O=4wt%. For the run products of annealing temperature less than 800°C, crystal size is less than 3 microns, whereas the run products of annealing temperature at 900°C contains crystals more than 5 microns across. Natural magmas may have crystallized at ca. 900°C judging from the compositions of Fe-Ti oxides in the groundmass. For runs with the annealing temperature of 900°C and H₂O=2wt%, crystallinity increases from 0 for the annealing time (t_a) of 0.2 hr, through 5% for t_a=1.0hr to 15% for t_a=30.4hr. For H₂O=4wt runs, crystallinity increases from 0 for t_a=0.2hr, through 2% for t_a=1hr to 4% for t_a=30.4hr. The extruded dacite of the 1991-1995 Unzen eruption contained 20-40 vol.% of microlites in the groundmass (Nakada and Motomura,1999JVGR), and it is conceived that the crystallinity of these lava samples may be attained by integration of the crystallization at various depth and water contents during the ascent of magmas. Present experimental results may compose a part of the data set to constrain the crystallization processes of microlites in the Unzen dacite.

P12-03

Cooling process of a granitic body deduced from the reaction textures during two sub-solidus stages: an example from the Okueyama granitic body, Kyushu, Japan

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This study describes quantitatively a difference in a cooling process according to the depth within a single magma chamber by studying the variation of the extents of sub-solidus reactions during exsolution coarsening stage(ECS) and deuteric coarsening stage(DCS) recorded in the Okueyama granitic body(OKG), central Kyushu, Japan. Perthitic microtextures in K-feldspar, myrmekite and the reaction rim, using the polarization microscope and HF-etching SEM works, imply that 1)the effective conditions for these texture formations are that of ECS for micropertite and that of DCS for patchperthite, myrmekite and the reaction rim, respectively and 2) DCS operated at a stage later than ECS. We measured six parameters of the extents: (1)width and (2)spacing of micropertite lamella, (3)width and (4)spacing of patchperthite lamella, (5)width of myrmekite, and (6)width of the reaction rim between plagioclase and K-feldspar. They show systematic downward increments from the roof boundary and do not show any systematic variations horizontally, which implies that OKG was cooled effectively and gradually from the roof.

Hornblende – plagioclase geothermometer and ternary feldspar thermometer give a temperature range between 710°C and 620°C, which implies the effective condition for ECS sub-solidus reactions. The thermal condition for DCS sub-solidus reactions is evaluated by using ternary feldspar thermometer, resulting in the temperature below 500°C.

The cooling duration for ECS is estimated by employing the 1-D heat transfer modelling, which is 820yrs. at the roof and 1,400-1,900yrs. at 1,000m below the roof. The cooling duration of EDS and DCS increases monotonously toward the bottom.

Chemical zoning formed by crystal growth of a solid solution controlled by the interface kinetics

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The origin of normal and reverse chemical zonings formed during crystal growth has been investigated using a mean field theory on the interface kinetics of growth of a solid solution from its melt in a binary system (Kitamura, M. and Matsumoto, N. 2004, *Journal of Crystal Growth*, 260, 243-254). The formulation in the present study reveals that reverse zoning results from inversion of compositional change under isothermal conditions, due to the increase of the departure of the liquid composition from equilibrium. The development of reverse zoning also depends on other factors such as cooling rate. The formulation clarifies that, even when the inversion exists, continuous cooling diminishes the possibility for the formation of reverse zoning. Calculation of chemical zoning by using a set of equations including the interface kinetics is also given. The present result gives a new insight into studies on the formation process of chemical zoning in minerals and their use in estimating *P-T* paths of metamorphic and igneous rocks.

Cation exchange between fluid and olivine in dunite controlled by grain boundary migration: Implications for mantle metasomatism

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Recently, Nakamura et al. (2005) showed experimentally that oxygen isotope exchange between aqueous fluid and synthesized quartzite in the lower crust condition was drastically accelerated by "grain boundary (GB) sweeping", a series of successive processes including GB diffusion, surface exchange reaction at GBs and migration of the isotopically-exchanged GBs. Similar phenomena was reported as an apparent increase of diffusion along migrating GBs in calcite (McCaig et al., 2003). To test the occurrence of GB seeping in other fluid-rock systems, we have examined Ni incorporation into forsterite in synthesized dunite as an analogue of a system being subjected to mantle metasomatism. Infiltration of aqueous fluid, an effective metasomatic agent, is expected to enhance GB migration (Karato, 1989; Nakamura and Watson, 2001) and thus to promote chemical exchange. Some microanalysis studies on peridotite xenoliths reported correlations between metasomatic signature and grain textures that suggest GB migration (e.g., Xu et al., 1998).

The experiments were carried out in a Pt-lined nickel capsule using a piston-cylinder apparatus at 1.2 GPa and 1200°C. Starting material was synthesized gel with 1-3 wt. % water. During the annealing experiments, nickel penetrated platinum all the way through and diffused into the fluid-saturated dunite (Ohuchi and Nakamura, 2006; this issue). The following observation showed that Ni-Mg exchange occurred dominantly in the area swept by the migrated GBs: 1) The large olivine grains are surrounded by thick Ni-rich rims, whereas small grain, thin. 2) The Ni-poor cores of the large grains have clear concave-outward outlines with sharp corners, showing relatively small contribution of lattice diffusion and original location of the GBs. 3) Ni-enrichment is conspicuous along the GBs without fluid film, rather than grain rims facing pore fluids. 4) Ni concentration profile shows trapezoidal form, not diffusional. The cation exchange flux between fluid and quartzite is much larger than by lattice diffusion from the stationary grain boundaries, as expected from the mass transfer mechanism diagram of Nakamura et al. (2005).

The experimental results imply that the larger grains with fast grain growth rate, which appear refractory to diffusive exchange, may be metasomatized deeply to the core. To the contrary, fine-grained domains, which often consist of polymineralic grains or contain secondary pinning phases, could be less-metasomatized in spite of their large surface area.

Growth patterns on ilmenite crystals in pyroclastic deposits

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Direct evidence of crystal growth can be obtained from surface observations. For minerals of magmatic origin, however, we can hardly secure as-grown surfaces which keep the features of growth at high temperature. This is because most surfaces have been changed owing to subsequent cooling and other geologic processes. Exceptionally, we expect ilmenite in pyroclastic deposits would preserve the as-grown features, since they were quenched by eruption and also because they could resist weathering considerably. This is the motivation of this study.

Ilmenite crystals were separated from pyroclastic flow deposits by the Quaternary volcanism in the Western Japan, and their surfaces were examined with DIM (differential interference microscope), SEM, and AFM in this study.

These observations have showed that the ilmenite crystals from the pyroclastic deposits take exclusively an euhedral and thick tablet morphology with (0001), and that they differ in weathering dependent not only on the origin but also on the sampling locality. When the sample was fresh and not weathered, the crystals were completely covered with a volcanic glass. But, as weathering goes on, the glass phase fades away and the surface appears. Thus exposed surfaces of ilmenite, which were mostly fresh and had a luster, showed the growth characteristics, which will be described in the presentation.

By the surface observations with DIM, circular growth steps were discerned exclusively, which are typical of the growth from the solution growth. Although thick steps were remarkable, which might be formed by bunching, thin steps and vicinal slopes were also observable between the thick steps. However, the detailed features, such as spiral growth patterns or growth centers from which the step generates, have not been distinguished in this study yet.

By AFM, the steps have been also detected. For the thick steps as an example, they measured 50nm. For thinner steps, however, we have failed to measure the height. This is because the surface was dusty and resulting noise disturbed the measurements. The dusty particles on the surface may be residual glasses, clay materials or oxidation products. Although some kinds of diluted acid were applied to remove these particle, the surface has not been cleaned up efficiently. Now, we are seeking another way of cleaning.

The effect of limited material transport in the matrix of the metamorphic rocks on the chemical composition trend of garnet

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The effect of diffusion transport in the matrix of metamorphic rocks is often discussed based on the crystal sizes of garnet porphyroblasts or their relative spatial distribution. It is, however, not always possible to observe the spatial relations between different garnet grains during their growth, due to possible deformation thereafter. On the other hand, sluggish diffusion transport in the matrix might have affected the chemical zonation trend in each grain. To investigate the influence of the sluggish diffusion transport on the chemical zonation trend of garnet, formation of zoned garnet from chlorite and quartz was calculated using a forward approach in the system MnO-FeO-MgO-Al₂O₃-SiO₂-H₂O. Sluggish diffusion transport was introduced by assuming limited equilibration volume in the matrix consisting of chlorite and quartz. It was assumed that only those matrix chlorite within certain diffusion distance from garnet surface were in equilibrium with garnet. Different transport ability was considered by giving different diffusion distance: 3.0, 1.0, 0.3, and 0.1 [mm]. Stepwise *P-T* conditions were given, and the amount and the chemical composition of garnet and chlorite in equilibrium were obtained at each *P-T*. Newly formed garnet was not considered in the next calculated step, to model the fractional crystallization. Calculations were carried out following the conditions obtained from the Sambagawa metamorphic belt, Japan. In the model without equilibration volume (where matrix chlorite was always homogeneous), the Mn content in garnet decreased from the core to the rim and neared zero before the Mg/(Mg+Fe) ratio in garnet started increasing. In contrast, shorter diffusion distance resulted in the rise of Mg/(Mg+Fe) ratio in garnet before Mn extremely decreased, which was more consistent with the observation of natural samples. Different diffusion distance little affected the chemical trend of the garnet, but only their size. Resulted radius of the garnet grain was largely proportional to the diffusion distance. The calculated amount of garnet growth increased dramatically as the temperature increased. The result indicates that the chemical composition trend in zoned garnet from the Sambagawa metamorphic belt is consistent with growth under sluggish material transport, and that the garnet porphyroblast might have grown far more rapidly in the higher temperature stages of the metamorphism.

Andalusite formation after kyanite and sillimanite in sheared HP Gföhl Granulites of Southern Bohemian massif, Czech Republic: Typical example of strain-assisted polymorphic reactions?

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The Blanský les massif is the largest body of the exposed mid-Paleozoic Variscan Gföhl Unit from the Moldanubian Zone in the southern Bohemian Massif, Czech Republic, where high-pressure quartz-feldspathic granulites occur containing blocks of garnet peridotite. The quartz-feldspathic granulite show variable features indicative of multiple stages of deformation and metamorphic recrystallization during exhumation. The kyanite + garnet + ternary feldspar + quartz is the primary mineral assemblage formed at the earliest and most high-pressure stage. Sillimanite with or without cordierite has been documented to replace kyanite to varying degrees during the subsequent high-temperature exhumation stage. Andalusite has also been known to occur rarely. However, we have newly found that andalusite is the major Al_2SiO_5 phase in some localized shear zones in the massif. The mylonite-ultramylonite in those shear zones has strong planar-linear fabric. In addition, abundant asymmetric structures are observed in the XZ sections of the sheared rocks, while such asymmetric structures are not seen in the YZ sections. Therefore, it is reasonable to assume a simple shear deformation. We estimate the magnitude of shear in the shear zone, using $S - C$ angles (θ°). The occurrence of Al_2SiO_5 minerals correlates well with the $S - C$ angle measured in the marginal part of a shear zone. Andalusite rarely occurs in the outermost part of the shear zone where $S - C$ angles $> 5^\circ$ (estimated shear strain $\gamma < 10$ ($\tan 2\theta^\circ = 2/\gamma$; Ramsay and Graham, 1970)). In contrast, andalusite is the major Al_2SiO_5 mineral and partial replacement of kyanite and sillimanite by andalusite is commonly observed in the central part of the shear zone where $S - C$ angles $\leq 5^\circ$ ($\gamma > 10$). Thus, polymorphic reactions from kyanite and sillimanite to andalusite may have been enhanced by strain at lower-temperature conditions than those during the preceding sillimanite forming stage.

Sulfide recrystallization experiments from hydrothermal solution circulating by thermal convection

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Hydrothermal fluid flow plays an important role in migration and fixation of elements through crystallization of minerals. Especially, sulfide minerals can contain either useful or toxic elements, and frequently shows characteristic textures, morphologies and mineral assemblages involving hydrothermal fluid flow at their crystallization. However, reproduction of crystallization with one-way flowing hydrothermal fluid is impossible in experiments with sealed containers. In this study, we designed a fluid circuit circulating hydrothermal fluid by thermal convection. Crystallization experiments of iron sulfides from flowing fluid were carried out with the hydrothermal fluid circuit.

A rectangular circuit (42.6 cm by 17.3 cm) of SUS316 pressure tubes with 5 mm in inner diameter was used as a reaction vessel. The rectangular plane was held to be 20 degrees inclination for thermal convection. One of the long sides of the rectangular was heated by an electric furnace. Volume of the circuit is approximately 24 ml. Starting material was filled in the heated side of the rectangular. The lower half of the starting material was a mixture of powdered natural pyrite (2g) and quartz grains (4g). The upper half was quartz grains only. Experimental fluid was 5 mol/l NH_4Cl solution. Volumes of the solution were 9 to 19 ml depending on the experimental pressures. Maximum temperature was controlled to 350°C at the center of the longer side, where was the upper boundary of the pyrite starting material. Experimental durations were 3, 5, 10 and 30 days. After the experiments, the run products were fixed with resin, and vertical sections were observed by SEM.

In the lower half of the starting material, pyrite decomposed and pyrrhotite formed around pyrite grains. Pyrite decomposition depended on the temperature and run durations. At the upper end of the heated side, where the temperature was approximately 110°C, tiny pyrite crystals occurred at the surface of the quartz grains. Submicron pyrite crystals formed framboidal aggregates or layer on quartz grains. Circulating hydrothermal fluid with sulfur provided by pyrite decomposition formed pyrrhotite at the higher temperature region, and pyrite at temperature decreasing region where high temperature vapor precipitated to liquid.

Characterization of defects in hydrothermally grown and natural beryl single crystals: A comparison

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Hydrothermal growth of emerald single crystals was done by the recrystallisation of natural beryl charges. Seed plates of both synthetic and natural beryl were used, which had been cut parallel to the (5 5 $\bar{1}$ 6)-plane. Crystals were grown under stationary heat field conditions (standard autoclave method) and under the action of rotation heat fields within the dissolution and crystallisation zones.

The grown crystals were of rather high quality. To study their defects, polarisation microscopy, X-ray topography and electron probe microanalysis have been used.

Two types of optical inhomogeneities can be observed. The first one is a system of bands corresponding to microface growth sector boundaries disintegrating the crystallisation front of the non-singular surface (5 5 $\bar{1}$ 6). This regeneration surface can be considered as a large number of parallel growing "subindividuals". During the growth process, their number is decreasing while each of the ones remaining is getting larger.

The second type of optical inhomogeneities are growth zones, which are marked by a set of bands corresponding to the growth isochrones. The distance between two nearest distinguishable zones is about 12 μ m. This growth zonality is due to non-uniform distribution of chromium within the crystals. The distribution of chromium along the growth direction measured by microprobe analysis appeared to be more uniform in crystals grown under the action of the rotating heat field than in those grown under standard conditions.

X-ray topography studies have indicated that there is a tilting between the grown crystals and the referring seed plates. The amount of the tilt angle depends on the composition difference between seed and grown crystal and on the growth conditions.

For comparison we started investigations on both natural emerald and natural colorless beryl crystals. The crystals are from different localities and reflect different mineralization conditions: hydrothermal, pegmatitic and metasomatic.

Ripple textures in volcanic alkali feldspars

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It has become to be widely accepted that plutonic alkali feldspars more or less undergo hydrothermal reactions. They show several types of microtextures due to fluid-feldspar reactions. A ripple texture was first reported for the Coldwell syenite alkali feldspars (Waldron and Parsons, 1992). Its origin has been attributed to high-temperature fluid-feldspar interactions.

Feldspars in alkaline volcanic rocks from Ischia island, Italy, have been studied by some workers (Rahman and Mackenzie, 1969; Poli et al., 1987; Crisci et al., 1989; etc.). Rahman and Mackenzie (1969) traced their path of fractional crystallization with magmatic resorption. They showed corresponding textures such as mantle and perthite-like textures. Up to date, however, any hydrothermal alteration has not been recognized for the feldspars. Feldspar textures in alkaline volcanic rocks from Oki-Dogo island, Japan, have also been produced by fractional crystallization with peritectic resorption (Nakano, 1992; Nakano and Akai, 1992; Nakano and Suwa, 1995; Nakano, 1996). They comprise mantle texture with saw-tooth interface (cuttle-fish texture) and perthite-like intergrowths of plagioclase-anorthoclase and sanidine. No signal of hydrothermal alterations has been recognized (Uchimizu 1966; Xu, 1988; Kobayashi and Sawada, 1998; Kobayashi, Sawada and Yoshida, 2002), as well as the case of Ischia.

Ripple textures, which are similar to the original one from the Coldwell syenite, have been found in the alkali feldspar phenocrysts from both the Ischia and Oki trachytes. The compositions of the Ischia alkali feldspar phenocrysts vary from Or14Ab79An7.5 to Or69Ab31An0.3 throughout their textures, which are higher in An content and wider in compositional range than those of the groundmass feldspars. As far as examined hitherto, the compositions of the Oki alkali feldspar phenocrysts vary from Or27Ab59An14 to Or54-57Ab43-40An3-2, which are much higher in An content than those of the groundmass feldspars. Their compositional differences between phenocryst and groundmass suggest their magmatic origin as well as the formation of other textures mentioned above.

Zircon textural and chronological evidence for Mesoproterozoic and Carboniferous mafic igneous complexes in the crystalline basement of NE Poland

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Zircon, because of its physical and chemical resistance to destructive geological processes, is widely used to study the origin and high-temperature history of crustal rocks. We have combined imaging of zircon growth textures by monochromatic cathodoluminescence (CL) and backscattered electron (BSE) with SHRIMP U-Pb microgeochronology to study samples from the basement of the SW part of the East European Craton in NE Poland.

Isolated deep boreholes in the Warmia area have intersected poorly defined tectonic structures containing high grade metamorphic rocks previously interpreted as enderbites (granulite grade metasediments), possibly representing either an enigmatic structure surrounded by western part of Mesoproterozoic Mazury Complex or westerly extension of the Mesoproterozoic Mazury Complex. However, basement zircon from drill holes at Malbork and Debowiec Warminski shows none of the textures expected in zircon from high grade metasediments (i.e. formerly-detrital cores surrounded by metamorphic zircon overgrowths). Instead the grains have the simple oscillatory growth zoning and lack of cores typical of crystallisation from an initially zircon-undersaturated magma. Consistent with this, all zircons from each sample have the same U-Pb age (Malbork - 1497 ± 21 Ma, Debowiec Warminski 1520 ± 21 Ma) and there is no evidence for inheritance. The Warmia structure is, at least in part, an igneous complex coeval with the Mesoproterozoic Mazury Complex, and probably and extension of that system.

Zircon from gabbro intersected by drilling at Pisz is much younger, 345.5 ± 5.1 Ma. The gabbro has previously been interpreted as a dismembered relic of a Palaeoproterozoic ophiolite sequence, but this is now considered unlikely. All the zircon grains have simple banded or concentric zoning consistent with growth in a fractionating mafic magma and have no metamorphic overgrowths. The gabbro is a product of Palaeozoic subcratonic magmatic activity. This requires the geological history of the area to be reinterpreted, but also resolves some previous problems.

On the Striated Prism Faces of the Tourmaline Crystals

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Tourmaline can be found in nature as short to long prismatic crystals with rounded triangular cross sections. Occasionally acicular and even fibrous crystals have been found. The prism faces are generally striated parallel to the *c* axis and this feature is considered as diagnostic for morphological tourmaline identification. Vertical striations are usually attributed either to juxtaposition of prismatic facets, that make curved prism surfaces, or to multiple parallel twinning. Nevertheless tourmaline crystals that appear striation-free, within the resolution limits of observations by Optical Microscopy-OM, have also been found. In particular, striated tourmaline is common in deposits of pegmatite origin, whereas striation-free crystals are found mainly in metamorphic rocks. Indeed, the origin of the striations in tourmaline remains a problem to be solved. Therefore in the present piece of work, the growth history reconstruction of tourmaline crystals from different occurrences and different growth environments have been carried out by means of Optical Microscopy-OM, X-Ray Diffraction Topography-XRDT and Electron Probe Microanalysis-EPMA. In particular, tourmaline crystals from pegmatite pockets of island of Elba (Italy) have been studied. These tourmalines are striated bi-colored crystals exhibiting greenish-yellow to colorless zoning perpendicular to and parallel to the *c* axis: the transition from the inner yellow regions to the colorless ones occurs suddenly. The present study indicates relationships between growth mechanisms of tourmaline and origin of the striations. In fact, two main growth stages were identified. The former stage, pegmatitic, corresponding to the greenish-yellow regions, resulted dislocation-free and developed by means of 2D growth mechanism. No crystal grain aggregation was observed. The latter stage is an overgrowth of colorless elbaite developed in hydrothermal stage of the pegmatite crystallization, chiefly by spiral-growth mechanism. It is characterized by dislocations normal to the growing faces and consists of homophase aggregation of crystal grains with the same chemical composition. In this growth stage, striations with prismatic facets and final rounded morphologies occur. Therefore, the striated prism faces can be considered as a result of near parallel intergrowth of small blocks elongated along the *c* axis. This relationship between parallel columnar intergrowth and striations has been confirmed by OM and XRDT in the other studied tourmaline crystals. In particular, tourmaline crystals from metamorphic rocks of Córdoba Province (Argentina) that appear striation-free by OM in reflected light, revealed their composite structure by OM in transmitted light and by XRDT. It is hard matter to apply the definition of single-crystal to these samples.

On the Diverse Etch Patterns of Magnetite by Hydrochloric Acid

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Several crystals of magnetite were corroded by hydrochloric acid and the characteristic features of etch patterns were evaluated as to reflect the growth condition of the mineral.

The degree of etching seems to be affected by the sort of solution, concentration, temperature, period, and so on. By the preliminary procedure, it is clear that 10 mol/l of hydrochloric acid is convenient for the etching. For the present experiments, the samples are magnetite from several types of occurrence such as metamorphic rocks, skarn, and others.

The observed etch patterns such as growth zoning, etch pits, and growth hills might reflect growth condition of the crystal. The zoning is most obvious on {001}, and is faint on {111}. In case of magnetite from skarn, etch patterns appear clearly especially on the {001} and weakly on the {111}. On the other hand, magnetite from metamorphic rocks shows very weak zoning independent of the crystal faces. The pits and the hills appear on {111}, and do not appear on {001}. On the triangular {111} faces, pits and hills both have triangular outlines. The hills have the same orientation as the {111} face (i.e., sides of "hill-triangles" are parallel to sides of the {111} face), whereas pits have the opposite orientation. The degrees of corrosion differ in each crystal face, that is, the crystal faces of {001} are corroded more strongly compared to {111}.

Inclusions in magnetite are also revealed by etching. In addition, the boundaries between magnetite and other minerals, such as hematite lamella, are emphasized clearly.

The difference and the degree of etching might suggest the diversity of the forming condition of the minerals.

O13-01

Modeling of the evolution of 3 dimensional polycrystalline structures

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Phase field model was originally designed as a model of the interphase boundary (typically solid-liquid interface). We extended the phase field model so that not only interphase boundaries but also grain boundaries can be described. Conventional phase field model does not include the information of orientations of crystals, thus could not express the polycrystalline structures. In order to construct an equation for the orientation in physically reasonable way, we developed a singular diffusivity theory, which treats the long distance interaction through infinitely large diffusivity. In 2D situation, we can take one angle variable as an expression of crystalline orientation, while the element of SO(3) must be adopted in 3D case. It means that we have to derive the model using SO(3)-valued variable (which has 3 degrees of freedom) including singular diffusivity, plus usual phase field variable. We will show our model equations can describe the solidification process from the multiple nuclei, the formation of the grain boundaries and the following grain structure evolution. Simulations of the model equation is demonstrated which is computed using the projection technique.

O13-03

Self-assembling of colloidal particles and nucleation problems

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It has been recognized the systems of the colloidal particles still obey the general theories of crystal growth, and thus the structurization of the nanomaterials is to be explained by the language of the crystal growth. According to the crystal growth theory, the self-assembling of the particles is a process of minimizing the free energy of the system through assembling a large number of thermally activated particles into the ordered large-scale lattices. Such kind of ordering processes are well formulated by the nucleation theory. From the view point of the precise fabrication of the nanomaterials self-assembling, the nucleation is very often related to the problems of the random and uncontrolled formation of the critical clusters in the undesirable manner which results in the erroneous assemblies of nanomaterials. The practical problem of the nucleation is how to control the formation of the critical clusters. We introduce several conditions to describe the dynamics of the particles self-assembling. 1) The size and mass of the assembling particles are large. This condition enables to manipulate the particle dynamics using the stochastic equation of motion known as the Langevin equation. 2) Initially systems are subjected to the metastable state. Under the metastable condition, the critical cluster plays the decisive rolls in determining the nucleation path which results in the possible structure of the target assemblies. 3) The particles are homogeneous. Only spherically symmetric and homogeneously structured particles are considered. According to these conditions, we can formulate a colloidal crystallization as a model system of the self-assembling of the particles.

O13-02

Quataron concept for crystal growth and nanomaterials formation

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In our recent works [1,2] we have described a set of ideas and principles dealing with structural self organization of substance in the nanorange. These ideas have been collectively referred to as the "quataron concept". Central in this new concept is the idea that there are specific nanosize clusters (quatarons) arising under non-equilibrium conditions. In this work is reported a new data about the peculiarities of quatarons and their role for formation of crystalline and noncrystalline materials. The formulated principles are used to explain the structure and origin of different types nanomaterials.

Quatarons are not actual new-phase nuclei. They cannot be described in terms of known states of substance. Actually quatarons represent a separate intermediate phase at the nanolevel. Quatarons are clusters a new species of the atomolecular organization of substance, a new state. This state referred to as a "latent" phase.

Quatarons are dynamic structures constantly changing their forms. Quatarons are the basis for all kinds of equilibrium nanostructures from ordinary tetra- and octahedral groupings to the widely known fullerenes or dense dodecahedral and icosahedral clusters, colloidal, fractal particles. In particular, quatarons are fullerenes predecessors [2].

It has been found that clusters more than 1.2 nm in size can become potential centers of crystallization. Only such clusters contain a minimal number of atoms necessary for crystal nucleation. At the same time, crystals grow by smaller clusters (quatarons), which are transformed to "two-dimensional" nuclei already on the growing crystal surface. Quatarons are ideal as growth units. Chemical composition of quatarons is the same as that of crystals. Topologically quatarons are close to structural modules of crystals. Variability of the structure allows quatarons to join any crystal surface.

This theory also broadens our understanding of the amorphous state. If for some reason quatarons or their aggregates fail to crystallize, then in the condensed state they give rise to a special class of solid ultradisperse materials of various degrees of ordering. The closest analogue of such materials is opal, a material made up of one-size spherical silica particles. The characteristic dimensions of structural units in opal-like materials are guaranteed at the second or third level of fractal aggregation of primary quatarons.

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O13-04

Formation of single-domain colloidal crystals by strong shear-flow

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Charged colloidal particles with an equal diameter are spontaneously organized into a three-dimensional periodic array in a liquid media. This ordered state is called the colloidal crystal, and has received considerable attention with respect to its possible application, particularly as photonic crystals. Although polycrystalline samples are easily prepared, producing large single-crystalline domains remains time-consuming and difficult. We have developed a fast and simple process for fabricating a single-domain film. A suspension of poly-crystalline colloidal crystals was charged in a flat capillary and processed by strong shear flow. The suspensions used are mono-dispersed polystyrene or silica particles (ca. 200nm in diameter) in water with particle volume fraction of about 10%, which form colloidal crystals diffracting visible light. Optical characterizations for the uniform samples indicate that almost all the capillary space (several square centimeters wide and 0.1mm thick) is filled with a single-domain crystal with a fixed crystallographic orientation determined by the cell geometry. The single-domain crystal can be fixed in a self-standing hydro-gel film by polymerizing gelation agents added in the suspension. The gelled colloidal crystals can be deformed by external stress and, therefore, work as tunable photonic crystals.

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The ability of in vivo biochemical systems to engineer complex materials to sustain life is evidently worth emulating in designing and constructing novel materials. However, bizarre as it can seem, purely inorganic processes can also yield self-assembled complex structures that are not controlled by crystallographic symmetry. I will present in this lecture a synthetic novel type of material that share with life complexity, morphology, hierarchy and self-organization yet it is remarkably simple in chemical terms. The synthesis is very simple, requiring only a source of carbonate ions (e.g. atmospheric CO₂), strong alkaline aqueous solutions, silica and alkaline-earth cations (Ba and Sr, Ca) at room temperature. Under these alkaline conditions, the precipitation of alkaline-earth carbonates (witherrite, strontianite or calcite/aragonite) coupled with silica interactions yields crystal aggregates made of millions of nanocrystals exhibiting self-assembled non-crystallographic morphologies (J.M. García-Ruiz, *Geology* 26 (1998) 843-846). These morphologies are highly reminiscent of the shape of primitive organisms, but the precipitate are clearly inorganic in origin and form without involvement of biological compounds or living organisms (J.M. García-Ruiz, et al., *Science* 302 (2003) 1194-1197). These crystal aggregates share with life complexity, morphology, hierarchy and self-organization, and therefore have been named "silica biomorphs". I will discuss the formation, morphological behavior and textural arrangement of these complex self-organized crystal aggregates as a function of the concentration silica and silicate species in the system, supersaturation value of the carbonate phase, pH and temperature. The study review a systematic characterization analysis including optical video microscopy, scanning and transmission electron microscopy, X-ray and electron diffraction and several spectroscopic techniques. At present, the formation of these types of precipitates under natural conditions is geochemically plausible, the probability increasing significantly for primitive Earth environments. I will review the geological niches where such mineral self-assembled structures may form and—as an application—I will finish with a discussion on the problem of the detection of primitive fossil life on Earth and Mars.

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The basic picture of heteroepitaxial growth can be summarized as formation of islands on a foreign substrate first, followed by horizontal expansion of the islands on the substrate. Previously little attention has been paid to how the interfacial tensions affect the horizontal expansion of a crystalline island over the substrate, which has recently been found to affect the physical property of thin film significantly. For example, tilting of crystallographic orientation has frequently been observed in epitaxial layers, and our understanding of such effect is very limited. In this talk I will focus on the lateral growth of NH₄Cl crystallite on a foreign substrate mediated by successive nucleation. With state-of-the-art structural and morphological characterization methods, we observed that the crystallographic orientation is consecutively rotated, leading to periodic structures on the surface of crystallite aggregate. We demonstrate that this unusual effect is related to the asymmetric surface/interface tensions in the early stage of nucleation, and should be enlightening for a class of thin film growth where nucleation plays a dominant role.

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Nucleation is found to be one of the key steps in crystalline micro/nano phase formation. In this presentation, I will give an overview on the latest development in nucleation mechanism and its role in the nano particles aggregation/assembly. Supramolecular functional materials consisting of 3D a self-organized micro/nano structure, have important applications in ultra-strong functional materials, photography, cosmetics, food, petroleum industries, drug delivery, lithography, catalyst supporters, scaffolds for tissue engineering, novel separation techniques for macromolecules, etc. Macroscopic properties are determined by the micro/nanostructure of continuous three-dimensional entangled networks in the liquid. In most cases, such materials with the desired structure and required properties are obtained by a large scale of screening different potential chemicals. The strategy of our research is to produce new supramolecular functional materials by a micro/nano scale architecture, which relies on our new understanding of the formation mechanism of the self-organized 3D nanostructures of supramolecular functional materials, and the correlation between the structure and macroscopic properties. Our research show that the formation of interconnected fibril networks often takes place through small angle crystallographic mismatch branching or wide angle crystallographic mismatch branching of the growing fibers. According to this principle, we can now achieve genuine architecture of nanofiber networks of supramolecular functional materials at a micro/nano scale, employing the so-called "branching generators" or other novel technologies. This progress opens up a new dimension in nanophase engineering, tissue engineering (scaffold), novel separation, drug delivery, and the engineering of multi structured functional materials (including superconductors, self-assembled quantum dots, etc.).

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Insulin, one of the most important hormone proteins, plays an essential role in controlling the amount of sugar in the blood. Not only the molecular insulin and its oligomer but also the suspended particles in solutions are utilized as a medicine for diabetes. For instance, the solution containing amorphous particles of zinc insulin shows a slightly slower therapeutic effect and that of its crystallites indicates rather retarded effect in comparison with the regular insulin solution, which are known as lente and ultralente insulins, respectively. Therefore, the control of the aggregation and crystallization of insulin in aqueous solutions is very important to improve a quality of the medicine. Recently, ten Wolde and Frenkel theoretically simulated a crystal nucleation process in colloidal solutions with a metastable liquid-liquid phase separation, and found that the appearance of the liquid-liquid phase separation drastically changes the generation pathway of a crystal nucleus and that the crystal nucleation rate increases with steps. Then, the two-step process has newly been proposed as a nucleation mechanism; at the first step small liquid droplets with a high protein concentration are generated from the mother solution, and next the nucleation of crystals occurs inside the droplets. The generation of these droplets makes us expect to promote and/or control the crystallization of proteins. Experimentally, the liquid droplet formation and the successive crystal nucleation have experimentally been observed for phosphoglucosylase and intact immunoglobulin. However, the nucleation and growth of the crystals are not detected inside the droplets but on the surfaces. These facts are inconsistent with the two-step mechanism. Thus, it is very interested to study how the droplets of insulin take part in the crystal nucleation process.

We succeeded in obtaining the liquid droplets in aqueous solutions of insulin by changing the pH values and Zn²⁺ concentrations of the mother solutions, and successive growth of insulin crystals generated on the surface of the droplets. The nucleation process belongs to the so-called heterogeneous nucleation mechanism occurred by using the surface of an external substance. Generation behavior of liquid droplets, however, is sensitively dependent upon pH values of the mother solutions. Such a pH-dependent nucleation and growth of insulin crystals via liquid droplets would also be applicable to control the nucleation of crystals and their micro assembly. In this session, we will report the new behaviors with reference to our previous results on crystal growth of insulin.

Synthesis and growth mechanism of rutile TiO₂ spherulites

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At ambient conditions TiO₂ can crystallize in three polymorphs, i.e., rutile, anatase and brookite. Among them rutile is the thermodynamically most stable phase. However, less attention has been paid to rutile TiO₂, possibly because of the expectation drawn from its larger energy band gap that it would yield a lower photovoltage than anatase. Recently, rutile has been proven to be very useful for dye-sensitized solar cells, optical devices such as waveguides, and catalyst for decomposing various toxic compounds. These findings suggest that additional research of rutile TiO₂ be interesting. Furthermore, detailed study of the growth properties of rutile is also considered to be very necessary as it has been reported to be capable of aggregation into some special morphologies.

In this presentation, we report synthesis and analysis of rutile TiO₂ spherulites. A spherulite is a polycrystalline structure with roughly spherical morphology, which consists of lath, fibrous or lamellar crystals emanating from a common centre with random misorientations. Here we will show that misorientations of the primary crystals can also be governed by a novel mechanism. The samples were fabricated by the microwave-assisted hydrothermal method at the typical reaction temperatures of 160–220 °C and time of 1 hour. Scanning and transmission electron microscopy (SEM, TEM), and electron backscattering diffraction (EBSD) are employed to study the morphologies and structures. It shows that the primary structure is rectangular rutile nanorods. The side surfaces of the nanorods are assigned to {110}, which is consistent with the calculated lowest surface energy of rutile {110}. Under certain reaction conditions, the nanorods are prone to form into various interesting secondary structures, where there are determined misorientations between the rods. We demonstrate that these structures are formed by multiply {101} twinning occurred during growth, and spherulites will be obtained when heavily branching of growing nanorods happens through consecutive multiply twinning. In addition, we show that self-organized array of the nanorods can be produced if twinning is suppressed.

Self-assemblage of extraterrestrial nano-magnetite particles

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Self-assembled nano-particles are extensively studied in the field of nano-technology. Similar textures have been recently recognized in the extraterrestrial iron oxide (magnetite Fe₃O₄) of Tagish Lake carbonaceous meteorites, which had experienced aqueous alteration. Detailed observation revealed the unusual structure in the particles, with an unique texture typical for self-assemblage. This knowledge can give us the possibility of new fabrication technique of self-assembled materials.

Magnetite crystalline in the fcc structure is commonly observed in terrestrial nature. It mostly appears as octahedron crystals surrounded by {111} faces. In extraterrestrial material, however, some nano-magnetite appears unusually shaped as "rhombic dodecahedron", along with {111} octahedron as terrestrials. The diameter of the observed particles varies in the range of 100-1000 nm (peak at 450 nm). The nano-magnetite particles were recognized to be form a self-assembled texture in the interstices (~500 nm) of the matrix part of this meteorite.

Using a Field emission scanning electronic microscopy, we obtained high-resolution images of the assembly of nano-magnetite. It was found that the size of the individual particles constructing the assembly is limited within a few hundred nm in diameter. Furthermore, only the particles sized around 200 nm exhibit the interesting structure. Electron diffraction analysis using a transmission electron microscopy revealed that they consist of only (110) faces that cannot be expected by crystallographical prediction for fcc crystals. However, if the particles are composed of four rhombohedral units {111}, their multiple twinning can form dodecahedron surrounded by {110}. This fact can consistently explain that the particles have the dodecahedron in shape, and so that they can be stacked in a close-packed configuration. In addition, certain edge of each particle seems to be depressed. High-resolution TEM investigations of the depressed edge exposed mismatch of lattice, which could result in the boundaries of the crystals. These morphologies and structures are similar to those of multiple twin particles, which are well known in ultra-fine particles (a few tens of nm). Extraterrestrial nano-magnetite particles oriented in a self-assembled texture might have seen formed under the conditions probably at asteroid body in which the gravity and/or magnetic field are different to the terrestrial environment.

Filamentary and skeletal sulphide (pyrite and galena) crystals embraced in large contemporaneously growing calcite crystal

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The calcite crystals sometimes include groups of peculiar filamentary, needle-like and skeletal crystals of sulphides with isometric crystal structure. The morphological and crystallographic features of such inclusions were observed after their extracting by selective dissolution of the enclosing calcite. Different techniques were applied in these studies: optical microscopy and goniometry, SEM, FESEM, EPMA, X-ray powder and single crystal methods. Three characteristic cases of calcite containing pyrite and galena inclusions were examined. (1) Pyrite filamentary inclusions from the Surneshko Kladenche copper vein deposit, Eastern Bulgaria (Bonev et al., 2005). The large calcite crystals show an internal habit evolution. The pyrite is presented by mm long transverse sub-parallel tortuous filaments with varying micron-sized thickness, starting from an internal calcite scalenohedral growth zone w{31-45} and reaching the crystal surface v{21-31}. Mostly, the not strongly straight filaments consist of parallel octahedral subindividuals and are elongated roughly in [001] direction. More dense and shorter pyrite crystals are additionally developed in the outermost zone of the same calcite crystals. (2) Another similar case comes from a Canadian locality where the inclusions are of cobaltian pyrite (11.3 wt.% Co). They form a zone of densely disposed subparallel filaments (up to 3 cm long) reaching the outer surface of the enclosing calcite. The spear-shaped inclusions are elongated along [111] and contain longitudinal (110) twin planes. Pyrite associates with two thin zones in calcite with abundant but much shorter hematite inclusions. In a similar case from the Caucasus, Zhabin (1986) described calcite crystals, containing internal zones of uniform fine elongated cinnabar crystals. (3) Skeletal and needle-like galena crystals were observed as internal zones within large-crystal calcite from the Zvezdel-Galenit vein Pb-Zn deposit, Bulgaria. Skeletons of various morphology have been found: hopper-like "tetragonal" pyramids elongated along [001] axes, star-shaped "trigonal" pyramids elongated along [111], triangle plates along [110] and complicated hopper-like macrospiral skeletons. Rare acicular crystals and [001] whiskers also occur.

All these cases characterize a specific simultaneous and competitive growth of large calcite crystals and a restricted number of small sulphide crystals on their surfaces. Sulphides continue their growth in transverse direction towards the available open space, being laterally limited by the spreading calcite growth layers. So, gradually, the sulphide seeds were developed as subparallel highly anisometric filamentary crystal-inclusions, oriented along their favourable growth directions. When the subordinate phase is of larger quantity, more developed skeletal forms arise, and this is the case with galena.

O14-01

An overview of seafloor hydrothermal activity in arc/backarc systems of the western Pacific

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Since the compilation of Ishibashi and Urabe (1995) and Glasby et al. (2000) on seafloor hydrothermal activity in northwestern Pacific, several important deep-sea hydrothermal mineralization sites were found in the region. These include Hakurei site in Izena Caldera, Okinawa Trough (Maeda et al., 1996), HAKUREI deposit in Bayonnaise knoll, northern Izu arc (Shiokawa et al., 2004), and on- and off-axis hydrothermal sites (Fryer, Archaean and Pika sites) of backarc spreading center of the southern Mariana Trough (Urabe et al., 2003). Other inferred sites include Sumisu caldera (Iizasa personal comm.) and other seamounts of Izu-Bonin arc which have caldera structure. Existence/paucity of sediments seems to have little influence on the mineralization. Suiyo caldera in Izu-Bonin arc is a seafloor hydrothermal site thoroughly studied during Archaean Park Project (Marumo et al., 2005, Urabe et al., 2005). It provides important information on the genesis of such deposits, that is, cooling volcanic conduit of dacitic magma that exists about 5 km beneath the summit caldera provides heat and mass to the hydrothermal fluid, water-rock interaction and subsequent dissolution of volcanic rocks provides channel of the high-temperature (310 deg-C) fluid, anhydrite-clay-cemented unit confine the channel and reservoir of the fluid as a cap-rock, and the sulfide orebody is limited to above or within a few meters beneath the seafloor. It should be noted that the distribution density of the known deposits is much more than expected based on the experience of land-based mineral exploration on VMS (volcanogenic massive sulfide) deposits that is believed to be the fossil equivalents of seafloor mineralization. This is particularly true if we consider that the mineralization epoch of Kuroko VMS deposits in northern Honshu Arc, Japan is limited to 15 Ma during the development of the arc since 22 Ma. As some of the newly discovered deposits have an estimated tonnage >1Mt, seafloor mining should be taken into consideration as an alternative source of mineral resources.

O14-03

Mercury and lead isotope ratios of the Suiyo seafloor hydrothermal system and Kuroko deposits

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Mineralization of the Suiyo Seamount in the Izu-Bonin Island-Arc, south of Japan, was studied using mercury and lead isotopes. Sulfide samples of the active venting sites of the Suiyo Seamount are characteristically high Au (<42 ppm), Ag (<1,500 ppm), As (<1,440 ppm), Hg (<55 ppm), Sb (<96 ppm), and Se (<44 ppm). EPMA analysis indicates that realgar, orpiment, and mimetite are major As-bearing minerals. The sulfides are also characterized by high Zn (>10 wt%) compared to Cu (<6%) and Pb (<0.6 wt%).

We analyzed Hg isotope (¹⁹⁶Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰²Hg, ²⁰⁴Hg) ratios of dacite lava and sulfide samples from the Suiyo seafloor hydrothermal system. These Hg isotopes were analyzed using a MC-ICP-MS (Thermo Finnigan Neptune). We also analyzed Hg isotope ratios sulfide and sedimentary rock samples from Middle Miocene fossil seafloor hydrothermal systems (Kuroko deposits) for comparison. ¹⁹⁶Hg/²⁰²Hg, ¹⁹⁹Hg/²⁰²Hg and ²⁰⁰Hg/²⁰²Hg ratios of Suiyo sulfides increase with increasing their mercury contents, suggesting light Hg isotopes accumulated during the mineralization. The Pb isotope ratios (²⁰⁶Pb/²⁰⁴Pb = 18.546–18.562, ²⁰⁷Pb/²⁰⁴Pb = 15.535–15.554, ²⁰⁸Pb/²⁰⁴Pb = 38.322–38.375) of the Suiyo sulfides are very similar to those of dacite lava (²⁰⁶Pb/²⁰⁴Pb = 18.552, ²⁰⁷Pb/²⁰⁴Pb = 15.539, ²⁰⁸Pb/²⁰⁴Pb = 38.333), suggesting that lead, as well as mercury, is of magmatic origin.

There is no such a relation between Hg isotope ratios and mercury contents in Kuroko sulfides, indicating complicated mercury mineralization of Kuroko deposits. The ¹⁹⁶Hg/²⁰²Hg, ¹⁹⁹Hg/²⁰²Hg and ²⁰⁰Hg/²⁰²Hg ratios of Kuroko sulfides may be explained assuming that the contribution of sedimentary mercury plays an important role for the mineralization. The lead isotope ratios reported in literatures also suggest the importance of the sediment lead for the Kuroko mineralization.

O14-02

Diversity in fluid chemistry and mineralization caused by phase separation in the active seafloor hydrothermal field at the Yonaguni Knoll IV, Okinawa Trough, southwest Japan.

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Phase separation is considered as one of important factors for occurrence of hydrothermal deposits, because it induces drastic change in fluid chemistry. Active seafloor hydrothermal systems in arc-backarc setting provide good test field for this discussion, because we can obtain samples both of hydrothermal precipitates and hydrothermal fluids. The Yonaguni Knoll IV active hydrothermal field is located at water depths of 1370–1385m in Southern Okinawa Trough. During YK03-05 and YK04-05 expeditions using submersible SHINKA16500 (JAMSTEC), we extensively collected hydrothermal samples. The active field is aligned along a small valley. The temperature of venting fluid (T=328 degC; close to the boiling point at this depth) was found at the top of a big chimney-mound complex structure, which is located at the middle of slope. While its fluid chemistry showed brine-rich signature (Cl=650 mM/kg), clear fluid (T=310 degC) emanating from the foot of the same mound structure showed vapor-rich signature (Cl=400 mM/kg). In the vicinity, another high temperature (T=326 degC) black smoker type chimney stood, which fluid chemistry was brine-rich signature (Cl=700 mM/kg). Contrary to this, in the lower part of the slope where filled with more thick sediment, rather low temperature (T=220 degC) clear fluid venting from the mound structure and weak shimmering discharging from the seafloor were observed. Moreover, at least some part of the sediment was revealed as occupied with liquid CO₂ and/or CO₂-hydrate based on the pore fluid chemistry. This CO₂-rich component would probably be migrated after sub-seafloor phase separation. Distinctive mineralogy was found between the black smoker type chimney-mound structure in the upper slope and the precipitates around sediment in the lower slope. The former deposits associate with brine-rich fluids contained sphalerite, marcasite, galena, and chalcopyrite, while the latter associate with CO₂-rich fluid consisted mainly of anhydrite, calcite, magnesite and was disseminated with sphalerite, galena, alabandite, tennantite and tetrahedrite. Diversity in mineralization was observed in the active sediment-hosted hydrothermal field at the Yonaguni Knoll IV is strongly related with diversity in fluid chemistry caused by phase separation.

O14-04

Seafloor hydrothermal mineralization at the off-axial vent sites of the southern Mariana Trough

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Extensive occurrences of massive sulfides and sulfates associated with active high temperature fluid venting were located at two off-axial vent sites (Archaean and Pika) in the southern Mariana Trough. Active and inactive chimney structures and massive sulfides were sampled from these two sites during the dive programs TN167A cruise in March 2004, using ROV ROPOS (CSSF) and R/V Thomas G. Thompson, and YK05-09 cruise in July to August 2005, using submersible SHINKA16500 (JAMSTEC) and R/V Yokosuka. The Archaean site (12°56.35'N, 143°38.0'E, water depth = 2990 m) is located at the ridge flank, about 2 km apart from the backarc-spreading axis. The hydrothermal field has several discrete hydrothermal mounds with active and/or inactive chimneys, one of them being as high as 50 m (the Archaean Colossal). The highest temperature of the discharging fluids was recorded as 343°C. Active chimney structures are composed of abundant pyrite/marcasite, common chalcopyrite and sphalerite, and rare isocubanite and Pb-As sulfosalt. Inactive chimney structures and massive sulfide rubbles from the mounds contain late barite infilling conduits and interstices of sulfide minerals similar to those found in active chimneys. The Pika site (12°55.1'N, 143°38.9'E, water depth = 2830 m), on the other hand, is located around the top of an off-axial seamount about 350 m high, which is about 5 km away from the spreading axis. Large sulfide mound about 30 m high has several hydrothermal discharges with a maximum temperature of 330°C. An inactive chimney structure about 30 m high was also observed during the dives. Active chimney structures consist of abundant cryptocrystalline pyrite/marcasite, common sphalerite and chalcopyrite, and rare Pb-As sulfosalt and barite, whereas massive sulfide rubbles from the mound are composed of coarse euhedral pyrite (pyritohedrons) and gypsum/anhydrite precipitated to fill cracks. It is suggested that the euhedral pyrite was formed by recrystallization of primary sulfide minerals.

Chemistry, isotope composition and temperature of fluids at East Pacific Rise 9° and 21°N

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A comparative study of mineral composition and chemistry, fluid chemistry, He, and S isotopes in minerals sampled from sulphide edifices in hydrothermal fields on at East Pacific Rise 9° and 21°N during 49 th cruise of Russia RV "Akademik Mstislav Keldysh" with "Mir" submersible in 2003 have been carried out. A fluid inclusion study showed that salinity of fluid trapped in anhydrite from EPR 9°N varies from 3 to 13 wt. % NaCl-equiv., this value estimated for fluid encapsulated in anhydrite from EPR 21°N is of 4.2 to 9.7 wt. % NaCl-equiv. These values are higher than those measured directly for fluids venting from vents. Phase separation of subcritical fluids is responsible for the fluid salinity higher than that of seawater. Gas chromatography detected that fluids trapped by sulphides contained light hydrocarbon gases (CH₄, C₂H₆, C₃H₈, C₄H₁₀, i-C₄H₁₀, n-C₄H₁₀, and n-C₅H₁₂). Homogenization temperatures of fluid inclusions in anhydrite EPR 21°N and 9°N varied from 132 to 346°C and from 320 to 370°C, respectively. True temperatures estimated for the formation of minerals from EPR 21°N and 9°N ranged from 335 to 385°C and 150 to 360°C, respectively. Sulfur isotope composition in minerals from EPR 9°N varied from +0.5 to +6.3‰, while that EPR 21°N range from +0.8 to +3.0‰. The R/Ra ratios = (³He/^{He}) / (³He/^{He})_{air} measured in fluids trapped by sulfides are of 7, 69 to 8, 44 (EPR 9°N) and from 5, 85 to 7, 13 (EPR 21°N). The R/Ra ratio indicates a contribution of upper mantle helium in hydrothermal systems. This study shown that the mature EPR 21°N "black smokers" are slightly richer in 4He and display a wider range of deposition temperatures. Fluid inclusion study revealed that salinity of fluids is higher values directly measured for venting fluids.

Recognition of Ordovician Escanaba type VMS deposits in the Scandinavian Caledonides

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Submarine volcanism and associated hydrothermal activity constitute by far the most common VMS-forming geological environment in modern and ancient terrains. These magmatic-hydrothermal processes are seldomly disturbed by sedimentary activity but such interference is locally significant in the eastern Pacific. This is best illustrated by the Escanaba Trough, offshore California, where the still active rift zone of the Gorda Ridge is covered by thick turbidite sequences, with detritus derived from the North American continent. As a result of the struggle between endogenic and exogenic forces, mafic sills intrude into the wet sediments and hydrothermal activity creates chlorite alteration within, and VMS deposition on top of, the most recent turbidite beds.

An almost perfect ancient analogue to the Escanaba environment can be recognized in the Middle Köli of the Scandinavian Caledonides, where numerous Zn-Cu-bearing massive sulphide deposits occur in metamorphosed Ordovician gabbro-intruded calcareous turbidites, stratigraphically overlying submarine volcanics and Tremadocian U-Mo-V-rich black schists. These VMS deposits were of major economic importance for more than 300 years at Roros (Norway) and are also well known from elsewhere in the orogen, including Ankarvatnet, Üsmeten and Ruonavagge (Sweden), thus constituting an ore-bearing tectonostratigraphic key unit for more than 600 km along the orogen. Violating earlier theories on an ophiolite association for the Sulitjelma sulphide ores (Norway), it is suggested that also these ores belong to this ore type. Pyrrhotite, sphalerite and chalcopyrite are the dominating sulphide species in most deposits while pyrite, galena and arsenopyrite occur in variable amounts. The alteration patterns, as documented at Ankarvatnet, grade from a chlorite quartzite close to the pyrrhotite-rich assemblages to a sericite quartzite close to the pyrite-rich assemblages.

The ore lead isotopic composition for this ore type is very homogeneous on orogen-scale (²⁰⁶Pb/²⁰⁷Pb ≈ 18.15) and slightly more radiogenic than true VMS deposits, interpreted that the main metal derivation was from hydrothermally active underlying ocean floor volcanics with a small contribution from Precambrian crustal sources, derived via detrital grains in the turbidites.

The recognition of an ancient analogue to Escanaba type VMS deposits in the Scandinavian Caledonides implies that this ore-forming sedimentary environment can not have been dramatically distant from a continent prior to nappe transport. A close link, both with respect to age and geochemical signature, between the Tremadocian black schists and the Dictyonema "alum" shale, constituting a wide-spread platform unit in Norway, Sweden, Estonia and Poland, suggests that this continent was Baltica.

From SEDEX to VMS – the Skorpion-Rosh Pinah massive sulphide district, Namibia

oral presentation under session 14: Sea-floor hydrothermal systems: Present and past examples

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The Skorpion-Rosh Pinah Zn-Pb mining district is located within the uppermost greenschist facies grade Late Proterozoic Gariep Belt in southernmost Namibia. Traditionally, the metallogenic style had been interpreted as sedimentary exhalative (SEDEX) although bi-modal volcanic rocks within the basin have been increasingly acknowledged by several authors. A full assessment of the volcanic inventory of the basin suggests that the 1st-order metalliferous system of the Skorpion-Rosh Pinah district is rather of a sediment-rich VMS-style than of SEDEX-affinity. The host rock of the Rosh Pinah deposit is mainly a high-energy turbiditic arkose. The sulphides at Skorpion, in contrast, are hosted by both high-energy arkose and rhyolitic tuff, tuffites, volcanoclastics and minor volcanic flows. Only a minute portion of the ore is hosted by low-energy sediments. Regionally, both ore deposits and neighboring sub-economic occurrences cluster around a major volcanic centre, the only one known within the basin to date. This volcanic centre is situated at the intersection of a 1st-order basin margin and a high angle transform fault. Basaltic flows and sills, emplaced along the main graben axis and a group of rhyolitic domes, flows and more wide-spread lapilli layers characterise the bi-modal volcanism in this part of the basin. Several pronounced vent and feeder systems have been identified in outcrop and drill core, showing hydrothermal features such as pervasive silicification and sericitisation. One of these vent systems contains anhydrite in the footwall of a systematically stacked pyrite-pyrrhotite VHMS system. The Zr-contents of the rhyolites range between 450 and 900 ppm, suggesting very high original melt temperatures, similar to some VMS deposits within the Abitibi Subprovince, Canada. Syn-volcanic intrusions to these high-temperature felsic melts would have been the principal thermal driving source of the metallogenic system. It appears unlikely that substantial hydrothermal ore systems would have developed without this volcanic component due to the rapid influx of large volumes of high energy sediments. Dilution from clastic sediments within the relatively deep graben-type basin would have obstructed the formation of true SEDEX-style ore bodies. Future base metal exploration will have to fully appreciate the role of volcanism within the magmatic, structural and sedimentological framework of the Gariep basin.

Hydrothermal alteration in the 2.77 Ga Mt Roe basalt, Pilbara, Western Australia

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The alteration on the 2.77 Ga Mt Roe basalt, Pilbara, Western Australia, is interesting in the standpoint of biological activity at late-Archean hydrothermal system. A fresh and consecutive ABDP core of Mt Roe basalt including alteration zones gives new and more detailed insight into this concern.

The core is composed of basaltic lavas with clastic sediments interbedded. The samples were studied mineralogically, paleomagnetically and organo-geochemically.

The results show that (1) the core is composed of at least three lava units which are separated by thick sedimentary units, (2) the sedimentary units are comprised of sandstone, siltstone and shale, all of which are black-colored and rich in organic carbon with the C isotopic ratios of -60 to -50 permil as well as of -20 to -35 permil, (3) the hydrothermally altered horizons of several meters were recognized just below these sedimentary units, (4) pyrite, pyrrhotite, sphalerite and other sulfide veins were observed in some parts of the sediments, (5) the major part of alteration zone is associated with the fine-grained, black and organic carbon-rich quartz vein, (6) all of the zone is characterizes by the depletion of Fe, Mg, Ca, Na and P and the enrichment of K, (7) organic carbons in hydrothermal vein show C isotopic ratios of -40 to -60 permil, (8) methane was the only gas detected from the fluid inclusions in quartz vein, and (9) the paleomagnetic normal direction is obtained from pyrrhotite although the reversed direction from fresh basalt.

These observations suggest the followings; (1) the alteration might relate to submarine hydrothermal activity at shallower depth, (2) the hydrothermal fluid might circulate through depositing sediment and top of erupted basalt, (3) methanogene could inhabitate in hydrothermal vein producing methane and made the fluid strongly reducing, (4) methanotroph could inhabitate around seafloor, (5) other microbes such as cyanobacteria (stromatolite) and sulfide reducing bacteria could also inhabitate in the sandstone near coast.

As the hydrothermal vein was not observed in uppermost massive lava unit, the timing of this alteration would have been essentially concurrent with the volcanic activity. This is concordant with the previously reported SHRIMP age of around 2.8 Ga for the hydrothermal vein.

The 2.77 Ga geomagnetic field was of reversed in direction. However, hydrothermal pyrrhotite reveal normal direction. The original reversed remanent magnetization of pyrrhotite changed to normal during later low grade metamorphism, although magnetite in basalt did not changed.

The isotopic and structural implications for the hydrothermal formation of karpatite from Picacho Peak, San Benito Country, California.

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Several rare polycyclic aromatic hydrocarbons (PAHs) minerals have been found to occur in nature (Gaines et al. 1997). Karpatite, which was identified as nearly pure coronene (C₂₄H₁₂; Blumer 1975; Wise et al. 1986), is one of PAHs minerals. Here we present results of the single-crystal structure analysis and carbon isotopic analysis of karpatite from the Picacho Peak for unraveling the formation process.

The coronene molecules in the crystal structure of karpatite are all isolated and the intermolecular distances correspond to van der Waals interactions; the properties of karpatite may be derived from those of the agglomeration of coronene molecule. In the last few decades the concept of aromaticity has been generally accepted (Krygowski and Cyranski 2001); aromatic compounds prefer substitution to addition, and hence, they exhibit a tendency to retain their π -electron structure. The aromaticity of coronene molecules in karpatite avoids formation of PAHs with more structural diversity.

The isotopic compositions of carbon were measured with a continuous flow isotope ratio mass spectrometer (CFIR-MS; Finnigan Delta Plus). The $\delta^{13}\text{C}$ value of the present karpatite was $-22.39 \pm 0.18\text{‰}$, which may be suggestive of its source to marine. Simoncic and Shoell (1995) reported that the isotopic compositions of coronene in hydrothermal petroleum from the Guaymas Basin located in the central Gulf of California are $-21.6 \pm 0.9\text{‰}$ and $-20.1 \pm 3.4\text{‰}$. In addition, they mentioned that hydrothermal alteration of the sedimentary kerogen yields the coronene in the hydrothermal petroleum. The Picacho Peak is about 100 km north from the Gulf of California; hence the isotopic composition and occurrence of karpatite derives its origin from sedimentary kerogen and its formation by hydrothermal alteration.

The karpatite is included in quartz vein; this reveals that the coronene molecules were transported by hot fluids whose temperature was high enough to produce a liquid silicate phase. The PAHs of lower molecular weight are depleted from high temperature fluids due to their greater solubilities in water and lower melting points. The PAHs of higher molecular weight had migrated through each process of crystallization, re-crystallization, decomposition and polymerization occurring along the fluid path. This series of reactions is accordant with the one-ring build-up mechanism (Simoneit and Fetzner 1996); hydrothermal reactions convert small PAHs into large ones such as coronene. The series of reactions probably leads to the concentration of coronene in the system. Consequently, the hydrothermal activity including various PAHs would terminate with the crystallization of karpatite.

Diversity of chemical and strontium isotopic compositions of land water from Bandai area, Japan

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Knowing the aspects the reacted rock at deep underground helps us consider fluid behavior in the volcano-hydrothermal systems. By identifying the reacted rock from fluid chemistry, the locus of the aquifer can be determined when geologic structure is compared with the rock. In present study, we focus on specifying the locus of the aquifer and proposing a model of hydrothermal system at Bandai area including Bandai volcano and Adatara volcano by chemical and strontium isotopic studies. Bandai volcano is an active volcano situated on the east of Aizu basin in Fukushima prefecture, northeastern Japan. Water samples from and around Bandai volcano were divided into five types (SO₄ type, Cl type, Cl-SO₄ type, HCO₃ type, Cl-HCO₃ type) based on the anion compositional classification. SO₄ type is shallow groundwater dissolving volcanic H₂S gases, and the water reacted with Quaternary volcanic rocks. Cl type is the NaCl water having character of fossil seawater or marine deposits. Most of the water are collected in Tertiary sediment. Cl-SO₄ type may be explained by mixing SO₄ type water with Cl type water. HCO₃ type is shallow groundwater dissolving volcanic CO₂ gases, and the water reacted with Quaternary volcanic rocks. Cl-HCO₃ type may be accounted for by the blend Cl type water into HCO₃ type water. Adatara volcano is an active volcanic chain situated on the east of Mt. Bandai. Water samples from and around Adatara volcano were also divided into some types based on the anion compositional classification. Strontium isotopic study showed most of the fluids reacted with Quaternary volcanic rocks or the basement rocks beneath volcanic rocks. Part of the strontium isotopic compositions of fluid cannot, however, be accounted for by reacting with rocks. Although strontium isotope can independently provide some constraints on the origin of the fluids, multi-element isotopic study will enable to establish more detailed origin of the fluids.

Alteration of felsic volcanics hosting gas reservoirs in the Minami-Nagaoka gas field, Niigata Prefecture, Japan -Comparison of the alteration styles of rhyolite on gas reservoirs with dacite associated with Kuroko deposits-

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Natural resources such as Kuroko deposits, petroleum deposits and natural gas accumulations are distributed in the Green Tuff region in which the geology of a back-arc basin (Sea of Japan) is widely exposed. Kuroko deposits and energy resources of petroleum and natural gas mainly occur in the central and western zones of Northeast Japan, respectively. Although altered felsic volcanics are present in these deposits, characteristics of alteration of rhyolite associated with natural gas accumulations are different from those of alteration of dacite associated with Kuroko mineralization. Emplacement of the rhyolite lavas for gas reservoirs took place prior to 15.6 Ma after formation of basaltic to andesitic volcanic successions associated with the back-arc spreading. The rhyolite lavas are characterized by aphanitic structure and intersertal texture. Alteration of the rhyolite is divided into two types: Types 1 and 2. Mineral assemblage of Type 1 consists of large amounts of quartz and albite with small amounts of illite, chlorite and siderite, while that of Type 2 is mainly composed of quartz and some albite with minor illite, chlorite and siderite. Mineral assemblage of porous altered rhyolite is large amounts of quartz and albite with a lesser amount of chlorite and small amounts of illite and siderite. These mineral assemblages are characterized by the presence of large amounts of carbonate minerals and clay minerals and compared to mineral assemblage of altered rocks associated with Kuroko mineralization. The rhyolite alteration took place in the order of albitization forming a quartz-albite assemblage under diagenetic conditions to hydrothermal alteration precipitating siderite and illite. Analyses based on AI (Ishikawa et al., 1976) and CCPI (Large et al., 2001) indices using the chemical compositions of altered rhyolite suggest that mobility of elements on the altered gas reservoir rhyolite is different from that of elements on altered Kuroko dacite and that the altered rhyolite was formed by overprinting of very weak illitization and carbonization and weak to moderate illitization and carbonization to the albitized altered rhyolite for Type 1 and Type 2, respectively. Gain and loss calculations reveal that SiO₂, Al₂O₃ and Na₂O contents decrease largely and that Fe₂O₃, MgO, CaO and K₂O contents increase slightly. The difference in alteration style between the altered gas reservoirs rhyolite and Kuroko dacite is thought to be due to the difference in water/rock ratios during these alterations.

O15-01

Unidirectional solidification textures, miarolitic cavities and orbicles: Field evidence for the magmatic to hydrothermal transition in intrusion-related mineral deposits

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Unidirectional solidification textures (UST's), miarolitic cavities and orbicles are features sometimes observed associated with or within mineralized felsic cupolas. The UST zones are comprised of irregular sub parallel layers of quartz crystals with orientated c-axis terminations. They are products of rhythmic precipitation of quartz and quartz plus feldspar during periods of fluctuating volatile overpressuring within a relatively small degassing felsic intrusion. Such textures have been observed in porphyry copper systems, tin, tungsten, molybdenum and gold-bearing intrusions. Mineralized UST's suggest that in some cases metals began to deposit at magmatic temperatures and pressures with subsequent transition to hydrothermal conditions and main stage deposition of mineralization. There also appears to be a close relationship between UST's and "A" veins in some porphyry copper and molybdenum deposits, in that both textures can sometimes be seen to coalesce. Miarolitic cavities are microscopic to metre size irregular voids which often underlie a UST zone. They can be infilled with pegmatitic and metallic assemblages which are considered to have been entrapped at magmatic temperatures and pressures during late-stage crystallization of the intrusion. Miarolitic cavity zones are relatively common in tin, tungsten, molybdenum and gold intrusion-hosted deposits. They are also known to occur in association with copper and gold-bearing systems. Orbicles are ovoid to spherical, microscopic to centimeter-sized concentrically zoned mineral assemblages which tend to occur as aggregates in some granitic to noritic intrusions, whilst they are not normally considered to be associated with mineralization, some examples have been noted to contain copper sulphides. It is concluded that the above textures, and in particular UST's, provide important evidence for initial metal sulphide deposition at magmatic temperatures and pressures in a large variety of intrusion-hosted mineral deposits. The mineralizing fluids subsequently evolve into a hydrothermal system as temperatures and pressures decrease.

O15-02

Transitions from porphyry environments: Ore versus barren epithermal systems determined by magma history?

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Recently the timing and genetic relationship has been demonstrated between the porphyry and epithermal environments. There is evidence for a relationship between the early potassic alteration stage of porphyry Cu deposits and the formation of more shallow advanced argillic alteration, commonly mushroomed into a lithocap. Many if not most lithocaps over intrusions are barren, <100 ppb Au with pyrite; a minority, however, host high-sulfidation state sulfides and Au mineralization. Why are only a few lithocaps mineralized? Is it related to fundamental controls of the intrusion, to whether or not there is underlying porphyry mineralization, or perhaps simply to geological setting and its effect on hydrology?

The potassic alteration of the Far Southeast porphyry deposit formed at 1.4 Ma, synchronous with leaching and alunite in the overlying lithocap, from a hypersaline liquid and vapor, respectively. Subsequent sericitic alteration of the porphyry, associated with chalcopyrite along structures, formed at 1.3 to 1.35 Ma; the temperature was lower, 350 vs 550 °C, and the fluid had a salinity of about 5 wt percent NaCl equiv. Within the previously formed lithocap, enargite deposited from a fluid with a salinity of 4 to 2 wt percent and corresponding temperature of 290 to 190 °C with increasing distance from the porphyry. A mixing diagram indicates that underlying sericite-chalcopyrite-stable fluid, upon cooling and dilution, is consistent with the composition of enargite-stable fluid. Thus, do porphyries with a sericitic overprint have greater potential to form a mineralized lithocap? Lithocap-hosted mineralization, where studied, forms from fluid with a salinity <10 wt percent. This is not surprising, given the high density of the early hypersaline liquid, whereas sericite-stage fluids typically have salinities <10 wt percent. Therefore, a well-developed sericite stage and associated fluid may be necessary for epithermal mineralization, within lithocaps as well as marginal veins.

In one endmember style of porphyry deposits, most of the high-grade copper ore consists of magnetite + bornite + digenite with high-temperature biotite ± K feldspar. At the other end of the spectrum, there are porphyries where most ore consists of chalcopyrite + pyrite with both the biotite + K feldspar as well as lower temperature sericite ± chlorite stages. This spectrum, as well as the generation of low-salinity epithermal fluids, may be due not only to the subsolidus pathway of the cooling system, but also to the intrinsic nature of the intrusion, both composition as well as crystallization history.

O15-03

Evolution of sulfur and copper in the magmas associated with porphyry-Cu mineralization at Santa Rita, New Mexico (U.S.A.)

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The magmatic processes leading to porphyry-Cu mineralization at Santa Rita were reconstructed on the basis of petrographic studies, thermobarometry, and LA-ICP-MS analyses of silicate melt and sulfide inclusions from samples ranging from basaltic andesite to rhyodacite. Combined results suggest that the magmatic evolution was similar to that of sulfur-rich volcanoes situated above subduction zones, being characterized by repeated injection of hot, mafic magma into an anhydrite-bearing magma chamber of rhyodacitic composition. The most mafic endmember identified at Santa Rita is a shoshonitic basaltic andesite that crystallized at 1000-1050 °C / 1-3 kbar and log fO₂ = NNO + (0.7-1.0). The presence of Cu-rich sulfide inclusions suggests that this magma was saturated in an immiscible sulfide melt and, therefore, the magma contained at least 0.1-0.2 wt% S. Copper contents of contemporary silicate melt inclusions range from 300 to 500 ppm. The most felsic endmember is represented by a rhyodacitic magma that crystallized at 730-760 °C and log fO₂ = NNO + (1.3-1.9) and contained 1-3 vol% anhydrite phenocrysts, implying a high magma sulfur content of 0.25-0.75 wt% S. Mixing between basaltic andesite and rhyodacitic magma caused precipitation of 0.1-0.2 wt% magmatic sulfides and an associated decrease in the Cu content of the silicate melt from 300-500 ppm to less than 20 ppm.

Sulfur solubilities, modal mineral abundances and measured mineral-melt and sulfide-melt partition coefficients were used to develop a quantitative model of the behavior of Cu during closed-system fractional crystallization. The results demonstrate that after 30% crystallization at sulfide-saturated conditions, 64 wt% of the total Cu is hosted by sulfides, 35 wt% Cu in the residual melt, and 1 wt% in the non-sulfide minerals. After the same amount of crystallization in a sulfide-undersaturated magma, 98 wt% of the total Cu is hosted by the residual melt, and 2 wt% in the (non-sulfide) minerals. Assuming that all sulfides are resorbed during fluid exsolution in the magma, the above modeling implies that magmatic sulfides do not significantly affect the amount of Cu ultimately available to the hydrothermal fluids. Magmatic sulfides therefore do not seem to be vital to the formation of porphyry-Cu deposits, unless a mechanism is required that holds back ore-forming metals fixed in sulfides until late in the evolution of the volcanic-plutonic system.

O15-04

Porphyry Cu-Mo and Base Metal Lodes at Butte, Montana: A World Class Ore Deposit Produced by Millions of Years of Magmatic-Hydrothermal Activity

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Butte, Montana, is one of the world's largest Cu-Mo-Ag resources (>37 million tonnes (MT) Cu and 1.2 MT Mo) with production dominated by >10 MT Cu and 22 T Ag from Main Stage lodes.

The porphyry Cu-Mo ores form two domical centers, the Anaconda and Pittsmt, ~1,500 m in diameter, that are genetically related to east-west striking, ~80-85°S-dipping "quartz" porphyry dikes. Both domes display near-identical sequence of 1-20-mm-wide veinlets. In order of decreased age, are 1) chalcopyrite - pyrite ± magnetite biotite-veinlets associated with biotite alteration of hornblende; 2) pyrite-chalcopyrite ± magnetite veinlets with pale green sericitic selvages; 3) quartz-molybdenite veinlets; 4) pyrite ± quartz veinlets with gray sericitic selvages; 5) Main Stage veins up to 10 m wide with "white" sericitic selvages. The gray sericitic zone affects >1 km² of rock from 1,600 m to sea level, where it contains sparse topaz and chalcocite similar to the Main Stage.

Porphyry Cu-Mo formed over a 2 m.y. period with the Pittsmt dome (~66-65 Ma) older than the Anaconda dome (~64 Ma). Over the next 1-2 m.y. the deep gray sericitic zone formed a feeder to the overlying the Main Stage Cu-As-Zn-Pb-Ag-Mn lodes, both with Ar-Ar ages of ~62-63 Ma.

Porphyry Cu-Mo ores formed at great depth (~8 km) from dilute (3-5 wt.% salts) magmatic aqueous fluids that contained 1000s of ppm Cu and Na and moved upward and outward to produce the domical ore-shell geometry. The highest Mo grades underlie the highest Cu grades, but quartz-molybdenite veinlets systematically post-date Cu-sulfide-bearing veins, which may indicate that isotherms moved upward to produce Cu deposition at ~500-550 °C followed by Mo deposition at ~650 °C.

The Main Stage lodes follow faults that root into the deep gray sericitic alteration. Some Cu in the Main Stage may have been supplied by hypogene leaching in this gray sericitic zone, but other elements such as As were supplied by new magmatic fluids. The Main Stage lodes are zoned from inner Cu (Ag) to intermediate Cu(Zn, Ag) and Zn-Mn-Ag(Cu, Pb, Au) to outer Mn-Ag(Pb) to outermost barren quartz corresponding to wall-rock alteration changing from advanced argillic to sericitic to weak sericitic-chlorite. Non-boiling Main Stage fluids with 3-5 wt.% dissolved salts at 300-350 °C suggest hydrostatic conditions at >2.5 km depth. Salinities and stable isotopes (O,H,S) suggest Main Stage ore fluids were magmatic, and that meteoric water incursion began at <300 °C.

Porphyry Cu Mineralization in Namosi District (Waivaka and Waisoi), Viti Levu, Republic of the Fiji Islands

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Copper mineralizations at Waivaka Corridor and Waisoi in the Namosi district, Viti Levu, are representative porphyry-type deposits in Fiji.

At Waivaka Corridor, Cu mineralization in Waivavaga is characterized by the ore mineral assemblage of bornite-chalcocopyrite associated with quartz-magnetite veinlet stockwork in diorite porphyry. Silicification is significant in the central part of mineralization associated with quartz-magnetite stockwork. Polyphase fluid inclusions in quartz-magnetite veinlets in high Cu grade zone show homogenization temperatures ranging from 390° to >500°C.

The Cu deposit at Waisoi is separated into two deposits; namely Waisoi East and Waisoi West. In the Waisoi East deposit, quartz porphyry is exposed whereas in the Waisoi West deposit, diorite porphyry is sporadically exposed in addition to a small body of quartz porphyry. The mineralization in the Waisoi East deposit is characterized by the bornite-chalcocopyrite-pyrite assemblage associated with trace of molybdenite and native gold. Polyphase fluid inclusions in quartz veinlets show homogenization temperatures ranging from 250° to 400°C. The high grade Cu mineralization in the Waisoi West deposit is characterized by the bornite-chalcocopyrite-pyrite assemblage accompanied with strong silicification and/or sheeted and stockwork quartz veinlets. Polyphase fluid inclusions sometimes containing hematite flake in quartz veinlets in the center of the Waisoi West deposit homogenize at temperatures ranging from 450° to >500°C. However, fluid inclusions in stockwork quartz veinlets in the periphery, homogenize at lower temperatures around 300°C. Both in the Waisoi East and Waisoi West deposits, primary bornite-chalcocopyrite-pyrite assemblage in the high Cu grade zone was deposited at the upper stability limit of chalcocopyrite with respect to sulfur fugacity. Thus, the principal Cu mineralization at the Waisoi deposits occurred at a high sulfur fugacity, i.e., high sulfidation environment.

Based on the elevated SO₂ contents of microphenocrystic apatite in diorite porphyry up to 0.57±0.13 wt% and the elevated whole rock Sr/Y ratios up to 58.4, diorite porphyry in the Namosi district show common characteristics exhibited by intermediate to silicic hydrous oxidizing intrusions that are associated with porphyry Cu deposits elsewhere in the world.

The occurrences of ore minerals and fluid inclusions in the Kingking porphyry copper deposit, Eastern Mindanao, Philippines

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The Kingking deposit is a gold-rich porphyry copper deposit located at Pantukan, Compostela Valley, Mindanao Island, Philippines, along the Eastern Mindanao Mineralized Belt. It has total mineable ore reserves of 353 million tonnes at 0.385% Cu and 0.439 g/t Au. The study area is underlain by sedimentary and volcanic rocks, presumably Cretaceous-Paleocene in age. These rocks are intruded by mineralized Miocene biotite-bearing diorite, hornblende diorite and diorite porphyries and by barren Miocene-Pliocene dacite and diorite porphyries. Two main alteration zones are identified in the study area, the inner potassic zone and the outer propylitic zone. These zones are further subdivided into different sub-zones named after the dominant mineral in the assemblage. Porphyry and epithermal type mineralization are reported and observed at Kingking and its surroundings. The biotite-bearing diorite and hornblende diorite porphyries are the primary host rocks of mineralization. Results of ore microscopic observations of drilled cores and other samples show two dominant primary copper minerals, bornite and chalcocopyrite with traces of talnakhite, in addition to minor secondary covellite and chalcocite. They usually occur as fracture fillings, associated with fine crystalline quartz veinlets or stockworks in the mineralized diorites. Bornite solid solution and intermediate solid solution must be primary Cu-Fe sulfide phases initially deposited from ore fluids. One notable characteristic of mineralization in Kingking is the occurrence of bornite clots (~5 cm in its longest axis) that are different from disseminations and are associated with volcanic rock xenoliths in biotite-bearing diorite porphyry. These clots of bornite are not associated with quartz veinlet stockworks. Fluid inclusion analyses were conducted on porphyry-type quartz veinlet stockworks and overprinting epithermal quartz veins from Kingking and surrounding areas. Results show two kinds of inclusions, polyphase hypersaline and two-phase fluid-rich inclusions from porphyry-type quartz veinlet stockworks. On the other hand, only two-phase fluid-rich inclusions are found in the epithermal quartz veins. The vapor-liquid homogenization temperatures (T_{HL}) of the polyphase hypersaline inclusions range from 200 °C up to >500 °C. The dissolution temperature of NaCl (T_{HNaCl}) ranges from 350°C up to >500 °C. In some cases, T_{HL} < T_{HNaCl}, indicating that some of the brine were saturated with NaCl at the time of entrapment. For the two-phase liquid-rich inclusions, the T_{HL} ranges from 244 °C up to >500 °C. Calculated salinity of the polyphase hypersaline inclusions ranges from 40% to 60% and 2% to 11% for the two-phase fluid-rich inclusions.

Tectonic setting of the Dexing porphyry Cu-Mo deposit in south China: Transitional setting from magmatic arc to contraction zone

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Dexing deposit, the largest porphyry Cu deposit in China, is located in the ENE-trending Jurassic magmatic belt along the southeastern margin of the Yangtze craton. The magmatic belt is separated from the central part of the Yangtze Craton with Dayin fault in the north, and from the Cathaysia zone with Jiangshan-Shaoxig fault in the south. The ENE-trending magmatic belt, as well as the Dayin and Jiangshan-Shaoxig faults, changes its strikes into east in the western Jiangxi province and into north-northeast in the western Hunan province, forming a 400 km-wide concave structure to the northwest. A block of Precambrian metamorphic rocks is exposed in the area of the concave structure in the Cathaysia zone. Contraction structures such as thrust faults and folds are developed in the Precambrian metamorphic rocks and overlying Lower Paleozoic rocks. The Dexing deposit is located at the eastern end of the concave structure, where Early to Middle Jurassic magmatic belt terminates. In the Dexing area, 180Ma porphyries and granites intrude in an ENE direction, whereas 170 Ma mineralized porphyries intrude in a NNW direction. This suggests that the stress field changed from arc-normal tension to arc-normal compression just before the mineralization. We interpret that the concave structure formed by the northward collision of the Precambrian block against the magmatic belt in the Yangtze craton during the Early to Middle Jurassic. A thick crust suggested by the presence of adakitic porphyry at Dexing may have formed by this collision. The Dexing porphyry Cu-Mo mineralization occurred during the period when arc-normal compressional stress was increasing at the transitional zone from the arc magmatism to collision.

Hydrothermal alteration and mineralization of the Dexing porphyry copper deposit, South China

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Dexing deposit, the largest porphyry copper deposit in China, is located in the NE-trending magmatic belt along the southeastern margin of the Yangtze Craton. The deposit contains 1000 Mt of ores with 0.7 % of Cu and 0.01 % of Mo. The deposit is hosted by a complex of Middle Jurassic granodiorite porphyries, which are divided into pre-mineral, intra-mineral and post-mineral ones. These porphyries intruded in pelitic schist of Proterozoic age. The deposit is centered on potassic alteration, and phyllic alteration is developed at the margin of the porphyry stocks. Phyllic alteration also overprints on the potassic alteration, reflected by hydrothermal biotite replaced by chlorite and sericite. Propylitic alteration, characterized by epidote, chlorite and calcite dominate in the marginal sedimentary rocks. Geochemical data indicate that the central and marginal parts of the deposit are enriched in Cu-Mo and Pb-Zn-Mn, respectively. Sulfide minerals of the deposit occur in quartz veins or are disseminated in the host granodiorite and metamorphosed sedimentary rocks. Several quartz vein stages that are characterized by different hydrothermal minerals are present. Early stage veins contain chalcocopyrite and bornite, and are associated with K-feldspar, magnetite, and biotite, whereas a majority of biotite is replaced by sericite and chlorite. Intermediate stage veins contain molybdenite and chalcocopyrite. Late stage veins contain pyrite and chalcocopyrite with or without sericite haloes. Feldspar-destructive alteration by muscovite and celadonite is dominant in the late stage. Early stage veins are frequently overprinted by late stage veins. Manganocalcite, calcite and barite veins are also present in the latest stage. Pyrite-replacing specularite is common. The $\delta^{34}\text{S}$ value of pyrite in quartz or pyrite veins range from -0.1‰ to 3 ‰, whereas $\delta^{34}\text{S}$ value of chalcocopyrite in calcite veins range from 4‰ to 5‰. The $\delta^{34}\text{S}$ range of pyrite, which is similar to the results by previous studies, suggests a magmatic origin for sulfur.

Geochemical variation caused by hydrothermal alteration at Oyu Tolgoi Cu-Au porphyry deposit

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The Late Devonian Oyu Tolgoi porphyry Cu-Au deposit is located in Paleozoic Gurbansayhan island arc terrane, in the South Gobi region of Mongolia. The Oyu Tolgoi deposit consists of a north northeast-trending 6 km long mineralized zone, with five porphyry Cu ± Au ore bodies: South Oyu, Southwest Oyu, and Central Oyu Tolgoi, Hugo Dummett South and Hugo Dummett North. These ore bodies are associated with quartz monzodiorite intrusions, which intruded into the basaltic to dacitic volcanic rocks and sedimentary rocks of the Late Devonian Alagbayan Formation. The Hugo Dummett ore bodies are intruded by post-mineralization biotite granodiorite dikes.

Petrographic and geochemical studies for drill core OTD 514, which cut a bonanza part of Hugo Dummett North ore body, was conducted. The drill core lithology changes from augite basalt to quartz monzodiorite intrusion at the 1245m interval. The ore body is located at the drill depth range from 1100m to 1500m and the upper and lower parts of the ore body are within augite basalt and quartz monzodiorite, respectively. The quartz monzodiorite intrusion can be divided into 3 parts, according to its alteration characteristics: 1. silica-rich quartz monzodiorite; 2. quartz monzodiorite with moderate quartz veining and 3. quartz monzodiorite with minor quartz veins. Silica rich part is located at the top of quartz monzodiorite, in depth from 1245 to 1370m and cut by much amount of ore mineral bearing quartz veins. Then gold rich part continues downward between 1370m to 1580m interval, containing up to 25% quartz veining. This part is reddish in color, which is caused due to K feldspar alteration. Quartz monzodiorite with minor quartz veins is located at the lowest part and it is relatively unaltered partly muscovite-altered and locally with quartz veining.

Result of analytic work indicates that copper content shows different tendency in each parts of quartz monzodiorite. Silica rich part is highest in copper, ranging from 0.025% to 5.9% and in the gold rich part copper moderately decreases (0.055-4.415), while gold shows highest grade (0.06-3.27ppm). Quartz monzodiorite with minor quartz veins is characterized lower content of gold (0.01-0.16ppm) and copper (0.015-1.5%).

Geochemical variation is detected on Sr, Nb, Rb, Y and Cr in relation with Cu content: Sr, Nb and Y tend to decrease but Rb and Cr increase with increasing Cu. Rb tend to be higher in the gold rich Qmd but Sr is lower.

Hydrothermal activity for auriferous vein and associated porphyry stock, in the sea shore side Ugusu-Arari, west Izu Peninsula

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Auriferous Qz-adularia veins are located in the sea shore side Arari, consist of mainly fine grained quartz-adularia and sulfide minerals, belong to epithermal deposits. Granite-porphyry is shown as a stock in the sea of Ugusu harbor (~ 20m depth), intruded into andesitic hyaloclastite breccia formations (the Yugashima formations), with propylitic alteration and associate chalcocopyrite-galenite-zincblende. There are distributed in the Miocene Green-Tuff region, Izu Peninsula. In the vicinity several Au mines were exploited, as the Seigoshi and Toi that were located near in the Toi harbor, also exploited the Ugusu Silica-Alunite deposits in mountaintop (600m high).

In Au deposit (Seigoshi mine), K-Ar ages range from 1.36 ± 0.33 to 1.83 ± 0.32 Ma (MITI,1987). Alunite deposit (Ugusu mine), range from 1.57 ± 0.28 to 1.42 ± 0.02 Ma (Hamazaki,2000). There are same hydrothermal activity. In Quaternary volcanic activity, there are distributed the Tanaba volcano, range from 1.52 Ma ~ 1.19 Ma (MITI,1987).

In the Ugusu Silica-Alunite deposits, there are shown high sulfidation (HS) deposits and formed zoning alteration (silicification-alunization- kaolinization), described by S. Iwao (1962). Although, the Seigoshi and Toi shown low sulfidation deposits (LS), belong to epithermal Au deposits, associated with bimodal volcanic suites. Auriferous Qz-adularia vein is shown about 50m length, NS direction along the shore.

Tectonic settings, the Ugusu-Arari area is distributed in plate-boundary, from western Izu Peninsula to Suruga bay. Also there are located in Southern Fossa Magna region and shown occurring compressive stress. This area contains porphyry Cu-Au and epithermal auriferous vein.

Characteristics of the Ciurug and Cikoret Veins: Genetic Reconstruction of the Pongkor Epithermal Deposit, West Java, Indonesia

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Abstract

The Pongkor deposit is located at the northeastern flank of the Bayah dome, West Java, Indonesia. Java form a part of the western Sunda-Banda arc and ore deposits associated with volcanism in West Java include some others epithermal gold deposits. Primary mineralization at the Pongkor mine is structurally controlled and occurs within veins system. The surrounding area of the Ciurug vein including the Cikoret area was recently explored to reveal the possibility of its extension. Tuff and lapilli tuff are the dominant rocks in the studied area, while andesite lava and siltstone are present locally. In this study, genetic model of the Pongkor Deposit is reconstructed based on the hydrothermal alteration mineral assemblages, reconstruction of paleo-surface and paleo-water table, evidence of boiling and mixing of ore fluids and vertical distribution of metallic mineral assemblage. Hydrothermal alteration is zoned and comprises deep regional propylitic alteration, whereas argillite, sericite, potassium feldspar and silicification form proximal alteration zones enveloping vein zone. The cristobalite, trydimite and smectite alteration zone occurs locally on the surface. The Ciurug vein shows four main mineralization stages where each discrete stage is characterized by a specific facies. These are, from early to late: carbonate-quartz, manganese carbonate-quartz, banded-massive quartz and gray sulfide-quartz facies. The Cikoret vein shows carbonate-quartz and banded-massive quartz facies. The major metallic minerals are pyrite, sphalerite, chalcocopyrite and galena; they occur in almost each mineralization stage and their abundance increases with depth. Bornite was observed locally in the deeper part of the Ciurug vein and shallow part of the Cikoret vein. Electrum and silver sulfides (mostly acanthite) are minor, whereas silver sulfosalts, stromeyerite, mckinstryite and covellite are in trace amounts. Most of the electrum occurs coexisting with other sulfide minerals, as inclusions in pyrite grains, with very little as inclusions in chalcocopyrite or sphalerite. Fluid inclusion microthermometry of calcite and quartz indicates deposition throughout the mineralized veins in the range from 170 to 230 °C and from low salinity fluids (predominantly 0-4 wt% NaCl equiv.). The homogenization temperatures of the Ciurug vein relatively increase with depth and the salinity of fluid inclusions also increase with depth. The homogenization temperature of the Ciurug vein at the shallow depth corresponds to a depth below the paleowater table of about 105 m. The texture of quartz-carbonate vein, fluid inclusion petrography and interpretation of Th-Tm data show evidence for boiling and mixing of ore fluid.

Gold and Silver Mineralization and Magnetic Susceptibility of Host Rock at the Asachinskoe Deposit in South Kamchatka, Russia

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Over twenty epithermal Au-Ag and base metal deposits are located in the Porozhistsko-Asachinskaya metallogenic province (100km×100km) of South Kamchatka. These epithermal deposits formed from Middle Miocene to Quaternary with ESE migration toward subduction zone based on formation ages.

Asachinskoe deposit consists of Au-Ag bearing quartz - adularia vein of low sulfidation, and its mining operation has been started in 2005 based on estimated reserves of about 20t Au and 42t Ag. The deposit consists of about 40 quartz - adularia veins with strikes N-S, steep dips 70-85 degrees, width 0.8-7.5 m, and vertical extension about 300m. Horizontal extension of a main vein is about 2km, and surface soil covers the deposit up to 10-120 m in thickness. Host rocks of the mineralized veins are tuffaceous rocks, rhyolite, rhyodacite, dacite and andesite with propylitic (epidote-albite-chlorite) and argillite (K-feldspar-sericite) hydrothermal alterations.

The quartz - adularia vein shows the well banded structure of quartz - adularia - sulfides. Representative ore minerals in the sulfide bands are electrum, Se-bearing polybasite group mineral, naumannite, argentite - aguilarite group mineral, As-pyrite, chalcocopyrite and Se-galenite. Modal composition of electrum is $Ag/(Au+Ag) = 40-65$ atomic% (average: 52 atomic%), while Au-rich electrum of 65-90 atomic% is also observed in minor mode. The quartz - adularia vein shows relatively high contents of adularia up to 40% in hand specimen, and a characteristic growth texture of the adularia is observed that interfingers with quartz. K-Ar dating of the adularia from the main vein with about 3m in width indicates a continuous mineralization ages to the center of vein as follows;

(1) 20cm from wall rock: 4.7 ± 0.2 Ma

(2) 40cm from wall rock: 4.4 ± 0.1 Ma and 4.5 ± 0.1 Ma (highest part of Au-Ag content)

(3) 120cm from wall rock: 3.1 ± 0.1 Ma

Host rocks of the Asachinskoe deposit and other deposits in the metallogenic province show variable magnetic susceptibilities, which is related to the decomposition of magnetite caused by water-rock reaction. Magnetic susceptibilities of each host rock vary 1.0×10^{-1} to 1.0×10^{-4} (S.I.) for andesite and diorite, 3.0×10^{-3} to 1.0×10^{-5} (S.I.) for rhyolite, rhyodacite and dacite, 1.0×10^{-2} to 1.0×10^{-5} (S.I.) for tuffaceous rocks, and 1.0×10^{-2} to 1.0×10^{-4} (S.I.) for sand stone and mud stone. The data indicates the decrease in magnetic susceptibility to 10-0.1% compared to the non-altered rocks by the hydrothermal alteration.

Genesis and thermal history of gold mineralization in the Remedios-Segovia mining district of northern Colombia

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Abstract

Remedios-Segovia mining district is located in northern part of the Colombian Andes. This area has historically been the most important gold producer in Colombia, however there are not works regarding to the genesis of these deposits and their relationships with host rocks. The deposit consists of a series of gold veins associated with andesitic to dacitic dikes emplaced in granodioritic rocks of the Segovia Batholith, and controlled structurally by Otú Fault.

Quartz sulfide veins are mainly composed by pyrite, sphalerite and galena with small amounts of chalcopyrite, pyrrhotite, electrum, tetrahedrite and argentite surrounded by a gangue of quartz and calcite. Tetrahedrite and argentite are identified in this deposit for first time. The alteration mineral assemblages within the wall rocks allow defining five types of alteration: phyllic, propylitic, sulphidation, calcification and silicification, however is common to find two of these alteration types combined.

EPMA analyses indicate that the relation of Au and Ag in electrum is 1:1, nevertheless Au was also found in small amounts within the rest of sulfides minerals. Moreover, Three types of sphalerite were identified; the most abundant is type 1, containing a lot of inclusions of chalcopyrite and showing FeS Mol % content around 12, the type 2 of sphalerite has similar content of FeS Mol % but occurs as inclusions within pyrite, in contrast, the type 3 has almost double of FeS Mol %, about 22, and occurs as small inclusions associated with pyrrhotite and enclosed by pyrite. These three types of sphalerite also contain small amounts of Mn (up 0.34 wt %), Bi (up 0.35 wt %) and Cd (1 – 2.2 wt %). Furthermore, an attempt was made to estimate the emplacement pressure of the sulfide-quartz veins using chemical composition of sphalerite coexisting in equilibrium with hexagonal-pyrrhotite and pyrite.

Additionally to the mineral chemical composition, preliminary fluid inclusion studies point out that homogenization temperatures (Th) in quartz decrease from 312°C peak in the south of the study area to 250°C peak in the north. In the same way, it was recognized a late hydrothermal event related to calcite with homogenization temperature around 200°C peak. On the other hand, measurements of melting temperature of ice in fluid inclusions show salinity of 1.9 % NaCl equiv. in the southern part and 8.4 % NaCl equiv. in the northern part of the study area. These preliminary results are suggesting probably two different hydrothermal sources for the veins in the study area.

Although the veins are intruded into granodioritic rocks of the Jurassic Segovia Batholith, there are also plutonic rocks of the Cretaceous Antioquian Batholith nearby; thus the veins have two possible hydrothermal sources, for that reason, fission track dating of apatite in granodiorites next to the veins, is currently being carried out with the purpose of finding the possible temporally related source for this hydrothermal system. Fission Track dating of zircon in the host rocks of Segovia Batholith will be also measure in order to establish the cooling history of this plutonic body.

The smallest base- and precious-metal deposits in the world and why we should care: Vesicle-hosted Cu-Sn-Co-Ag alloys

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Recent investigations of the mobility and behavior of Cu in young (<50 ybp) Kilauean (Hawaii) lava samples revealed the presence of unusual Cu-Co-Sn alloys present in vesicles. We inferred that the metals for these alloys were transported (in part) as chloride complexes, and that the metal ratios in the alloys may be a function of S/Cl. Despite their small size (approx. 100 microns), their ubiquitous presence and variable composition encouraged us to look for alloys in other mafic lava flows. Consequently, we chose to investigate vesicle-lining minerals in other Hawaiian volcanoes (Mauna Kea and Mauna Loa) as well as the mafic alkaline volcanoes of Etna, Vesuvius, and Stromboli.

All of the young Hawaiian (OIB) lavas we investigated have comparable alloys present in vesicles. Compositions are extremely heterogeneous with Co concentrations from 2% to 36%, Cu from 35% to 83%, and Sn from 9% to 35%. Element maps of individual grains show a covariance of Cu and Sn while Co concentrations vary independently. Grain morphologies exhibit a cockscomb structure toward the inside of the vesicle in some cases. Element maps of the alloys reveal that chlorides are occasionally present in the same vesicles as the alloys. Sulphur content of the metal alloys rarely exceeds about 0.4 wt%. Other elements found in low concentrations in the Kilauean alloys include Fe (0.05 to 0.65%) as well as detectable amounts of Ni, Pb, Zn, As, and Ag. Alloys found in Vesuvian, Strombolian and Etna lava vesicles are very similar in size, morphology and composition except that Co and Ag are far more abundant reaching maximum concentrations of 85% and 43% respectively. Our current model for the origin of the alloys suggests that the metals are transported to vesicles as chlorides and then deposited as sulphides and/or native metals followed by oxidation and removal of most of the S.

These data suggest that in some circumstances Cu and Ag are readily partitioned into escaping magmatic volatiles during quenching of mafic magma. If broadly similar processes occur at the base of porphyry Cu magmatic systems during episodes of magma mixing then significant amounts of Cu, S, Cl, and H₂O may be transferred to the intermediate magma or ore-related fluids. Additionally, the seemingly widespread occurrences of these alloys exclusively in very young lavas allows the possibility that they may often readily dissolve and serve as source material for a wide variety of other Cu-Co-Ag-rich low-T deposits.

Petrogenesis of Eocene-Oligocene magmatism of the Sulphur Spring Range, central Nevada: The role of magma mixing

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Widespread base- and precious-metal anomalies, altered porphyry intrusions and oxidized veins occur in a portion of the Sulphur Springs Range, Nevada (adjacent to the Carlin Trend). Some of the Eocene-Oligocene age intrusions and cogenetic volcanic rocks in the range exhibit evidence of magma mixing and invite comparisons with other mineralized, Eocene mixed magma systems such as the Bingham porphyry Cu deposit 300 km further inboard (east). Tectonic discrimination diagrams show that both of these volcanic/intrusive centers are overwhelmingly continental arc-related magmas. The Sulphur Springs (SS) igneous suite ranges through rhyolite, dacite, andesite and basalt (or trachybasalt) on the IUGS chemical classification diagram but is less alkaline than the Bingham suite. However, Sulphur Springs suite alkali contents are similar to other Eocene igneous rocks along the Carlin Trend. The Bingham suite ranges compositionally from rhyolite to trachyte, latite, shoshonite, and basanite. The unusual geochemical signature of the Bingham igneous suite, enrichment in Cr, Ni, and Ba, is generally not found in the unaltered Sulphur Springs suite, but a weakly altered intrusive suite may be both alkaline and Ba-rich. Hydrothermal barite is abundant and widespread in the range. High Cr concentrations are present in many altered intermediate and silicic dikes from the Sulphur Springs range and probably represent a magmatic suite distinct from the unaltered volcanic rocks. Both the Bingham and Sulphur Springs volcanic suites show extensive mixing of mafic magma with intermediate compositions. The Bingham suite demonstrates mixing mineralogically by the presence of altered olivine and pyroxene in intermediate composition rocks. One of the disequilibrium Sulphur Springs rocks vividly expresses magma mixing as "andesite" containing plagioclase, biotite, clinopyroxene, orthopyroxene, and olivine, concurrent with heavily resorbed megacrysts of quartz and K-feldspar. The Sulphur Springs mixed magma also contains abundant late-stage accessory magnetite and resorbed and oxidized garnet. The most likely parental magmas for this rock are garnet-bearing biotite quartz porphyry and olivine-bearing andesite which are present in the range. We suspect that magma mixing may be operative in the genesis of other Sulphur Springs rocks as well, although in a less dramatic fashion.

Questions these data raise include: 1) Was there an unusual tectonic setting operative during the Eocene of the western United States that promoted both magma mixing and base- and precious-metal mineralization? 2) How vital might mixing processes be in delivering large amounts of S and chalcophile metals from mafic magmas to the shallow crust and eventual ore deposits?

Why is indium rich in the Japanese island-arc magmatic belts?

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There have been two primary sources for industrial indium; one from massive sulfides such as Kidd Creek, Broken Hill, Sullivan, Brunswick, Neves-Corvo etc, while the others are dissemination-veins and skarns, such as Mt. Pleasant, Toyoha, Ikuno, Akenobe, Kawayama, Nakatatsu, and Taishu. The latter group of the In-bearing deposits occur typically in the Japanese Islands, and indium is contained as In-minerals such as sakuraiite (CuZnFeAg₃(InSn)₄), roquesite CuInS₂, laforetite AgInS₂ and many unidentified minerals, and also occurs substituting zinc and copper sulfides. Average ore grades of the ores from which indium may be extracted vary from 10 ppm (e.g., Broken Hill) to 200 ppm (Toyoha).

The arc plutonism of the Japanese islands is seen most widely in the late Cretaceous – Paleogene Inner Zone of SW Japan, then in the Cretaceous NE Japan. The indium-rich ore deposits are limited to the ilmenite-series Sanyo Belt of SW Japan. The late Cenozoic plutonism is also composed of reduced ilmenite series in the Outer Zone of SW Japan and the Hidaka Belt, and oxic magnetite-series of the Inner Zones. The indium-rich deposits tend to occur in the ilmenite-series terranes, however, the largest Toyoha deposits occur in the magnetite-series Green Tuff Belt. Granitoids have never exposed there, but indium occurs in the reducing environment shown by abundant pyrrhotite and tin minerals in the southeastern mine claim.

Sedimentary source rocks are necessary to have indium-rich granitic magma which is reduced by contained sedimentary carbon, thus small possibility to expel sulfur compounds out of the magma chamber. On the contrary, magnetite-series magmatism can provide abundant sulfur to the ore systems. Therefore, we need the two magmatic activities differing in oxygen fugacity for the concentration of indium in ore deposits. The Japanese islands are, fortunately, composed of magnetite/ilmenite-series paired belts, and mixed zones occurs between two belts. The sedimentary source materials and changing oxygen fugacity at the site of ore deposition seem most critical for the formation of In-bearing ore deposits.

Genesis of metallogenic provinces from the viewpoint of global material recycling

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Deposits of chalcophile (Cu, Zn, Pb, and Mo) and lithophile elements (Sn and W) in Mesozoic - Cenozoic plutonic belts in the circum-Pacific region tend to be distributed in separate metallogenic provinces. These metallogenic provinces are characterized not only by their metallic elements but also by petrography of their host rocks: the chalcophile elements are generally accompanied by magnetite-series granites and lithophile elements by ilmenite-series granites.

As chalcophile elements are much more soluble in seawater than lithophile elements, the former do not usually occur as precipitates on the ocean floor, while the latter do especially when they enter the sea from land. The global-scale differentiation between the distribution of chalcophile and lithophile elements has been steadily taking place in the ocean throughout geologic history.

Chalcophile elements are steadily removed to the oceanic crust from seawater by alteration processes of mid-ocean ridge basalts (MORB). In the hydrothermal system of the mid-oceanic ridges, sulfate ions in the seawater are reduced to hydrogen sulfide by ferrous iron in MORB, and the hydrogen sulfide reacts with chalcophile elements, precipitating then as sulfides. Iron oxides (magnetite and hematite) are also precipitated. When the altered MORB is drawn into the upper mantle by plate subduction, because of heating, the sulfides are oxidized and decomposed by reacting with coexisting iron oxides. The chalcophile elements and sulfur dioxide separated from subducting oceanic plates become incorporated into magma generated in the subduction zones. When the magma is consolidated in the upper crust, the chalcophile elements (probably as chlorides in magma) are precipitated as sulfide deposits in magnetite-series granites.

Lithophile elements supplied from land areas are mainly incorporated into terrigenous marine sediments. A part of the sediments is drawn into the upper mantle by plate subduction, and the rest form accretionary complexes in the crust. In both cases, when the sediments melt, the lithophile elements are partitioned into magma. Sn and W deposits are formed in ilmenite-series granites because the magma is reduced by carbonaceous materials contained in the sediments.

Spatial and temporal variations of the metallogenic provinces are due mainly to the supply and properties of subducting materials beneath a given region.

P15-01

Origin of iron on Miocene Fe skarn mineralization of the Oohinata deposit in the active uplifting region of central Japan

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The Oohinata iron skarn deposit, which is located in the eastern part of the active uplifting region of central Japan, occurs in Jurassic strata (mudstone including limestone, chert and basic tuffs) around Miocene hornblende granodiorites. Granitoids around the Oohinata deposit are divided into four facies: hornblende granite porphyry, hornblende granodiorite, biotite-hornblende granodiorite and biotite granite. These granitoids are classified into magnetite-series except the ilmenite-series biotite granite. The latest biotite granite intruded into the biotite-hornblende granodiorite. The iron mineralization is thought to be due to the activity of hornblende granodiorite based on geological data. The variation of major elements of these granitic rocks shows the geochemical variations of calc-alkali granitic rocks. Negative Eu anomalies of the biotite granite is larger than those of other types of granitic rocks in the Oohinata area, although chondrite-normalized REE patterns are similar one another among the granitic rocks. These facts suggest that iron mineralization is caused by emplacement of moderately differentiated granitic bodies, not that of highly differentiated granitic bodies. Fluid inclusions in granitoids and iron ores of the Oohinata area are classified into three types: Type 1 (vapor + liquid phases), Type 2 (vapor + liquid phases +/- KCl + NaCl) and Type 3 (vapor + liquid phases + KCl + NaCl + various solid phases). The solid phases identified are mostly iron chloride with some CaCl₂, hematite, chalcocopyrite and anhydrite. Type 3 fluid inclusions containing iron chloride, hematite and CaCl₂ as daughter minerals are recognized in the quartz crystals of the hornblende granite porphyry, hornblende granodiorite and recrystallized chert from an outcrop showing iron mineralization near the Oohinata deposit in addition to Types 1 and 2 fluid inclusions. The homogenization temperatures and salinities of Type 3 fluid inclusions are above 450°C and above 50 wt % NaCl equivalent, respectively. The fact that Type 3 fluid inclusions often coexist with vapor-rich fluid inclusions indicates that phase separation took place during a late stage of emplacement of hornblende granodiorite in the shallower part of the crust. The presence of Type 3 fluid inclusions in the granodiorite and recrystallized chert associated with iron ores suggests that iron on iron mineralization of the Oohinata deposit was transported by high-temperature and high-saline fluid formed by phase separation of fluid coexisting with melt of the hornblende granodiorite.

P15-02

A study on the quartz veins and associated ore minerals at the deep part of the Batu Hijau porphyry copper deposit, Sumbawa, Indonesia

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At the Batu Hijau porphyry copper-gold deposit, four types of quartz veins called A, B, C and D veins have been recognized. Copper sulfides associated with quartz veins are bornite, chalcocopyrite, digenite and chalcocite. The A veins contain mainly bornite, often associated with digenite and chalcocite. In addition, magnetite occurs in A veins. However, at the deep part of the deposit, quartz veins are associated with magnetite, but with little copper sulfides such as bornite and chalcocopyrite (quartz veins in the studied drill hole SBD257). The cause of absence of copper sulfides in these veins is discussed and compared with quartz veins associated with magnetite and abundant copper sulfides (veins in drill hole SBD194). There are abundant polyphase fluid inclusions in quartz veins in addition to gas-rich inclusions. Homogenization temperature (Th) of vapor and dissolution temperature (Td) of NaCl daughter crystal of polyphase inclusions are measured in both types of quartz veins. The average Th in quartz veins contained in SBD257 ranges from about 300°C to 340°C, and about 320°C to 360°C in SBD194. However, Th in each quartz vein all varies widely. Therefore no difference is found in the Th of quartz veins between SBD257 and SBD194. In addition, there is little difference in salinity between SBD257 and SBD194. Fluids inclusions are trapped from aqueous immiscible region into brine and vapor. Therefore, it is possible that the vapor present was trapped along with the brine. The obtained average Th tends to be higher at shallower elevation. This reverse relationship of average apparent Th-depth is attributed to the entrapment of immiscible vapor phase in addition to brine. Therefore, at the shallow part the real temperature of fluid is considered to be lower than apparent Th obtained. A model taking note of the proportion of the ratio of vapor to brine is proposed to give an answer to the above-mentioned scenario. At shallow part, there may have been higher ratio of vapor compared to the deep part. This is due to lower pressure in the shallow part or the lower density of vapor compared to the brine. Copper is dissolved in brine, and becomes concentrated through the removal of vapor from brine. Therefore, copper sulfides are easily deposited at shallow part.

P15-03

The time and spatial distribution of mineralization at the southeastern part of Toyoha deposits in southwest of Hokkaido

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The Toyoha mine, located in southwest of Hokkaido, is classified into polymetallic epithermal vein-type deposit. It is well known that produce tin, tungsten, cobalt, bismuth, indium, arsenic, and antimony besides base-metals. The deposits are composed of more than fifty veins distributed in the area with 2km at N-S and 4km at E-W, where the mineralized area is almost extended to NW-SE direction with distinguishable 3 types of vein system such as NW-SE, N-S and E-W. They are estimated to be young formation of about 0.5-3.0Ma and the host rock temperature is around 170-200°C. Taking into consideration of these facts, it is assumed that the hydrothermal activity and the related mineralization are still going on even now. The Toyoha deposits are divided into seven mineralization stages based on the cross-cutting and brecciation relationships among the ores in underground and hand-specimen, where Stages I-II are classified into the Earlier stage and Stages III-VII are into the Later stage. Considering the past studies especially by fluid inclusions, the deposits might be formed by the invasion of hydrothermal water with SE to NW trend from the Shinano vein, where the mineralization might be occurred slowly by the mixing of ore fluids with underground geothermal water. In this study, the collected samples from the Izumo and the Iwami veins of west extension from the Shinano vein, recognized as the principal ascending zone of hydrothermal water, were investigated in detail. These veins are assumed to be most suitable ones to discuss about the genesis and the characteristics of the mineralizations related with hydrothermal activity accompanying the transportation of heavy metals. Ore microscopy, chemical analyses by EPMA and fluid inclusion studies have been done for the samples from those veins to clarify the mineralizations of this deposit in detail. Based on the laboratory works as mentioned above, both veins are composed of polymetallic massive sulfide minerals such as pyrite, sphalerite, galena, chalcocopyrite, arsenopyrite and stannite, with the mineralization characteristics classified into the later stage. Taking into consider the results of fluid inclusions study, the hydrothermal activity of high temperature fluids with about 250-270°C were also detected at the lower level of the Iwami vein. It indicates the existence of independent ascending zone of hydrothermal water in the vein different from the Shinano one. Moreover, the hydrothermal water with higher temperature of about 230-250°C are also found even in the upper level of the Iwami vein. It suggests that the much complicated behavior and movement path of the hydrothermal water could be existed in this area.

Mineralization process of Au-Ag deposit at the Koryu mine, southwest Hokkaido, JapanH. Matsueda¹, T. Shimizu², and A. Sato³¹The Hokkaido University Museum, Hokkaido University, N10 W8, Sapporo, 060-0810, Japan

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Koryu Au-Ag deposits are composed of eight major veins hosted in Miocene black mudstone with E-W trending steep shear veins of maximum two meters in width. They are estimated as the formation of 1.4 to 0.85Ma in ages based on the K-Ar dating for adularia in the vein. The veins distribute vertically extended more than 100m, and horizontally about 1,200m. Gold-bearing ore veins are characterized by the abundant occurrence of multi-crusted quartz and adularia with clay minerals that show the variable crystal growth texture in the vein. The mineralizations are divided into two episodes of the Earlier and the Later with three and seven stages according to the cross-cutting and brecciation relationships of the veins in underground, respectively. Major gold mineralizations are characterized by the stages of L-III with chlorite/smectite mixed layered clay minerals and lesser by those of L-IV and L-V. The representative gold-silver bearing minerals in the ore are electrum, acanthite-agularite, polybasite-pearceite, pyrrargyrite-proustite, mckinstryite, jalpaite, hessite, Ag-Te-Se-S mineral and tetrahedrite on the basis of ore microscopy and EPMA analysis.

Based on the fluid inclusion study, the formation temperature (°C) and the salinity (NaCl eq. wt%) in each episode are 250-270 and 2.0-2.7 (the Earlier), 200-260, 0.5-3.3 (the Later), respectively. It seems to occur the boiling phenomena for ascending fluids in the shallow level so that gold precipitation might be started around the level of about -20mL. In concordant with this estimation, well development of adularia and "Gin-guro" bands rich in Au-Ag minerals are observed upper than about -20mL in the vein. Furthermore, it may be assumed to happen the mixing of ore fluids with ground water upper than +60mL according to the fluid inclusions data. This mixing might have inspired the effective gold precipitation at the upper level. Estimated paleodepth of the vein formation is about 430-850m in this deposit.

Results of stable isotopic study for oxygen, hydrogen and carbon of vein and host rock suggest that the circulating meteoric water interacted with surrounding rocks could have strongly contributed for the Au-Ag mineralizations at the Koryu deposits.

Chlorine geochemistry of volcanic rocks in the Hokusatsu gold mining district in Kyushu, JapanM. Furusawa¹ and M. Nedachi¹¹Graduate School of Science and Engineering, Kagoshima University, Kagoshima, 890-0065, Japan

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The Hokusatsu district (50 kmNS x 70 kmEW) in Kyushu, Japan, is located in the west of the Kirishima volcanic belt, and is characterized by the intensive volcanism across the district, and by the numerous gold mineralization of relatively high Au/Ag ratio. The magmatic eruptions have occurred roughly from the west (~9 Ma) to the east (present volcanic front), and well coincide temporally with gold mineralization (Izawa et al., 1992). In this study, the geochemistry of volcanic rocks is described to understand the contribution of magmatism to gold mineralization.

The volcanic rocks of the district are of tholeiite or calc-alkaline rock without significant geochemical features over whole area. The rock-forming Fe oxide minerals are magnetite and ilmenite, implying the rocks of oxidized type. However, the some areas are recognized to be enriched in incompatible elements such as K, Cl, and Rb. Those areas are elongated to NNE-SSW direction, parallel to the present volcanic front line. Referred to the transitional change from the front to back arc system in Northeast Japan (Tatsumi, 1995), the similar but obscure transition might repeat in this district, although the width of the transition zoning is rather narrow (20 to 30 km). The transitional set has skipped from western end toward the present volcanic front. The cause might be the discontinuous move of subducted slab toward the ocean side.

Gold mineralization distributes in the areas enriched in Cl and other incompatible elements: Hishikari-Ohra-Ohnoyama-Yamagano area and Kushikino-Iriki-Fuke-Oguchi area. The typical example is observed in the Hishikari gold mining area. The volcanisms in this area are characterized by bimodal compositions (andesite and dacite). The phenocrysts of apatite, biotite (phlogopite) and hornblende of these volcanic rocks are rich in Cl and Cl/OH. Geobarometer indicates that the dacitic magma reservoir might be emplaced into about 2km depth, and was almost saturated in water. These suggest that gold was discharged from magma as chloro-complex. The lack of the evidence of Cl rich hydrothermal solution in the Hishikari ore deposits suggests that Au was converted from chloro-complex to bisulfide complex in reduced country rock (Accretion carbonaceous greywacke; Shimanto Supergroup), and that Au was precipitated when the bisulfide complex was decomposed in the volcanic rocks of oxidized type, or by mixing with oxidized meteoric water.

Gangue minerals associated with the precipitation of gold at the Hishikari low-sulfidation epithermal gold deposit, Japan

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The Hishikari low-sulfidation epithermal gold deposit located in southern Kyushu, Japan is well known as the large gold deposit with high grade ore. Gold-bearing quartz-adularia veins are hosted by the Cretaceous sedimentary basement rock and Pliocene-Pleistocene andesitic volcanic rocks which unconformably overlie the basement rock. The veins consisting of quartz, adularia and clay minerals (mostly smectite) with a small amount of calcite and truscottite. Ore minerals are electrum, pyrite, marcasite and chalcocopyrite with a small amount of sphalerite, galena, stibnite, tetrahedrite, bornite (without pyrite), miargyrite, arcanthite, Au-Ag selenide and telluride. The quartz veins are observed from +100 to -20 m relative to sea level in the mine at present. The gold grades of quartz veins are high in the vicinity of the unconformity, becoming lower with decrease in depth.

Macroscopic and microscopic observations were conducted to compare the gangue minerals and their textures associated with gold deposition between the upper levels and lower levels. Sulfide-rich (Ginguro) bands abundant in gold are commonly observed in veins with banding structure at upper levels, whereas relatively scarce at lower levels. Bladed calcite and quartz and columnar adularia that indicate boiling of hydrothermal fluids which is considered to be an essential event for the mineralization of gold are commonly observed at any level. Truscottite also suggests boiling of hydrothermal fluids and it is considered to be precursors of pseudo-acicular calcite and quartz. The truscottite has been observed mainly at upper levels, whereas pseudo-acicular calcite and quartz are observed at any level. These minerals and textures suggest that the boiling occurred commonly at different levels at the Hishikari deposit, however they do not necessarily accompany gold. The mineral assemblage of fine-grained quartz $\pm$ fine-grained adularia $\pm$ smectite observed in crustiform quartz veins shows the physico-chemical variation of hydrothermal fluids. The quartz vein with this mineral assemblage is commonly abundant in gold at any level.

Tertiary sedimentary rock-hosted, low-sulfidation epithermal deposits and prospects in the Eastern Rhodopes, Bulgaria: New geological, stable isotope and fluid inclusion constraintsI. Márton¹, R. Moritz¹, P. Marchev², N. Bonev³, S. Hasson⁴, T. Vennemann⁵¹University of Geneva, Section des Sciences de la Terre, 1205 Genève, rue des Maraichers 13, Switzerland

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The recently discovered Tertiary epithermal gold deposits with a low-sulfidation character at Ada-Tepe and surrounding prospects are dominantly hosted by syn-detachment sedimentary rocks of Maastrichtian-Paleocene age. A low angle normal fault between the metamorphic basement and the sedimentary rocks constitutes the major ore-controlling associated structure. The geometry of the ore bodies reveals the structural and lithological controls on the mineralization. They include: (a) strongly faulted rocks of the highly permeable sedimentary unit that offered a favorable channel-way for fluid circulation generating open space filling bonanza type mineralization in veins with a general E-W direction; (b) in contrast, the deformed metamorphic rocks with a ductile fabric and the cataclastic deformed detachment zone were the loci for focused fluid flow, toward lower pressure areas, where a massive, tabular ore body was formed immediately above the detachment fault. These zones consist of strongly altered rocks, replaced by silica, adularia, sericite, pyrite and carbonate minerals. On the basis of the alteration mineralogy and textural relationships gold may have been deposited as a consequence of different physical-chemical processes in the various prospects. Abundant bladed quartz pseudomorphs replacing platy calcite suggest boiling in different prospects, including Ada Tepe, Kuklitsa and Kupel. Boiling textures are absent in other prospects, such as Rosino, Sumak, Kremenitz and Skalak, where fluid-rock interaction may be responsible for gold deposition, affecting the pH and Eh conditions of the gold-transporting fluid. Areas enriched in organic carbon were identified at Ada Tepe, Sumak and Rosino, which correlate with high Au grades, likely revealing intense, local reduction of the hydrothermal fluids. Fluid inclusion microthermometry of the two phase fluid inclusions from early stage carbonates at Ada Tepe suggest deposition temperatures about 180-210 °C from very diluted fluids. According to preliminary stable isotope analyses the calculated $\delta^{18}\text{O}$ values (vs. V-SMOW) of water in equilibrium with analyzed quartz and adularia samples are about -3.6 to 0.1‰. The Ada Tepe and Sumak pyrite samples have comparable $\delta^{34}\text{S}$ values (vs. CDT) between -3.7‰ and 0.2‰. The stable isotopic compositions can be interpreted as typical for mineralizing fluids with a dominantly magmatic/metamorphic character, or a surficial fluid that has been equilibrated with magmatic and metamorphic rocks, especially if we consider the very dilute nature of the fluids on the basis of microthermometric fluid inclusion data.

Spectroscopic study of gold(I) and silver(I) thiosulfate adsorbed on Al_2O_3 K. Yonezu¹, T. Yokoyama², A. Imai¹, and K. Watanabe¹¹Department of Earth Resource Engineering, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan. yone@mine.kyushu-u.ac.jp²Department of Chemistry, Graduate School of Science, Kyushu University, 4-2-1 Ropponmatsu, Chuo-ku, Fukuoka, 810-8560, Japan.

In order to elucidate the concentration mechanism of Au and Ag and formation of electrum during the formation of epithermal gold deposit, adsorption experiment of Au(I) and Ag(I) thiosulfate complex anions on Al_2O_3 was carried out. The adsorption reaction is regarded as a model reaction for the concentration of gold in low sulfidation epithermal gold deposit. To clarify the chemical state of Au and Ag adsorbed on Al_2O_3 , XANES (X-ray Absorption Near Edge Structure), MAS (¹⁹⁷Au Mössbauer Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) were used. The XANES spectra for gold adsorbed on Al_2O_3 show that gold is present as Au(0), i. e., elemental gold, referred to the reference materials. The MAS spectrum for gold adsorbed on Al_2O_3 is divided into two components. One component is characterized by a singlet which is assigned to Au(0), and the other component is characterized by a quadrupole splitting doublet which correspond to Au(I) state in terms of isomer shift (IS) and quadrupole splitting (QS). The MAS spectrum for gold-silver system adsorbed on Al_2O_3 is similar to that for gold system adsorbed on Al_2O_3 . The MAS results suggest that Au(I) thiosulfate was partly reduced to Au(0) due to disproportionation of Au(I) to Au(0) and Au(III) in spite of coexistence of silver, and spontaneous reduction of the resulting Au(III) species occurred at the surface of Al_2O_3 . The XPS spectra of Au 4f region for both gold system and gold-silver system adsorbed on Al_2O_3 is assigned to binding energy of Au(0). The XPS spectrum of Ag 3d region for gold-silver system adsorbed Al_2O_3 is divided into two doublets having 6 eV of spin orbital splitting. One doublet completely corresponds to Ag(0), elemental silver. The other component is shifted to about 1 eV in the direction of lower binding energy, suggesting alloying with gold (electrum). These data suggest that both Au(I) and Ag(I) thiosulfate are reduced to elemental gold and silver state on the surface of Al_2O_3 . These facts emphasize the important role of the surface of Al_2O_3 in concentrating and reducing of gold and silver from ore-forming fluid in epithermal environment.

Rare earth mineralizations in clay sediments related to weathered granitic rocks in JapanH. Murakami¹, S. Ishihara², and Y. Watanabe¹¹Institute for Geo-resources and Environment, Geological Survey of Japan, AIST Central 7, Higashi 1-1-1, Tsukuba, 305-8567, Japan h-murakami@aist.go.jp²Special Councillor, AIST, AIST Central 7, Higashi 1-1-1, Tsukuba, 305-8567, Japan

Rare earth elements (REEs) are important and attractive mineral resources for modern high technology industry. Ion-absorption-type REE deposits, which are now known only in southern China, have recently become a major source of heavy REEs. Thus it is important to know concentration of REEs during weathering condition of various geological and climatic settings. Here we report several case studies of REE mineralization in the weathered granitic crust in SW Japan.

In the Ashizuri-misaki area, Mioocene granitic rocks consist of quartz syenite, alkaline and fluorine-rich granite with high content of light REEs such as La and Ce. The Tanakami and the Naegi areas were underlain by late Cretaceous I-type, ilmenite-series biotite granite. The Naegi granite has moderate alkaline compositions with A-type affinity, and is more enriched in fluorine and heavy REEs than the other I-type ilmenite series granitic rocks. The REE enrichment within these granitic rocks reflects the amounts of accessory REE-bearing minerals such as zircon, xenotime, and possibly multiple oxides.

The weathered crusts are more depleted in REEs more than the underlying granitic rocks in all three areas. The weathered crust in the Ashizuri-misaki area records the highest value (av. $\Sigma\text{REE}+\text{Y}=342$ ppm) among those in the Tanakami (av. $\Sigma\text{REE}+\text{Y}=165$ ppm) and Naegi (av. $\Sigma\text{REE}+\text{Y}=232$ ppm) areas. The Tanakami and Naegi granitic rocks are sporadically overlain by the Quaternary clay sediments, reworked products from the weathered granite, which filled local basins. The clay sediments consist of alternating beds of halloysite and sandy sediments of quartz with minor plagioclase in a clay matrix. The maximum thickness of the clay sediments are of more than 20 and 50 meters for Tanakami and Naegi areas, respectively. The halloysite-rich layers have higher REE contents ($\Sigma\text{REE}+\text{Y}>400$ ppm for Naegi and Tanakami areas) with maximum contents of $\Sigma\text{REE}+\text{Y}$ over 700 ppm for Naegi area. These values are equivalent to those of the ion-absorption-type REE deposits in southern China. In these two areas, REEs are concentrated in the reworked clay sediments derived from the weathered granites, but not in the weathered crust on the granite such as the Ashizuri-misaki area. The enrichment of REEs, particularly HREE in clay sediments relative to the underlying granitic rocks corresponds mainly to halloysite content.

O16-01

Possibilities and limitations of trace element characterization (fingerprinting) of precious materials

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A major problem in South Africa is the theft of precious material (anything from ore to refinery products) from the gold mines of the Witwatersrand Basin and the platinum mines of the Bushveld Complex. Often this material is illegally processed to convert it into metals and then introduced into the economy by various means (e.g. sold as scrap metal). Metal to the value of several hundred million US\$ annually is thought to be "laundered" in this way.

Trace element fingerprinting of gold and platinum-containing materials is aimed at the unique characterization of materials from ores and precious metal minerals, materials at different stages in the beneficiation and refining process, and commercially available products. Using data obtained from a range of analytical techniques, specially designed statistical software allocates individual analyses to material groups and performs a probabilistic comparison with other analyses in the database.

A method for identifying illegally smelted metal has been the object of much research, which up to now has focused on the determination of the geological origin, because differences or changes in the ore forming processes should be reflected in the trace element pattern of ore minerals (or associated minerals which are introduced into the beneficiation process).

Both gold and platinum-group metals have unique problems associated with source identification. In either commodity the challenge is to use trace element fingerprinting to identify the source despite different beneficiation procedures by companies and illegal syndicates. The degree of processing needed for the manufacture of metals means that matching them to their raw material sources is difficult. Attempts to do this based on comparisons between the major and minor element geochemistry of metal and potential ores and more recently on their stable isotope geochemistry have met with limited success. A major reason for this is that ore sampling strategies have either been neglected or based upon an incomplete understanding of the mineralogical and geochemical complexities inherent in any metalliferous ore deposit.

In South Africa, the driving economic force behind this research is the need to identify the source of precious metal materials recovered during police operations in order to return them to their rightful owners. While the comprehensive understanding of the factors controlling metal trace element characteristics remains a goal, the rapid identification of a particular batch of gold as "stolen" or "legal" is now possible.

O16-02

New insights into pyrite textures from the application of electron backscatter diffraction

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Textures in many of the world's sulphide ore-deposits provide evidence for both the primary environment of ore formation and also for subsequent modification during secondary metamorphism and/or deformation. Many common sulphide minerals (e.g. galena, chalcocopyrite, and sphalerite) are rheologically weak and easily modified. Their history is effectively erased by recrystallisation, even at only slightly elevated temperatures. On the other hand, pyrite is relatively strong and refractory. It can preserve evidence from its primary formation right through to its near destruction in some orogenic environments. However, because pyrite is opaque and cubic, its inner secrets are not easily given up by traditional methods of reflected-light microscopy and backscattered electron atomic-number-contrast imaging in the SEM. Recent and ongoing collaborative studies at the University of Liverpool have demonstrated the utility of SEM-based electron backscatter diffraction (EBSD) coupled with focussed electron orientation-contrast imaging as a tools to decipher the history of pyrite, and as a result understand sulphide ore genesis and evolution better.

A number of case studies will be presented to illustrate the utility of EBSD and orientation contrast imaging, and their scope in providing new insights into an opaque mineral:

1. implications for self-organisation of pyrite microcrysts from crystallographic ordering in framboidal and colloform pyrite microstructures;
2. implications for the pyrite deformation-mechanisms map from the microstructure of experimentally and naturally deformed massive-sulphide ore;
3. implications for apparently simple texture interpretations from detailed study of pyrite replacement by magnetite textures and pyrite foam textures.

O16-03

The silver-bearing and related minerals in El Zencudo deposit, Antioquia, Colombia and their genetic processes.

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El Zencudo mine is a silver-gold deposit located in the left flank of the central mountain range, Antioquia prefecture, Colombia. It is hosted mainly in green schist. Its origin has been considered to be related to the igneous activity of some Miocene porphyritic intrusion. The ores occur mainly with breccia and show banded structure. The ore deposit is generally associated with a large altered zone which contains kaolinite, muscovite and illite. The ores contain sphalerite, pyrite, arsenopyrite, galena, tetrahedrite-freibergite, miargyrite, andorite, boulangerite, bournonite, jamesonite and minor proportions of chalcocopyrite, electrum and native silver. The textural relation and chemical compositions of the ore minerals is complex and suggest several stages of mineralization. According to the textural relation, the mineral assemblages have been divided into three groups corresponding to three main mineralization stages: the assemblage of the first stage includes sphalerite, pyrite, arsenopyrite, galena and electrum; in the second stage, the sulfosalts are associated with galena; the final stage is defined by sphalerite and pyrite.

By the high iron content in sphalerite, ranging from 3 to 13 wt% and according to the FeS mol% distribution, this deposit is classified into "Cu-Pb-Zn vein deposit" type. The pyrite is rich arsenic (0-2.7wt%) and the variation of arsenic content marks episodes of crystallization. In galena grains silver up to 1wt% has been detected, and antimony and bismuth are also contained. Boulangerite, bournonite and jamesonite are broad dispersing in the samples and are close to their ideal formulas: $Pb_5Sb_4S_{11}$, $CuPbSbS_3$, and $Pb_4FeSb_6S_{14}$ respectively. Tetrahedrite-freibergite minerals, $(Ag,Cu)_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$, are poor arsenic and rich silver: the silver content ranges from 4 to 32wt% with average of 18.86wt%, and arsenic is around 3wt% at the maximum. This feature between silver and arsenic in tetrahedrite-freibergite may be due to a poor arsenic fluid that increases the antimony content allowing silver enrichment. Miargyrite ($AgSbS_2$) is shown in average 0.57wt% of arsenic content and the molar relation $As/As+Sb$ percentage is less than 8%, which has been reported for epithermal miargyrite. The Andorite formula is $PbAgSb_3S_6$, it occurs in wide solid solutions with strong variations in the lead-antimony content.

In terms of the mineralogical data, El Zencudo deposit is considered as a product of hydrothermal activity and could be classified as epithermal type ore deposit.

O16-04

Distribution of Cu-Ag-S-Se phases in epithermal deposits of the Hauraki Goldfield, New Zealand

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The Hauraki Goldfield of New Zealand is a classic epithermal province, with approximately 50 adularia-sericite epithermal deposits. Electrum is the only significant Au-bearing mineral in the quartz veins that form orebodies in the goldfield, but Ag occurs in electrum and in several other minerals in the Cu-Ag-S-Se group. There is considerable substitution in the Cu-Ag-S-Se group, and the epithermal deposits of the goldfield show a range of minerals from this group.

Acanthite (Ag_2S) is the most abundant silver-bearing mineral in the goldfield, as it occurs in most deposits. In some deposits, such as the deep veins of Karangahake, and the shallow veins of Golden Cross, acanthite is commonly stoichiometric. However, acanthite in the deep veins of Waihi and the shallow veins of Broken Hills, contains up to 10 wt% Se. Selenium also occurs in naumannite (Ag_2Se) and/or aguilarite (Ag_2SeS), as reported from the Te Ahumata, Ohui, Broken Hills, Maratoto, Waihi, and Favona deposits. Both minerals are orthorhombic, with a space group of P212121. Naumannite commonly shows some sulfur substitution; a typical microprobe analysis could yield a formula of $Ag_{1.84}Au_{0.05}Fe_{0.05}Se_{0.83}S_{0.17}$. Some samples contain a Ag-Cu-Se-S phase with a Se:S ratio of 2:1, and a representative formula of $Ag_{1.96}Cu_{0.02}Fe_{0.01}Se_{0.66}S_{0.34}$, which presumably reflects substitution in the naumannite-aguilarite group.

In most deposits, Cu occurs exclusively in chalcocopyrite, and therefore Ag-bearing ore minerals are restricted to Ag-S-Se space. However, in some deposits, such as Favona, there is significant Cu locally, resulting in the formation of chalcocite (Cu_2S), and one or more minerals whose compositions fall in the stromeyerite ($CuAgS$) to mckinstryite [$(Ag,Cu)_{25}$] group. These range from $Ag_{0.95}Cu_{0.94}Au_{0.02}Zn_{0.01}S_{0.99}Se_{0.01}$ to $Ag_{1.31}Cu_{0.67}Au_{0.05}Zn_{0.01}S_{0.91}Se_{0.09}$.

In the Hauraki Goldfield deposits, there is a strong positive co-variation between weight percent Se and weight percent Ag in the Cu-Ag-S-Se phase. Where Se and Ag increase, S and Cu decrease respectively. The high Se content of acanthite and other minerals does not correlate with the depth at which the veins formed. Instead, this likely reflects a relatively oxidizing environment, which is favorable for maximum Au solubility. Although some veins with bonanza grades do not contain significant Se-bearing phases, most veins with Se-bearing phases have high grades, and many contain greater than 30 ppm Au. Other Se-bearing high grade epithermal Au deposits worldwide include Hishikari, Japan; Sleeper, Nevada; and Pongkor, Indonesia.

Mineralogical and genetic characteristics of the Dohgamaru skarn and vein type ore deposits, Shimane Prefecture, Japan

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Ore deposits of Dohgamaru mine, Ohchi-gun, Shimane Prefecture, Japan, were investigated to examine ore types of the deposits, to reveal occurrence of ore minerals containing silver and other metals, to establish ore mineralization sequence and to consider the evolution of ore mineralization in the San-in district.

The ore deposits occur in rhyolite-dacite lava and/or pyroclastic rocks of Ohchi Formation, Cretaceous in age, and were associated with Onbara granite of 60-65 Ma (Shibata and Ishihara, 1974; Hattori, 1983). The host rocks are extremely silicified. The deposits were distributed at the shallow part and partly mined in open pits.

The samples are divided into vein-type ones and skarn type ones. In addition to common ore minerals such as pyrite, chalcopyrite, and sphalerite, silver minerals were found from this mine for the first time.

Pyrite contains arsenic up to 4.69wt%. Pyrite and chalcopyrite contain 0.1 to 0.9wt% silver or gold, although any silver- and gold-bearing mineral was not observed, suggesting very fine invisible electrum with nm order in size. Galena contains 0.1 to 0.4wt% of Ag and Bi, which is common in vein type ore deposit. There are two types of fine (<10 μm) silver-bearing minerals: one is Cu-Ag-S phase (70.8wt.% Ag), and another Cu-Ag-Fe-S phase (27.4wt.% Ag).

Main skarn minerals are garnet, hedenbergite and epidote. Garnets are extremely rich in almandine. Total Fe₂O₃ content in epidote attains up to 21.2wt%. Pinkish epidote and piemontite also occur.

Homogenization temperatures of fluid inclusions in quartz (223-358°C) are different from those from Neogene ore deposits in San-in district, but are similar to those of Tsumo mine. They indicate that hydrothermal solution experienced boiling stage.

Sulfur fugacity of this deposit is similar to those of Tsumo mine and other Neogene ores in San-in district.

Three mineralization stages can be recognized: at the early stage, skarn ores were formed; at the middle stage, vein type ores were deposited; at later stage, sulfates were crystallized.

The Dohgamaru mine is characterized by higher genetic temperatures and lower Bi content than other metallic deposits such as Tsumo mine (skarn deposit), Iwami Kuroko deposit and Ohmori Eikyū deposit, which is interpreted in terms of the historical evolution of ore mineralization caused by a change of nature of magma activity.

Another look at nagyágite from Săcărîmb (Romania)

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We have investigated chemical heterogeneity among lamellae of nagyágite of different sizes, textures and morphologies in specimens from the type locality (Săcărîmb, Romania). The aim of the study was to complement existing compositional data for this mineral. Based on the structural formula, [(Pb₃(Pb, Sb, As))₂Si₂](Au,Te₂)₂], we note three sets of compositional variation: (i) As substitution for Sb, beyond previously recognised limits to an end-member almost free of Sb, and a tendency towards irregular As distribution in individual lamellae; (ii) variation in the Au:Te ratio from ~0.2 to ~0.4 in lamellae with close-to-end-member Sb content; and (iii) variation in the Pb/(Pb+Sb+As) ratio, independent of As/(As+Sb). The last of these variations is expressed by co-existing 'high-Pb' and 'low-Pb' varieties that occur within the same short-plate grains, <30 μm in size, typically within fringes that seal areas with exsolutions of other Au-Ag-tellurides. High-Pb (~4.7 to 5.0 a.p.f.u Pb) and low-Pb (~3.9 to 4.2 a.p.f.u Pb) varieties are readily distinguishable from one another in back-scattered electron images as distinct zones within the same plate grain. We have tracked correlations between the different variables and note correlation between Te, and implicitly also Σ(Au+Te), with Σ(Pb) content; the low-Pb variety contains consistently >3 a.p.f.u. Σ(Au+Te).

Both Sb- and As-rich varieties of nagyágite were observed to coexist in the same sample and throughout the width of the veins; textures indicate, however, that the former crystallized earlier. The more restricted occurrence of the short plate grains with Pb-rich and -poor varieties indicates formation from local residual fluids that first deposited Ag-Au-assemblages (atypical for the veins). As-bearing nagyágite is mainly found in vein selvages formed during reopening of those veins. In this case shear-induced deformation of lamellae is observed to go from microscopic- down to nano-scale, since shearing of the lattice fringes was observed in As-bearing nagyágite using HRTEM. Solid solution is a viable mechanism for As⇌Sb exchange in the structure since no stacking disorder was noted.

However, given that nagyágite is the N=1 member of the nagyágite homologous series, with N=2 represented by buckhornite, [(Pb₃Bi)₂Si₂](Au,Te₂)₂], with a further related species, museumite, [(Pb₃Pb,Sb)₂Si₂](Te,Au)₂], also known, we consider it likely that disordered lattice-scale intergrowths may be present, especially in the species with variable Pb contents. Alternatively, co-existing 'high-' and 'low-Pb' varieties within the same grain may represent chemical modulation within derivative structures. Future work, using focussed-ion-beam HRTEM techniques, aims to address the structural characteristics and order-disorder state of the small plate-lamella.

Breccias with high-grade Ag-Sn mineralization at Pirquitas, Argentina

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The Ag-Sn deposit Pirquitas, Province of Jujuy, NW-Argentina, represents the southernmost member of the Cenozoic tin belt of the Central Andes. Total reserves (proven and probable) are reported to be 34 million tons with an average grade of 5.1 oz Ag/t, 0.6 % Zn and 0.2 % Sn. The mineralization is hosted by Ordovician siliclastic sediments of the Acoite Formation. High-grade mineralization is characterized by NW-trending subvertical veins crosscutting the bedding of the host rocks at the hinges of NNE-trending anticlines.

The most remarkable ore concentration of the deposit which covers an area of 1.5 x 2 km is the Oplaca vein system situated at the hinge zones of the San Pedro anticlinal structure. The high-grade Ag-Sn ore at Oplaca is exposed underground between a major crosscut (level 9) at 4250 m and an adit at 4370 m above sea level, close to the surface. The ore mineralization is associated with a tectonic breccia of a pipe-like shape (20x30 m in cross section) which extends from level 7 (4300 m above sea level) through 6 sublevels up to the surface. This breccia is penetrated by several extensional veins with typical pinch and swell structure, and ranging in thickness from a few cm's up to 0.5 m. Open space filling is indicated by crustiform and colloform banding, cockade textures and frequent vugs.

At Oplaca, a great variety of exotic mineral assemblages occur which were precipitated in several superimposed pulses, commonly recognized as telescoping in this deposit type. In-bearing sphalerite and wurtzite are the dominant sulfides in the breccia and the veins, and occur in bands of colloform texture. The ubiquitous tin minerals in both the breccia and the veins are franckite-potosite, suredate (particularly in fine crystals), coiraitite, (PbSn²⁺)₁₂As₃Fe²⁺Sn⁴⁺S₂₈, and cylindrite-icaite. These are associated with an earlier generation of Sn-bearing minerals such as, cassiterite and members of the hocarite-pirquitasite, rhodostannite-toyohaite and stannite-kesterite solid solution series. Silver-bearing sulfosalts (miargyrite, pyrargyrite, andlorite-fizelyite-randohrite) are especially abundant in the breccia. Locally, a Bi-Te mineralization (bismuthinite, pavonite-benjaminite, tetradyomite, Te-canfieldite) may be associated with the Zn-Sn ore.

The first results of an extensive fluid inclusion study reveal homogenization temperatures for hocarite ranging between 242 and 259°C (6.5 - 7.8 wt.% NaCl equiv.). The bulk of the Sn mineralization (sulfosalts, suredate) which is closely associated with sphalerite-wurtzite is assumed to have been formed at the same temperature range as the zinc sulfides (205 - 227°C, 0.8 - 2.3 wt.% NaCl equiv.).

High-resolution transmission electron microscopy study of natural Bi-chalcogenides of the tetradyomite group

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Bismuth chalcogenides of the tetradyomite group [Bi₂X₃ (X=Te,Se,S)], crystallise as rhombohedral or trigonal layer structures. These are interpreted as distinct stacking sequences between two types of layers, i.e. 2-atom 'BiBi' and 5-atom 'XBixBiX' layers. Although numerous intermediate compounds can be structurally derived in this way and have been synthesised, minerals are known only for a more limited set of Bi:X ratios, i.e., 2:3, 3:4, 1:1, 4:3 and 7:3. Members of each iseries are derived from the tetradyomite structure (555) by inserting a single 2-atom layer at different periodicities of the 5-atom layers, i.e., x4 (Bi₂X₄), x2 (BiX), x1 (Bi₄X₃). Hedleyite (Bi₇Te₃) comprises sequences of (22) and (222) alternating with a single 5-atom layer. Lattice scale disorder and a different interpretation of the stacking sequences, i.e., a 7-atom layer instead of the 2-atom layer, is given for synthetic compounds with composition M₂X₃ (M=Sb, Bi; X=Se, Te; 0<x<0.4) in previous high-resolution transmission electron microscopy (HRTEM) studies. A general structural model was interpreted for the group using superspace formalism, where the average distance between homoatomic layers (q) is linked to the composition (between Bi₂X₃ and Bi₄X₃).

We employed HRTEM to characterise minerals from all, except Bi₂X₄, iseries (i) Bi₂X₃ - tetradyomite, tellurobismuthite; (ii) Bi₄X₃ - pilsenite, laitakarite; (iii) BiX - tsumoite; and hedleyite. The studied samples are from Au deposits in the Fennoscandian Shield, hydrothermally altered fields adjacent to epithermal Au mineralisation within the Transcarpathians and Au skarn at Hedley (Canada). Our results indicate that (i) the model with 2- and 5-, rather than 7-atom layer is more suitable for interpretation of observed stacking sequences; (ii) stacking disorder is found as lattice scale intergrowths between units of tellurobismuthite and tsumoite in orogenic Au veins (Moberg, Norway) but not in metamorphosed epithermal Au at Orivesi (Finland); (iii) sequences of (225) are present in both pilsenite and hedleyite; laitakarite from metamorphosed VMS at Orijarvi (Finland) is ordered; (iv) q value obtained from electron diffraction patterns is suitable to identify different stoichiometries within the group; hedleyite has q=1.66.

Our preliminary LA-ICPMS measurements of Au within Bi-chalcogenides from various types of Au deposits indicate that they contain Au at X-xxx ppm levels. Since we observed that the OD state varies for a given species from one deposit to another, this is a good premise to consider a correlation between OD state and Au content; data presented here is prior to LA-ICPMS investigation on these specimens.

Kuroko and Besshi-type volcanogenic massive sulfide deposits in Japan

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In Japan, there exist two groups of volcanogenic massive sulfide deposits (VMSDs) termed with Japanese words as "Besshi-type" and "Kuroko" ore deposits. Besshi is the world-class mine's name of the Paleozoic VMSD on Shikoku Island. The other Japanese "Kuroko" has a meaning of black-colored ore. This paper attempts to provide geological, petrological and geochemical views of these two VMS systems, with descriptions of the tectonic and igneous processes involved in VMS formation and of important examples representing a variety of VMSDs in Japan.

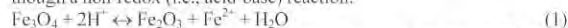
The Besshi-type deposits are characterized by conformable and stratiform ore-sheets with the mineral assemblages of massive pyrite and/or pyrrhotite with variable contents of chalcopyrite, sphalerite, and rare galena with the close relationships to basaltic volcanics. Most of the deposits occur in the Sanbagawa metamorphic belt, with some occurrences in weakly metamorphosed Jurassic and Cretaceous accretionary terrains. The deposits are divided into two groups; the sediment-baren group is hosted by basalt-chert sequences, whereas the sediment-covered group is hosted by basalt-shale sequences. Geochemical characteristics of REE patterns of weakly metamorphosed greenstones and even metamorphosed amphibolites and Pb isotopic compositions of the first group Besshi-type deposits in Japan show the similarities to those of MORB. The Besshi-type ores are also characterized by S isotopic trends similar to those of sea-floor deposits now forming at mid-oceanic ridges (Sato and Kase, 1996). However, Pb isotope data for the second group ores such as Shimokawa deposits tend to have slightly higher radiogenic values (Sato and Sasaki, 1980). Those data indicate that the Shimokawa deposit formed in relation to volcanism along a mid-oceanic ridge where elastic materials were supplied, and the deposit was accreted shortly after mineralization. Combining geological observations, the Shimokawa deposit is likely to be formed during the ridge-subducting setting beneath the ancient continent of Hokkaido. Kuroko deposits in Japan are closely associated with submarine felsic volcanism. The volcanic and sedimentary rocks have been strongly, hydrothermally altered into so-called "Green-tuff" of Middle Miocene age. Kuroko deposits are also characterized by conformable and lenticular orebodies with the assemblages of massive sphalerite and galena with variable contents of chalcopyrite, pyrite, tetrahedrite, barite and so on. They represent a significant source of the world's Cu, Zn, Pb, Au, and Ag ores, with some products. The stratiform orebodies are mostly underlain by stock-work siliceous orebodies. Trace element analyses by laser ablation ICP mass spectrometry are carried out for felsic lavas and tuffs. REE patterns are similar for both the felsic volcanic rocks from the pre- and post-Kuroko stages with negative anomalies of Eu and high concentration of LREE. MORB-normalized spider diagrams show some concentration of enriched large ion lithophile elements. It is likely that the felsic volcanics are implied to the volcanic suite associated with island arc volcanisms of initial stage. The slight Nb negative anomalies show the felsic volcanics from the contemporary and post-Kuroko stages could be formed by initial stage island arc volcanisms. Nd isotopic data are also supporting the same conclusion. Kuroko deposits of the Hokuroku district is likely to be formed in transitional tectonic stages from back-arc to initial-stage arc volcanic setting.

Non-redox transformation of magnetite - hematite under H₂-rich hydrothermal conditionsT. Otake¹, D. J. Wesolowski², L. M. Anovitz², L. F. Allard, Jr.³ and H. Ohmoto¹¹Department of Geosciences, Pennsylvania State University, University Park, 16803, USA.

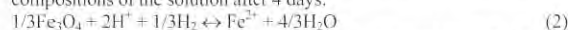
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Magnetite (Fe₃O₄) and hematite (Fe₂O₃) are used to constrain the redox conditions of fluid (or melt) from their presence or absence in rocks. Magnetite-rich Banded Iron Formations (BIFs) and secondary hematite-rich iron ore formations have been linked to the oxygenation of the ocean and atmosphere, assuming redox transformation of magnetite - hematite. However, magnetite - hematite transformation may proceed through a non-redox (i.e., acid-base) reaction:



Magnetite is transformed to hematite as a result of leaching Fe²⁺ from magnetite while hematite is transformed to magnetite as a result of incorporating Fe²⁺ into hematite. We have examined the reactions (forward and reverse) using a hydrothermal cell with hydrogen electrodes for pH measurements and a hydrogen-permeable membrane for P_{H₂} measurements. The experiments were conducted at 100 - 250°C under highly reducing conditions (P_{H₂} = 0.5 - 50 bar) and mildly acid conditions (pH = 4 - 6). After the system reached a steady state, iron concentration in the withdrawn sample solutions was measured by ICP-AES. The residual solid was analyzed using XRD, SEM and IRTEM. Our experiments have demonstrated that euhedral crystals of hexagonal dipyrmidal hematite grow rapidly by reaction between magnetite and acid solutions at T ≤ 200 °C, suggesting dissolution and reprecipitation of Fe²⁺ under highly reducing conditions. Rapid dissolution and reprecipitation of Fe²⁺ may be promoted by the presence of Fe²⁺ in the solution through electron transfer and/or indicate the importance of nanoparticle or aqueous Fe₂O₃(aq) for crystallization of hematite. Chemical composition of the experimental solution at the given temperatures are independent of the H₂ pressure and remain constant over weeks, controlled by reaction (1). Reaction (1) is reversible, although the reverse reaction is more sluggish than the forward reaction. However, at T = 250°C, reductive dissolution of magnetite (i.e., redox reaction) controls the chemical compositions of the solution after 4 days:



No hematite was found in the residual solid from experiments at the temperature.

The results of our studies suggest magnetite and hematite act as an acid-base buffer, rather than a redox buffer in low temperature environments. Because magnetite - hematite transformation does not require a redox reaction, secondary hematite-rich iron ore developed from BIFs may have formed by subsurface reaction between magnetite and acidic hydrothermal solutions at T ≤ 200 °C.

The Role of Reaction Kinetics In the Growth of Sphalerite in MVT Deposits

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The reasons for variations in the size and morphology of crystals in ore deposits are poorly understood, but it seems certain that the degree of supersaturation during growth is a major factor. In Mississippi Valley-type (MVT) lead-zinc deposits, sphalerite is commonly fine-grained to colloform, but occasionally occurs as well-formed centimeter-sized crystals, for example in the deposits of Central Tennessee. If this variation is attributed to differing degrees of supersaturation during growth, two different scenarios for the origin of the reduced sulfur (as H₂S) are indicated. In general, H₂S is thought to result from reduction of seawater sulfate, but typical MVT ore formation temperatures of 150±50°C are too high for bacterial reduction, and thermochemical sulfate reduction (TSR) is known to be extremely slow at these temperatures. For these reasons sulfate reduction is commonly held to occur *before* ore deposition, with the H₂S held in a trap later intersected by a metal-bearing solution. Such mixing (the "mixing hypothesis") should result in a high degree of supersaturation and hence fine-grained or colloform textures. In this case the kinetics of the TSR reaction is not a genetic factor, and there are theoretically few limits to the amount of ore produced. Compilation of all available data, including some recent data of our own, shows that at a temperature of 150°C, the first order rate constant for the overall TSR reaction lies between 10⁰ and 10⁻⁴, depending on the reductant and other factors. An alternative to sulfate reduction is the release of H₂S from organic material such as petroleum or organic-rich shale. Our preliminary data on the rate constant for the release of H₂S from organic-rich shale lies in the same range. Although very slow, a simple flow model shows that rates in this range are fast enough to generate small ore bodies, with H₂S generation taking place *during* ore formation. This slow generation of H₂S should result in low degrees of supersaturation and relatively large, well-formed crystals. Although ore formation with H₂S generation taking place during ore formation is thus kinetically permissible, the concentration of ore in specific localities becomes more difficult to explain. These problems are discussed in relation to the ores of Central Tennessee.

Some crystallochemical peculiarities of PGM with As, Te, Sb, and Sn

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Among Platinum Group Minerals (PGM) the large number presents compounds with As, Te, Sb, and Sn. Their physical properties are typical for metals - high reflectivity, metallic luster, malleability. Structures of these minerals generally are characterized by interaction "PGE"- "PGE" due to the shortened interatomic distances, leading to some metallic character of chemical bonds. Significant variations of As, Te, Sb, Sn (and Bi, Pb) content, and significant isomorphous substitutions among these elements are also typical. Sometimes it is not so easy to calculate the adequate formula based on the microprobe analyses. Many problems are caused by the small PGM grain dimensions (from first microns till some hundreds microns), and by complex character of their occurrence in nature, i.e. close association of some PGM and other ore minerals. That is why it is necessary to apply the model synthesis for obtaining the detail characteristics of PGM, conditions of PGM and of PGM-bearing association formation. Now the homogeneity and morphology of PGM, as well as their fine structures are analyzed using the scanning electron microscope equipped by ED detector. This equipment is one of the most powerful tools of modern mineralogist. Results of its application to study some PGM (majakite, telargapite, vincentite, etc.) and synthesized phases in (Pd,Ag)₃₋₄Te, (Pd,Ni)₂As Pd₈(As,Te,Sn,Bi), etc. systems are presented. Series (Pd,Ag)₃₋₄Te was chosen for determine the composition limits of telargapite. The synthesized (Pd,Ag)₃Te phase differs from mineral in composition, and is characterized by Ag content ~3-5 Wt%. The heightened "Pd+Ag" apfu (>3) in synthetic telargapite is caused by (Ag,Pd) submicroinclusions, <0.05 μm, in "telargapite" grains. The majakite-like compounds, ("PGE",Ni)₂As, have been obtained only in systems with Pd, Rh, and Ru. (Pd,Ni)₂As series presents the large solid solution with some ordered phases, characterized by stoichiometric Pd:Ni:As ratios - i.e., Pd₃Ni₁As₂, Pd₃Ni₁As₁, Ni₃Pd₁As₂. The positive composition deviation from stoichiometry A₂B is caused by tiny submicroscopic inclusions of Ni-arsenides. The sophisticated treatment of published data on mineral vincentite and other Pd-(Te,Sb) minerals has been carried out. Relationships and composition peculiarities of Pd₃(Te,Sb) phases have been adjusted by experimental study of Pd₃Te-Pd₃Sb series. Results of EPMA and SEM+EDS study of palartanide series, Pd₃₋₄(As,Sn)₂₋₃, prove the high heterogeneity of synthesized phases and some mineral grains at submicroscopic level. This fact could explain some disagreements on the palartanide formula. Pursuance of researches included DTA study of synthesized (Pd,Ni)₂As, (Pd,Ag)₃Te, and some of Pd-(As,Sn) phases for determine temperatures and conditions of their formation.

Ore Mineral Paragenesis and Sulfur Isotope Characteristics of Volcanogenic Massive Sulfide Deposits of Turkey occurring in the Eastern Pontides (NE Turkey): Are They True Kuroko-type Deposits?

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The upper Cretaceous volcanogenic massive sulfide deposits (VMS), occurring in northeastern Turkey known as the eastern Pontide tectonic belt are considered as the largest sources for base metals in the country. The Turkish VMS deposits, about 60 known occurrences throughout the eastern Pontide tectonic belt, share common attributes. They are all hosted by the felsic volcanic pile of late Cretaceous age and have a strata-bound nature. Based on ore mineral paragenesis these deposits belong mainly to the Cu-Zn-type, but Cu-Zn-Pb- (e.g., Lahanos deposit), Cu- (e.g., Murgul deposit), and Zn-Pb-Cu-types (e.g., Köprübaşı deposit) are also present in the region. All the deposits were deposited at temperatures ranging from 320°C to 160°C. The salinities of the fluid inclusions range between 0.5 – 6 wt. % eq. NaCl. Fluid inclusions are generally liquid-rich and have consistent liquid-to-vapor ratios. Almost all of the VMS deposits exhibit a very high Cu/Cu+Zn ratio relative to the Japanese counterparts. The sulfur isotope compositions of selected major sulfide minerals for all of the major deposits fall in a very narrow range suggesting a homogeneous source and temperature formation.

Structural control and rheological properties of the hydrothermal mineralization: a case of a mineralized mafic dike outcropping near Lula, Sardinia, Italy

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In the mid-eastern Sardinia, Italy, most base-metal deposits are linked to complex magmatic-hydrothermal activity related to the evolution of subduction-related magmatism (Hercynian). The Lula area is a classical mining district for hydrothermal Pb-Zn-Ag ore deposits, already known during Roman Empire. They were mined until the end of the Second World War. This area is characterized by a complex magmatic-metamorphic environment composed of a metamorphic complex intruded by granites and by a complex system of dikes (Hercynian). We report structural and paragenetic data, and the chemical composition of minerals forming the hydrothermal veins cutting a mafic dike, which is hosted by schists. Two sets of nearly orthogonal arrays of veins cut the mafic dike. They strike N210 and N300°, with dips of 70° on average. Both sets of veins are filled by composite associations of tourmaline + sulfides + sulfate and carbonate. This fracture system does not penetrate the schistose host-rocks, suggesting a contrast in the rheological properties during ongoing deformation. The minerals in all veins have a similar composition; schorl-dravite predominates over sulfides (galena – sphalerite ± chalcopryite), sulfates (barite) and carbonates. In some veins, the tourmaline coexists with Ba-rich K-feldspar. Near the mineralized veins, the paragenetic assemblage in the wallrock is: K-feldspar – amphibole – epidote ± titanite ± chlorite. The metamorphic rocks, hosting mafic dike, were affected by three episodes of deformation, D1, D2 and D3, followed by circulation of late hydrothermal fluids (D4). A textural analysis allowed us to recognize D1, due to regional metamorphism. We derived an estimate of the peak conditions of metamorphism at 600-700°C and <3 kbar using garnet-biotite geothermometry. The D1 episode is considered to be contemporaneous with an overprint D2 due to contact-metamorphic effects. The widespread crystallization of late-kinematic chlorite forms part of a retrograde assemblage that marks D3. The mesothermal deposits of the Guzzurra (Ag-rich galena – sphalerite and a gangue of quartz – barite or fluorite or quartz – siderite hosted by black schist) and Sos Enattos (galena – sphalerite – barite and a gangue of quartz – calcite) both occurring in the area, suggest that a system of hydrothermal circulation was activated, in which local structural control is evident. The mafic dike shows the same attitude even where it does not host the mineralization; as it was affected by the same hydrothermal process, it offers a natural "micro- laboratory" in which to evaluate structural control, rheological properties, paragenetic assemblages and the chemical composition of the mineralized veins.

Metallogenic constraints on the origin of hypogene zinc ores at Angouran Mine, Iran

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The Angouran zinc deposit in NW-Iran consists of 4 Mt of hypogene sulphide-dominated sulphide-carbonate ore @ 40.4%Zn, 1.9%Pb and 18 Mt zinc-carbonate-dominated ore @ 28.1%Zn, 4.2%Pb, which is partly supergene. The hypogene ore is in part matrix to a hydraulic breccia in Late Proterozoic quartz-sericite schist but also in overlying Cambrian marble. Both units have been thrust over young (18.42±0.18 Ma) rhyolitic tuffs. Due to the lack of drill core information it is not clear, if the basal breccia reaches below the thrust or is rooted therein. Hypogene metallogeny comprised multiple Zn-Pb-sulphide stages as well as a zinc-carbonate stage due to an abrupt change of fluid composition and pressures. C- and O-isotope data suggest fluid mixing of a zinc-bearing fluid with CO₂/CO₂H-rich meteoric fluids percolating through the hangingwall marble. Sulphide precipitation was from ZnCl₂ ± ZnNa₂Cl₄-rich (F_m ~ -65°C to -63°C) hypersaline brines (~35 wt % ZnCl₂, L_m ~ -27.5 °C). Homogenisation temperatures (T_h 110-170 °C) are close to the temperature of entrapment, since fluid pressures are very low. Subsequent hypogene Zn-carbonate formed from very low salinity fluids (F_m=L_m= 0 to 2 °C) at low temperatures (T_h = 120 °C). The constant existence of low density gas cavities suggests low lithostatic pressures (i.e. shallow mineralisation levels). We classify the Angouran hypogene sulphide-carbonate ore as a new deposit type derived from a low-T hydrothermal fluid. Current information does not yet allow the exclusion of one of the following concepts: i) A thrust-related model, with seismic pumping as the major driving force for metalliferous fluids. In such a model, ore formation immediately followed hydraulic fracturing when hydrostatic fluid pressure exceeded lithostatic pressure. The ore body formed in a hydraulic trap at the schist marble/interface above the thrust plane. ii) A hydrothermal origin, associated with young (18 Ma) magmatism, in which metalliferous fluids have pierced the thrust plane and ascended to the schist/marble contact, where hypogene ore formation took place. Rare breccia clasts, probably of felsic pyroclastic origin, within the sphalerite ore currently favour the latter model, in which ore formation post-dated thrusting.

Alteration minerals in adularia-sericite epithermal deposits as indicators of mineralisation potential: Examples from the Hauraki Goldfield, New Zealand

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In geothermal fields, which are the active analogues of epithermal adularia-sericite deposits, there is a close correlation between the amount of dissolved gold, H₂S and CO₂ in alkali chloride waters. Gold is principally transported as a bisulfide complex and precipitates due to cooling and gas loss via boiling. The amount of CO₂ helps control mineralogy, with high CO₂ levels favouring the formation of calcite and inhibiting zeolites and epidote formation. Accordingly, geothermal fields with ore-grade precipitates of gold and silver such as Rotokawa, Broadlands-Ohaaki, and Kawerau in New Zealand have high levels of dissolved CO₂ (>0.5 molal), abundant calcite and lack zeolites. In contrast, fields that lack gold precipitates, like Wairakei and Orakeikorako have low CO₂ levels (0.01 molal), abundant zeolites, epidote and generally lack calcite. Waiotapu, with low to intermediate CO₂ concentrations (0.05 molal) has both zeolites and calcite; gold is locally associated with arsenic and antimony colloids.

In epithermal adularia-sericite deposits of the Hauraki Goldfield in New Zealand, alteration and peripheral vein minerals can indicate economic versus sub-economic deposits. Orebodies are surrounded by widespread quartz, adularia, chlorite, illite, interstratified illite-smectite, and pyrite alteration together with or without calcite or zeolites. Extensive calcite alteration and veins at the Golden Cross deposit (0.8 Moz Au) coupled with a lack of zeolites is consistent with formation from a fluid with high CO₂ levels and the occurrence of economically mineralised quartz veins. Similarly, the lack of zeolites at the world class Waihi deposit (+6.7 Moz Au) also suggests high CO₂ concentrations, although calcite is only locally abundant. Here, late stage CO₂-rich waters that form overprinting calcite appear to have been largely removed due to hydrological controls, thereby indicating that a lack of calcite may not always reflect low CO₂. In contrast, several subeconomic prospects in the Hauraki Goldfield have epidote at depth and a mixture of zeolites (laumontite, clinoptilolite, mordenite) and calcite at shallower and marginal levels suggestive of low to intermediate CO₂. This intergrowth of calcite and zeolites suggest fluctuating low CO₂ concentrations that vary as a function of boiling depth and could explain why veins are essentially barren and only locally mineralised. Therefore, when prospecting for epithermal deposits the occurrence or lack of zeolites and calcite veins and alteration can indirectly provide valuable insight into CO₂ levels and the potential for ore-grade veins.

Placer platinum-group minerals from Ivalojoiki and Lemmenjoiki rivers, Finnish Lapland

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The platinum group minerals (PGM) from the Ivalojoiki and Lemmenjoiki tributaries, Finnish Lapland, were studied from samples taken from till of the bedrock surface, river sand and gravel, sluice box ends and heavy mineral "black" sands from the prospectors. Gold washing has been done in the Ivalo and Inari rivers since the 19th century. The bedrock in the area belongs to the granulite belt of northernmost Finland. The granulites are metasedimentary rocks with mafic to ultramafic intrusions metamorphosed in granulite facies conditions. The dyke rocks consist of crosscutting and conform pegmatites, quartz-feldspar-porphyry veins and quartz-hematite veins, which cut generally the rocks of the granulite complex and have a general strike N-S with a vertical dip. Mafic diabase dykes are found in the Saariselkä area. The age determinations (Rb-Sr, monazite) suggest an age of ca. 2 Ga for the granulites. In the northern part of the granulite belt there is an Archean window with a minimum age of 2600 Ma by the whole rock common lead method.

A total of 45 PGM phases have been found as single macro or micro grains or as inclusions in other PGM. The minerals were analyzed with a Link EDS and Cameca SX 100 WDS at the University of Hamburg, Germany and previously with Cameca SX50 at GSF in Finland. The most common PGM phases are sperrylite PtAs₂, isoferroplatinum Pt₃Fe, cooperite PtS and braggite (Pt,Pd)S. The less common PGM are native Pt, Pt oxide, native Pt₂Pd, isomertieite Pd₁₁Sb₃As₂, mertieite I (Pd,Pt)₁₁(Sb,As)₄ and II (Pd,Pt)₈(Sb,As)₃, arsenopalladinite Pd₈AsSb₃, guanginitite Pd₃As, stibiopalladinite Pd₅Sb₂ stillwaterite Pd₈As₃, rustenburgite Pt₃Sn, moncheite PtTe₂, kotulskite Pd(Te,Bi), platarsite (Pt,Rh,Ru)AsS, hollingworthite (Rh,Pt,Pd)AsS, irarsite IrAsS, osarsite (Os,Ru)AsS, ruarsite RuAsS, laurite RuS₂, cuproiridsite CuIr₂S₄, cuprorhodite CuRh₂S₄, erlichmanite OsS₂, Os-Ir-Ru alloy, Ru-Ir-Os alloy, native Os, Os-Ir alloy, (Au, Ag)₄(Pd,Cu), (Au,Ag)₂(Pd,Cu), Pt-Cu, Pt-Fe-Cu, Au-Ag-Pd, Au-Pd-Cu alloys, xingzhongite (Ir,Rh,Pt)(Cu,Fe,Pb,Ni)₂S₄, hongshite PtCu, Cu-bearing isoferroplatinum, undefined PtTe, Pd₅As₂, Pd₁₁Te₂As₂, Pd₁₁Sb₃As₂ Pd₃(Sb,As,Sn) and Pd₁₁Te₂Se₂. The wide variety of the PGM in the placers studied indicates a complex and probably multi-stage PGE mineralization and alteration.

P16-01

Ore mineralogy of a high-grade epithermal silver mineralization at El Quevar, Argentina

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The epithermal mineralization of El Quevar occurs on the southeastern flank of a large stratovolcano complex (QSC) which covers roughly 1500 km² of the Puna High Plateau and ranges in elevation from ~ 4300 m up to 5780 m above sea level. The ore deposits are located in the valley of Incahuasi at an elevation between 4370 m (Mina Vince) and 4750 m (Mina Quespejahuar) above sea level, 270 km to the west of Salta which is the capital of the province. They were intermittently mined between 1939 and 1971, and exploration continued until 1989. High-grade ore contained up to 2000 oz of Ag/t.

The polymetallic mineralization is genetically associated with an Upper Miocene K-rich dacitic eruption which occurred along a major NW-SE trending wrench corridor (Calama-Olacapato-El Toro lineament). Alteration (argillic, advanced argillic, silicification) is very conspicuous, covers an area of 50 km² and can be traced over a vertical distance of 1000 m. The epithermal system is controlled by NE-SW oriented normal faults with a sinistral strike slip element.

The Ag-Pb-Zn-Sb-Bi-As ores preferably occur along the same structures. Three different ore types can be distinguished: vein type mineralization, ore pockets of an irregular shape and disseminated ore. A bonanza-grade ore shoot (Mina Armonia) measured 3 m in thickness and was hosted within a strongly silicified vuggy breccia dyke. Two ore-forming stages can be discerned. The early one is characterized by a fine-grained Ag-rich mineral assemblage in deeply interpenetrating textures. The assemblage consists of andorite type phases, aramayoite-baumstarkite, boumonite-seligmannite, diaphorite (including "brongniardite"), famatinite, freieslebenite, galena, members of the lillianite-homologous series, miargyrite, owyheeite, polybasite-pearceite, pyrrargyrite-proustite and zoubekite. EMPA revealed the presence of the Bi-analogues of diaphorite, freieslebenite and "brongniardite" as well as several compositionally unnamed mineral species in the ternary system Ag₂S-Pb₂S₂-S₂(Bi,Sb)₂S₃. Chemical zoning is very pronounced and the content/ratio of the semimetals strongly varying. The late ore-forming stage is dominated by galena, sphalerite and Pb-Sb(As) sulfosalts (boulangerite, robinsonite, plagiogite, laumayite, geocronite-jordanite).

The Ag-rich deposits of El Quevar are typical for a HS epithermal environment with a transition to the IS type in the peripheral parts. Ore formation took place at a depth between 250 and 500 m below surface at T < 280°C and at low P. The complex mineral assemblages and the chemical zonation of the minerals are indicative for a significant change of T, P and pH of the mineralizing fluids during formation of the ore deposit.

P16-02

Microparagenesis of germanium mineralization in polymetallic deposits of Bolivia and Argentina

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Germanium is an important high-tech element which is predominantly recovered as a by-product from low-temperature hydrothermal and carbonate-hosted Zn-Pb ores, from Kipushi-type Cu-Pb-Zn-Ge mineralization and coal deposits. Epithermal environments of Bolivia and Argentina might be another source of high-grade Ge mineralization. Significant Ge concentrations associated with bonanza-grade Ag ore occur at Porco, (Department of Potosí, Bolivia), which is one of the large Zn-Pb-Ag-Sn deposits in the Bolivian Ag-Sn belt. Porco is a typical vein-type deposit within a large caldera which is hosted by Ordovician metasediments. The high-grade Ag-Ge mineralization is confined to ribbon ore shoots in the upper parts of Zn-rich veins which show all the characteristics of open-space filling. The principal Ge mineral that accompanies the Ag-rich ore is argyrodite, Ag₂GeS₈, which is observed in massive ore bodies, in veins and veinlets, and rarely as highly complex crystals ranging in size from microscopic inclusions up to a few cm's. The associated minerals are Ag-(Pb)-Sb sulfosalts (pyrrargyrite, miargyrite, stephanite and diaphorite), sphalerite, galena and quartz. Acanthite, native silver, polybasite and pyrostilpnite were formed during supergene enrichment processes which resulted in a considerable increase of the grade of silver in the ore. The largest ore-shoot which contains high-grade Ge mineralization measured some 100 m along strike and dip with a maximum thickness of several meters. Capillitas is an epithermal deposit situated in the Miocene Farallon Negro Volcanic Complex of Catamarca, Argentina. Two different types of Ge mineralization can be distinguished. Type 1 belongs to the intermediate-sulphidation stage and is characterized by the presence of argyrodite and "arsenian argyrodite" with a As:Ge ratio of 2:1. The Ge-bearing ore is commonly associated with proustite, pearceite, acanthite and native silver and accompanied by sphalerite, galena, quartz and rhodochrosite. Type 2 was detected in an environment typical for the high-sulphidation stage. The mineral paragenesis is composed of enargite-luzonite, tennantite-goldfieldite, hübnertite, Sn-sulfides (e.g. colusite-nekrasovite and stannoidite) and tellurides (e.g. hessite and krennerite). Supergene enrichment processes led to the formation of high-grade bornite ore. This sulfide is host of several Ge minerals such as putzite, (Cu₄Ag_{1.4})₂GeS₆, catamarcaite, Cu₆GeWS₈, the Ge analogue of stannoidite, Cu₈Fe₂ZnGe₂S₁₂, and briartite. The assemblage of these Ge minerals - three of them represent new mineral species - is unique and has not been reported elsewhere. In the epithermal environment of both ore deposits, the Ge-sulfides have been formed at low temperatures (< 250° C) from solutions with a high sulphur fugacity.

P16-03

The Os-Mo-S system, a crystal-chemical and experimental approach

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The interest in the Os-Mo-S system is on the rise in connection with the increasing importance of the Re - Os geochronometer applied to molybdenite from ore deposits. The resistance of molybdenite to post-crystallization events is a key feature, and it depends primarily on the mode of presence of Os in the molybdenite structure. Phase relations in the limiting binaries have been reported in detail in literature (Brewer *et al.*, 1980; Fischman *et al.*, 1992; Taylor *et al.*, 1962), but the ternary Os-Mo-S system has not been studied. Therefore, we started an investigation of the phase relations in the Os-Mo-S system at 1000°C using the evacuated silica glass tube technique. Four minerals are known from the system: MoS₂ - molybdenite, OsS₂ - erlichmanite and native sulphur and osmium. Beside the minerals, a compound Mo₂S₃ (stable above 630 °C) and two intermetallic compounds Mo₃Os and Mo₂Os have also been reported. The ionic radius of Mo⁴⁺ is 0.65 Å, which is close to that of Os⁴⁺ (0.63 Å). Yet, MoS₂ and OsS₂ are far from isostructural. Molybdenite has a layer structure that occurs in the form of the more common 2H₁ polytype (hexagonal, P6₃/mmc) or the more rare 3R polytype (rhombohedral, R3m). The structure of molybdenite is based on the stacking of planar close-packed S-Mo-S layers. Each Mo atom is surrounded by 6 S in a trigonal prismatic VI-fold coordination. Erlichmanite is cubic (Pa³), and Os too is VI-coordinated, but the S atoms form a regular octahedron. Nonetheless, the similar atomic radii of Mo⁴⁺ and Os⁴⁺ make the possibility of Os substitution in molybdenite likely. According to the first results in the 1000°C isothermal sections, molybdenite and erlichmanite form a stable assemblage with Os. The phase Mo₂S₃ forms stable assemblages with Mo, Os and intermetallic phases Mo₃Os and Mo₂Os. The experiments performed so far indicate a low solubility of Os in MoS₂. At 1000°C, the solubility of Os in MoS₂ barely exceeds 0.15 at % Os. Not surprisingly, the Os contents of natural molybdenites are generally very low, on the order of p.p.b (Stein *et al.* 2001). It appears rather unlikely that the solubility limit of Os in MoS₂ would be exceeded in natural conditions, and consequently, all Os present must be dissolved in the molybdenite structure.

P16-04

Bieber – a widely unknown ancient Ore – Deposit in the Spessart – Mountains (Germany)

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The Bieber – locality includes at least three different types of historically mined ore – deposits:

- “Kupferschiefer” (blackshale) with mainly tennantite and galena (both silver – containing) and additional chalcopryrite,
- “Kobaltrücken”: hydrothermal veins with Co-, As-, Ba-, Fe – mineralization,
- „Eisensteinlager”: oxidic iron – ore deposit in upper permian limestones.

These occurrences have been described first by CANCRIN (1787) and then by BÜCKING (1892) more than hundred years ago. A new investigation of the former ore – deposits has been carried out in the last ten years with a special focussing on mineral assemblages and up to now not defined minerals.

Moreover Bieber/Spessart is type – locality for bieberite and rösslerite.

P16-06

Uranyl-selenites, unique minerals of Musonoï Mine, Katanga, DRCC. Pirard¹, F. Hateri¹¹ Laboratory of Mineralogy and, B18, University of Liège, B-4000 Liège, Belgium.
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Musonoï Mine lies in the western part of the Katanga copperbelt, in the Kolwezi thrust outlier. This Cu-Co mine shows a tectonic unit called thrust-slice 2400 (‘*écaillé 2400*’) which has a typical Cu-U-Se mineralization. This ore body has given magnificent examples of uranium-bearing minerals such as vandenbrandeite, cuprosklodowskite or torbernite but it has also provided 4 new species of uranyl-selenites which were described in the 70’s.

The present study has permitted to make an inventory of the minerals occurring at Musonoï, and to better characterize their chemical compositions by using electron microprobe. The growing environment of uranyl-selenites and their sequences of crystallization together with other minerals are also discussed.

Selenian digenite [Cu₂(S,Se)₂], berzelianite [Cu₂Se] and trogtalite [(Co,Cu,Pd)Se₂] are the primary minerals. Their main alteration products are chalcomenite [CuSeO₃·2H₂O] and cobaltomenite [CoSeO₃·2H₂O], which can be found in several places through the deposit. These electric-blue and red-pink crystals are common oxidation products in selenium-bearing rocks.

Four of the seven known uranyl-selenites have been first described at Musonoï Mine and do not seem to occur elsewhere in significant amounts. Guilleminite [Ba(UO₂)₂(SeO₃)₂·O₂·3H₂O], marthozite [Cu(UO₂)₂(SeO₃)₂·8H₂O], and its dehydrated equivalent with 6H₂O, are frequent in cavities filled by their yellow and green plates. Relationships with other copper- and uranium-bearing phases indicate that these two minerals crystallize at all stages of the alteration process. Bottle-green pinacoids of demesmaekerite [Pb₂Cu₃(UO₂)₂(SeO₃)₆(OH)₆·2H₂O], frequently dehydrated in brownish crystals and olive-green derriksite [Cu₄(UO₂)₂(SeO₃)₂(OH)₆], are far less common and generally occur as crusts on cobaltoan malachite. Genetic relationships seems to show that demesmaekerite appears quite early in the deposit, just after the crystallization of barium-bearing minerals (guilleminite, barite) and before the crystallization of vanadates (sengierite, volborthite). Derriksite is a late phase crystallizing with the last uranyl-sulfates (cuprosklodowskite, α-uranophane).

During this work, at least one new uranyl-selenite has been discovered, with a (H₃O)₄(Cu,Mg,Ca)(UO₂)₂(SeO₃)₂(CO₃)₄·H₂O composition. The yellow-green platy crystals are associated with marthozite and seem to be related with the latest deposition of rutherfordine and soddyite in the ore body.

P16-05

Tephrochronology of the manganese wad deposit at the Akan Yunotaki hotspringH. Miura¹, K. Wada², and Y. Katsui¹¹Department of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8, Sapporo, 060-0810, Japan.

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An outcrop of manganese oxide about one meter thick, inter-bedded with several volcanic ash layers, is found at the Yunotaki hotspring, Hokkaido, Japan. The manganese wad is precipitated from hydrothermal water. On the basis of the previously known age of the inter-bedded volcanic ash layers, linked to well-known eruptions, it has been possible to determine the chronology of the manganese oxide precipitation. The ash layers were identified by the chemical composition of the separated volcanic glasses. Since the lowermost manganese oxide layer occurs immediately above the mud flow of Mt. Ponnmachineshira without the presence of any intermediate soil layer between them, its age of formation could be near the age of the mud flow, i.e. 4500 – 5000 years BP. The manganese oxide layers in the top 50 cm of the outcrop are comparatively softer than those occurring below 50 cm and commonly have the texture of the aggregate of a filament structure. Manganese oxide layers occurring below 50 cm is hard and has a diagenetically altered texture reflecting change in the filament structure to a grain aggregate structure. These oxides have lost their structural water and the mineralogy has begun to change from 10 Å phase to 7 Å phase during the diagenetic process.

P16-07

New phase relations of the system Fe–Ni–S at temperatures from 875 to 450°C as the pentlandite ore-genesisA. Sugaki¹ and A. Kitakaze²¹Kadan 4-30-503, Aoba-ku, Sendai, 980-0815, Japan

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High-form pentlandite (Fe_{4.94}Ni_{4.06}S_{8.00}) first crystallizes as a product of a pseudoperitectic reaction between monosulfide solid-solution and liquid at 870°C and forms a limited solid-solution from Fe_{5.07}Ni_{3.93}S_{7.85} to Fe_{3.74}Ni_{5.26}S_{7.85} at 850°C. This solid-solution grows rapidly toward the Ni-rich side with decreasing temperature and joins β₂(Ni_{3.77}S_{3.00}) on the Ni–S boundary at 806°C. β₁(Ni_{2.65}S_{2.00}) first appears on the Ni–S boundary at 800°C and forms independently a limited solid-solution (Fe_{0.36}Ni_{2.63}S_{2.00} to Ni_{2.85}–3.43S_{2.00}) jutting from the Ni-S boundary into a ternary field at 600°C. Crystallization of the Fe- and metal-rich extreme high-form pentlandite from liquid finishes at 762 and 739°C, respectively, because of tie-line changes. Consequently, crystallization of high-form pentlandite from liquid finishes at 739°C. Liquid occupies a wide field in the metal-rich portion of the system above 850°C. However, its field reduces and retreats to the Ni-rich side with decreasing temperature, and finally disappears at its eutectic of 637°C and Ni_{0.67}S_{0.33}. Pentlandite (Fe_{3.59}Ni_{3.41}S_{7.85}) first appears due to a phase-transition of Fe-rich extreme high-form pentlandite at 625°C, grows as limited solid-solutions from Fe_{5.62}Ni_{3.38}S_{7.82} to Fe_{3.24}Ni_{5.76}S_{7.85} at 600°C and from Fe_{5.63}Ni_{3.35}S_{7.92} to Fe_{2.42}Ni_{6.58}S_{7.92} at 500°C due to a continuing phase-transition (625 to ~550°C), exsolution (625 to 503°C) and breakdowns (pseudo-eutectoids at 625 to 579°C and 579 to 503°C) of high-form pentlandite and exsolution (below 579°C) and breakdown (pseudo-eutectoid at 579 to 484°C) of β₁. Pentlandite solid-solution also grows slightly fat in S-composition due to exsolution (below 625°C) of monosulfide solid-solution. Pentlandite coexists with high-form pentlandite (625 to 503°C), monosulfide solid-solution (below 625°C), γ (below 617°C) and/or β₁ (579 to 484°C). A metal-rich portion of the high-form pentlandite solid-solution still remains stably below 600°C, but retreats to the Ni-rich side with decreasing temperature and finally disappears by breakdown to pentlandite, high-form godlevskite and β₁ at 503°C and Fe_{1.01}Ni_{7.97}S_{6.94} (eutectoid). β₁ also breaks down to pentlandite, heazlewoodite and γ at 484°C and Fe_{0.26}Ni_{2.87}S_{2.00} (another eutectoid). The assemblages with pentlandite and high-form godlevskite or heazlewoodite first appear at 568 or 498°C, respectively. This study shows that pentlandite in the Ni-Cu ores can form at temperatures from 625 to 500°C or less due to phase-transition, eutectoid and exsolution of high-form pentlandite, monosulfide solid-solution and β₁, which are the primary phases that would crystallize from sulfide magma (liquid in the system Fe–Ni–S) at around 1,000 to ~750°C.

Sodalite from Cerro Sapo, Bolivia: Bridge between archeology and mineral sciences

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Ancient societies in the Central Andean region much appreciated blue sodalite, as shown from archeological sites located especially in northern Peru. Cylinder-shaped or round beads and ritual objects made of sodalite have been found in the cultural manifestations corresponding to the Formative Period both in the highland, i.e. Cerro Blanco (1300-1200 BC) and Kuntur Wasi (1100-800 BC), and on the Pacific coast, i.e. Puemape (1300-1200 BC) and Morro de Etan (800 BC). Common features such as color, paragenesis, texture and chemistry of the sodalite-bearing samples suggest that this material was derived from the same place. The sodalite-ankerite-sulfides association omnipresent in the beads links to the Cerro Sapo mine, located 1800 km south in the Ayopaya alkaline province of Bolivia. At Cerro Sapo the carbonatite-alkaline rock association of Cretaceous age, unique in South America, includes a nepheline-syenitic stock associated with a small intrusion of carbonatite and a variety of dikes. The sodalite-ankerite-barite dike, the youngest rock unit of the alkaline complex, 3 km long and up to 8 m thick is mined for blue sodalite identical to that from the archeological sites. Sodalite occurs as nearly monomineralic bodies, up to several meters large, and with ankerite, in magmatic textures as irregular patches or narrow rhythmic layering suggesting crystallization from concomitant carbonatite and silicatemelts (Schultz et al., 2004). Spots and fine veinlets of chalcopyrite, galena, pyrite, magnetite, ilmenite, analcime, natrolite and goethite are also observed. The magnetite-ilmenite pair suggests formation temperatures of 500-600°C based on data by Ghiorsio and Sack (1991). In the central part of the dike, the sodalite is accompanied by ankerite, and sodalite-ankerite-barite occur in the marginal zone; "pegmatitic veins" and veins cross-cut the magmatic textures. Preliminary microthermometric measurements on sodalite and barite show homogenization temperatures between 240 and 380°C, indicative of a hydrothermal environment. The contemporaneous liquid-rich and vapor-rich inclusions homogenize to liquid and vapor, respectively, and denote that immiscibility was involved. This assumption is supported by the array of fluid inclusions apparently trapping hydrocarbon- and/or CO₂-H₂O fluids with a very different volume ratio, located close to minute specks of an unknown dark material. The present study reveals the location of the source of sodalite found in archeological sites of northern Peru which was transported over about 1800 km of distance. Thus the gemstone from Cerro Sapo serves as a valuable indicator of "trade" paths across South America during the Formative Period and helps to understand the cultural development of the Central Andean region.

Cathodoluminescence study of gold ore at the Harmony mine, Witwatersrand Basin, South Africa

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The genesis of the gold ores in the Witwatersrand Basin, the world's largest gold-producing province of South Africa, has been a controversial topic for many years. A modified palaeoplacer model, grains of gold as well as rounded pyrite and uraninite grains were detrital in origin and they deposited together with host conglomerates under reduced atmosphere, has been predominantly believed. However, some researchers proposed that these minerals precipitated from a hydrothermal fluid. In this study, mineralogy and texture of minerals in the Harmony gold mine will be described. These samples were also observed by cathodoluminescence microscope, and this technique will help understanding the genesis of gold ore.

The gold ore of the Harmony mine is hosted by conglomerate of the Basal Reef, Central Rand Group. The conglomerate contains detrital rock fragments such as quartzite, shale, with minor greenstone. It accompanies mineral fragments of quartz, feldspar, zircon, chromite, pyrite, uraninite and minor gold. Quartz grains in the studied samples typically occur as rounded pebbles or granules. Under a cathodoluminescence microscope, quartz shows various colors, light blue, bluish purple, reddish purple, orange and brown. Preservation of several colors suggests that the metamorphic grade of conglomerate is very low. Grains of quartz were probably supplied from different source rocks because luminescence colors of quartz pebble are variable even in neighboring pairs. Quartz grain shows zonal texture with inner part and thin rim under the cathodoluminescence microscope. A thin layer with reddish luminescence typically over grows the inner part of a quartz grain, which shows bluish to brownish luminescence. Such texture of quartz suggests that the inner parts of quartz grains represent detrital part, and that the outer parts were formed during the diagenetic stage. The relationship between detrital grain of gold and overgrowth part of quartz will be discussed.

Structural and textural variations of epithermal Au-Ag vein quartz -Koryu deposit in Hokkaido, Japan

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This study presents a review of quartz morphology of Koryu Au-Ag veins and an assessment of morphological variations of quartz between the Koryu deposit and Japan's biggest Au-Ag deposit, Hishikari. Koryu was a small gold-silver quartz vein deposit in Hokkaido, Japan. The deposit occurred in the Pleistocene (1.4-0.85Ma) within Miocene sedimentary rocks. Shimizu et al. (1998) showed that two mineralization episodes-earlier and later, have been identified based on the cross-cutting relationship of the veins. The earlier and later episodes are further divided into three and seven mineralization stages, respectively. Koryu veins were characterized by well-developed quartz banding with various structures (on macroscopic scale) and textures (on microscopic scale): The structures mainly consist of comb, fine-grained, colloform and cockade while textures are composed of comb, feathery, microcrystalline and colloform. Microcrystalline quartz is associated with electrum. Although the veins locally show complicated brecciation and spatially restricted mineral assemblage, the individual mineralization stages were traced over a distance of 60 meter vertically and 100 meter horizontally because of their distinct physical appearance such as color, structures and textures in the veins. Fluid inclusion study showed that the paleodepth of bonanza zone was estimated at 430-850 m. The quartz morphology combined with fluid inclusion study suggest that boiling of hydrothermal fluids occurred repeatedly, leading to silica-supersaturated conditions with respect to quartz and resulting in the formation of the banded vein with various quartz structures and textures. Compared to the Hishikari deposit, Koryu has several characteristic features: 1. Koryu veins occur in a smaller zone of about 0.5km² than that of Hishikari (~2km²). 2. Koryu bonanza veins show more conspicuous morphological changes of quartz (e.g., line-grained to coarse-comb crystals with geometrical selection). 3. Fluid inclusion study showed that representative vein-formation temperatures (233-283°C) were higher than those of Hishikari (210-230°C, Sanematsu et al., 2005). 4. Electrum usually occurred in Ginguro bands enriched with Pb-Zn-Cu-Fe sulfides. These characteristic features suggest that the distinct morphological changes of quartz in Koryu bonanza veins could represent a smaller, hotter and deeper epithermal vein system than that of Hishikari.

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Geochemistry and species of major and rare elements in Fe-Mn crusts from sub-sea mountains of NW Pacific Ocean

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According to the results of combined investigation of geochemistry, mineralogy and technological features of Fe-Mn crusts from sub-sea mountains, their major and rare elements assume several forms such as being sorbed on Mn and Fe hydroxides as well as entering the lattice of major and accessory minerals or forming their own minerals including native metals or intermetallic compounds. Mn and Fe form mineral phases such as vernadite, being the principle one, asbolane, todorokite, goethite and feroxyhite. According to experimental results and interelement correlations, Co, Pb, Zn, Ni and most of Ce relate to Mn phase whereas Pb and V are partly related to Fe phase. As for Co and Zn, they enter partly the lattice of ferruginous vernadite (Co) and heterolite (Zn). The rare Co-hydroxide heterogenite is also found. Along with oxides the crusts host some trace amounts of sulfides including pyrite, chalcopyrite, sphalerite, galena, covellite, chalcocite, molybdenite, bornite, tennantite, argentite and some others, as well as rare silicides, carbides and chlorides. The native metals are represented by Fe, Al, Cr, Ta, Co, Ni, Cu, Pb, Zn, Pt, Au and Ag. Pt is found forming relatively large plate, flaky or drop-shaped particles. The occurrence of Pt increases evidently in the regions being abundant in Ca and P, but depleted in Mn and Fe. The most abundant among the non-metal minerals is apatite (carbonate-apatite, fluorapatite, hydroxylapatite) which is hosting Sr, Ba, and F along with rare earths and U minerals. Monazite and bastnasite particles less than 0.5 microns in size are found in the carbonate-phosphate material presented in the ore parts of the crusts. Xenotime is found forming crystals of square section of size 0.3 microns in the fine-dispersed aggregate of vernadite. In general the crusts are polygenetic owing their growth to the supply of ore material from various sources including deposition from sea water, seeping from underlying weathered rocks and episodic input from postvolcanic hydrothermal activity.

Mineralogical description and their Biosignatures of Kuroko Ore minerals

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Kuroko is multi-metallic ore of Cu, Pb, and Zn etc. and characteristically occurs in Japan. The ore consists of sphalerite, galena, chalcopyrite, barite etc. The geologic age of the Kuroko is Miocene. The genesis had variously been discussed. Kajiura (1983) has proposed PUMOS (Primitive Undifferentiated Metallic Organic Sediments) and suggested the same origin of petroleum and the Kuroko ore. Some sulfide isotopic data (Komuro, 1987) support this idea. However, no detailed mineralogical data suggesting biogenic origin have been shown yet.

We carried out detailed observation of textures and structure by microscopic methods. Enohji (1987) classified Kuroko ores into three types; type I, II and III. Based on this classification we examined many ore samples. Type I has fine grained textures. The ore samples of type I often have varieties of spherulite, concentric thin band (Baumkuchen-like) texture and colloform textures. Some of the colloform textures which consist of pyrite have characteristic stromatolitic structure. This suggests biogenic origin of Kuroko ore.

Fe-precipitation is estimated at earlier stage (Komuro, 1987). Furthermore, sphalerite in type I has thin lamellar twin structures. On the other hand, sphalerite of type II and III ores having nano scale GP zone structures has been found. No stromatolitic textures were found in type II and III ore samples. The correspondence of these nano structures, ore types and biosignature in type I is characteristic, based on ore formation process.

GP zone has enrichment of Cu and Fe in the disk region. These are due to Cu and Fe-containing solid solution in sphalerite which correspond to the sphalerite growth under Cu rich environment in later stage of the Kuroko formation processes. On the other hand, sphalerite in type I with less Cu contents corresponds to the earlier of formation stages with stronger biological activities.

Bismuth-bearing minerals in some tin-silver-lead-zinc deposits of Verkhoyansk fold belt (Sakha-Yakutiya, Russia)

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Tin-silver-lead-zinc deposits of Verkhoyansk fold belt (Sakha-Yakutiya, Russia) that composed of carbonate-quartz-sulphide veins contain numerous bismuth and bismuth-bearing minerals. These veins are located in Tryassic sandstones and claystones and associated with post-collision granitoids. Major constituents of veins are rhythmically-zoned coarse-grained carbonate-sulphide and fine-grained quartz-sulphide mineral aggregates. These bismuth and bismuth-bearing minerals are part of a complex sulphide-sulfosalts assemblage of microscopic to submicroscopic (<10 µm) intimately-intergrown accessory phases. They are intimately associated with chalcopyrite and tetrahedrite. Results of electron probe micro analysis (EPMA) allowed to identify minerals of bismuthinite-aikinite ($\text{Bi}_2\text{S}_3\text{-CuPbBiS}_3$) and lillianite-gustavite ($\text{Pb}_3\text{BiS}_6\text{-AgPbBiS}_6$) series, bismuthian miargyrite. EPMA data points lies within compositional ranges ascribed to friedrichite ($\text{Cu}_{15.00-1.97}\text{Pb}_{4.96-4.85}\text{Bi}_{6.88-6.94}\text{S}_{18.04-18.12}$) with $n_6 = 84-83$ (where n_6 - percentage of the CuPbBiS_3 end-member in the $\text{Bi}_2\text{S}_3\text{-CuPbBiS}_3$ series in accordance with classification of E. & M. Makovicky), lindstromite ($\text{Cu}_{12.70}\text{Pb}_{2.68}\text{Bi}_{6.71}\text{S}_{15.80}$) with $n_6 = 57$, gladiite ($\text{Cu}_{10.96}\text{Pb}_{0.95}\text{Bi}_{4.63}\text{S}_{9.41}$) with $n_6 = 34$ and between those characteristic of peckoite ($\text{Cu}_{1.24}\text{Pb}_{1.39}\text{Bi}_{0.90}\text{S}_{18.27}$) and gladiite with $n_6 = 24$. Nearly continuous compositional range intermediate between gustavite and andorite was found. The Sb/(Sb+Bi) ratio in these compounds varies from 0.1 to 0.93. Two line of explanation for this phenomena could be suggested: 1) this compositional trend is due to analysis of sub- to nanoscale intergrowths of gustavite and andorite. 2) the substantial isomorphous substitution of Sb for Bi in andorite and Bi for Sb in gustavite can occur. The substitution of Bi for Sb was found in bismuthinite. This mineral contains up to 32.8 wt. % of Sb. An occurrence of coexisting grains of antimonian bismuthinite different in the Sb content (3 to 9 wt. %) suggests the immiscibility gap between bismuthinite and stibnite. High bismuth content (up to 15 wt. %) in miargyrite, while coexisting pyrrhotite and stephanite do not incorporate bismuth. EPMA data points obtained are interpreted as isomorphous substitution between high temperature cubic modifications $\beta\text{-AgSbS}_2$ and $\beta\text{-AgBiS}_2$. A considerable isomorphous substitution of Bi for Sb in low temperature of 150 to 220°C (based on fluid inclusion study) seems to be resulted from a metastable crystallization of minerals from supersaturated fluids due their supercooling.

Sulfur Isotope Characteristics of Carbonate-Hosted Pb-Zn Deposits Occurring in the Central Taurus Mountains (Southern Central Turkey)*

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A great number of carbonate-hosted Pb-Zn mineralizations occur in the central Taurus Mountains known as Aladağlar-Bolkardağ range. Majority of these deposits mainly have potentials for lead and zinc, to a lesser extent, for gold and silver. In this study, all the mineralizations occurring from Yahyalı (Kayseri) to Anamur (Mersin) area have been sampled for sulfur isotope analyses.

Most of the deposits occur in an area known as Aladağlar and Bolkardağ districts, which are divided by the Gülek through. About 22 occurrences have been recorded. For most of the deposits, galena was selected for isotope analyses since it is the only primary sulfide mineral survived pervasive oxidation due mainly to its relatively higher resistance to surficial conditions. Where it is not found or present either pyrite or sphalerite was employed.

Two methods were utilized for sample preparation. For one set of samples, galena crystals were picked under a stereomicroscope with the aid of tweezers from crushed/semi-powdered samples. For the second set, samples were acquired from polished plugs or hand-size slabs by employing a micro-driller. Sulfur isotope results from both sets representing identical samples well agreed. $\delta^{34}\text{S}$ values range between +0.46 and +11.73 ‰. Most of the values are considered within a narrow magmatic range. Higher values are attributed to enrichment in ^{32}S due to oxidation and/or contributions by evaporitic formations contained by the regions rocks. The Horozköy mineralization was considered to be of distinct origin with different ore mineral paragenesis.

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TEM mineralogy of Mn oxide in sedimentary and biogenic manganese ore in relation to origin of trilling in todorokite

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Varieties of manganese dioxide have complex structure. They are classified into layer structure and chain structure, based on different sharing of MnO_6 octahedra (Golden et al, 1987). Buserite and birnessite are the examples of layer structure type, and todorokite is the example of manganese oxide with chain structure. In todorokite edge-sharing chains of MnO_6 octahedra form tunnel structure.

Sedimentary manganese ores of Miyazaki mine, Shitada mine and Ikeshiro mine which are in green tuff region in Japan, and modern and recent manganese precipitation at Yunotaki (Mita, 1994) were comparatively examined. They are composed mainly of todorokite and manganite.

In the sedimentary manganese ores from Miyazaki mine, banded structures which are similar to stromatolite-like structure were found under microscope. In HRTEM observation of the samples from sedimentary ores, trillings of todorokite are often found.

In recent Yunotaki ore specimens, nucleation stage of trilling was found. TEM image shows that on the 7 Å lattices, a few narrow of lattices of 9.8 Å ~ 19.9 Å in three equivalent directions with rotation of 120° were found. 10 Å ~ 20 Å lattices may correspond to chain-width disorder todorokite. It suggests that primary mineral of buserite formed by bacterial activities at Yunotaki has changed to precursor mineral of todorokite which had initial stage of trilling structure. Transformation of buserite to todorokite in immersed into hot water has already been reported by Halka (2002). The recent Yunotaki sample is probably some hundreds or thousand years old. So, in these relatively young precipitations, diagenetical change has not perfectly completed. This means that origin of todorokite trilling may be originally planar birnessite (Post and Bish, 1988), buserite, or similar planar type manganese oxide mineral of sedimentary or bacterial origins.

Trilling of todorokite was found in stromatolite-like structure in the manganese ore of Miyazaki mine. From structural characteristics, it might also have been originally planar manganese oxide mineral like Yunotaki minerals. Characteristics of chain-width disorder were described for each sample by HRTEM.

Micro-scale mineralogical study on the Toarcian manganese ore deposit, Úrkút, Hungary

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The Úrkút, Hungary manganese ore deposit, the largest, still mined, manganese accumulation in Europe related to the Toarcian Anoxic Event, has been studied by many authors for several decades by applying different, mainly geochemistry and/or sedimentology centred scientific approaches. Many theories have been introduced on the formation and the subsequent overprinting processes of the deposit, but, due to the complexity of the locality, without any general acceptance. Our current systematic micro-scale mineralogical studies are going to give a solid base for the further reconstruction of the ore forming processes.

The sedimentary complex consists of a lamellar pyritic dark, mainly grey-black, radiolarian marl ("black shale") sequence containing two manganese-bearing horizons. The lower horizon of a maximum thickness of 10–12 m ("Main Ore Bed") and the upper horizon ("Bed #2"; maximum thickness 4 m) are separated by 8–15 m-thick dark grey-black radiolarian marl. Manganese occurs both in carbonate and oxide phases in the ore, with the major part of the oxide being a secondary product. Both ore beds have fine lamellar structure representing the same sedimentological background as the hosting black shale. The radiolarian marl sequence is covered by a brown chert bed of 0.2–0.3 m thickness.

A complete section ("Profile C") was sampled in a drift of the active mine (shaft #3; level 175 m). The fine lamellar samples with alternating dark and light laminae were embedded in epoxy resin and thin sections were prepared under dry conditions to avoid the washing out of clay. Thin sections were studied by polarised light microscopy and scanning electron microscopy (equipped with EDX system). Systematic XPD measurements were carried out on full and separated samples through the complete section.

The mineral composition is highly variable throughout the sequence. One of the key features of the whole profile is the large variability of mixed Mn–Ca(–Fe)–Mg carbonates. The lower horizon contains a characteristic Ca-bearing rhodochrosite ($d_{104}=2.85$ Å). The upper horizon differs significantly from any other beds of the complex with the unique presence of three carbonate types; almost pure calcite ($d_{104}=3.03$ Å), rhodochrosite with Ca substitution ($d_{104}=2.87$ Å) and rhodochrosite with Fe and Ca substitution ($d_{104}=2.83$ Å). Double carbonates ($d_{104}=2.89$ – 2.90 Å) are also present in limited amount in some parts of the profile. The textural connection of the different carbonate phases just as well as the role of pyrite originally present or missing in particular beds are also discussed.

PT constraints on the formation of large brucite deposits: a case study from the Apuseni Mnts., Romania

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In the Apuseni Mts. (NW Romania) various hornfelses, skarns, and hydrated metasomatic rocks formed at the contact between Mesozoic sedimentary rocks and two large Late Cretaceous-Early Paleogene granodioritic intrusives (*banatites*). Large brucite-bearing zones occur in the Anisian calcitic-dolomitic marbles forming two main deposits: Budureasa in the north and Pietroasa in the south. The irregular, sometimes lens-shaped brucite-bearing zones range from several meters up to tens of meters in width and from tens to hundreds of meters in length. The bulk chemical analyses of the brucite-bearing dolomitic limestones point to an inhomogeneous brucite distribution inside both deposits, with either brucite-rich (up to 40%) or brucite-poor domains (less than 5% brucite).

Brucite occurs mainly as small thin lamellas, grouped in three types of clusters: a) small, isometric clusters, rarely containing relics of periclase; b) large, irregular-shaped clusters, often containing carbonate relics; c) oval-shaped clusters, with brucite associated with forsterite relics and serpentine minerals. Microprobe investigations show 86.05–86.51% of MgO in brucite, and the presence of the same mixture of calcite + dolomite grains inside the brucite cluster as in the surrounding carbonate mass.

The studies carried out on the formation of brucite reveal a model of heating and cooling sequences under an assumed pressure of 0.1 GPa for the contact metamorphism, inferred from the field relations. The brucite-bearing assemblages can be described in the system: CaO–MgO–SiO₂–H₂O–CO₂. The following minerals were considered: calcite-dolomite-periclase-brucite-forsterite-antigorite. The phase diagrams show that the stability field of brucite is restricted to the very low X_{CO_2} in a wide range of temperatures. The upper temperature stability limit of brucite is near 600–610°C, according to a prograde reaction, which generated periclase: dolomite → periclase + calcite + CO₂, followed by a retrograde reaction, which generated brucite by the decomposition of periclase: periclase + H₂O → brucite. The direct decomposition of dolomite into brucite and calcite can take place over a wide range of temperatures, from 600 down to ~350°C. Lower temperatures, close to 400°C, can be estimated from the decomposition of forsterite into brucite and antigorite.

O17-01

The magmatic-hydrothermal transition in barren vs. mineralized intrusions

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The magmatic-hydrothermal transition is one of the most critical stages in the development of magmatic-hydrothermal ore deposits. Our current understanding of the processes operating at this stage is based almost exclusively on experimental and theoretical work, because corresponding natural samples are difficult to find, and because the in-situ quantitative analysis of co-existing fluid and melt inclusions is a non-trivial task. Some fundamental questions concerning the mineralization process have thus remained unanswered: (1) Were the fluids in mineralized intrusions more metal-rich than those in barren intrusions? (2) If not, why did the barren intrusions not become mineralized? (3) If yes, what was the cause for the higher metal content in the fluid from the mineralized intrusions?

To shed more light on these questions we present new and already published LA-ICP-MS data from fluid inclusions and coexisting melt inclusions (where available) from four barren intrusions, four porphyry-Cu deposit, two porphyry-Mo deposits, one Sn/W-granite and one REE-mineralized intrusion. The data are complemented by information on the physical state of the fluids at the time of unmixing from the residual silicate melt (single-phase vs. two-phase), corresponding fluid salinities, and reconstructed P/T-conditions of inclusion formation.

The results suggest that the mineralization potential of the studied intrusions already was pre-determined by the metal-content of the exsolving fluids, as the lowest metal concentrations generally were found in fluids from barren intrusions, the highest Cu-concentrations in fluids from porphyry-Cu systems, and so on. Hence, the absence of economic mineralization in the barren intrusions was caused by a lack of metal-rich fluids rather than by a lack of fluid focusing or metal precipitation. The higher metal content in the fluids from mineralized intrusions could be either due to a higher metal concentration in the magma from which the fluids exsolved, and/or due to a more efficient metal fractionation into the fluid. The first possibility is difficult to test because the metal content of residual melts constantly changes during crystallization and concomitant fluid exsolution. The second possibility seems to be supported by a higher fluid/melt partition coefficient of copper in Santa Rita compared to that in barren systems. Consequently, the question remains as to whether parental magmas of mineralization are already enriched in ore elements relative to barren magmas.

O17-02

Study on melt inclusions in zircon in igneous rocks from various regions in China

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Melt inclusions in zircon in igneous rocks such as granite, alkaline rock, and basalt from over 20 rock mass of different regions in China were studied. Observed inclusions included single-phase solid, two-phase, multi-phase and immiscible phase melt inclusions, in shapes mostly ellipse, strip or irregular. Their prolate axis is often parallel to the C axis and sizes various from 3x6 µm to 20x60 µm, a few up to 6x142 µm. Gaseous phase is 1-25%.

The homogenization temperature of melt inclusions in zircon were measured with the following results.

Acid rocks: Granite and quartz porphyry is 780-1,200°C. Among these, REE, W and Sn bearing rocks from Lianhuashan, Guangdong and Gejiu, Yunnan is 800-1,200°C that is higher than 780 ~ 980 °C of Au bearing granite from Taishang and Hetai, Guangdong. In same region, for instance Gejiu, Yunnan, earlier phase (porphyritic biotite granite 900-1,200 °C) is higher than later phase (fine-to-medium grain biotite granite 800-1,000 °C). Homogenization temperature of younger age granite such as Neoproterozoic rock mass (950-1,100 °C) of Hannan, Shanxi is slightly higher than the elder Proterozoic Erxianzi rock mass (950-1,000 °C) in same region.

Neutral to acid rocks: In the middle to lower Yantse River region, the homogenization temperature of melt inclusions in zircon in granite and diorite is 740-1,080 °C. In the same rock mass in Gaozi-Xiashu, Jiangsu, the margin phase is 900-1,080 °C, the intermediate 880-900 °C, and center 740-840 °C.

Alkaline rocks: Melt inclusions in zircon in magmatic origin alkaline syenite from Saima, Liaoning is 950-1,000 °C.

Basic rocks: Melt inclusions in zircon in basalt from Penglai and Leizhou Peninsular in Hainan Island are 1,040-1,100 °C and 1,050-1,080 °C, respectively.

Scanning electron microscopy energy spectrum was utilized to conduct compositional analyses of inclusions in zircon. Data from 10 measuring points in melt inclusions in zircon in Gejiu granite indicate that SiO₂ is 52.89-75.05%, Al₂O₃ 3.29-35.90%, ZrO₂ 0.76-17.88%. The majority are zirconium bearing silico aluminate and glass. Comparing to the source rock components, P, Zn, Ti, and Cr are higher while Na, K, Ca, Fe, and Si lower, which is the character of earlier phase zirconium bearing salic magma. Zirconium bearing silicate glass and other 4 daughter minerals were detected from 16 measuring points of the melt inclusions in zircon in mylonite from Hetai gold deposit granite.

O17-03

The significance of hematite-filled nano-inclusions in feldspars

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Transmission Electron Microscopy shows that red-clouded alkali feldspars from granitic rocks contain numerous pores up to several hundred nanometres in cross section, and that almost every pore contains rosettes or needles of crystalline hematite. In the samples described here, the hematite forms at the reaction interfaces at which plagioclase feldspar is hydrothermally replaced by alkali feldspar. The replacement is pseudomorphic involving a coupled dissolution-reprecipitation mechanism. This generates a porosity within which hematite is precipitated from an Fe-bearing fluid phase and preserved within fluid inclusions. The generation of porosity due to such fluid-rock interaction processes depends on both the molar volume changes involved and more importantly, on the relative solubilities of the parent and product phases in the fluid. Both fluid and melt inclusions can be generated whenever a solid phase reequilibrates in the presence of a fluid or melt. Other examples include the generation of melt inclusions in 'dusty' plagioclase rims which have resulted from reequilibration in magma, described by Nakamura and Shimitaka (EPSL, 1998), and also the formation of monazite within fluid inclusions in reequilibrated fluorapatite, described by Harlov et al. (CMP, 2005).

O17-04

Origin of the fluorite mineralization in the Tajno alkaline Massif (NE Poland) - evidence from fluid inclusions and petrological study

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The Tajno Massif is a differentiated pluto-volcanic alkaline-carbonatite complex intruding the Proterozoic crystalline basement in NE Poland, that is a part of East European Craton. It is a 5 sq. km intrusion covered by 600 m thick Phanerozoic sediments. The Tajno rocks are composed of clinopyroxenites and syenites with a 800 m diatreme pipe which contains chimney breccia cemented by carbonatites with fluorite mineralization. The only published K-Ar age of the Tajno massif is 327 Ma but new U-Pb data measured recently by SHRIMP (work in progress) have indicated Carboniferous ages contemporaneous with Kola Alkaline Province of NW Russia. Three stages of carbonatite emplacement have been documented. They form veins (up to 50 cm thick) of calcium, magnesium, iron, manganese and REE carbonates with up to 60% of fluorite. The late-stage carbonatite activity in the Tajno massif is mainly Mg- and then Fe-rich, as compared to the Ca-rich carbonatites formed at early stage. These late carbonatites contain quartz and silicate minerals eg. zeolites and REE-rich minerals. The following REE bearing minerals are the most abundant in the Tajno carbonatites – burbankite, parisite, synchysite and bastnaesite. The average REE content for the complex, in terms of oxides, is estimated to be 0.33 wt.%. The rocks are very unusual by their low Nb(Ta) content.

The cathodoluminescence (CL) studies revealed crushed and healed grains of carbonatites and fluorites as an evidence of unstable tectonic environment. Mosaic zoning and presence of REE (mainly Ce, Gd, Er and Dy) in fluorite structure were noticed due to CL investigations too.

Total of 103 fluid inclusions in fluorite were investigated in heating-freezing stage and also 10 after opening by electron microprobe. Seven types of inclusions were recognised, filled by: a) aqueous solution, gas bubble and 4-5 daughter minerals like halite, sylvite, calcite, brenkite, dawsonite, burbankite, parisite-(Ce) and synchysite-(Y); b) aqueous solution, gas and halite; c) aqueous solution, liquid and gas carbon dioxide; d) liquid and gas carbon dioxide; e-g) three inclusion types of aqueous solution plus gas. The determined formation temperature ranged from 500 to 240°C and pressure from 1.2 to 0.5 kbar. Thus, carbonatites formed from dense saline to diluted solutions with CO₂ under variable pre- or post-explosive conditions.

The Tajno massif is comparable in many respects (e.g. Late Palaeozoic age, mineralogy, geochemistry and p-T condition) to the Kola-Karelia carbonatite province and can be the south-western extension of this province into NE Poland.

Nahcolite and carbonaceous matters in fluid inclusions in quartz veins from the Ryoke metamorphic belt, SW Japan

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Two topics will be discussed in the presentation.

1) Nahcolite

Nahcolite (NaHCO₃) has been found in fluid inclusions in quartz veins in the biotite zone of the Ryoke metamorphic rocks in Kasado-Jima (Island), Yamaguchi Prefecture, Japan (Hoshino et al., submitted). Extremely large volume fractions of nahcolite solids in the inclusions indicate their origin as accidentally trapped ones. The nahcolite-bearing fluids show various ratios of aqueous (H₂O-NaCl) and gaseous (CO₂-CH₄) phases, suggesting an immiscible condition prevailing during their entrapment. The $X_{CH_4}/(X_{CO_2}+X_{CH_4})$ ratios of the latter phases are about 0.05. Salinities of the aqueous phases are lower than 4 wt. % NaCl eq..

A thermodynamic calculation of the nahcolite stability and a phase analysis of the fluids show $\log a_{NaHCO_3} = 7.4 - pH$ as the minimum activity at $P = 100$ MPa and $T = 270^\circ\text{C}$ where the neutral pH = 5.6. Hence, it can be concluded that the original (prior to immiscible state) liquids might have contained high Na⁺ and low Cl⁻ yielded by an interaction of a low-salinity fluid and Na-bearing minerals such as plagioclase in the host metamorphic rocks below the fractures now occupied by quartz.

2) Carbonaceous matter (CM)

Daughter minerals of CM have been observed in fluid inclusions in quartz veins in the biotite zone of the Ryoke metamorphic rocks in the Yanai district, Yamaguchi Prefecture, Japan. The veins were formed during retrograde metamorphism, probably above 300°C (Yamamoto et al., 2004). Fluids with CM's in the inclusions are gaseous (CO₂-CH₄) and aqueous (H₂O-NaCl) phases. The $X_{CH_4}/(X_{CO_2}+X_{CH_4})$ ratios of the former are about 0.1-0.2. Salinities of the latter estimated by Raman spectra of the stretching band of water (Dubessy et al., 2002) are low, ranging from 0 to 4 wt. % NaCl eq..

The degrees of organization of CM's measured by Raman microspectrometry (Beyssac et al., 2002) indicate their organization temperatures of 530-610°C averaging about 550°C. On the other hand, the CM's in the host pelitic schist of the biotite zone show the temperatures of 450-550°C. It should be noted that large CM's growing along cleavages of biotite in highly metamorphosed rocks in the K-feldspar-cordierite and garnet-cordierite zones show high temperatures, while those surrounded by quartz indicate lower and variable temperatures. Since the organization of CM has so far been believed to be an irreversible process, the above evidence suggests that the low-temperature CM's in high-grade metamorphic rocks were formed during the retrograde metamorphism.

P17-01

The effect of sulfur on the vapor-liquid distribution of Cu and Zn in boiling hydrothermal fluid by SRXRF microanalysis of synthetic fluid inclusions

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In the formation of porphyry-Cu deposits, the boiling of hydrothermal fluid has been considered to be an important process for the selective extraction of copper. For example, the analyses of fluid inclusions trapped boiling hydrothermal solutions (e.g., Heinrich et al., 1992) suggests that fluid inclusions trapping magmatic vapor frequently contain more copper than other heavy metals, while liquid-rich inclusions contain more iron, zinc and lead than copper. To know the copper enrichment in vapor inclusions in detail, especially the role of sulfur, vapor-liquid partitioning coefficients of Cu and Zn for sulfur-bearing and sulfur-free aqueous fluid are experimentally obtained. Synthetic fluid inclusion technique proposed by Bodnar and Sterner (1987) was employed as an experimental method. Fluid inclusions were synthesized in quartz cores fractured by thermal shock. The starting materials were 1500–12000 ppm Cu and Zn with 10–30 wt% NaCl aqueous solutions and 0–1.8 mol/kg H₂O elemental sulfur. The core, the starting materials and quartz powder (to promote crack healing) were loaded in a gold capsule and it was kept at 500–650 °C and 35–100 MPa, which are the boiling conditions of the experimental solutions, for about 7 days in an autoclave. During this procedure, fluid inclusions were formed by the recrystallization of quartz. After the experiment, the coexistence of vapor-rich and liquid-rich inclusions was observed in the specimens by microscopic observations, and these individual inclusions were analyzed quantitatively by synchrotron radiation x-ray fluorescence (SRXRF). The analysis shows that Cu-rich and Zn-poor vapor inclusions and Cu-poor and Zn-rich liquid inclusions were coexisting at sulfur-bearing conditions, and Cu, Zn-poor vapor inclusions and Cu, Zn-rich liquid inclusions were coexisting at sulfur-free conditions. K_D [= (concentrations in vapor) / (concentrations in liquid)], the vapor-liquid distribution coefficient of solutes suggests that the chemical species of copper at sulfur-rich conditions may be different from that in sulfur-free conditions. The $\log K_D$ value for Cu gradually increases with sulfur content and becomes $K_D = 25$ for sulfur-rich conditions. On the other hand, the $\log K_D$ value for Zn is independent on sulfur content. For sulfur-free conditions, the $\log K_D$ value of Cu is roughly equals to that of Zn. These results demonstrate that the hypothesis proposed by Heinrich et al. (1992) that sulfur is responsible for copper enrichment in vapor.

P17-02

Analyzing volatiles in silicate melt inclusions by FTIR spectrometry

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The study of the concentration and speciation of volatiles in silicate melt inclusions has largely been performed by in situ measurements using Fourier Transform InfraRed (FTIR) spectrometry. However, this technique has two significant drawbacks: the need for difficult and time consuming double polishing of small (tens of microns) inclusions; and the inability to precisely measure the thickness of the inclusion, introducing a significant error to the results. It has been suggested that in order to simplify sample preparation, reflection infrared spectroscopy be used to determine volatile contents. However, this becomes problematic on inclusions less than ~ 100 µm, as it is difficult to position the beam solely on the inclusion, resulting in a contribution to the reflectance spectrum from the host crystal overprinting the volatile spectral bands of the inclusion. In transmission spectra the bands of olivine (or other host minerals such as feldspar) do not overlap with the total water peak allowing the peak to be detected while analyzing through the host crystal. However, in order to obtain volatile contents the thickness of the inclusion is still required. We examine whether it is possible to use the difference between the spectral bands of the host crystal measured with and without an inclusion in the beam path to indirectly calculate the thickness of the inclusion within the crystal. We have analyzed many inclusions, with a wide range of volatile contents, hosted in olivine and feldspar crystals from basaltic samples by single beam and imaging FTIR techniques, and examined them optically. If this technique is successful it will greatly ease the preparation of inclusions for FTIR analysis. Furthermore, if a crystal hosts several inclusions it will allow all of them to have their volatile concentrations measured. Inclusions will not be lost as one is doubly exposed and polished.

P17-03

Thermal history of the Nabeyama sericite mine, NE Shimane, SW Japan, based on fission track and fluid inclusion studies

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The Nabeyama sericite mine is located in NE Shimane Prefecture, and is the only mine of its type currently in production in SW Japan. High quality sericite is produced through sedimentation techniques. The host rock of the mineralization is Cretaceous granitoids. The sericite ore body consists of a 200m x 30m fissure filling vein striking N55W. The sericite ore body has been considered to be genetically related to a hydrothermal system following the emplacement of host granitoids, based on previous studies of polytypes and K-Ar age of sericites. However, detailed study of the thermal history of the mine has not yet been made. Sericite ore color, hardness and quality vary considerably along the mine drive, sometimes with clear boundary, due to variable hydrothermal alteration. Constituent minerals of the ore are mainly sericite, calcite and quartz, with subordinate chlorite, anatase and gypsum. Under the microscope, modes of the sericite can be divided into three types, namely large subhedral, rounded, and very small crystals. The very small sericite grains appear to infiltrate calcites. Euhedral hexagonal quartz precipitated at an early stage is sometimes common. Homogenization temperatures of fluid inclusions in coexisting calcite show several modes at 235°C, 280°C and 320°C. The mode at 235°C is common in all samples, but the higher temperatures are recognized only in samples which contain abundant hexagonal quartz crystals. NaCl equivalent salinities range from 0% to 1.6%. The fluid inclusion data suggest that successive influxes of hydrothermal fluids with different temperatures may have passed through the fissure during the sericite formation stage.

Fission track ages of zircons from within the ore bodies (50.3–53.9Ma) compare well with ages from surrounding unaltered host granitoids (50.5–53.4Ma), but FT ages of apatite from the ore bodies (36.6–40.5Ma) are slightly older than apatite ages from surrounding granitoids (32.2–34.1Ma). These older ages and low fluid salinities data suggest that the ore body cooled faster than the surrounding host granitoids, probably due to inflow of cool meteoric water into the fissures of the ore body. However, more detailed examination of the alteration stages of the constituent minerals and the chemical composition of the sericites is required to further refine the genesis of the Nabeyama sericite deposit.

P17-04

Fluid inclusion compositions of the Kofu granite body, central Japan: significance for chemistries of deep groundwater in the granite body

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Although common fluid inclusions are intactly remained after formation, a leakage of inclusion fluid can be occurred by fracturing during rock deformation and by reequilibration due to environmental changes. The fluid leaked mix with surface water, can affecting a composition of deep groundwater. Granites often contain high-saline fluid inclusions with high metal contents, so a release of the inclusion fluids is important to chemistries of the groundwater. For some granitic bodies in Sweden and Finland, a hyper-saline groundwater has been reported, and a contribution of inclusion fluids has been considered as the origin of the high salinity. Granitic bodies are an important model site for geological disposal of radioactive waste, so studies on the fluid-inclusion compositions are significant to understanding the groundwater chemistries. Thus, we have determined elemental compositions of single fluid inclusions in quartz from the Kofu granitic body using particle-induced X-ray emission (PIXE). The Kofu granitic body consists of biotite granite and granodiorite and intruded into marine sediments at the Middle Miocene. The quartz samples were collected from granites, miarolitic cavities, quartz veins, and hydrothermal ore deposit from the biotite-granite part. The PIXE analyses were performed for the quartz-vein and the miarolitic-cavity samples with distinctive formation stages to understand the origin of the fluids. Main fluid inclusions in the granite-related rocks are a low salinity (5-10 wt.%NaCl eq. and 300-450°C Th), and those in the miarolitic cavities contained Fe, Cu, Ge, Br, Rb, and Pb with concentration of a few to several tens wt. ppm. On the one hand, granite-related rocks of the upper part of the body often contain halite-bearing fluid inclusions (30-38 wt.%NaCl eq. and 350-450°C Th). The polyphase inclusions contained large amounts of Ca, Fe (wt.%), and Mn. Zn, Cu, Br, Rb, Sr, and Pb (hundreds to thousands wt.ppm). The hyper-saline and metal-enriched fluid can be formed by boiling of the main fluid during adiabatic ascending from a deep part along the cooling joints of the body. Some cold springs in the upper part of the body where the polyphase inclusions concentrate are relatively saline. Br/Cl ratios of the spring waters agreed with values of mixing of the polyphase inclusions and surface water and differ from those of spring waters in the surrounding marine sediments. Thus, the inclusion fluids can affect the groundwater chemistry of the granitic body. A boiling of granitic fluids may be important to examine groundwater chemistries in granite.

P17-05

The thermal properties of the crystallized inclusions in minerals from Kogarasu-yama granodiorite, Kofu, Japan

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The thermal properties of the crystallized inclusions in mineral from Kogarasu-yama granodiorite, Kofu, central Japan, were investigated by heating experiments with high temperature type heating stage. The validity and the trouble on the heating procedure are discussed here.

Kogarasu-yama granodiorite distributes in the northern part of Kofu, Yamanashi. The rock is one of the youngest plutons in Japan, whose K-Ar age ranges 4.27-4.38 Ma (Shibata et al., 1984). The crystallized inclusions are found in plagioclase and quartz of the granodiorite. They consist of solid phase that often shows anisotropism and vapor phase. The crystallized inclusions in quartz contain several transparent minerals and those in plagioclase are often opaque. The crystallized inclusions are 20 µm in maximum length.

The heating equipment used in this study is the programmable Linkam TS1500 heating stage mounted on the optical microscope. Samples were heated at 5°C/min from room temperature to 500°C and then 3°C/min until homogenization.

The crystallized inclusions in quartz began to melt at 600-900 °C and homogenized at 1,250-1,290. They begin to melt the host quartz from the part on the rim of the inclusion, and the shapes become more round. Those in quartz look transparent and colorless during homogenizing. When keeping homogenized temperature of the inclusion in quartz for 4 hours, the volume increase was not found. The crystallized inclusions in feldspar began to melt at 1,110°C and homogenized at 1,200°C. Those in feldspar look transparent and brown during homogenizing. When heating was continued after homogenization, the melting contents of inclusion in feldspar were leaked out.

P17-06

The formation of rhyolite from Nagahama Volcano, Kozu-shima, Tokyo, Japan

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Kozu-shima of the Izu Islands is located on the Izu-Mariana Islands Arc. It consists of rhyolitic monogenetic volcanoes that spouted out on the Zenisu Ridge with Nii-jima and Shikine-jima located in the northeast. While nearby O-shima, Miyake-jima and Hachijo-jima consist of basaltic stratovolcanos. Kozu-shima consists of lava domes, thick lava flow, and thick pyroclastic deposits. The island is known as one of the major producer of obsidian.

Rhyolite used in this study is from Nagahama volcano which is in the northwest of the island, and is the oldest volcano in the island. The petrography and the thermal characteristics of submicroscopic grains were investigated.

Rhyolite from the Nagumi-wan lava consists of phenocrysts and mesostasis. Phenocrysts consist of plagioclase, quartz, cummingtonite and a few amounts of magnetite and ilmenite. They are mostly euhedral in shape.

Glass inclusions are found in phenocrysts of quartz and plagioclase. The mesostasis consists of the glassy groundmass, with submicroscopic grains such as crystallites, microlites, spherulites and microspherules. Rhyolite partly shows distinct flow texture and partly with foam structure. It seems that these microstructures are genetically related to the formation of rhyolite.

From the heating experiment of the submicroscopic grains and glass inclusions, Formation process of the Nagahama volcano lava flow is thought to be as follows. The phenocrysts were crystallized in magma before the lava extrusion, and glass inclusions were formed in the process of the growth of phenocrysts. Microlites, crystallites, microspherules and glass were formed during rapid cooling at the time of the lava extrusion. The differences of properties in the submicroscopic grains were caused by the difference of cooling rates of magma. Spherulites were formed by devitrification after the magma cooling. It seems that there were hydrothermal activities related to the partly devitrification of rhyolite. The formation of foam in the glassy mesostasis was occurred at the time of the lava extrusion. Thus the porous rocks were formed during these geological processes.

P17-07

Fluid inclusions in the high-grade Abukuma metamorphic rocks from Hanazono district, northeast Japan

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We present a systematic fluid inclusion data from the Cretaceous Abukuma metamorphic belt, which is a classic example of low-P/high-T type (Abukuma-type) granulite-facies metamorphic complex in northeast Japan. Our detailed field mapping indicates that the major lithologies of the studied Hanazono district are composed of pelitic, psammitic, siliceous, and granitic gneisses with minor calc-silicate gneiss, amphibolite, ultramafic rocks, and intrusive granitoids. The examined pelitic and granitic gneisses have a common mineral assemblage of quartz + garnet + biotite + plagioclase + K-feldspar ± orthopyroxene ± cordierite ± sillimanite ± graphite. The trapped fluid inclusions within undeformed quartz in pelitic and granitic gneisses are petrographically subdivided into two categories; primary to pseudo-secondary and secondary inclusions. The dominant category of early-stage primary to pseudo-secondary fluid inclusions comprises monophasic carbonic fluids with melting temperatures of -64.2 to -56.6 °C, indicating a CO₂-rich composition of the fluid, with minor CH₄ and/or N₂. The carbonic inclusions with higher melting temperatures (T_m = -60.0 to -56.6 °C) homogenize into the liquid phase at temperatures in the range of -49.4 to +26.7 °C, translating into CO₂ densities of 0.683-1.153 g/cm³. In contrast, secondary aqueous inclusions show melting and homogenization temperatures ranging from -9.9 to 0 °C and from +101.7 to +254.7 °C, respectively. Densities of the carbonic inclusions can be divided into two categories; high-density (1.121-1.153 g/cm³) and medium-density (0.683-1.111 g/cm³) inclusions. The former category that we report in this study is by far the highest yet recorded for CO₂-rich fluids from Phanerozoic granulite-facies rocks. The fluid densities of the later inclusions when computed into isochores indicate entrapment of CO₂ at the peak P-T condition of the studied area (2.8-5.2 kbar at 770-850 °C). In contrast, isochores of high-density category do not intersect the clockwise P-T trajectory of Hanazono district, although those are consistent with the high-pressure condition of the Abukuma metamorphic rocks in Takanuki area (8 kbar at 750-800 °C) inferred from the occurrence of prograde kyanite. We therefore infer that CO₂ was the dominant fluid types preserved during the Abukuma high-grade metamorphism, and also interpret that the fluid inclusions preserved traces of a symmetamorphic fluid. The presence of CO₂-rich fluid at the peak stage probably buffered the H₂O-activity to low levels in the Abukuma metamorphic rocks to stabilize granulite assemblages. This study provides unequivocal evidence for the involvement of extremely high-density CO₂ in Phanerozoic granulite formation.

Characteristics and significant role of fluid inclusion from high-grade metamorphic rocks in Sri Lanka

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Sri Lanka is located to southeast India and is famous for its various mineral resources such as gem stone, graphite and so on. It is mainly composed of Precambrian high-grade metamorphic rocks of so-called Highland Series, Vijayan Complex and Wannu Complex, and is noted as a fragment of Gondwana continent. The Highland Series are characterized by granulite facies metamorphic rocks, while the Vijayan and the Wannu Complex by amphibolite facies ones. The border between the Highland Series and the Vijayan Complex is transitional, but that between the Highland Series and the Wannu complex is assumed to be divided by thrust.

Fluid inclusions containing CO₂, H₂O and CH₄ are frequently observed in these metamorphic rocks, and it is considered that dry fluids, especially CO₂ fluid, have largely contributed to the formation process of Precambrian high-grade metamorphic rocks.

In this study, it is aimed to clarify the characteristics and detailed mode of occurrence of fluid inclusions from granulite facies metamorphic rocks and to discuss on the significant role of the fluids through the metamorphism. As a result of microscopic observation and Laser Raman Spectrometry, it is found that primary CO₂ fluid inclusions tend to distribute mainly at the western part of the Highland Series. This suggests that CO₂ fluids might have played an important role in the formation of charnockite and graphite deposits with similar distribution. In contrast, secondary H₂O inclusions mainly distribute in the central and the eastern parts of the Highland Series. CH₄ inclusions, almost secondary, rarely distribute to the central and the eastern Highland Series. In consequence of heating and cooling experiments for the inclusions, CO₂ fluid tends to show high density and high degree of purity, while, H₂O fluid shows low density and low salinity. It is assumed that CO₂ fluids had been active in the early stage of retrogressive metamorphism, then H₂O and CH₄ fluids might become active in the later stage of metamorphism. Based on the P-T estimation using secondary fluid inclusions, some H₂O inclusion and the low density CO₂ inclusion are trapped at the low temperatures (200–250°C) and the pressures (1–1.2 Kbar) during the later stage of metamorphism. Considering the noted transitional stage from CO₂ dominant to H₂O dominant phases, it is inferred that the formations of graphite deposits and overprint of the charnockite occurred in this stage.

O18-01

Missing link between ultra-high pressure (UHP) and ultra-high temperature metamorphism (UHT): A case study in the Bohemian massif

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Ultra-high pressure (UHP) and ultra-high temperature (UHT) metamorphic rocks represent the extreme metamorphism which attracts many attentions during these decades. The formation of UHP rock can be explained by the subduction of crustal materials at least to upper mantle depths and the subsequent exhumation to the surface escaping from the pervasive re-crystallization in the crust. The formation of UHT rocks needs local/regional heating up to 900-1100°C under almost H₂O free conditions. UHP and UHT rocks are found from more than 20 areas each other until 2005 and addition of their new locality is not doubtful in near future. Most of UHP rocks are exposed in the continent-continent collision zones which formed mainly during Phanerozoic, but most of UHT rocks were formed before late Paleozoic. Therefore, the metamorphic belt which contains both UHP and UHT rocks is scarce, but the Bohemian massif is an exceptional case. In Bohemian massif, Ky-bearing leucocratic granulite showing a sign of UHT condition is widespread. UHP rocks *sensu stricto*, metamorphosed crustal rocks containing coesite or diamond, however, occur only in the Saxothuringian zone, but not in the Moldanubian zone, where UHP conditions were mainly recorded in Grt-peridotite and Ky-eclogite which are enclosed in leucocratic (Gföhl) granulite or migmatite. Our co-operative study newly found omphacite granulite at Rohy in the Blanský les massif of southern Bohemia, and the pair of omphacite (X_{jd}=30 and Tsch=15) and Grt (Prp₁₈₋₂₇Alm₃₈₋₄₁Grs₃₄₋₄₀Sps₁) gave highest-P (ca. 22 kbar at 1000°C) for the granulite in the relevant area. Newly found Grt-peridotite hosted by the granulite at Plesovice in the Blanský les massif recorded peak P-T conditions of 900-1000°C and 27-32kbar. The peak temperature is almost identical among the omphacite granulite and the Grt-peridotite, but there is a significant pressure gap at peak conditions. Re-evaluation of peak P-T conditions of Ky-eclogite associated with Grt-peridotite hosted by migmatite at Nove Dvory gave 1050-1150°C and 45-49kbar, which are well concordant to those of the host peridotite. Zoning structure of Opx in Plesovice Grt-peridotite and that of Grt in Ky-eclogite at Nove Dvory suggest the host rocks experienced the subduction. To exhume heavy (ultra)basic rocks from the upper mantle to the lower crust, light density and/or partial melt of leucocratic rocks may play an important role.

O18-02

Do Ultrahigh Temperature and Ultrahigh Pressure Metamorphic Belts Record Secular Change in Tectonic Regime on Earth?

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I will address fundamental questions about metamorphism under extreme P-T conditions, secular change and tectonic regimes. We may speculate about how robust are age interpretations and maximum calculated/inferred P-T conditions for rocks that record extreme values, but high temperatures and pressures are unequivocal and linking ages to P-T is now commonly practiced. Furthermore, compilation of data from metamorphic belts indicates step changes in thermal regimes, suggesting punctuated tectonic evolution of Earth. Archean rocks exhibit moderate-P-high-T metamorphic facies; neither blueschists nor any record of deep continental subduction is documented. Medium-temperature eclogites are preserved in the Neoproterozoic Belomorian Belt, Orosirian Usagaran Orogen and Grenvillian belts of the Proto-Atlantic. HP granulite metamorphism is predominantly a Proterozoic-Phanerozoic phenomenon related to subduction-to-collision orogenesis. Abundance and scale of ultrahigh temperature (UHT) belts from Neoproterozoic to Neoproterozoic imply transient sites of high heat flow during much of Earth evolution. Continental crust may be metamorphosed in various settings, but many UHT belts appear to have developed in back-arcs closed by crustal aggregation/supercontinent formation. Is this a requirement for UHT metamorphism? Blueschists appear in the Neoproterozoic Era, becoming common through the Phanerozoic Eon; they record low thermal gradients associated with modern subduction. Ultrahigh pressure (UHP) metamorphism is predominantly a Phanerozoic phenomenon related to deep continental subduction within subduction-to-collision orogens. Many UHP belts have developed where a magmatic arc is absent from the hanging wall; is this condition necessary for UHP metamorphism? The Archean-Proterozoic Eons are characterized by higher mean mantle temperatures and radioactive heat production (RHP), and thinner TBL with shorter residence time than modern Earth. Modeling the effect of increased RHP on thermal evolution of thickened crust indicates ancient collisional orogens should have experienced higher maximum temperatures than recorded in modern collisional orogens, but there is no evidence of this – the Archean record is dominated by 'ordinary' P-T conditions and low-T melting, and bimodality in thermal regimes appears only since the Neoproterozoic Era. Thus, the Archean-to-Proterozoic transition may register introduction of a 'Proterozoic plate tectonics regime', evidenced by bimodality in thermal regimes in the rock record – MT eclogite/HP granulite and UHT belts, but total ridge length and number of plates undoubtedly were larger at that time than on modern Earth, and the style of tectonics likely was different. The Neoproterozoic transition to the 'modern plate tectonics regime' registers change to deep continental subduction, perhaps recording whole mantle convection as oceanic lithosphere became thicker with decreased thermal gradients.

O18-03

Art of Petrography: An Amazing Tool for Snap-Shots of the Journey of UHT Rocks

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An important aspect of petrological investigation is the art of petrography. Petrography exerts strong influence on framework of observation and interpretation in petrology. Textures in metamorphic rocks, spectacular as they are, hint at the extraordinary potential information they conceal within their tiny domain. The pieces of rock fragments are like memory chips bearing signatures of geological event. Thus essence of art of petrography is directed towards utilizing the complementary line of evidence from textures through the eyes of a petrographer and mind of a petrologist. There is a great deal to be learnt from the study of rocks under microscope. Half the charm of the study is lost when the rock is powdered and its tiny crushed fraction is settled to claim big results. Finally, the textures help us to look beyond novel journey of rocks and are capable of weaving the metamorphic P-T paths and tectonic regime during orogenic processes. Some workers balk at this projection and prefer to discount the importance of textures generally over the computer generated intricate curves for the UHT rocks.

However, what is envisioned today in metamorphic petrology is determination of vectors of the P-T path from the mineral assemblages and reaction textures that provide insight into crustal-scale processes. Preservation of contrasting mineral compositions and subtly different reaction textures provide snap-shot of the P-T evolution. Both silica-undersaturated and quartz-bearing metapelites have been reported from number of UHT terrains worldwide. It is not surprising that strongly refractory UHT assemblage domains (garnet, spinel, corundum, sapphirine, kornupine, cordierite, hypersthene, osumilite) and a range of related reaction textures provide a direct record of their P-T evolution. Disequilibrium textures portrayed eloquently in UHT rocks are promising contestants for detailed petrological examination. Partial pseudomorphs, coronas, reaction rims, symplectites and resorption textures are a few striking disequilibrium textures which reflect continuous/discontinuous reactions under changing P-T conditions. Texture of metamorphic tectonites resulting from nucleation, grain growth and various recrystallization mechanisms are strongly controlled by temperature, time and strain/stress ratio. Therefore, the analysis of metamorphic textures is a plausible method that is capable of distinguishing between two metamorphic events under similar P-T conditions of different durations. These observations bolster the opinion that the textural interpretation of mineral assemblages have greater propensity to understanding the UHT metamorphic rocks.

O18-04

Collision zone metamorphism under extreme P-T conditions in Vietnam and adjacent SE-Asia

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Continental crust in Southeast Asia including Vietnam has been considered to be developed by the micro-continent collision during Permo-Triassic time (ca. 270-240 Ma). Many kinds of ultrahigh-temperature (UHT) and ultrahigh-pressure (UHP) metamorphic rocks are found in the Kontum Massif and the Song Ma suture zone, which were formed during the collision between Indochina and South China cratons in Vietnam region.

The UHT pelitic metamorphic rocks in the Kontum Massif are Grt-Opx-Sil-Crd gneiss, Opx-bearing Grt-Crd-Sil-Bt gneiss and Grt-Opx charnockitic gneiss. The highest-grade metamorphic condition is determined from Grt-Opx-Sil-Crd gneiss, which indicates multi-stage symplectite formation during retrograde stage started from isothermal decompression at UHT condition (>1000 °C) owing to high-Prp in Grt and high-Al₂O₃ in Opx. The Grt-Cpx-Opx granulites (eclogitic UHT mafic granulite) as blocks in Dia-bearing felsic Grt-Opx gneiss from the Kontum Massif, a series of change in divariant assemblages from Grt-Cpx-Qtz to Hbl-Qtz through Cpx-Opx-Pl-Grt is identified as a result of their metamorphic evolution of isothermal decompression followed by nearly isobaric cooling. This type of eclogitic mafic granulite characteristically contains hyper-silicic Cpx and abundant Rt-needles, Cz and Ky included Grt.

The UHT and UHP metamorphic rocks from the Kontum Massif, which expose along the Dac To Kan shear zone, show a clockwise P-T path with the peak metamorphic condition of 12-13 kbar and c. 1050 °C (M1 stage). The previous UHP metamorphism (>40 kbar, ca. 900 °C; M0 stage) as part of prograde metamorphism and low-pressure (but still high-temperature) metamorphism (8-9 kbar, c. 800 °C; M2 stage) as part of retrograde metamorphism during the clockwise P-T evolution are also recognized.

A newly found rather low-temperature UHP mafic metamorphic rock (Grt-Cpx-Hbl-Qtz eclogite) from the Song Ma suture zone contains Id-rich Cpx, Grs- and Prp-rich Grt, Na-rich Hbl, Phg and Qtz. Estimated the peak-pressure P-T conditions of the eclogite show ca. 650-700 °C and ca. 25 kbar with clockwise P-T evolution.

Based on the combination of P-T paths from the Kontum Massif and the Song Ma suture zone, two-stages of metamorphic field gradient would be identified. An earlier high-P/T gradient is recognized by using assumed peak-pressure conditions from the UHP metamorphic rocks as an early of Permo-Triassic continental collision event (M0). A later low-P/T gradient is also identified by the connection of peak UHT metamorphic conditions from those areas as the M1 stage caused by very high-temperature magmatic intrusion or asthenosphere upwelling.

Multiple tectonothermal events in high-grade gneisses of the Kontum massif, central Vietnam: Geochronological constraints and geodynamic implications

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High-grade gneisses in the Kontum massif (Central Vietnam) are grouped into three crystalline basement complexes known as the "Archean" Kannack Complex, the "Paleoproterozoic" Ngoc Linh Complex and the Neoproterozoic Kham Duc Formation. Recent studies have revealed that some gneisses record extreme metamorphic conditions of UHT granulite-facies and UHP eclogite-facies. A wide range of geochronological data have been obtained for the high-grade gneisses in the Kontum massif. UHT granulites and eclogitic rocks within the Dak To Kan shear zone were dated at 245–260 Ma. Granodiorite-amphibolites south of the Dak To Kan shear zone recorded U-Pb zircon ages of 444–451 Ma. A similar U-Pb zircon age of 436 Ma was obtained for hornblende-biotite gneiss that is far from the Dak To Kan shear zone to the north, and of 407–418 Ma for hornblende-biotite gneiss in the Da Nang – Dai Loc shear zone that is the northernmost part of the Kontum massif. A minor data were also obtained such as ca. 480–500 Ma CHIME monazite, ca. 670 Ma Sm-Nd, and SHRIMP U-Pb dates of 860, 1400 and 2540 Ma for inherited zircon cores.

From available data, it is now clearly that high- to UHT metamorphism has affected crystalline basement complexes in the Kontum massif during Permo-Triassic Indosinian times (245–260 Ma). This metamorphic event could be linked with continental collision in East Asia and it opens a possibility that Kontum massif is a site of collision boundary between Indochina and South China cratons. Event recorded by U-Pb zircon ages of ca. 410–450 Ma in crystalline basement complexes, that is interpreted as the magmatic-crystallization age, indicates a strong tectono-magmatic activation in Ordo-Silurian times. The Pan-African metamorphic event has also left its clue in the massif as the age range of 480–500 Ma to 670 Ma was obtained. Some inherited zircon cores from the crystalline basement complexes record ages of 860 Ma, 1400 Ma and 2540 Ma, suggesting old crustal relics and Neoproterozoic thermal events, though their tectono-metamorphic significance is still unclear.

Ultrahigh-temperature Metamorphism and Crustal Anatexis Caused by Mantle Plume in Collision Zone, the Kontum Massif, Central Vietnam

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The Late Permian continental growth in Asia accounts for collage tectonics due to the collision of micro-continents. Extreme metamorphism and syn- to post-collisional magmatism occurred along the boundary zone of continental collision. In this study, we report two types of granitic rocks, garnet granite (Grt granite) and orthopyroxene granite (Opx granite), as well as fine-grained gabbro from the Kontum massif, central Vietnam, which is situated on the continental collision zone between the South China and Indochina cratons. Ultrahigh-pressure (UHP) and ultrahigh-temperature (UHT) metamorphism took place in the same zone. However, the genetic relationship between the extreme metamorphism and the magma activity has not understood completely.

Grt granite and Opx granite intrude discordantly into the host high-grade gneisses, thereby suggesting the magma activity of these granitic rocks corresponds to post-collisional magmatism. The field relationship between Grt granite and fine-grained gabbro reveals that both rocks are coeval intrusive rocks. Based on the petrological and geochemical study, Grt granite is derived from pelitic gneisses by partial melting, whereas Opx granite is produced by the partial melting of garnet-bearing mafic granulites. The geochemistry of fine-grained gabbro possesses the subduction related signature such as Rb, K, and Ba enrichment and Nb, Ta, and Ti depletion; however, concentrations of the incompatible elements of fine-grained gabbro are higher than those of arc and continental margin basalts. These geochemical signatures represent post-collisional high-K basalts derived from enriched source, possibly metasomatized lithosphere, occurring in collision zones.

The geochronological data for the HT to UHT metamorphic rocks and the granitic rocks reveal that the time of formation of granitic magma corresponds to the metamorphic events from the peak to decompression stages during the Late Permian (260 – 250 Ma). We inferred that a significantly high-geothermal gradient is required to produce the granitic and basaltic magmatism and related HT to UHT metamorphism in the Kontum massif. Plume-related basaltic rocks, e.g., Emeishan basalt in south China and Song Da komatiite in northern Vietnam, erupted around the collision zone between the South China and Indochina cratons during the Permo-Triassic. Therefore, this geotherm may be attributed to upwelling mantle plume beneath the Kontum massif during the Late Permian.

Madurai Block, Southern India: A classic terrain for Petrotectonic Implication

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The Madurai Block is a classic terrain that may be regarded as a model for Precambrian crustal evolution, lies between the Palghat-Cauvery and the Achankovil shear zones. The Madurai block has attracted the attention of petrologists on account of UHT granulites that serve as a window into the mid-lower continental crust. Common mineral assemblages of constituent metapelites include garnet, cordierite, sapphirine, orthopyroxene, spinel and sillimanite. The garnet-cordierite-sapphirine-bearing assemblages dominantly occur in the central part of the highland massif, whereas garnet-sillimanite-bearing assemblages prevail in the Ganguvarpatti-Andipatti-Usilampatti lowland massif. Marble and calc-silicate are the carbonate lithologies that in addition locally contain quartzites and ultramafics. Sapphirine bearing granulites have been reported previously from a number of localities in the central and northern parts of the Madurai block. These sapphirine-bearing granulites revealed UHT metamorphism in several localities, e.g. Rajapalayam, Perumalmalai, Ganguvarpatti, Usilampatti, Lachmanapatti, Malappatti, Sengal, Sakkarakottai, Paramatti at the Palghat-Cauvery zone. Mafic granulites of the Madurai block preserve its metamorphic history in the form of reaction textures and symplectites have high potential to elucidate the conditions of HT/UHT metamorphism. The metamorphic P-T conditions recorded in the Madurai block point strongly to a decompressional history. The rocks of Madurai block document a clockwise decompression P-T trajectory, consistent with crustal thickening followed by extensional collapse. Constraints from model Nd ages provide evidence for Paleoproterozoic magmatism restricted to the Madurai block in the Southern Granulite Terrain. The early part of the crustal evolution of the Madurai block could be coeval with the Paleoproterozoic event. Subsequent development of symplectitic assemblages via near-isothermal decompression can be ascribed to a distinctly later tectonic event. Available U-Pb and Sm-Nd mineral dates suggest a widespread Pan-African tectonothermal event in the Madurai block. Given the general recognition of UHT (Ultrahigh-temperature) and ITD (Isothermal decompression) in Pan-African age metamorphism in the EAAO (East-African-Antarctic Orogen), the Madurai block UHT history is considered to be part of this record. A possible correlation of similar post-peak decompression texture and comparable UHT conditions in high-grade granulites in the continental fragments of southern India, Sri Lanka, Madagascar and East Antarctica support the possibility that they share a common metamorphic P-T history and form an integral part within East Gondwana framework. Future isotopic data from this region would provide important constraints on exhumation history of the Madurai block.

Ferromagnesian phosphates as products of anatexis in granulite-facies paragneisses from the Larsemann Hills, Prydz Bay, East Antarctica

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In the Larsemann Hills, a coastal exposure at 69° 25' S, 76° 10' E, biotite paragneisses containing borosilicate segregations and fluorapatite nodules form a distinctive lithologic unit that had been extensively melted at peak conditions (800–860 °C, 6–7 kbar) or during subsequent decompression. Wagnerite, (Mg,Fe)₂PO₄(F,OH), forms nodules, mantles around apatite nodules or is included in fluorapatite. Two new ferromagnesian phosphates are also enclosed in fluorapatite. Y-dominant analogue of chladniite, (Y,Ca)Na₄(Ca,Nb)₃(Mg,Fe)₄(PO₄)₃₆ (IMA 2005-040, approved) forms anhedral, subhedral or euhedral grains with hexagonal or rhombic outlines up to 1 × 0.25 mm across. Y + REE (predominantly Yb) range 0.523–0.949, and atomic Mg/(Mg + Fe) ratio, 0.684–0.749. Structure refinement shows that Y and Yb are fully ordered at the (0, 0, 0) site. The Mg-dominant analogue of sarcopside, (Mg_{2.30}Fe_{0.86}Ca_{0.02}Mn_{0.01})(P_{1.95}Si_{0.02})O₈ (IMA 2006-004, submitted), forms completely isolated anhedral grains 0.1 × 0.4 mm to 0.2 × 0.6 mm across in fluorapatite. Ti-rich biotite (up to 6.64 wt% TiO₂) has partially broken down to hercynite + Fe-Ti oxide + K-feldspar; biotite and its breakdown products are separated by a wagnerite mantle from enclosing fluorapatite. Feldspar P₂O₅ contents are 0.1–1.1 wt% (Kfs) and 0.3 wt% (Pl, An17–18); P is incorporated by the substitution PAISi₂. Fluorapatite has relatively high Cl, Y₂O₃, MgO, and FeO (2.39 – 3.23 wt%) contents, REE + Y contents (0.024–0.039, one to 0.068 per 12.5 O) average ~70% of Na content, less than predicted by Na(Y, REE)/Ca₂. Fluorapatite FeO contents suggest that the nodules formed at high temperatures in the presence of a permeating anatectic melt; this subsequently crystallized to graphic intergrowth of quartz and K-feldspar, whose composition suggests melt P₂O₅ contents might have also reached 1 wt%. By analogy with the reactions proposed by David London and colleagues, the development of wagnerite coronas around biotite are attributed to the reaction Bt + P₂O₅ (in melt) = fluorapatite + Kfs + Hc + Mgt + Ilm + wagnerite. In cases where the Y-dominant analogue of chladniite occurs around K-feldspar, we infer that the permeating melt was sufficiently enriched in MgO, FeO and P₂O₅ from interaction with fluorapatite and biotite in one part of a fluorapatite nodule for ferromagnesian phosphates to crystallize in a part lacking biotite, whereas isolated ferromagnesian phosphate inclusions in fluorapatite or interstitial to fluorapatite grains could be sites from which the melt had been completely extracted after precipitation of the ferromagnesian phosphate.

Garnet-scapolite intergrowths and multistage garnet coronas in UHT calc-silicate boudins from Rundvågshetta, East Antarctica: Insights for P-T-X- f_{O_2} evolution

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Calc-silicate rocks are well known for preserving vital clues on the metamorphic history of high-grade rocks, especially in high to ultra-high temperature conditions. Significantly, these rocks are resistant to anatexis, but vulnerable to changes in fluid composition. We present here the results on the ultra-high temperature imprint of calc-silicate assemblages and reaction textures from Rundvågshetta, in the Lützow-Holm Bay, East Antarctica. Granulites in Rundvågshetta formed from diverse protoliths, including pelitic, psammitic and basic to ultrabasic rocks, and less commonly impure carbonates. In the metapelite rocks orthopyroxene + sillimanite-bearing and sapphirine-bearing assemblages imply UHT conditions of ~1000°C and ~11 kbar were attained during the Pan-African peak metamorphism.

The Rundvågshetta calc-silicate boudins, up to 2 m thick and several meters in length, are enclosed in pyroxene-gneiss containing alternations of metapelite layers and blocks of basic granulites. Mineralogically calc-silicate rocks comprises of three zones with modal variations within the assemblage of grandite-garnet + scapolite + clinopyroxene + plagioclase + titanite +/- calcite +/- quartz. The core zone contains garnet porphyroblasts in a matrix of scapolite + quartz. The intermediate zone is characterized by alternations of scapolite + garnet or plagioclase + garnet intergrowths with subordinate amounts of clinopyroxene, quartz and calcite; where as the rim portion of the boudin does not contain garnet. The peculiarity of the Rundvågshetta calc-silicate rock is the presence of stable calcite + quartz instead of wollastonite, except a rare occurrence of relict wollastonite. Melonitic scapolite (EqAn = 0.94), coexists with anorthite (An₉₈) suggesting a minimum peak metamorphic temperature of ~850°C. Retrograde textures include several generations of garnet corona and scapolite breakdown to form anorthite + calcite +/- quartz. Textural features and mineral chemistry revealed at least four types of grandite-garnet and three types of chemically distinct clinopyroxene.

Activity corrected partial petrogenetic grids were constructed in the CAFSV system for the mineral reactions in accordance with the texture vs. chemical variations observed in various minerals. During the peak metamorphism moderate to high X_{CO_2} fluid composition was present, whereas retrogression was attended by hydrous-rich fluids. The oxygen fugacity conditions during each stage of the metamorphic history were estimated. The P-T-X- f_{O_2} evolution estimated using calc-silicate equilibria were then supplemented with the existing models on P-T evolution obtained from metapelite rocks, to evaluate the geodynamic evolution of the Rundvågshetta granulites within the Lützow-Holm Complex.

Pressure-temperature path of spinel-garnet peridotite at the Plešovice quarry in the Blanský les granulite massif, southern Bohemia

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The thermal history of the newly found garnet peridotite lenses enclosed within the Gföhl granulite at Plešovice quarry was investigated. This quarry is located at the eastern margin of the Blanský les granulite massif in the Czech part of the Moldanubian Zone. The spinel inclusions in garnet and the aluminous core (Al₂O₃ wt % ~ 3.0 wt %) of an orthopyroxene megacryst may suggest that the peridotite once experienced high-temperature conditions at the early stage (Stage I). Witt-Eickchen & Seck (1991)'s Al-Cr orthopyroxene thermometer yields 1030 °C in the spinel peridotite facies. Olivine, orthopyroxene, clinopyroxene and spinel ($Y^{Cr}=0.55-0.57$) form porphyroclasts (1-3 mm) along with the fine-grained matrix (< 1mm). Garnet occurs as large spheroidal grains (~ 10 mm in diameter) containing many inclusions (mainly orthopyroxene and Cr-spinel), and is replaced by kelyphite with various degree at the margin. Al contents of orthopyroxene inclusions in garnet, porphyroclasts and matrix-grains are similar (Al₂O₃ wt % = 1.4-1.6 wt %) in their cores. Therefore it can be regarded that all these minerals have once equilibrated with garnet. The mineral assemblage at stage II is defined by minerals that have equilibrated with Grt. Two-pyroxene thermometer (Taylor, 1998), Grt-Cpx thermometer (Krogh-Ravna, 2000), Grt-Opx barometer (Brey & Köhler, 1990), Grt-Cpx barometer (Nimis & Taylor, 2000) and empirical Spl barometer for Spl-Grt lherzolite (O'Neill, 1981) yield the consistent estimate: 26-34 kbar and 900-1050 °C. The stage III is defined by aluminous pyroxene and spinel in the kelyphite. Its temperature condition is estimated as ca. 700 °C based on the two-pyroxene geothermometer (Taylor, 1998). The obtained P-T path is characterized by the pressure increase at earlier stage that triggered the garnet formation. The possible tectonics that drove the pressure-increase might be the subduction. For the comparison of the P-T conditions of Grt-bearing assemblage at Stage II of Plešovice peridotite with those of other Czech peridotites, we have re-evaluated the P-T conditions of other Czech peridotites using the same combination of geothermo-barometries, using the data in the literature and in-house analyses of several peridotites localities. The re-estimated P-T conditions for Grt-bearing assemblage in the Czech peridotites range 850-1050 °C and 15-40 kbar. The relatively narrow range of temperature condition of our P-T re-estimations indicate that Grt lherzolite paragenesis was formed in a tectonic setting where the temperature condition is nearly constant from shallow to deeper level. One of the possible tectonic settings may be the upper part of the subducted crust.

Perrierite in sapphirine-quartz gneiss: geochemical and geochronological features and implications for accessory phase paragenesis of UHT metamorphism

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Al-rich variety of perrierite, Ti-REE silicates - (La,Ce,Ca)₂(Fe²⁺,Mg)₂(Ti,Al,Fe³⁺)₂Si₄O₂₂ (e.g., Macdonald & Belkin 2002), has been found in a sapphirine-orthopyroxene-quartz-bearing ultrahigh-temperature (UHT) pelitic gneiss from Mt. Riiser-Larsen, Napier Complex, East Antarctica. Major constituents of this UHT gneiss are quartz, orthopyroxene, sapphirine, osumilite, with minor biotite, K-feldspar and secondary cordierite. Zircon, monazite, perrierite and rutile are accessory phases. Sapphirine is commonly associated with quartz and orthopyroxene. Thin (20-50µm) film of cordierite occurs between sapphirine and quartz, and fine-grained (less than a few µm) aggregates of cordierite-K-feldspar-quartz-orthopyroxene symplectite are developed around osumilite crystals. These reaction textures are thought to have formed during the near-isobaric cooling from the peak ~1100°C conditions down to 900-800°C. Perrierite is commonly 50-500µm in diameter, and is relatively abundant (>10-20 grains in one thin section) compared with monazite (only a few tiny grains in one thin section). Electron microprobe analyses for perrierite, monazite and zircon in terms of REE chemistry and U-Th-Pb chemical ages have been carried out using JEOL JXA-8800 at the National Institute of Polar Research, Japan. Approximate chemical composition of perrierite in this sample is (La_{0.7}Ce_{1.6}Pr_{0.2}Nd_{0.6}Sm_{0.1}Y_{0.3}Ca_{0.3})(Fe_{0.5}Mg_{0.7}Al_{1.0})(Ti_{2.0}Al_{1.0})Si_{4.0}O₂₂, which is similar chemistry with 'Mg-Al-rich perrierite' reported from a granulite xenolith in Vestfold Hills, East Antarctica (Harley 1994). The perrierite grains of the studied sample have no significant compositional variation with respect to major and REE chemistry (e.g., La₂O₃=10.7±0.3 wt%, Ce₂O₃=21.1±0.6 wt%) and show the chondrite-normalized REE patterns (Ce_n/Dy_n=10-16) similar with monazites (Ce_n/Dy_n=12-24). Zircons suggest M-HREE (Gd, Dy, Er, Yb) concentrations up to 0.1 wt %, which are markedly high compared with normal zircon compositions. Monazite, zircon and perrierite gave equivalent c.2500-2460 Ma U-Th-total Pb ages with a few younger monazites (c.2200-1900 Ma) and older inherited? zircons (c.3300-2600 Ma), that are consistent ages with those reported for the metamorphic events including the UHT at the same area (e.g., Hokada et al. 2004). These imply that the perrierite might have stably coexisted with zircon and monazite at least the end of UHT event, and the occurrence of perrierite is possibly controlled by the relatively low phosphorous and high REE and titanium contents.

Windows to the very-low-temperature subduction process: a Review of worldwide lawsonite eclogites

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Lawsonite eclogites preserve a record of very-low-temperature conditions in subduction zones. All occur at active margin settings, typically characterized by accretionary complex lithologies, and as tectonic blocks within serpentinite-matrix mélange. Peak lawsonite-eclogite facies mineral assemblages (garnet + omphacite + lawsonite + rutile) typically occur in prograde-zoned garnet porphyroblasts. Their matrix is commonly overprinted by higher-temperature epidote-bearing greenschist- or amphibolite-facies assemblages. Pseudomorphs of various assemblages after lawsonite occur, particularly in some blueschist/eclogite transitional facies rocks. Coesite-bearing lawsonite-eclogite xenoliths in kimberlitic pipes and lawsonite pseudomorphs in some relatively low-temperature ultrahigh-pressure eclogites are known. Using inclusion assemblages in garnet, lawsonite eclogites can be classified into two types: L-type, such as those from Guatemala and British Columbia, contain garnet porphyroblasts that grew only within the lawsonite stability field, and E-type, such as those from the Dominican Republic, record the maximum temperature in the epidote-stability field. The inferred prograde P-T trajectory of the L-type lies near a geotherm of ~5°C km⁻¹, comparable to the calculated thermal structures of the NE Japan and the Alaska Range subduction zones.

Formation and preservation of lawsonite-eclogites requires cold subduction to mantle depths and rapid exhumation. The earliest occurrences of lawsonite-eclogite facies mineral assemblages have Early Paleozoic age in Spitsbergen and the New England fold belt of Australia; this suggests that since the Phanerozoic, secular cooling of Earth and subduction-zone thermal structures evolved the necessary high pressure/temperature conditions. Buoyancy of serpentinite and oblique convergence with a major strike-slip component may facilitate the exhumation of lawsonite eclogites from mantle depths.

Laser Raman microspectrometry of metamorphic quartz: A simple and effective method for comparison of metamorphic pressures

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Laser Raman microspectroscopy was used to study quartz from metamorphic rocks formed under various *P-T* conditions to discuss the quantitative correlation between the Raman shift and metamorphic pressure. Quartz inclusions show internal pressures specific to the individual host crystal: in eclogite the most intense Raman band, located at about 464 cm⁻¹ under room temperature and atmospheric pressure conditions, shifts up to 471, 472, 467 and 467 cm⁻¹ in quartz inclusions of garnet, kyanite, omphacite and epidote, respectively. These observations imply that the residual pressures retained by quartz inclusions depend on elastic parameters of the host crystals as discussed by previous researchers. Major Raman bands of quartz inclusion in garnet systematically shift up to 471, 225 and 132 cm⁻¹ in quartz-eclogite facies samples, 468, 217 and 130 cm⁻¹ in epidote-amphibolite facies samples and 465, 208 and 128 cm⁻¹ in amphibolite facies samples. Calibrations based on the experimental works suggest that the measured frequency shifts signify residual pressures of 0.7-0.8, 0.4 and 0.1 GPa for these three groups of metamorphic rocks, respectively. Normal stresses (internal pressures) of quartz inclusions in garnet numerically simulated adopting an elastic model and inferred pressure-temperature conditions at peak metamorphic stage are compatible with the residual pressures estimated based on the Raman frequency shifts. Laser Raman microspectroscopic analysis of quartz is a simple and effective method for (1) comparison of pressure conditions in metamorphic rocks formed under various *P-T* conditions, and (2) detection of higher-pressure signature in metamorphic rocks extensively recrystallized during the subsequent exhumation and hydration stage.

Ca-rich garnet-clinopyroxene rocks at Hujialin in the Su-Lu terrane (Eastern China): deeply subducted arc cumulates?

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Layers of Ca-rich garnet-clinopyroxene rocks enclosed in a serpentinite body at Hujialin, in the Su-Lu terrane of eastern China, preserve igneous textures, relict spinel in garnet, and exsolution lamellae of Ca-rich garnet, ilmenite/magnetite, Fe-rich spinel, and also amphibole in clinopyroxene. In terms of their major and trace element compositions, the studied samples form a trend from arc cumulates towards Fe-Ti gabbros. On diagrams of Al₂O₃ vs. Mg/(Mg+Fe²⁺), Al^{IV} vs. Ti, and Ca-Mg-Fe proportions, the reconstructed augite compositions fall on the trends for clinopyroxene in arc cumulates. These data, combined with the presence of pargasite inclusions in clinopyroxene, the high Fe³⁺ contents, and isotope compositions, suggest that the Hujialin clinopyroxenites crystallised from a hydrous, subduction-related, magma beneath an arc. Their relatively low Mg/(Mg+Fe), Cr and Ni, and high Al, Ti, Zr, and V contents suggest that they were not cumulates from primary magmas in equilibrium with the mantle, but from magmas which had differentiated to variable extents. The Ca-rich garnet + diopside assemblage is inferred to have formed by compressing Ca-rich augite, whereas the relatively Mg-rich cores of garnet porphyroblasts may have formed at the expense of spinel. The protolith cumulates were subducted from near the crust-mantle boundary (c. 1 GPa) deep into the upper mantle (4.8 ± 0.6 GPa and 750 ± 50 °C). Negatively sloped *PT* paths proposed by some earlier workers for the Hujialin garnet-clinopyroxene rocks are not conclusive. Cooling with, or without, decompression of the cumulates after the igneous stage likely occurred prior to deep subduction. In any case, such *PT* paths should not be used to argue for corner flow and mantle wedge subduction, because the Hujialin spinel clinopyroxenites most likely crystallised in the lithosphere near the crust-mantle boundary, rather than in the asthenospheric mantle.

Crystal-Chemistry of Phosphorus at Ultra High Pressures : Petrological Implications

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In many instances, ultra-high pressure conditions in continental and upper-mantle rocks can be assessed or confirmed from the unusual minor element contents of minerals. The phosphorus potential as high-pressure indicator has already been suggested (Thompson, 1975) but never really evaluated because of the lack of crystal-chemistry data for this element at high-pressure.

Phosphorus is a minor element with a chondritic abundance of ca. 0.25 wt. % P₂O₅. In the continental crust, where P₂O₅ concentrations amount to around a weight percent, the phosphorus budget is mainly controlled by apatite, Ca₅(PO₄)₃(OH,F,Cl), and monazite REEPO₄. Chemical data on peridotite xenoliths, UHP garnets and inclusions in deep-seated diamonds indicate that under high-pressure conditions, phosphorus tends to be incorporated in silicates. This crystal-chemical feature is likely to change the geochemical behaviour of phosphorus which has, for long, been associated to that of apatite. In order to illustrate the positive dependency of P - Si exchanges with pressure, we have carried out syntheses along the Mg₃Al₂(PO₄)₃ - Na₃Al₂(PO₄)₃ join, in the range 15-17 GPa at temperatures between 1200 and 1600 °C. An Na₃Al₂(PO₄)₃ compound of garnet structure with a cubic-cell parameter of 11.579 Å was obtained and a complete solid-solution series between this phosphate garnet and pyrope was evidenced. Along with the UHP ellenbergerite series, this is the second example of complete P - Si solid-solution at high pressure. In order to extend this result obtained on a simplified chemical system to nature, we conducted a series of experiments at ca. 18 GPa and 1873 K in a multi-component system. The starting material was an oxide mixture of pyrolytic composition (McDonough and Sun, 1995), to which around 2 wt. % P₂O₅ were added. Ringwoodite (Mg_{0.89}Fe_{0.11})₂SiO₄ along with phosphorus-bearing garnet are the dominant phases in the run product. EDS-SEM characterization revealed the presence of a Ca-dominant phosphate, (Ca_{2.3}Mg_{0.4}Na_{0.1})(PO₄)₂. From the derived stoichiometry, a structural similarity with the dense polymorph of Ca₃(PO₄)₂ (Murayama et al., 1986) can be envisaged.

This study shows (1) that phosphorus in high-pressure silicates can be used to track UHP conditions and (2) that the phosphorus geochemistry in the upper mantle is likely to be controlled by garnet and/or a calcium phosphate depending on bulk P₂O₅ composition.

Meso-Neoproterozoic compressional reworking of UHT metamorphosed granulites: first petrological evidence from the Eastern Ghats Belt, India

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Aluminous granulites exposed in high-grade terrains all over the world exhibit spectacular reaction textures that could be profitably harnessed to infer the *P-T-t* evolution of regional granulite terrains. This rock type preserves the textural evidences for both prograde and retrograde paths of evolution. Additionally, these rocks are instrumental to characterize the extreme conditions of metamorphism, e.g. UHT peak metamorphic conditions. In this study we describe both field and petrographic data from aluminous granulite exposed at Panirangini in the Eastern Ghats Belt. Large-scale field features imply superposition of three generations folding producing regional scale fabric pattern. A localized shear zone is developed at a very low angle to the major foliation in this region. Aluminous granulite occurs as a small lensoid body within foliated garnet-quartz-feldspar gneiss (leptynite). Macroscopically the aluminous granulite occurs in three modal varieties. Type A variety is foliated with alternate orthopyroxene-spinel-rich layer and quartzofeldspathic layer. Type B is massive with orthopyroxene and cordierite porphyroblasts. Type C is massive too with profusion of porphyroblastic garnet. The foliation in type A variety is mylonitic and characterized by recrystallized ribbon quartz in a pool of finer grained quartzofeldspathic matrix. Textural features in all these rocks indicate the stabilization of the assemblage aluminous orthopyroxene + spinel_{ss} + sapphirine at the UHT peak condition (> 1000 °C, 8-9 kbar) that changes to orthopyroxene (corona) + sillimanite (corona) + cordierite (poikiloblastic) ± biotite (late replacement) assemblage during retrogressive decompressive cooling. Cordierite grains show conspicuous and intensive breakdown to orthopyroxene + sillimanite + quartz + garnet fine intergrowth that possibly resulted due to loading synchronous to development of mylonitic fabric in the rock. This metamorphic and structural event is definitely unrelated to the early UHT one (the latter is tentatively dated as Mesoproterozoic c. > 1.7 Ga). Available petrological and geochronological data suggest that this second event is a manifestation of probably late Mesoproterozoic to Neoproterozoic orogeny. This is the first time that a loading event synchronous to a deep crustal shearing during this period could be characterized.

Pan-African High-Pressure and Ultrahigh-Temperature Metamorphism in the Palghat-Cauvery Shear Zone System: Implications for Crustal Evolution in Southern India

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The Palghat-Cauvery Shear Zone System (PCSS) at the northern margin of the Madurai Granulite Block in southern India is an extensive crust-scale shear zone between the Archean terrane in the north and Proterozoic granulite blocks in the south. A series of highly deformed lithologies that are composed mainly of charnockite, hornblende-biotite orthogneiss, pelitic and mafic gneisses, and sapphirine- and corundum-bearing Mg-Al rocks along the PCSS which have been subjected to high-grade metamorphism during the late Pan-African orogeny. Silica-deficient Mg-Al rocks from Sevitturampatti in Namakkal district located at the central domain of the PCSS have common mineral assemblages such as garnet + gedrite + sillimanite, Fe-rich staurolite + sillimanite + garnet, and biotite + corundum + sapphirine. Occurrences of garnet + corundum assemblage as well as Mg-rich ($X_{Mg} = 0.52$) staurolite and kyanite inclusions in poikiloblastic garnet suggest that the rocks underwent prograde high-pressure ($P > 11$ kbar) metamorphism, probably in the field of eclogite. They subsequently underwent ultrahigh-temperature (UHT) event of $\sim 990^\circ\text{C}$ at 7–8 kbar at the lower crustal level along a decompression path, as inferred from spinel-sapphirine and garnet-plagioclase-sillimanite assemblages. Various retrograde symplectite textures such as cordierite + spinel and cordierite + sapphirine between garnet and sillimanite, and cordierite + corundum between garnet and Fe-rich staurolite suggest the exhumation of rocks from lower to mid-crustal levels (600–700°C and ~ 4 kbar). The results suggest a single clockwise P - T trajectory for this crustal section. The high-pressure (HP) prograde metamorphism and following UHT event recorded in the rocks from Namakkal area are coincident with the timing of final amalgamation of the East and West Gondwana blocks into the Gondwana supercontinent. Due to the closure of the Mozambique Ocean and a subsequent continent-continent collision, subducted oceanic crust may have undergone HP (eclogite-facies) metamorphism. Subsequent slab delamination probably triggering heat input from mantle-derived magmas could explain the exhumation of the rocks to a lower crustal level, re-heating at extreme thermal conditions at UHT, and rapid uplift along a clockwise P - T trajectory.

New textural evidences of anomalously high thermal conditions in deep continental crust from Eastern Ghats granulite belt, India

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Recent study on some aluminous granulites of Eastern Ghats, India shows the presence of highly aluminous orthopyroxene, co-existing with sapphirine, cordierite, sillimanite, quartz and garnet in various combinations, that forms the granulite mosaic peak metamorphic assemblages. Orthopyroxene contains four types of intergrowths: (a) involving sapphirine with or without cordierite, (b) involving spinel, but without sapphirine, (c) involving cordierite, but without sapphirine, and spinel, and (d) involving garnet, without sapphirine, spinel or cordierite. Textural and compositional data indicate that the origin of the intergrowths is due to breakdown of Mg-Tschermak component, locally also involving Fe- and Ti-Tschermak. An attempt is made to compute the "pre-breakdown" compositions of orthopyroxene by image analysis, which shows maximum Al_2O_3 content of 13.4 wt.% in the pristine orthopyroxene. Geothermometry, phase equilibria consideration and application of existing experimental data on alumina solubility in orthopyroxene coexisting with sapphirine and quartz, collectively indicate extreme thermal conditions of metamorphism ($> 1000^\circ\text{C}$) for the studied assemblages. This re-affirms the notion that Al_2O_3 solubility in orthopyroxene is the most powerful indicator of UHT metamorphism (Harley, 2004). The intergrowths are considered to have formed due to cooling from the thermal peak spanning a temperature range of approximately 150°C . Appearance of diverse types of intergrowths is probably related to subtle differences in bulk composition, particularly Fe:Mg ratios. Moreover, the reaction textures and mineral chemistry at certain domains in similar aluminous granulite are consistent with prograde metamorphism. Of particular interest is a unique intergrowth texture as observed in garnet porphyroblasts from such domain. Lamellar to vermicular intergrowth of spinel solid solution occurs in garnet, particularly in the central part of the porphyroblast. Locally, sapphirine, overgrowing spinel, is also intergrown with garnet. Three possible mechanisms are discussed to account for the garnet-spinel intergrowth, viz. (a) from early stabilized orthopyroxene + sillimanite, (b) spinel pseudomorphing early sillimanite inclusions in garnet, and (c) from an early stabilized hypothetical highly aluminous orthopyroxene involving a complex reaction between the (Fe,Mg)-Tschermak and Fe^{3+} -Tschermak components. Sapphirine is produced by a reaction involving spinel and aluminous pyroxene. Regardless of the exact mechanism, available thermodynamic data suggest that all such reactions presumably occurred due to loading and/or heating during prograde metamorphism consistent with the conclusion from the other domain. Such an intergrowth texture has so far not been reported in aluminous granulite parageneses, but these could provide crucial information regarding the prograde segment of the metamorphic evolution of deep crustal rocks.

Metamorphic Evolution of the Kodaikanal Metapelite Belt, Southern India

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The Kodaikanal Metapelite Belt within the Madurai block in Southern India is a vast supracrustal belt that has undergone high grade metamorphism during the late Neoproterozoic, coinciding with the assembly of Gondwana supercontinent. The major rock types in this belt include Grt-Bt gneiss (Grt-Bt-Spl-Pl-Kfs-Qtz±Sil, Type 1), Grt-Crd-Bt gneiss (Grt-Crd-Bt-Spl-Pl-Kfs-Qtz±Sil±Cm, Type 2), and Grt-Sil-Spl-Crd gneiss (Grt-Sil-Spl-Crd-Pl-Kfs-Qtz±Bt, Type 3). This study describes the metamorphic conditions from this metapelite belt through detailed petrological and fluid inclusion studies.

The salient finding in this investigation is the first report of the occurrence of spinel and quartz in direct association within garnet, which is one of the key evidences for ultrahigh-temperature metamorphism in this belt. Spinel in equilibrium with quartz has moderate X_{Mg} ratio (0.42) and is characterized by low ZnO content (0.5 wt.%). The temperatures and pressures estimated from conventional thermobarometry are, however, slightly lower: Grt-Bt gneiss from 830 to 870°C and 5.4 to 7.2 kbar, Grt-Crd-Bt gneiss from 840 to 910°C and 5.0 to 8.0 kbar, and Grt-Sil-Spl-Crd gneiss from 840 to 920°C and 6.0 to 8.0 kbar. The pressure-temperature values estimated in this study fall within the general pressure and temperature conditions of granulites facies rocks. However, Grt-Crd geothermometer temperatures shows relatively low values $T = 780^\circ\text{C}$ as compared to the Grt-Bt geothermometer, in spite of using the compositional pair with X_{Mg} value of garnet and cordierite with most close distribution coefficient (K_D) value from $K_D = 1$. Besides it was also found that the reaction texture $\text{Grt} + \text{Sil} + \text{Qtz} = \text{Crd}$ is common in both type 2 and 3 rocks, indicating a retrograde stage. These observations suggest that almost all cordierite in the metapelites from Kodaikanal were possibly formed during retrograde metamorphism. Thus, these rocks do not preserve high temperature stable cordierite which is in equilibrium with garnet. The results of fluid inclusion heating-freezing experiment clearly show that the fluids were captured during the retrograde lower pressure regime.

This study reveals that the metapelites from Kodaikanal belt experienced retrograde metamorphism characterized by decompression, subsequent to peak conditions of ultrahigh-temperature metamorphism. The rocks preserve evidence for the UHT conditions only within inclusions in garnet, and the matrix assemblage has re-equilibrated during retrograde metamorphism.

Fluid-Rock Interaction in High-Grade Calc-Silicate Rocks from the Madurai Granulite Block, Southern India: Evidence from Scapolite Chemistry

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Granulite-facies calc-silicate rocks exhibit a wide variation in mineral assemblages and chemistry depending on pressure, temperature, fluid activity, and bulk-rock chemistry. Scapolite, a common mineral in high-grade calc-silicate rocks, generally contains Cl, CO_2 or SO_2 in its structure. Concentration of such mobile phases in scapolite is likely to be controlled by the composition of fluid present during its growth or recrystallization. Quantitative analysis of Cl, C, and S in scapolite is therefore a powerful tool for monitoring compositions of fluid and its flow mechanism in deep continental crust. The Madurai Granulite Block in southern India, a late Pan-African ultrahigh-temperature terrane, contains lenses or layers of marble and calc-silicate rock enclosed in charnockites and pelitic gneisses. The studied calc-silicate rock has a common mineral assemblage of K-feldspar + calcite + scapolite + clinopyroxene + sphene + graphite. Scapolite in the sample is textually divided into three types: Scp-I, IIa, and IIb. Subhedral and coarse-grained Scp-I occurs along the contact between marble and pelitic gneiss. Scp-IIa and IIb in pelitic gneiss are about 1–3 cm apart from the contact. Scp-IIa intergrows with K-feldspar and is elongated along the foliation. Scp-IIb locally overgrows around Scp-IIa. The Scp-IIa shows higher Cl content of 0.90–0.94 wt.% than that of Scp-I (0.33–0.48 wt.%) and Scp-IIb (0.38–0.51 wt.%). The Cl contents show a positive correlation with Na and K contents, suggesting a possible presence of saline fluid. According to EMP analysis of carbon by our new analytical technique, CO_2 content of Scp-I (5.68–5.96 wt.%) is higher than that of Scp-IIa (3.57–4.21 wt.%), while Scp-IIb contains a moderate CO_2 of 3.72–5.35 wt.%. All scapolites are almost free from sulfur. The results indicate a negative correlation between CO_2 and Cl contents for all scapolites. The compositional variation among the three types of scapolite is probably controlled by fluid-rock interaction along the boundary of marble and pelitic gneiss. Scapolite adjacent to marble underwent a significant effect of CO_2 influx from marble, forming high- CO_2 and low-Cl scapolite (Scp-I). In contrast, Na- and Cl-rich, and CO_2 -poor Scp-IIa crystallized in pelitic gneiss where saline aqueous fluid was dominant. Scp-IIb, which is textually a later product around Scp-IIa, may have been formed by introduction of post-peak Cl-poor fluid possibly from the marble. The results indicate that fluid composition differs within a thin (~ 3 cm) layer. Detailed study on scapolite chemistry therefore has an advantage in monitoring fluid-rock interaction at high-grade metamorphism.

Metamorphism and Fluids of Ultrahigh-Temperature Garnet-Orthopyroxene-Cordierite Granulites from the Achankovil Zone, Southern India

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The Achankovil Zone (ACZ) of southern India, a NW-SE trending lineament of 8-10 km in width and >100 km in length, is regarded to mark the boundary between the Madurai Granulite Block (MGB) in the north and the Trivandrum Granulite Block (TGB) in the south. Both the MGB and TGB show evidence for Pan-African ultrahigh-temperature (UHT) metamorphism, although their exhumation styles are markedly different. Several bands, layers and lenses of cordierite gneiss occur along the ACZ with common mineral assemblages of Crd + Grt + Qtz + Pl or Crd + Grt + Opx + Qtz + Pl with or without Spl, Ilm, Mag, Bt, Kfs, and Sil. The rocks occur within charnockite (Pl + Kfs (Pth) + Qtz + Opx + Bt + Mag + Ilm), and are locally intruded by concordant or discordant pinkish alkali-feldspar granite (Qtz + Pth). Geothermobarometric studies indicate that the rocks within the ACZ also underwent peak UHT metamorphism at 8.5-9.5 kbar and 940-1040°C followed by multistage exhumation history with retrograde conditions of 3.5-4.5 kbar and 720 ± 60°C. Such a multistage uplifting path has been reported from several UHT localities in the MGB. Similar P-T paths obtained from both the ACZ and the MGB suggest that the ACZ is not a unit of the TGB but the southern flank of the MGB. Cordierite gneisses and charnockites of the ACZ examined in this study contain fluid inclusions in garnet and quartz, and rarely in cordierite. Most of them occur as secondary phases along healed fractures probably formed by post-peak deformation associated with exhumation. Fluid inclusions in garnet (10-50 μm) are aligned along NNE-SSW trending cracks that cross-cut the gneiss foliation. The fluids are monophase at room temperature and show melting and homogenization temperatures of -56.9 to -56.1°C and +17.0 to +24.4°C, respectively, which corresponds to CO₂-rich fluid with densities of 0.72-0.80 g/cm³. These low-density carbonic inclusions were probably trapped during late Pan-African major shearing that affected the ACZ at low to middle crustal level of approximately 700°C at 2-3 kbar as inferred from calculated isochors. The fluid activity is probably related to an intracrustal suturing during the final amalgamation of Gondwana supercontinent.

Sulfide evolution in high-temperature to ultrahigh-temperature metamorphic rocks from Lützow-Holm Complex, East Antarctica

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The upper amphibolite to granulite facies high-temperature (HT) metamorphic rocks and the ultrahigh-temperature (UHT) metamorphic rocks from Lützow-Holm Complex, East Antarctica show a systematic difference between sulfide assemblages in the rock matrix and those found as inclusions in the silicates stable in high-temperatures. Matrix sulfides are commonly pyrite with or without pentlandite and chalcopyrite. On the other hand, inclusion sulfides are pyrrhotite with or without pentlandite and chalcopyrite lamellae. When recalculated into integrated single-phase sulfide compositions, inclusion sulfides from the UHT region showed a wider range of solid-solution composition than the inclusion sulfides from the HT region. The host minerals of the sulfides with extreme solid-solution compositions are those stable at the peak of metamorphism such as orthopyroxene and garnet. One of the most extreme ones is included in orthopyroxene coexisting with sillimanite ± quartz, which is the diagnostic mineral assemblage of UHT metamorphism. These observations suggest that sulfide inclusions preserve their peak metamorphic compositions. Both in HT and UHT samples, most of the integrated single-phase sulfide compositions belong to the solid phase compositional fields obtained from the experimental studies. Integrated single-phase sulfide compositions that belong to the melt fields are rare. This implies that inclusion sulfides in HT and UHT metamorphic rocks are in most cases restitic rather than melts. Pyrrhotite did not revert to pyrite because of the closed system behavior of sulfur in inclusion sulfides. On the other hand, sulfides in the rock matrix and inclusion sulfides connected to the rock matrix via cracks were partly to completely altered by the later fluid activity because the open system behavior of sulfur is permitted, and no longer preserve the original compositions. Inclusion sulfides that are completely isolated from the rock matrix, therefore, can be a potential thermometer as well as the good target of Re-Os dating.

Metamorphic evolution and partial melting under ultrahigh-temperature conditions: The Howard Hills UHT rocks, Napier Complex, East Antarctica

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The Napier Complex of East Antarctica preserves imprints of extreme crustal metamorphism at ultrahigh-temperature (UHT) conditions and is hence an important terrane in understanding the development and evolution of continental crust during Archaean to early Proterozoic. The Howard Hills area consists predominantly of garnet felsic gneiss, orthopyroxene felsic gneiss and aluminous gneiss with garnet, sapphirine and sillimanite in various amounts. We report the characteristic assemblage of sapphirine + quartz from quartz-feldspathic layers within the aluminous gneiss, which indicates that these rocks reached the stability field of sapphirine + quartz during peak metamorphism. P-T conditions changed from the stability field of sapphirine + quartz to that of garnet + cordierite + sillimanite. The peak metamorphic temperatures were around 1050-1150°C, as estimated by plotting the inferred original compositions of mesoperthites from garnet felsic gneiss, orthopyroxene felsic gneiss and aluminous gneiss on an An-Ab-Or ternary diagram. Quartz inclusions in the cores of garnets from silica-undersaturated layers within the aluminous gneiss from Howard Hills indicate that the garnets crystallized under the silica-oversaturated condition. This implies mass transfer within the aluminous gneiss, probably involving partial melting that also led to high Y concentrations in garnet cores, high An values for plagioclase, and high Ba contents in mesoperthites in the aluminous gneiss. Furthermore, garnet in garnet felsic gneiss exhibits compositional zoning of Y and P, indicating a marked change in the trace element distribution coefficient during the evolution of this rock. Trace element concentrations of aluminous gneiss and garnet felsic gneiss normalized to the upper continental crust in the Archaean show identical patterns; LILE-elements such as Rb and Ba are depleted and HFS-elements such as Zr, Ti and Y are enriched, typical of restitic pattern. The aluminous gneiss shows relatively higher abundance of HFS-elements than garnet felsic gneiss. This feature suggests that the aluminous gneiss has undergone relatively high degree of partial melting. Aluminous gneiss and garnet felsic gneiss presumably represent the restite fraction, and the anhydrous nature resulted from the separation and segregation of a melt phase. Partial melt from aluminous gneiss and garnet felsic gneiss were generated during prograde metamorphism with subsequent melt segregation while the restite was subjected to ultrahigh-temperature metamorphism.

Time tracks of cooling after UHT metamorphism in Howard Hills, Napier Complex, east Antarctica

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Large blocks of metamorphic rock with mafic to ultramafic compositions occur in felsic gneiss in the northern Howard Hills, Napier Complex, east Antarctica. The ultramafic core is separated from felsic gneiss by a mantle of pyroxene granulite, mostly composed of orthopyroxene with granoblastic polygonal texture. In places the mantle of pyroxene granulites is rich in the phlogopite. Adjacent samples of phlogopite-bearing pyroxene granulite and orthopyroxene felsic gneiss were taken from the edge of the mafic block. In the granulite sapphirine occurs as porphyroblasts with core of greenish spinel, or as thin films with quartz along the grain boundaries of granoblastic orthopyroxene. Rutile occurs along grain boundaries and as acicular inclusions in orthopyroxene. Phlogopite is rich in fluorine (nearly 4wt.%; Sato et al., 2004) and poor in H₂O (H₂O(-)=0.06wt.%, H₂O(+)=0.54wt.%). In the adjacent felsic gneiss alkali feldspar is perthite to mesoperthite. Peak metamorphic conditions of the gneisses have been estimated to 1150-1200°C (Yoshimura et al., 2000). Rb-Sr and Sm-Nd isotope data of the metamorphic rocks arranged lines on isochron diagrams with contemporaneous apparent ages about 2.65Ga within analytical errors with intercept of ordinate with ⁸⁷Sr/⁸⁶Sr=0.7357±0.0024 and ¹⁴³Nd/¹⁴⁴Nd=0.50856±0.00004 ($\epsilon_{\text{Nd,CHUR}}=-12.3\pm0.9$). No evidence regarding the isochrons as productions of mechanical mixing was found from texture nor compositions of the metamorphic rocks. This age is interpreted as the starting or peak time of UHT metamorphism with partial melting of LILE-enriched protoliths with high Sr isotope ratio. Phlogopite, orthopyroxene, feldspar and rutile in phlogopite-bearing pyroxene granulite and zircon in orthopyroxene felsic gneiss were extracted for specifying the temperature-time (T-t) tracks on and after the UHT metamorphism. Zircon grains from the felsic gneiss yielded near concordant U-Pb isotopic ages of about 2.5Ga by conventional isotope dilution methods and defined a discordia with 2.44±0.02Ga lower intercept age. This age shows the last of a period of UHT metamorphism in Howard Hills. Fluorophlogopite fractions from pyroxene granulite yielded Rb-Sr model ages of about 1.85Ga. Internal Sm-Nd isochron of the same granulite shows 1.85±0.15Ga. These ages record a time when the metamorphic rocks underwent medium to high-grade metamorphism. Rutile fractions from pyroxene granulite yielded near concordant U-Pb isotopic age of about 1.5Ga. This age is interpreted as the last episode of regional thermal activity except local igneous intrusions in the Napier Complex.

Sapphirine + Quartz Corona around Mg-Staurolite in Garnet Granulite from the Limpopo Belt, Southern Africa: Evidence for Ultrahigh-Temperature Metamorphism?

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Equilibrium sapphirine and quartz-bearing assemblages have been newly discovered in garnet granulites from the Central Zone of the Neoproterozoic Limpopo Belt in Zimbabwe, located between the Zimbabwe Craton in the north and the Kaapvaal Craton in the south. Poikiloblastic garnet in a pelitic granulite contains numerous inclusions of sapphirine + staurolite, sapphirine + quartz + staurolite, sillimanite + sapphirine, and orthopyroxene + cordierite, as well as monophase inclusions. The garnet is mantled by a corona of orthopyroxene + cordierite suggesting a clockwise nature of its P-T history. Sapphirine ($X_{Mg} = 0.83-0.87$) and quartz occur as a symplectitic intergrowth between garnet ($Alm_{38-40}Py_{57-59}Gr_{52-3}Sp_{50-1}$) and inclusions of unusually Mg-rich staurolite that is more Mg-rich ($X_{Mg} = 0.52-0.54$) than previously reported magnesian staurolite from the Central Zone. The core of a coarse-grained staurolite inclusion has the highest Mg content of $X_{Mg} = 0.55-0.58$. Sapphirine and quartz show a direct grain contact with no evidence of reaction texture, and the presented texture suggests that the following prograde dehydration reaction resulted in the formation of sapphirine + quartz:



Progress of the reaction is supported by the presence of fine-grained staurolite inclusions in product sapphirine and quartz. Available experimental and thermodynamic investigations suggest that the presence of equilibrium sapphirine + quartz in a granulite is a robust evidence of $T > 1000^\circ C$ ultrahigh-temperature (UHT) metamorphism. However, the peak P-T conditions obtained from this sample ($T = 850^\circ C$) is significantly lower than the inferred temperature condition of sapphirine + quartz stability, but not inconsistent with available peak P-T conditions of the Central Zone inferred from ternary-feldspar geothermometry and Al-solubility in orthopyroxene ($T = 900-950^\circ C$ at 8-9 kbar). It is known that high oxygen fugacity, high H_2O activity, and Fe-rich bulk chemistry could lower the stability field of sapphirine + quartz. Also, the reaction of sapphirine + quartz formation from staurolite has not been studied quantitatively. A preliminary thermodynamic calculations of the above reaction in the FMASH system indicate that, at $a_{H_2O} = 0.5$, sapphirine + quartz can be formed at $900^\circ C$ and 9-10 kbar, which is consistent with the peak P-T condition recorded from this zone. Our results therefore confirm that sapphirine + quartz can be formed from garnet and staurolite at lower temperature conditions ($T \sim 900^\circ C$), rather than during UHT.

Precursor high-pressure evidence in the Grt-Bt-Sil-Crd gneiss in the Lhenice shear zone (Moldanubian Zone of the southern Bohemian Massif), Czech Republic, and its geological significance

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Zoned garnet was newly found from low-pressure/high-temperature type gneiss with garnet, biotite, sillimanite and cordierite at Ktiš in the Lhenice shear zone of the southern Bohemian Massif, Czech Republic. This rock accompanies with various kind of partial melting structures such as leucosomes, parallel with foliation or in interboudin partitions, and leucocratic veins. Although most of fine-grained (0.8 mm in average) and coarse-grained (> 3 mm) garnets are homogeneous with a composition range of $X_{Alm} = 0.69 \sim 0.79$, $X_{Prp} = 0.19 \sim 0.25$, $X_{Grs} = 0.01 \sim 0.09$ and $X_{Sps} = 0.005 \sim 0.009$, Ca-content shows a silk-hat shape in some large grains; the core composition of $X_{Alm} = 0.66 \sim 0.68$, $X_{Prp} = 0.03 \sim 0.06$, $X_{Grs} = 0.24 \sim 0.25$ and $X_{Sps} = 0.03 \sim 0.05$, and the rim with identical composition with those of the homogeneous type. This zoning pattern is quite similar with those of the prograde type zoned garnet reported in Gföhl granulite (Carswell & O'Brien, 1993; Svojtka et al., 2002). The combination of Grt-Bt and Grt-Crd geothermometers and Grt-Als-Qtz-Pl and Grt-Crd-Sil-Qtz geobarometers evaluates $760-880^\circ C$ and 7.4-11.3 kbar for the equilibrium conditions for the matrix (rim) stage. Partial melting synchronously took place with the rim formation, as the fine-grained and coarse-grained garnets are contained in leucosome and residue (i.e. melanocratic part). Although Ky is not found from this specimen, a tentative use of the Grt-Als-Qtz-Pl geobarometer predicts that Ca-rich core once equilibrated with Ky in the early stage of the metamorphism, e.g. gives > 14 kbar at $600^\circ C$ and > 22 kbar at $900^\circ C$ for coarse-grained garnet core condition. These facts suggest that the garnets from LP/HP Ktiš gneiss experienced a higher pressure metamorphism and then suffered the low-pressure re-equilibration which formed the matrix assemblage represented by Ca-poor garnet along with biotite, sillimanite and cordierite. This P-T history resembles to that of the Gföhl granulite. Partial melting should play important roles for not only the exhumation of both the Gföhl granulite and the Lhenice shear zone, but also masking the precursor history of the Variscan metamorphism.

Low-pressure metamorphism on the Ryoke metamorphic rocks from Kasado-jima Island, SW Japan

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The Cretaceous low-pressure/high-temperature Ryoke metamorphic belt contains abundant granitoids of the Ryoke and San-yo granitoids that intruded at various crustal depths during or after the formation of the belt. To clarify the tectono-metamorphic history of the belt, it is necessary to evaluate the thermal effects of the intrusion of the different types of granitoids. Kasado-jima Island, SW Japan, contains metasedimentary rocks, massive biotite granite, and migmatitic biotite tonalite. The granite and tonalite occur in the central and southern areas, respectively. In the central area, the granite intrudes into metasedimentary rocks and cuts across bedding-parallel schistosity within the metapelites; this indicates that intrusion postdates the Ryoke metamorphism. In contrast, tonalite in the southern area was emplaced parallel to the schistosity. On the basis of the field occurrences and the petrographic characteristics of these granitoids, we correlate the biotite tonalite and biotite granite to the Older Ryoke and to the San-yo granitoids, respectively. Based on the paragenesis of schistosity-forming minerals of metapelites, we identify two mineral zones, biotite zone and cordierite zone. The biotite zone is characterized by a mineral assemblage of muscovite + biotite $\pm$ garnet, while the cordierite zone is characterized by the assemblage muscovite + biotite + K-feldspar + cordierite or garnet. On the basis of a mineral chemistry, we estimate peak metamorphic conditions for the biotite zone to be $\sim 470^\circ C$, and $\sim 550^\circ C$ and 250 MPa for the cordierite zone. In the central area, a contact aureole adjacent to the biotite granite is identified by the occurrence of randomly oriented muscovite and very large dendritic cordierite porphyroblasts. These randomly oriented porphyroblasts may have formed at a high degree of supersaturation due to a thermal perturbation by a shallow intrusion of the biotite granite to the cooler crust. In the southern area, most metamorphic minerals have the similar grain size and their longer axes are aligned to form a unique schistosity, suggesting a small degree of thermal perturbation and/or a high strain rate. This implies that the biotite tonalite as a deep-seated granitoids was related to the regional low-pressure/high-temperature metamorphism on Kasado-jima Island.

Interphase boundary diffusion rates and their effect on retrograde zoning patterns of metamorphic minerals

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During cooling from granulite facies conditions cation exchange equilibrium along the rims of garnet porphyroblasts is often restricted to interphase boundary segments, where garnet is in contact with its cation exchange partners such as pyroxene or biotite. This behavior indicates slow diffusion along interphase boundaries, which allows for the development and preservation of disequilibrium cation partitioning on the scale of individual grains. We have constructed a two-dimensional numerical diffusion model that allows for the simulation of retrograde zoning patterns in minerals at triple points, where a cation exchange reaction occurs between two minerals, and the third mineral does not take part in cation exchange. During retrogression element re-distribution between the exchange partners leads to compositional variations along their interface. This causes compositional gradients and diffusion along the entire interphase boundary network and ultimately modifies the compositions of the exchange partners also along their interfaces with the non-reactive third phase. For any reasonable cooling rate our simulations indicate that cation exchange equilibrium is maintained along interphase boundaries on the scale of individual grains only if diffusion along the interphase boundaries is several orders of magnitude faster than volume diffusion in the adjacent grains. For slower diffusion along interphase boundaries, compositional variations develop along the interphase boundaries depending on the local environment. In general, equilibration domains become successively smaller with decreasing temperature. Our calculations indicate that the development of equilibration domains during cooling does not only depend on standard enthalpy change for the exchange reaction, the cooling rate and the ratio of the diffusion coefficients in the reactive minerals, but is also influenced by the rates of diffusion along interphase boundaries. We applied our model to high-pressure granulite-facies metapelites from the Mozambique belt, SE-Kenya. There garnet porphyroblasts show retrograde zoning patterns, which involve non-equilibrated compositions along garnet-quartz interphase boundaries at garnet-biotite-quartz triple points. For an initial temperature of $820^\circ C$, a cooling rate of $5^\circ C/my$ and for an assumed grain boundary width, between 1 and 10 nm, our numerical model predicts the observed compositional pattern of garnet around the triple points, if diffusion along the interphase boundaries is about 5-7 log-units faster than within garnet. For these interphase boundary diffusivities measurable deviations from equilibrium cation partitioning begin to form when the rocks cool below about $550-600^\circ C$.

Experimental Studies of Melting Phase Relation of Garnet-Sillimanite Felsic Gneiss and Distribution of Minor Elements between Garnet and Melt under Ultrahigh-Temperature Metamorphic Condition

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Present study has two main objectives of unveiling the evolution processes of Archaean crust that is focused on Napier Complex in East Antarctica. First objective is an experimental demonstration of partial melting that could be accompanied with ultrahigh-temperature (UHT) metamorphism (e.g., Sheraton et al., 1987, *Bur. Miner. Resource Bull.*; Hokada et al., 1999, *Polar Geosci.*; Osanai et al., 1999, *Polar Geosci.*; Yoshimura et al., 2000, *Polar Geosci.*; Miyamoto et al., 2004, *Polar Geosci.*). Second one is a detailed description of distribution of minor elements between mineral and molten phase under the UHT metamorphic condition. In this experiment, garnet-sillimanite felsic gneiss (sample no. YY9812290702; Yoshimura et al., 2000), which was collected from the Napier Complex, was used as a starting material. Experiments were carried out using a piston-cylinder apparatus at P = 12-16 kbar and T = 1100-1200 degree-C. The high pressure experiments revealed that melt coexisting with mineral phases was produced in the specific conditions at P = 12-14 kbar and T = 1150 degree-C, and at P = 16 kbar and T = 1175 degree-C. Thermal peak of UHT metamorphism in the Napier Complex has been reported as over 1120 degree-C (Harley and Motoyoshi, 2000, *Contrib. Mineral. Petrol.*). Agreement in the P-T conditions supports the possibility of partial melting in the complex. At present, partitioning relation of minor elements between garnet and melt in a run product, which was obtained at 12 kbar and 1120 degree-C, was also investigated using an ICP-mass spectrometer coupled with a laser ablation system (at TITech). This result will be useful for constraints on the evolutionary process under the UHT metamorphic condition. In this talk, we will present following topics: (1) experimental data of the melting phase relation, and (2) analytical data of the distribution of minor elements.

First Report of h  gbomite from ultrahigh temperature metapelite along the Ranotsara Shear Zone in Southern Madagascar

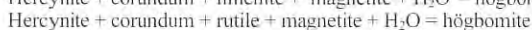
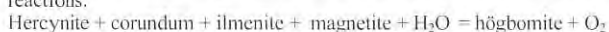
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We report new occurrences of h  gbomite from Pan-African (630-520Ma) granulite facies metapelites along the Ranotsara Shear Zone in Southern Madagascar. The h  gbomite-bearing rocks were suffered intense deformation and ultrahigh temperature metamorphism evidenced by the occurrences of corundum-quartz and hercynite-quartz assemblages. The rocks consist mainly of Mt + Ilm + Sill + Crd + Pl + Kfs + Bt + Qtz + Grt + Hc, and minor amount of corundum and h  gbomite. The h  gbomite occurs along the fractures and grain boundaries of magnetite and ilmenite. It associates with Mt + Hc + Ilm + Crn + Rt + Pseudorutile. The petrographical observations suggest that the h  gbomite crystallized under retrogressive metamorphic stage after the ultrahigh temperature metamorphic conditions where hercynite + quartz and corundum + quartz are stable. Hercynite, magnetite, corundum, ilmenite, rutile and probably melt are involved in the h  gbomite formation. We suggest following h  gbomite forming reactions:



XRD analyses suggest that the present h  gbomite is probably the 2N2S type. Electron microprobe analyses of the h  gbomite yield: ZnO (0.00-8.78 wt%), Al₂O₃ (59.91-63.04 wt%), Cr₂O₃ (0.00-0.50 wt%), FeO (21.53-29.27 wt%), MgO (2.98-5.58 wt%), MnO (0.00-1.35 wt%), TiO₂ (3.88-6.09 wt%), CaO (0.00-0.27 wt%), K₂O (0.00-0.01 wt%), Na₂O (0.00-0.11 wt%), SiO₂ (0.00-0.86 wt%). The similarity in chemistry of the present h  gbomite to those in literatures (Gatehouse and Grey, 1982; Armbruster, 2002 and Hejny et al., 2002) permits us to apply the structural formula: (Fe²⁺ZnMgAl)₆(Al³⁺Fe³⁺Ti⁴⁺)₁₆O₃₀(OH)₂.

The chemical analyses suggest that compositional variation in the present h  gbomite is governed by the substitution of Zn²⁺ by Mg²⁺+Mn²⁺+Fe²⁺. There is weak core-rim zoning in individual grains. The zinc content in the h  gbomite grain highly depends on the associated mineral.

Keywords: H  gbomite, ultrahigh temperature metamorphism, corundum + quartz, Ranotsara Shear Zone, Southern Madagascar.

Corundum Replacing Al₂SiO₅ Minerals in the Vicinity of Quartz in both High-pressure and High-temperature Metamorphic Rocks: Evidence for Brief Partial Melting during Exhumation

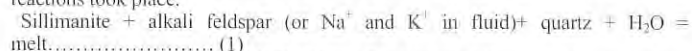
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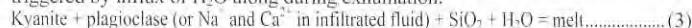
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It is not uncommon for corundum to occur in quartz-bearing rocks. However, the question of whether or not corundum-quartz association is stable has been long debated. We have found corundum replacing preexisting Al₂SiO₅ minerals in metamorphic rocks formed under widely different conditions (from UHT-HT to UHP). In UHT-HT metamorphic rocks (graphitic garnet-sillimanite gneiss) from Sri Lanka and East Antarctica, sillimanite is partially replaced by symplectitic intergrowths of corundum and alkali feldspar (or albite and orthoclase). Corundum is always separated from quartz by thin films of alkali feldspar. In addition, textural features clearly show that quartz was consumed during corundum formation. These observations imply the following congruent and incongruent reactions took place.



The rocks lack hydrous minerals and we suggest partial melting was triggered by influx of H₂O which resulted in local superheating. These reactions are estimated to take place at temperatures around 800   C.

In the case of UHP metamorphic rock from Donghe, SE China, kyanite is partially replaced by symplectitic intergrowths of corundum and plagioclase in epidote-phengite-kyanite-bearing "quartz" pools developed in eclogites. The symplectites are separated from quartz by thin film of albite and are commonly accompanied by paragonite. The mineral textures are most satisfactorily explained by the following partial melting reactions, which we also suggest were triggered by influx of H₂O along during exhumation.



These reactions may have taken place at temperatures below 700   C.

Both in the UHT-HT and the UHP metamorphics, the feldspar films separating corundum from quartz are probably produced from melts. These films are as thin as 0.1 mm indicating an extremely short duration for the partial melting event.

Ultrahigh-pressure metamorphism recorded in ultrahigh-temperature mafic granulite from the Kontum Massif, central Vietnam

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Ultrahigh-temperature (UHT) metamorphic rocks in the world usually contain well-developed decompression textures that are useful to understand the metamorphic evolution after the peak metamorphism. However, it is quite difficult to identify the peak-pressure conditions of such UHT granulites in most cases. Because the high-pressure minerals are easily replaced by high-temperature mineral assemblages under its extremely high-temperature condition. In this presentation, we discuss the pressure limit and detail pressure-temperature (P-T) path of the UHT mafic granulite from the Kontum massif in central Vietnam. The Kontum massif is composed mainly of amphibolite- to granulite-facies metamorphic rocks. The mineral parageneses and mineral chemistries including isotopic data of some granulites suggest the UHT metamorphism took place in part of this massif at the Permo-Triassic. The UHT metamorphism is considered to be due to the continental collision event in Asia that characterized by ultrahigh-pressure (UHP) metamorphism in the Dabie-Sulu belt. UHT mafic granulite studied here, occurs as block, as lens and as disrupted layer within pelitic or felsic gneisses. The mafic granulite consists of coarse-grained granoblastic Grt, Cpx, Rt and Qtz as well as fine-grained Opx+Pl+Mag+Spl symplectites. The symplectites well develop around Grt and show decompressional evolution during UHT conditions (1.3 GPa at 1050  C to 0.8 GPa at 850  C). High-pressure relicts in UHT mafic granulite are observed as Qtz rods in Cpx and Rt needle in Grt. The recalculated precursor Cpx and Grt show supersilicic and supertitanic compositions, respectively. In addition, micro-Dia is also present within Zrn in host pelitic gneiss, which suggests the possibility of UHP metamorphism prior to UHT conditions. Sm-Nd internal isochron ages of host pelitic gneiss and mafic block yield 247 and 240 Ma, respectively. U-Pb SHRIMP analysis of Zrn including micro-Dia reveals 268 Ma. These ages propose the UHT mafic granulite was metamorphosed together with host pelitic gneiss and experienced UHP condition before decompression. The P-T conditions of peak-pressure stage were estimated by minimum pressure of Dia stability and Grt-Cpx thermometry using recalculated supertitanic Grt and supersilicic Cpx. The result shows P-T conditions of ca. 900-930   C and >4 GPa. From the conditions, the rock subsequently decompressed to relatively low-pressure UHT metamorphic condition. It is a first report of Dia occurred in UHT granulite in the world. The extreme P-T path is thus significant to realize the tectonic evolution of continental collision among SE-Asian continental crusts, especially for the uplift process from mantle depth.

Pressure and temperature trajectory of the kyanite-quartz eclogite from the Sambagawa metamorphic belt, Japan

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The prograde stage pressure and temperature trajectory of the kyanite-quartz eclogite from the Besshi area, the Sambagawa metamorphic belt, Japan, is investigated using the petrogenetic grid and the Gibbs' method. The mineral assemblage of the kyanite-quartz eclogite is mainly constituted by quartz, garnet, omphacite, phengite, and epidote. In addition, kyanite appears in the leucocratic part and hornblende in the melanocratic part. In the leucocratic part, the poikiloblastic texture of the porphyroblastic garnet core characterizes the pre-peak stage mineral assemblage, including quartz, phengite, paragonite, epidote, chlorite, albite, and hornblende/glaucophane. Omphacite and kyanite are never found in the garnet core but appear in the garnet mantle and the matrix. The inclusion-poor mantle of the porphyroblastic garnet and the ubiquitous fine-grained euhedral garnet indicate the extensive garnet growth and nucleation during the prograde stage. The garnet core of the leucocratic part (Alm44-54Sps2-4Prp24-36Grs14-20) is richer in almandine and poorer in grossular than that of the melanocratic part (Alm34-41Sps2-3Prp32-40Grs20-25). The garnet rim composition of the leucocratic part varies from sample to another ranging from Alm43-47Sps1-2Prp32-39Grs15-20 to Alm38-44Sps0-1 Prp39-46Grs15-20. The latter is almost the same composition as the garnet rim of the melanocratic part. The analysis of the petrogenetic grid in the $\text{Na}_2\text{O}-\text{CaO}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (NCFMASH)-system with quartz, phengite and H_2O as excess phases indicates that (1) the assemblage of garnet, omphacite and kyanite was stabilized after crossing the tie-line switching reaction of garnet + hornblende + paragonite + zoisite = omphacite + kyanite, and (2) the increase of Mg# in garnet enhanced the creation of garnet through the continuous reaction of hornblende = omphacite + garnet. Peak pressure and temperature conditions of 650-700°C and 2.5 GPa are estimated by the garnet-clinopyroxene-phengite-kyanite-quartz geothermobarometer (Krogh Ravna and Terry, 2004). Pressure and temperature trajectories are inverted applying the Gibbs' Method to the garnet zoning incorporating the Al/Fe^{3+} ratio of epidote and Si/Al ratio of phengite in the garnet-omphacite-kyanite-epidote-phengite-quartz-water assemblage and the $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{FeO}-\text{MgO}-\text{CaO}-\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{H}_2\text{O}$ system. The clinozoisite content of epidote is assumed to have linear relation with the grossular content of garnet. Phengite Si/Al ratio is assumed to be constant. Garnet zonings of both grossular-decrease and -constant are inverted along almost the same pressure and temperature gradient of 0.7 GPa/100°C, which is similar to the conditions of the top of the subducting Philippine Sea plate in south-west Japan.

Protolith and polymetamorphic evolution of the Tonaru eclogite-bearing metagabbro body in the Sambagawa belt, central Shikoku, Japan: implications for the tectonic process of oceanic crust in subduction zone

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The protolith and metamorphic evolution of the Tonaru eclogite-bearing metagabbro body in the Sambagawa metamorphic belt exposed in central Shikoku, Japan, were investigated for understanding a tectonic process of subducted oceanic crust and related high- P/T metamorphism. The Tonaru metagabbro body occurring as a tectonic block in the high-grade portions of the Sambagawa belt consists mainly of garnet-epidote amphibolites with minor eclogites and diopside amphibolites. The major protolith of the Tonaru body is of layered gabbro, but the local occurrence of such intercalated metasedimentary rocks as pelitic schists and marbles suggests a possibility of sedimentary origin for a part of the body. The original rocks of the Tonaru body underwent three events of prograde metamorphism: the high- T/P metamorphism, the high- P/T metamorphism of the eclogite facies and the Sambagawa prograde metamorphism of the epidote amphibolite facies. The first high- T/P metamorphism probably attained to the amphibolite or granulite facies on the basis of the occurrence of relict Mg-rich garnets and TiO_2 - and Al_2O_3 -rich taramite-pargasite inclusions in garnets in the eclogites and garnet-epidote amphibolites. This high- T/P event might be explained as ocean-floor metamorphism or dynamothermal metamorphism such as metamorphic soles beneath ophiolites before the high- P/T subduction zone metamorphism. The second high- P/T event consists of three stages, i.e. pre-peak- and post-eclogite stages. Epidote and glaucophane inclusions in eclogitic garnet suggest a $P-T$ condition of the epidote-blueschist facies ($T = 300 - 450^\circ\text{C}$ and $P = 0.7 - 1.1$ GPa) before the attainment of the peak metamorphic conditions of the eclogite facies ($T = 700 - 730^\circ\text{C}$ and $P \geq 1.5$ GPa). The Tonaru body was retrograded into the epidote amphibolite facies during the post-eclogite stage. After the high- P/T metamorphism the Tonaru mass has experienced the Sambagawa prograde metamorphism, together with surrounding Sambagawa schists, until the conditions prevalent in the oligoclase-biotite zone (ca. 600 °C, 0.9 - 1.1 GPa) which is the highest metamorphic grade in the Sambagawa belt in central Shikoku were reached. The Tonaru metagabbro body is probably derived from an oceanic lower crust, and it underwent to the high- T/P metamorphism with the inception of subduction. Subsequently, it subducted to a depth of over 50 km in the eclogite facies during the high- P/T metamorphism in subduction zone.

Two generations of talc in the Sanbagawa metamorphic rock at the Kotsu area, eastern Shikoku, Japan

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Various modes of the occurrence of talc were identified in piemontite-quartz schists collected from the schist and the eclogite units in the Kotsu area of Sanbagawa belt, Japan. They were classified into following three types: A) Later stage talc than the matrix phases, B) Matrix talc associated with Na-pyroxene (NaCpx) or Na-amphibole (NaAmp) in the eclogite unit sample, and C) Matrix talc associated with albite or chlorite in the schist unit sample. The representative A) type talc is developed at pull apart of NaAmp along with albite, chlorite and phengite in samples from both the schist and the eclogite units, suggesting that the these talc were produced consuming NaAmp. Microstructures, such as rare paragonite inclusion in piemontite porphyroblast and talc-NaAmp intercalation in albite porphyroblast in the eclogite unit, suggest that NaAmp-talc-paragonite-phengite assemblage was stable at an early stage and talc-albite-chlorite-phengite was stable in a later stage. Talc-NaCpx-phengite association was found from a thin layer with higher Na_2O (1.64 wt%) content in the eclogite unit. NaCpx shows a chemical zoning of decreasing jadeite and increasing aegirine content from the core (ca $\text{Jd}_{40}\text{Aeg}_{60}\text{Di}_{20}$) to the rim (ca $\text{Jd}_{23}\text{Aeg}_{33}\text{Di}_{24}$). Some NaCpx was rimmed by secondary winchite and albite with various degrees and tiny idiomorphic winchite developed sticking into a talc-NaCpx pool. These textures suggest that talc-NaCpx (core)-phengite assemblage once equilibrated during an early stage. Using an internally consistent thermodynamic dataset, the plausible petrogenetic grid was selected in the system of CNKMA-Fe³⁺-SH with excess piemontite (regarded as epidote), hematite, and quartz. This grid suggests that the talc-NaCpx-phengite assemblage is stable at higher pressure condition (ca >11 kbar) and that talc-albite-phengite assemblage is stable at around 9-10 kbar. The results suggest that the pull apart talc of the eclogite unit was produced by the following reaction; crossite + paragonite = talc + albite during the decompression stage. Pseudosection analysis for the NaCpx-bearing layer suggests that talc-NaCpx-phengite assemblage is stable at around 550-620 °C and 16-20 kbar. This P-T condition is concordant to that of Kotsu glaucophane eclogite (20 kbar, 600 °C; Matsumoto *et al.*, 2003). The pull apart talc associated with phengite and albite can be stable at around 565-580 °C and 9.5-10.5 kbar. These facts suggest that the piemontite-quartz schist from the eclogite unit first experienced a high pressure metamorphism at about 50-60 km depth and then exhumed to ca 30 km depth under adiabatic conditions, where the eclogite unit and the schist unit may have juxtaposed each other.

The origin of jadeite-quartz rocks in the Kamuikotan metamorphic terrane, Japan

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The Kamuikotan metamorphic terrane consists of high P/T metamorphic rocks with glaucophane-lawsonite assemblage, and is characterized by the appearance of large amounts of serpentinite. The rocks consisting mostly of jadeite and quartz (referred to as "jadeite-quartz rock") are found in and around the serpentinite masses. The formation of these rocks needs the remarkable high-pressure/low-temperature metamorphic conditions. To reveal the protolith of these rocks is important to understand the Kamuikotan metamorphism and the tectonic environment of the Kamuikotan metamorphic terrane. Boulders of jadeite-quartz rocks have been well known in the Etanbetsu-Daihasen River (type 1). Takayama (1986) suggested that these rocks had been derived from plagiogranite, and metamorphosed under the condition of 200 °C and 1 GPa. Another type of jadeite-quartz rocks (type 2) were newly found as several boulders in the Osamunai-Horonai River. The type 2 rocks are composed mainly of jadeite (Jd_{95-100}), quartz, phengite, K-feldspar, lawsonite, and albite. They are massive and do not have any foliation. The bulk rock analyses indicate that they are acidic in composition (i.e., $\text{SiO}_2 = 75-77\text{wt\%}$, $\text{Na}_2\text{O} = 5.4-5.8\text{wt\%}$, $\text{K}_2\text{O} = 1.9-2.5\text{wt\%}$). A peculiar texture is recognized in the type 2 rocks; that is, relatively coarse-grained jadeite crystals of 1-2 mm in diameter are scattered in the matrix which mainly consists of the aggregate of fine-grained crystals of quartz and jadeite. The coarse-grained jadeite has many inclusions of quartz, phengite and K-feldspar in the core, and of quartz, lawsonite, phengite and K-feldspar in the rim. Slender 10 to 20 μm lawsonite crystal with random direction is characteristically abundant in the rim. The mineral associations of core and rim suggest that the coarse-grained jadeite was primarily a K-feldspar mantled with plagioclase. The compositions inferred from ratios of each constituent mineral in the core and the rim are roughly consistent with K-feldspar and plagioclase, respectively. This type of feldspar is common in rapakivi granite from Northern Europe. Small but similar feldspar was also reported from granite in Ashizuri Cape, Japan. It is highly probable that the protolith of type 2 rocks is granite with rapakivi feldspar. During the Late Jurassic to Cretaceous time, granitic rocks had been supplied into the trench from once developed island-arc or continent, dragged down into deeper part, and consequently changed into jadeite-quartz rocks by metamorphism. Thereafter, the rocks were uplifted by serpentinite diapir to the region where the lower-grade high P/T Kamuikotan metamorphism was prevailed.

Phase relationships of the eclogite in the southern Eclogitic Micaschist Complex of the Sesia zone, Italy

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We briefly introduce the relationship between the phase relationships of the eclogite in the Orco Valley area in the southern Eclogitic Micaschist Complex (EMC) of the Sesia Zone. Studied samples were collected from around Pont Canavese (PC; along the Orco Valley) and St. Maria (SM; northern slope of the Orco Valley). PC eclogite occurs along with lawsonite (Lws)-bearing rock and its main mineral paragenesis is garnet (Grt) + omphacite (Omp) + glaucophane (Gln) + clinozoisite (Cz) + paragonite (Pg) + phengite (Phn) + quartz (Qtz) + titanite (Ttn) + rutile. SM eclogite lacks Cz and Ttn as matrix phases and does not accompany with Lws-bearing rock. The pair among the highest X_{Grs} in Grt, X_{Gln} in Omp and X_{Cz} in Phn gives following peak metamorphic P-T conditions, using Powell (1985) and Waters & Martin (1993) thermobarometry; 512 ± 20 °C and 16.8 ± 0.6 kb for PC eclogite and 562 ± 22 °C and 18.1 ± 0.9 kb for SM eclogite. The latter gives significantly higher temperature. This estimation of SM eclogite is almost identical to those of previous studies in the central EMC by Tropper & Essene (2002) and Zucali et al. (2002). The phase equilibrium relation of the eclogites was examined by PT pseudosection for the model NCKFMASH system with Qtz, Phn and water in excess combined with the bulk composition of both PC and SM eclogites. The obtained PT pseudosections for both PC and SM eclogites show the divariant field of Grt+Omp+Gln+Cz+Pg (<540 - 570 °C and 13 - 16 kb) located at lower temperature side to the trivariant field of Grt+Omp+Gln+Pg (>540 - 570 °C and 14 - 20 kb). These PT conditions of the predicted mineral paragenesis are well concordant with the PT estimation by the conventional geothermometry for SM eclogite, but show slightly lower pressure (2 - 3 kb) for PC eclogite. The modal amount of hydrous mineral decreases from PC (lower T) to SM (higher T) eclogite with relatively constant Phn amount, such as Gln (20% to 2), Pg (20 to 1) and Cz (10 to 0). These data suggest that the successive dehydration proceeded from the divariant field of Grt+Omp+Gln+Cz+Pg to higher PT trivariant field of Grt+Omp+Gln+Pg. As the result, water content decreases from ca. 1.6 wt% (PC eclogite) to ca. 0.9 wt% (SM eclogite). The water contents of continental crust origin SM eclogite is slightly lower than that of New Caledonian barrosite eclogite (ca. 1.5 wt%; oceanic crust origin) and Field F of Schmidt & Poli (1998) in K-free basalt system, where are identical PT conditions to SM eclogite. This difference between 0.9 and 1.5 - 2.3 wt% may characterize the dry circumstance of the original rock, i.e. continental dry basalt vs. oceanic hydrous basalt.

Characterization of polymetamorphism in the Austroalpine basement east of the Tauern Window using garnet isopleth geothermobarometry

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The Austroalpine basement was affected by at least two metamorphic events during pre-Eo-Alpine times. A first metamorphic overprint is usually ascribed to the Variscan orogeny. In addition some Austroalpine units were affected by extensional tectonics accompanied by magmatism and high temperature/low pressure (HT/LP) metamorphism during Permo-Triassic times. Due to intense Eo-Alpine metamorphism and deformation during the Cretaceous the rock fabrics and mineral parageneses from the pre-Eo-Alpine evolution were almost completely obliterated. Usually garnet porphyroblasts in metapelites from the Upper Austroalpine basement nappes are the only remnants of the polymetamorphic evolution. In many cases these garnets show several distinct growth zones, and the original compositional growth zoning appears to have been preserved. The systematics of garnet core compositions suggests that chemical equilibrium was attained over the scale of a hand specimen, at least during the incipient stages of garnet growth. A Rayleigh fractionation model is employed to estimate the shifts of the thermodynamically relevant composition due to the crystallization of garnet. The P-T estimates obtained from garnet isopleth geothermobarometry fall into three distinct groups, which represent three different metamorphic events. For the incipient growth stages of the Permian garnet generation, which together with inclusions of quartz and ilmenite represents the only remnants of the HT/LP metamorphic event, temperatures of about 540 °C $\pm$ 15 K and pressures of 4 ± 0.5 kbar are inferred. This testifies to garnet growth at a geotherm of about 40 K per kilometre during the Permian. These conditions clearly differ from the P-T estimates obtained for the Variscan and the Eo-Alpine events: Incipient growth of Cretaceous garnet occurred at about 535 °C $\pm$ 10 K and 6.75 ± 0.5 kbar, i.e. at a geothermal gradient of about 20 K per kilometre. This is markedly cooler than a thermally relaxed continental geotherm and probably indicates that Eo-Alpine garnets started to grow during fast subduction, where thermal relaxation could not keep up with rapid pressure increase. The third set of P-T estimates clusters around 535 °C $\pm$ 20 K and 5.5 ± 0.5 kbar, i.e. at a geothermal gradient of about 30 K per kilometre. This is clearly separated in P-T space from the Permian and Cretaceous garnet generations. This suggests that the respective garnet generation pertains to a different metamorphic event, presumably of Variscan age.

Eclogites and UHP metamorphic rocks in the Kyrgyz Tien-Shan

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There are three HP and UHP metamorphic areas in the Kyrgyz Tien-Shan, i.e. the Makbal and the Aktyuz areas in the Northern Tien-Shan and the Atbashi Range in the Southern Tien-Shan, and preliminary introduction of these metamorphic rocks has been already published (e.g. Sobolev et al., 1986; Tagiri and Bakirov, 1990; Tagiri et al., 1995; Puelles and Takasu, 1996; Bakirov et al., 1998). The recent progress in our research is being presented in this paper. In the Makbal area garnet-chloritoid-talc schists area intercalated in quartzites, and eclogites and amphibolites probably derived from the eclogites occur as lens or sheet-like bodies within the quartzite layers. Coesites and quartz pseudomorphs after coesite occur as inclusions in the garnets in the garnet-chloritoid-talc schists (Ishida et al., 2004). The peak metamorphic conditions of the garnet-chloritoid-talc schists are estimated as >29 kbar and c. 600 °C. Eclogites (540 - 650 °C, >14 kbar) suffered a prograde metamorphism through the epidote amphibolite facies, and after the eclogite metamorphism some of them experienced the second HP prograde metamorphism from the greenschist facies to the epidote amphibolite facies. In the Aktyuz area eclogites and amphibolitized eclogites occur as lenses layers in pelitic gneisses and gneissose-granites, and three metamorphic events are distinguished in the eclogites, i.e. the first relatively LP-HT metamorphic event, the second HP metamorphic event to get to the eclogite facies (690 ± 30 °C, >16 kbar) and the third relatively LP-HT metamorphic event of the amphibolite facies. Field occurrence and petrography of eclogites and the country rocks gneisses have shared at least the last metamorphic event (Orozbaev et al., 2006; IMA-Kobe). In the Atbashi area eclogites have two modes of occurrence, i.e. layers in pelitic schists and massive blocks within the alternations of layer eclogites and pelitic schists. Layer eclogites and pelitic schists have a similar mineral assemblage including garnet, omphacite, glaucophane, phengite and quartz, and the peak metamorphic conditions are >11 - 14 kbar and 400 - 500 °C. Tagiri et al. (1995) estimated the UHP metamorphic condition for a massive eclogite according to the occurrence of quartz pseudomorph after coesite and talc-albite aggregate in garnet and omphacite. There are at least three tectonic and related HP-UHP metamorphic events (Aktyuz: 750 Ma, Makbal: 480 - 510 Ma, Atbashi: 270 Ma) in the Kyrgyz Tien-Shan (Tagiri et al., 1995, 2005).

The Garnets from Conțu-Negovanu Pegmatitic Field (Lotru-Cibin Mts. – Romania)

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The Conțu-Negovanu pegmatitic field is located in the Lotru-Cibin Mts. (South Carpathians, Romania). The pegmatite bodies are hosted by mesometamorphic rocks (kyanite-staurolite-bearing micaschists, biotite paragneisses) of the Sebeș-Lotru Group within the Getic Realm. In the Conțu-Negovanu field there are feldspar pegmatites and albite-spodumene pegmatites – their mineralogical composition, bulk chemistry and geochemical signatures suggest that they both represent successive stages of the pegmatitogenesis, which are related to the late crystallization fluid. Selected garnet crystals belonging to the albite-spodumene pegmatites, feldspar pegmatites and to the metapelites were analysed for major elements (Si, Al, Mg, Ca, Mn, Fe) – by EMPA and XRF techniques, and for trace elements – by ICP-MS.

The investigated garnet samples generally display a normal chemical composition. In metapelites and in feldspar pegmatites, almandine is predominant (73-86% alm.), whereas in the albite-spodumene pegmatites the garnet composition becomes more spessartinic (max. 53,18% spess.). In this respect, the X_{Mg} values are relevant, as they decrease with at least one order of magnitude in the spessartinic garnet type compared to the almandine rich garnets. The minor element contents are also differentiated: Sc, V, Cr, Co and Ni display higher contents in the metamorphic garnets than in the pegmatitic ones, showing in fact their immobility during the pegmatitic stages. Y which concentrates in the nucleus of metamorphic garnets is less mobile and therefore, it has 20-30 times lower contents in the garnets belonging to the pegmatites. Other trace elements, like Nb and Ta (especially Ta), which concentrate in the final pegmatitic fluids, show higher contents in the pegmatitic garnets. The chondrite normalized REE patterns display a characteristic trend for the metamorphic garnets, whereas in the pegmatitic garnets the REE contents are lower and also present an abnormal trend of these patterns. The decrease of the REE contents in the pegmatitic garnets as compared to the metamorphic ones, by at least one order of magnitude, is normal considering the immobility of these elements versus the pegmatitic fluid. The REE anomalies of the garnets belonging to the albite-spodumene pegmatites may be induced by the minute REE rich phosphate inclusions, which are not yet fully identified. In the metamorphic garnets and to a lesser extent in the pegmatitic ones, the tetrad effect may be observed, the $T_{1,3}$ value being higher than 1.1.

Phytofulgurites: new type of atmogenic electric-discharge metamorphismA. Lysiuk¹, G. Yurgenson², N. Yushkin¹¹Institute of Geology, Russian Academy of Science, Ural Branch, 54, Pervomaiskaya st., Syktyvkar, 167982, Russia
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Fulgurites are a geological consequence of a lightning stroke to rocks. They are tubular or drop-shaped form composed of glass, relics of surrounding rocks and new mineral formations.

Two types of fulgurites are noted. They are determined by target rocks: clastofulgurites (aleuro- or psammito-) formed on different porous rocks, and petrofulgurites resulted from lightning discharge on exposed hard rocks. We have discovered a new type of fulgurites – phytofulgurites which formed on plants.

A lightning stroke to a dry haycock (village of Podvolok, Chita region, Russia; August 2002) resulted in grass inflammation and its partial coking in the lower part without air access. On the ground among ash a cake-like body was found which had rolled fibrous structure and size of 15 x 16 cm, 1 cm thick, its weight was about 90 g. It was presented by a complex hydrocarbon polymer $C_{411}H_{182}N_{26}S$ corresponding to natural medium anthraxolite, similar to oil coke. The following elements compose both fulgurites and inclusions captured from soil and new mineral phases: O, Si, Ca, Mg, Mn (about 1% and less), Fe, Ti, Al, Sr, K, P, Cu, Zn, Pb, Co (less than 1%). Isotopic ratio $\delta^{13}C/^{12}C$ -27,795 corresponds to earth plants. Determined phytofulgurite differs from other natural bitumen by extraordinary high content of amino acids (2.36 mg/g) with the predominance of L-modifications. Relic and new inclusions compose 10-15% of volume. Relic inclusions are presented by fossilized diatoms composed of silica. New inclusions are presented by silica, quartz, calcium-magnesium carbonates, sulphates, leaded brass.

The process of atmogenic electric discharge transformation of plants into bitumen is interesting not only scientifically, but also technologically.

O19-01

Contributions of Slab Fluid, Wedge Mantle, and Crust to the Origin of Quaternary Lavas in the NE Japan Arc

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Quaternary lavas from the Northeast (NE) Japan arc show geochemical evidence of mixing between mantle-derived basalts and crustal melts from the magmatic front, whereas significant crustal signals are not detected from the rear arc lavas. The along arc chemical variations in lavas from the magmatic front are attributable almost entirely to geochemical variations in the crustal melts that were mixed with a common mantle-derived basalt. The mantle-derived basalt is slightly enriched than in the rear arc in Nd-Sr-Pb isotopic compositions but the variation is less pronounced if crustal contributions were eliminated. Therefore, the source mantle compositions and slab-derived fluxes are relatively uniform across and along the arc. Despite this, incompatible element concentrations are significantly higher in the rear arc basalts. We examine an open system, fluid fluxed melting model, assuming that depleted MORB source mantle melted by the addition of fluids derived from subducted oceanic crust (MORB) and sediment (SED) hybrids at mixing rate 7% and 3% SED in frontal and rear arc sources. The results reproduce the chemical variations found across the NE Japan arc with the conditions: 0.2 % fluid flux with degree of melting $F = 3\%$ at 2 GPa in the garnet peridotite field for the rear arc, and 0.7% fluid flux rate with $F = 20\%$ at 1 GPa in the spinel peridotite field beneath the magmatic front. The chemical process operating in the mantle wedge requires: (a) various SED-MORB slab hybrid fluids; (b) various fluid flux rate; (c) a common depleted mantle source; with (d) different melting parameters for the origin of across-arc chemical variations.

O19-02

Magma feeding system beneath the Gassan volcano, NE Japan

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Gassan volcano is a Quaternary stratovolcano (ca.0.5 to 0.3 Ma) in back arc side of the northeast Japan arc. Based on detailed geologic and petrologic data, we examined the magma feeding system beneath this volcano. The eruptive products can be divided into eight units, NGL, GLL, GUL, GPL, UBL, USL, UPL and 1688L in ascending order. Most rocks are medium-K andesite and have plagioclase, clinopyroxene, orthopyroxene and Fe-Ti oxides as phenocrysts, with or without olivine, hornblende, quartz or biotite. Mafic inclusions, which are observed in all units, are basalt to basaltic andesite, have plagioclase, clinopyroxene, orthopyroxene, olivine(±) and hornblende(±) as phenocrysts. Petrographic and mineralogic features observed in host and mafic inclusions, such as disequilibrium phenocrysts and resorbed textures, suggest magma mixing/mingling. Whole rock compositions of both host rocks and mafic inclusions from a geologic unit show linear trends in variation diagrams, which suggest rocks are derived from magma mixing/mingling between mafic and felsic end-members. The mixing trends can be classified to high- and low-Cr types. Rocks from GUL, GPL, UBL and USL units draw the former type trend and those from NGL, GLL, UPL and 1688L units draw the latter one. The felsic end-members have ca.65% in silica content for every geologic unit, while the mafic end-members of high- and low-Cr types have ca.50% and 51-52% in silica content, respectively. The felsic end-member magmas may be partial melts of crustal materials and stored in the crustal magma chamber, while the mafic end-member magmas come from the depth. Rb/K, Ba/K, and Zr/Y ratios of the mafic end-members are similar among geologic units, and the mafic end-members of low-Cr type tend to have higher contents of incompatible elements than those of high-Cr one. These data indicate the low-Cr type mafic end-member magma is derived from high-Cr type one by fractional crystallization process. As the high-Cr type appeared in the middle part of the Gassan activity, it is probable that most of the high-Cr type mafic magma differentiated to the low-Cr one before the mixing in the dawning and waning periods, whereas the both types mafic magmas injected to the crustal felsic magma chamber and mixed with the felsic end-member in the flourish period.

O19-03

Evolving mantle source regions and crustal growth in the Philippines

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The present location of the Philippine archipelago along a complex boundary among three plates, Eurasian, Philippine, and Indo-Australian, makes it a natural laboratory for studying and understanding the early stages of continental growth. Prior to this present stage, the archipelago may have undergone previous histories of multiple arc and back-arc basin generation, crustal accretion, as well as tectonic displacements from a more southerly location. The arc's tectonic evolution from its birth to its present stage of development is reflected in the available data from combined studies of igneous rocks of Cretaceous to recent ages, which also reveal a record of the changing or evolving mantle source regions that accompanies the arc's evolution.

The results of the geochemical study of ~100 Ma basement rocks of the eastern margins of Luzon, the largest island, suggest that an Indian MORB-type mantle may have underlain the archipelago since the Cretaceous. This mantle signature continues to be tapped by the younger volcanic products and plutonic rocks emplaced along the eastern side of the island. The western margin of the island is currently being modified by active subduction and collision with the Eurasian margin. As a result, the geochemical signatures of igneous rocks suggest that local processes tend to modify the nature of this pre-existing mantle as a result of changing tectonic setting and subduction recycling of materials from previously rifted fragment of the Eurasian margin.

O19-04

Petrochemical variations of island arc volcanics and sources for these discrepancies: observation from Java island, Sunda arc, Indonesia

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Java island, a classic example of island arc, is built through multiple Cenozoic arc magmatism events. Its long history, simple geologic setting, and presence of various volcanoes (single and double chains, backarc volcanoes) makes this region ideal to observe all variations of arc volcanics produced by subduction factory.

The most evident petrochemical variation is increasing of potassium contents towards younger ages and towards backarc-side from the trench. Volcanics are dominated by low-K magmas during Lower Tertiary, then evolved into medium-K during Upper Tertiary. Quaternary volcanics hold most varied compositions, from medium-K to high-K (dominant) to shoshonitic-leucititic. Boundary of high-K vs shoshonitic approximates boundary island arc vs backarc volcanoes. Study on Quaternary Merapi-Merbabu-Telomoyo-Ungaran-Muriah-Bawean across-arc volcanoes shows that spatial-temporal magma variations can be discriminated by combination of potassium, strontium, and rubidium. Trench-ward magmas decrease in K/Rb and Rb/Sr ratios, while younger magmas move oppositely. Adakite classification chart can be another discriminant for three volcanic fields: normal-arc volcanics (low Sr/Y, high Y), adakite (high Sr/Y, low Y) and backarc magmatism (high Sr/Y, high Y). Sources of spatial variations are likely due to different materials to be melted and different degree of partial melting, while temporal variations are less conclusive but demonstrate systematic evolutions of magmas. Backarc volcanoes show mixture arc and non-arc characters and, with support of geophysical evidence, we speculate that backarc magmas are produced from combination of subduction-related materials and deeper mantle sources induced by slab detachment.

Effects of crustal compositions on Java volcanics may result in overall higher silica contents in western Java (continental crust) than eastern part (oceanic crust). Most volcanics, regardless the setting, have upper limit of SiO₂ level at about 63% weight. Only calderas produce >70% SiO₂, suggesting an extraordinary fractional crystallization to produce large-scale eruptions. ⁸⁷Sr/⁸⁶Sr radioisotope values show irregular patterns than the expected decreasing values towards the oceanic crust. Variations among nearby volcanoes and within individual volcano are also notably that suggest local geologic-tectonic controls are more influential on determining ⁸⁷Sr/⁸⁶Sr ratios. On contrary, Cenozoic adakitic volcanics are exclusively present in eastern Java and can be attributed to regional presence of basalts underplate and/or younger subducted plate. Arc volcanics should be viewed as dynamic products of combining materials and processes at different scales and four dimensionally.

Spatial and temporal variability of intra-oceanic island arc magma sources: new observations from Oligocene Izu-Bonin arc

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Recent studies on Quaternary Izu-Bonin arc volcanism have revealed that the magma source has the following characteristics: 1) In the northern arc (north of 27°N) the slab-derived component is dominated by fluid released from subducting oceanic crust and pelagic sediment; 2) South of 27°N the contribution of fluid and/or melt from Pacific seamounts with HIMU isotopic characteristics becomes significant, and reflects the greater number of seamounts on the Pacific Plate; 3) Around the Iojima Island an influx of melt from pelagic sediment is recognized as a significant contribution to magmas; 4) A systematic along-arc variation is observed in Pb isotope ratios that may reflect the character of the mantle wedge prior to slab addition.

The Kyushu-Palau Ridge (KPR) is regarded as a remnant arc separated from the Izu-Bonin-Mariana arc by the spreading of the Shikoku and Parece Vela back-arc basins. Samples were collected on the KPR and also from the ridges extending west into the palaeo rear-arc. Dating results indicate that most of the collected samples collected are in the age range 25 and 27 Ma, implying these samples represent the last stage of arc volcanism on the KPR.

Chemical characteristics of the basaltic to andesitic lavas from KPR show enrichment in large-ion-lithophile elements and depletion in high-field-strength elements such as Nb relative to MORB, confirming its island arc character. Positive correlation between Sr isotopes and fluid-mobile element enrichment (Ba, Cs) implies that slab-derived fluid played an important role in the Oligocene magma source as is the case for the Quaternary northern Izu-Bonin arc. Samples from rear arc side of the KPR show lower ⁸⁷Sr/⁸⁶Sr and ²⁰⁶Pb/²⁰⁴Pb associated with a weaker enrichment in fluid-mobile elements relative to the main KPR, implying less significant slab fluid contribution to the rear arc source.

On Pb-Pb isotopic plots, the KPR arc defines a different trend to the Quaternary Izu-Bonin. Where the Quaternary arc forms trends to high $\Delta 7/4$ and $\Delta 8/4$ with increasing ²⁰⁶Pb/²⁰⁴Pb the KPR defines a trend with decreasing $\Delta 7/4$ and $\Delta 8/4$. This implies that one of the slab-derived components in the KPR magma source was different to the Quaternary arc, and that this component had isotopic characteristics similar to HIMU. Combined with the differing along arc trace element variations between Izu-Bonin and the KPR this implies a temporal variation in the composition and/or geometry of the subducting plate.

History of volcanism of the Izu-Bonin Arc deduced from the chemical composition of heavy minerals of volcanoclastics

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Lower Oligocene to Present volcanoclastics, volcanic sands and sandstones, recovered from the Izu-Bonin Arc during Ocean Drilling Program (ODP) Leg 126 were all derived from Izu-Bonin Arc volcanism. Individual grains of the sediments consist of volcanic glass, pumice, scoria, basaltic or andesitic fragments, plagioclase, and minor olivine and hornblende. In Pliocene-Pleistocene (PP) samples, plagioclase and heavy minerals in the volcanoclastic sands and sandstones are present in the following abundance: plagioclase > orthopyroxene > clinopyroxene > pigeonite > olivine. In contrast plagioclase and heavy minerals found in Oligocene-Miocene (OM) samples occur in the following order: plagioclase > clinopyroxene > orthopyroxene > hornblende. The lower concentration of Al, Ti, and Cr in calcium-rich clinopyroxene in Oligocene to Present sediments suggests that the sources of the volcanoclastic sediments were non-alkalic igneous rocks. There are, however, some distinct differences in the chemical composition of the pyroxene between the PP and OM volcanoclastic sands and sandstones. Orthopyroxene belong to the hyperthene-ferrohypersthene series (Fe-rich) in PP sediments and the bronzite-hypersthene series (Mg-rich) in OM ones. Clinopyroxene is characterized by augite and pigeonite in PP sediments, and by the diopside-augite series in OM ones.

Mineral assemblages and mineral chemistry of the volcanoclastic sands and sandstones reflect those of the volcanic source rocks, that is Izu-Bonin Arc magmatism records. Therefore, the observed changes in mineralogy record the change in volcanism of the Izu-Bonin Arc in time. The mineralogy is consistent with the geochemistry of the volcanoclastic sands and sandstones and the geochemistry of forearc volcanic rocks of the Izu-Bonin Arc since the Oligocene.

Magmatic evolution in the central Izu-Bonin arc: a 3-D perspective and the possible role of phengite

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We investigate two-dimensional, along-arc and across-arc variations of magma chemistry in the central Izu-Bonin arc, an area that contains the frontal volcanoes Sumisu (31.5°N, 140°E) and Torishima (30.5°N, 140.3°E) and the backarc volcano Horeki (30.3°N, 139.2°E). These three volcanoes, similar in size, rise as relatively isolated edifices from the seafloor and collectively can provide 2-dimensional information relating to arc magma genesis. The frontal volcanoes of Sumisu and Torishima contain low-K basalts originating from both wet and dry basaltic magmas (low-Zr basalts and high-Zr basalts, respectively). These basalts result from different degrees of melting of the same source mantle (~20 % and ~10 % for wet and dry basaltic magmas, respectively). Assuming that the wet basalts contain greater abundances of slab-derived components than their dry counterparts, geochemical comparison of these two basaltic types permits the identification of the specific elements involved in fluid transport from the subducting slab. Using the abundant geochemical data from Torishima, where the downgoing slab is about 100 km deep, we find that Pb, Ba, and Sr are selectively concentrated in the slab-derived metasomatic fluids below this arc-front volcano, but K and Rb are not. However, at Horeki, 110 km to the west and where the slab is >100-140 km deep, slab-derived fluids contain abundant K and Rb. We suggest that the K-rich mica, phengite, plays an important role in determining the makeup of fluids released from the downgoing slab. In arc-front settings, where slab depth is <100 km, phengite is stable, and released fluids contain little K. In backarc settings, slab depth is 100-140 km, phengite is unstable, and K-rich fluids are released. We conclude that cross-arc variations of K and Rb are likely related to differing compositions of fluids released rather than the commonly held view that such variations are controlled by the degree of partial melting.

Experimental constraints on olivine LPO under water-rich conditions and implications for seismic anisotropy in subduction zones

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The complex seismic anisotropy is reported in subduction zone upper mantle, in which fast shear wave polarization is normal to the subduction direction (parallel to trench) while most of oceanic mantle show the fast propagation direction parallel to the plate motion. In previous studies, this is considered due to complex flow geometry in the wedge mantle. However, we found the dominant lattice-preferred orientation (LPO) in olivine, which controls the seismic anisotropy in the upper mantle, is sensitive to water content and temperature as well as differential stress by performing high-pressure deformation experiments. In this presentation, we will show that the complex seismic anisotropy in subduction zone can be caused by changes in the dominant type of olivine LPO due to the spatial variation in water content and temperature in subduction zone rather than the complexity in flow pattern.

Allanite as an indicator of origin and tectonic setting for granitic rocks, Japan: implications for fractionation in manganese and rare earth elements, and for difference in Sr-Nd isotope compositions.

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Twenty-six samples of allanites originating from granitic rocks, Japan, were examined by EPMA. Fourteen analyzed allanites contain appreciable amounts of MnO (0.14-0.59 a.p.f.u.). Therefore, the present allanites are significantly divided into Mn-rich (more than 0.14 a.p.f.u.) and Mn-poor (less than 0.14 a.p.f.u.) types. The relationship between Mn-rich and Mn-poor allanites is established by the coupled substitution: $Mn^{2+} + (MREE, HREE)^{3+} [Mn\text{-rich types}] \leftrightarrow Ca^{2+} + LREE^{3+} [Mn\text{-poor types}]$. Moreover Mn-rich and Mn-poor allanites differ considerably from each other in chondrite-normalized REE concentration: Mn-poor allanites have some chondrite-normalized patterns indicative of the LREE enrichment, while such patterns in Mn-rich ones show the MREE enrichment. Mn-rich allanites are characteristic of the allanites from granitic rocks in Japan (Hoshino et al. 2006). Primary magmatic allanites (e.g., Chesner & Etlinger 1989) have the same patterns, reflecting LREE-enrichment, as observed in the studied Mn-poor ones. On the other hand, secondary allanites (e.g., Exley 1980), influenced by hydrothermal fluid, have the REE patterns similar to those of the Mn-rich allanites. These geochemical characters may represent that Mn-rich and Mn-poor allanites derive their origins from hydrothermal fluid and magmatic melt, respectively.

Complication of the chemical compositions of the present allanites which reveals Th-incorporation as the coupled substitution of $3Th^{4+} + \square \leftrightarrow 4REE^{3+}$, provides an explanation for the observation that higher Th concentrations characterize allanites from the island arcs. Moreover, from the global viewpoint of allanite mineralogy, the ternary Al_2O_3 - Fe_2O_3 - SiO_2 diagram illustrates that allanites are grouped, according to their origins, into three classes suggestive of tectonic backgrounds for the crystallization localities: (1) intracontinental, (2) island arc and (3) continental margin. Therefore Mn, REE and major element contents in allanites become an indicator for both the origins of the host rocks and the crystallization localities of allanites from granitic rocks.

The isotopic compositions of Sr and Nd were analyzed for seventeen allanites (11 samples of an Mn-rich type, and 6 samples of an Mn-poor type) of the present samples by mass spectrometer. The analyzed Mn-rich samples have $^{87}Sr/^{86}Sr$ ratio of 0.70812-0.71379 and $^{143}Nd/^{144}Nd$ ratio of 0.512454-0.512067, while Mn-poor samples have $^{87}Sr/^{86}Sr$ ratio of 0.70637-0.70711 and $^{143}Nd/^{144}Nd$ ratio of 0.512583-0.512529. In other words, there is a negative correlation between $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios for the analyzed Mn-rich and Mn-poor allanites. The above identifying characteristics suggest that the geneses of Mn-rich and Mn-poor allanites are consistent with the origins of ilmenite-series and magnetite-series granitoid, respectively.

O19-10

Large sulfur supplies by mafic magma injection into the magma systems of the volcanic front of the northeast to central Japan arc: Melt inclusion evidence

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Melt inclusion studies found very sulfur-rich mafic melts trapped in olivine phenocrysts from island arc volcanoes. Subduction-related magmas of island arc are expected to transport large amounts of sulfur, inherited and recycled from the subduction slabs, to the frontal volcanic systems, and most of sulfur is explosively discharged to the atmosphere. To investigate the characteristics of the melt compositions and to estimate sulfur supplies in the magma systems of the volcanic front, we performed microprobe analyses of sulfur as well as major components of the olivine-hosted melt inclusions from younger tephra from the frontal volcanoes (Tarumai, Kuttara, Iwate, Nasu, Asama, Yatsugatake, Hakone, Fuji volcanoes). In these volcanoes, major phenocrysts (ortho- and clinopyroxene, plagioclase, Fe-Ti oxides) were derived from the long-lived felsic magma reservoir and trapped sulfur-poor, crust-derived felsic magma (< 500 ppm S, 66-75 wt% SiO_2). Instead, olivine (Fo₇₅₋₈₅), a rare phenocryst, trapped sulfur-rich mafic melt inclusions of basalt to basaltic andesite compositions (SiO_2 46-58%), recording the information of the primary volatile contents of the subduction-related mafic magma.

Our melt inclusion study revealed the characteristic features of subduction-related mafic magma at the volcanic front: 1) High sulfur concentrations in primary mafic magmas (< 3500 ppm S). 2) Water-rich and, in many cases, water-saturation of mafic magma, indicated by heterogeneous trapping of melt and bubbles, and common inclusions of pargasitic amphiboles in olivine phenocryst. 3) Relatively high oxygen fugacities and correspondingly high sulfur solubility of the magma, in response to sulfate-dominated species for sulfur, and the frequent inclusions of aluminous clinopyroxene with a large $CaFe^{3+}AlSiO_6$ components.

The melt inclusion data revealed that the mafic magma was originally hydrous, and sulfur content of the mafic magma strongly decreased (from 3500 ppm to 400 ppm level) before the mixing, mainly due to distillation by water exsolution of magma and partly by sulfide precipitation. It is likely that magma temperature was beyond the stability regions of hydrous phases, and a large part of dissolved water eventually exsolved, incorporated with sulfur, and was discharged to the atmosphere. The melt inclusion evidence reliably records that hydrous, oxidized mafic magma transported a large amount of sulfur to the frontal volcanic systems from the subduction slabs in the source region.

O19-11

Polymetamorphism of the Aktyuz eclogites in the Northern Tien-Shan, Kyrgyzstan

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The Aktyuz Formation is located in the Zaily Range of Northern Tien-Shan in the Kyrgyzstan and consists of pelitic gneisses and gneissose-granites, in which eclogites and garnet amphibolites occur as lenses or boudins. We recognized three different metamorphic events in the Aktyuz eclogites. The inclusions of Fe-rich staurolite ($Mg\# < 0.29$), Mg-taramite, oligoclase and augite included in the core of the eclogitic garnets represent an evidence of the first LP-HT metamorphic event.

The inclusions of Gln, Pg, Phe, Ep, Rt and Ab in prograde zoned garnets suggest epidote-blueschist facies stage before getting to the peak metamorphic conditions of the eclogite facies. The eclogite (Grt+Omp(Jd₅₃)+Phn+Pg+Qtz+Rt) P-T conditions are estimated as $690 \pm 30^\circ C$ at 16 kbar using of Powell (1985) and Krogh (1988). The break down of omphacite into symplectites of Cpx+Ab or Cpx+Amp+Ab in eclogites suggest the first retrograde metamorphism under the epidote-amphibolite conditions according to the mineral assemblage of Omp(Jd₁₆₋₂₆)+(Na-Ca)-Amp+Ab+Ep+Phn+Pg. These three metamorphic stages belong to the second metamorphic event and show a clockwise P-T path.

The third metamorphism was maintained together with the country rock gneisses, and they were experienced LP-HT metamorphism from the epidote-amphibolite facies to the amphibolite facies conditions. The presence of migmatites suggest minimum temperature $c. 600^\circ C$ for the country rocks, and the maximum $Si = 3.35$ p.f.u. ($O = 11$) in phengites gave 6 kbar (Massonne & Schreyer, 1987). Field occurrence of eclogites as lenses and boudins in the country rocks gneisses suggest that they have shared at least the last metamorphism. The zoning of matrix amphibole with Na-Ca amphibole core and pargasite or Fe-pargasite rim, and zoning of albite core (An_8) to oligoclase (An_{35}) rim support a prograde metamorphism in the Aktyuz eclogites, and the representative mineral assemblage is Ca-Amp+Pl(An_{35}). The eclogites and the country rock gneisses were retrograded into the greenschist facies.

The first HT-LP metamorphic event, probably took place in the oceanic crust at the inception of subduction zone metamorphism. The second HP-LT metamorphism took place within a subduction zone. The third LP-HT metamorphic event is probably due to the collision of continental crust after the eclogites and country rocks tectonically juxtaposed along subduction zone.

O19-12

Zircon thermometry and inheritance kinetics reveal ultra-fast magma generation processes during Cambro-Ordovician times in Iberia

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The Variscan basement of Central Iberia contains abundant metagranitoids and metavolcanites of Cambro-Ordovician age with two notable features. First, they were apparently produced with no connection to any major tectonic or metamorphic event. Second, they have an unusually high zircon inheritance. U-Pb micro-analysis combined with cathodoluminescence imaging revealed that about 70-80%, in some cases nearer 100%, of zircon grains contain inherited cores. In our knowledge, such a high inheritance factor has never been found in volcanic rocks or alioctonous granitoids and is only approached by low-temperature pegmatoid anatectic mobilizates. The whole-rock zircon-saturation temperature of these rocks is about 800-840 °C. The Ti-in-zircon temperature of the Cambro-Ordovician grains is 850-900 °C, enough, therefore, for dissolving all zircon of the protolith. The fact that the dissolution was so incomplete can only be attributed to kinetic factors. Three-dimensional modeling of the zircon dissolution rates for melts with a composition similar to the Cambro-Ordovician magmas indicates that the survival of zircons with a dimension of 300 x 100 microns in a magma that reached 900 °C requires extremely fast heating and cooling rates. These conditions can only be achieved when small batches of mafic magma underplate a cold (hence rigid) fertile felsic crust. Heat transfer from the crystallizing mafic magma would produce a small pulse of felsic magma which, assuming an extensional regime, can then be quickly transferred to higher crustal levels and cooled in volcanic or subvolcanic conditions. Thermal modeling indicates that for assuring a zircon survival such that found in the Iberian Cambro-Ordovician magmas, the total process for a single magmatic pulse, from the beginning of melting up to final emplacement, should have spanned for less than 0.01-0.02 Ma. The lineal arrangement of Cambro-Ordovician magmatic rocks in Central Iberia, the small volume of individual magmatic bodies, and their chronology, suggest that small volumes of mafic magmas were repeatedly emplaced during ca. 20 Ma along lineal mantle structures probably related to the detachment of Iberia from West Gondwanaland and the opening of the Rheic ocean. The lack of regional metamorphism can be attributed to fast melt transfer through the crust, the small volume of magma involved, and the episodic nature of the magmatism.

Modeling silicate-rich fluids at high pressures: The system K_2O - Na_2O - CaO - Al_2O_3 - SiO_2 - H_2O (KNCASH)

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Comprehension of rock-forming processes at depths corresponding to the lower crust and active subduction zones requires an understanding of silicate-rich fluids coexisting with rock-forming minerals. However, existing models for aqueous silicate solutions are difficult to extrapolate to pressures higher than 0.5 – 1.0 GPa. An alternative approach is to treat H_2O in terms of a statistical thermodynamic model involving a dynamic equilibrium between "gas-like" disordered and "liquid-like" clustered molecules (Gerya and Perchuk, *Petrology*, 5, 366–380, 1997), where $X(\text{liq})$ is the mole fraction of the latter. Gerya et al. (*Eur. J. Mineralogy*, 17, 269–283, 2004) successfully tested this approach for SiO_2 - H_2O solutions to 1300°C and 2 GPa. We use it here to combine both available and also new experimental high-pressure solubility data for quartz (SiO_2), corundum (Al_2O_3), wollastonite ($CaSiO_3$), grossular ($Ca_3Al_2Si_3O_{12}$), zoisite ($Ca_2Al_3Si_3O_{12}(OH)$), sanidine ($K_{0.9}Na_{0.1}AlSi_3O_8$) and albite ($NaAlSi_3O_8$) in pure H_2O , as well as quartz and corundum solubilities in KOH solutions, to develop a simple thermodynamic description for aqueous fluids in the model system KNCASH. ΔG_r of dissolution reactions is thus expressed in terms of the standard-state molar thermodynamic parameters ΔH_r , ΔS_r , ΔC_p , ΔV_r , the molality of the dissolved species and $X(\text{liq})$. The model successfully returns the available experimental data. The formalism requires data on speciation to define the influence of $X(\text{liq})$ on the reaction and to determine the number of species and reactions involved. However, a simplified "component" approach for oxides can be developed to approximately model KNCASH fluids from 0.2 to 3 GPa. "Mixing terms" are needed for interacting oxide pairs like SiO_2/Al_2O_3 , SiO_2/K_2O , Al_2O_3/K_2O , Al_2O_3/Na_2O , etc.. These can be directly derived from comparison of the different experimentally investigated fluid-solid systems. Very strong interaction is observed for alkali oxide/ SiO_2 and alkali oxide/ Al_2O_3 . For Al_2O_3 , the solubility is up to 2.5 orders of magnitude higher in potassium-bearing systems than in pure H_2O . On the other hand, almost no interaction is indicated for CaO/SiO_2 .

Origin of atoll garnets in eclogite and its implication for the mobility of trace elements in continental subduction zone

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Chemical zoning of metamorphic garnets has been regarded as the key to deciphering P-T paths of metamorphism, to elucidating evolution of the metamorphic fluids and deformation, and to interpreting the ages of metamorphism because of its occurrence in a wide range of bulk compositions over a wide range of metamorphic grades, and also because cation diffusion in garnet is sufficiently slow to retain compositional differences even within single grain. On the other hand, metamorphic garnets may display various special microstructures, such as corona, symplectite, fishnet, atoll and patch. The intriguing atoll microstructure is thought to be a special type of coronas consisting of a mostly garnet ring surrounding a mixture of several other phases and/or island-shaped garnet fractions. Although atoll garnets have been documented long ago and several genetic mechanisms have been proposed, such as overgrowth, selective replacement, multiply nucleation and coalescence, its genesis still remains essentially unclear. Furthermore, to understand the genesis of atoll garnets in high-pressure metamorphic eclogite may gain further insight into the continental slab subduction and/or exhumation processes. To unravel the origin of atoll garnets, a detailed electron and ion microprobe study was carried out on atoll-shaped and complete garnets in ultra-high pressure metamorphic eclogite from Dabie. Compositional profiles of both complete and rings of atoll garnets show well-preserved growth zoning with decrease in Mn, Ca and HREEs and increase in Mg towards rims. Nevertheless Mn annuli and MREEs humps were observed near garnet rims. Island and peninsula garnets inside atoll garnets are homogeneous in major elements and show the same composition as garnet rims, whereas the HREE concentrations are similar to the complete garnet cores. The atoll garnets were likely formed on the consumption of former cores with the fluid released from both hydroxyl exsolution and lawsonite decomposition at the onset of exhumation following peak pressure, i.e. garnets breakdown from inside and grow from outside in. Because garnet is readily acting as a sink of HREEs and because of the refractory nature of zircon, large scale release of HREEs and HFSEs during continental slab deep subduction or exhumation is unlikely. In order to elucidate the evolution of metamorphic rocks correctly, linking the chemical composition of minerals with their microstructures is critically important.

Temporal and spatial variation of petrochemistry of the Tertiary volcanic rocks in the Oga Peninsula, NE Honshu arc

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Ninety major and trace elemental analyses were carried out for the Eocene to early Miocene volcanic rocks from the Oga peninsula. Excluding altered specimens by using Na_2O+K_2O - Na_2O/K_2O diagram (Miyashiro, 1975) and Al_2O_3 - K_2O - $CaO+Na_2O$ diagram (Nesbitt and Young, 1989), 69 specimens are classified by the activity age and the mode of occurrence. The K_2O contents of volcanic rocks from the same age group show a linear trend from basalt to rhyolite, and these trends gradually decreasing the inclination on the SiO_2 - K_2O diagram with time from Eocene to early Miocene. Some other incompatible elements also decrease with time from Eocene Monzen basalts to early Miocene Nomuragawa basalts named by Kobayashi et al. (2004).

Transition from the Eocene continental basalts with high Zr ratio in $Zr/4-2Nb-Y$ diagram (Meschede, 1986) to the early Miocene island arc basalts with higher Y ratio at about 21 Ma is coincident to the inception of the back-arc spreading in the Yamato Basin. It has been thought that the transition from the Eocene Monzen basalts to early Miocene island arc Nomuragawa basalts were closely related with the injection of asthenospheric mantle at about 21 Ma in Yamato Basin. Moreover, present results suggest that this chemical transition from the Monzen basalts to the Nomuragawa basalts may caused by interaction among the injected asthenosphere, the sub-continental lithosphere and one other source mantle which might be sub-arc lithosphere.

Decompression-induced phenocryst crystallization in arc basalt magma from Hakkoda, Northern Japan

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Crystallization process was petrographically investigated for hydrous arc basalt from Hakkoda, northern Honshu. Plagioclase in the basalt are as calcic as An80-90, indicating the magmas contained more than 3 wt% H_2O . Observed phenocryst assemblages are ol + pl, ol + pl + opx, ol + pl + opx + aug, and pl + opx + cpx + magnetite. These phenocryst assemblages imply that the order of crystallization is olivine, plagioclase, orthopyroxene, augite, and magnetite. Nevertheless, variation trends of whole rock compositions demonstrate early fractionation of augite preceding plagioclase crystallization. The distinct increase in Al_2O_3/CaO during early stage differentiation can be accounted for by augite fractionation without plagioclase fractionation. It is feasible that augite fractionation occurred at deep magma chamber whereas phenocrysts crystallized at shallow level. For these basalts, we propose the crystallization model involving isothermal decompression-induced phenocryst crystallization in hydrous magma. Compared with the phase equilibrium calculation by MELTS for the hydrous basalt, the petrological features correspond with isothermal decompression rather than multistage cooling which is often stressed in the classical polybaric crystallization models. When the initial water content is fixed (ex. 3 wt%), the magma is saturated with water at low pressures ($P_{\text{total}} = P_{H_2O}$), whereas it is not saturated with H_2O at high pressures. Then, slopes of crystallization curves vary according to pressures. At low pressures ($P_{\text{total}} = P_{H_2O}$), slopes of the crystallization curves are negative on P-T space, whereas they are positive at high pressures except for plagioclase. Many minerals have minimum melting temperatures at the cross point with the water saturation curve. Isothermal decompression results in melting of minerals or reverse reaction (pyroxene $\rightarrow$ olivine) at high pressures, and in crystallization at low pressures. Petrographical features can be accounted for by the isothermal decompression for the most primitive basalt in which phenocryst assemblage is olivine + plagioclase. Pyroxene inclusions captured in olivine phenocrysts must have been crystallized under high pressure. Pyroxenes exposed to melt must have disappeared by resorption at low pressures. Rare olivine reaction rim around orthopyroxene is the evidence that the magma passed through the reaction curve of orthopyroxene + melt = olivine from high pressure to low pressure. Corroded form of olivine crystals can also be accounted for by decompression at water undersaturated conditions. The MELTS calculation demonstrates the phenocryst plagioclase crystallized at $P < 2$ kb.

Evolution of the Northeast Honshu Arc - Arc volcanism from Cretaceous to Present -

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The NE Honshu Arc is one of the typical trench-arc-back arc basin systems. NE Honshu shows a zonal arrangement of geological and geophysical features from the trench to the back-arc side such as geomorphology, structure of crust, gravity anomalies, heat flow, seismic activity and lateral chemical variations. NE Honshu consists of pre-Tertiary basement rocks, Tertiary volcano-sedimentary strata with many large calderas, and Quaternary volcanoes. In the late Jurassic to Paleocene, accretionary prism and a collided block formed part of the eastern margin of the Asian continent of which Japan was a part. In the Early Cretaceous, oblique subduction of the Izanagi plate generated the Kitakami magmatic arc. After formation of the Early Cretaceous Kitakami arc, the volcano-plutonic activity shifted westward, and continued along the Asian continental margin through the Paleocene. The collided continental block composed of Paleozoic granites and sedimentary rocks forms the basement of south Kitakami, and the Jurassic accretionary prism now underlies north Kitakami Province. The batholithic roots of the Kitakami magmatic arc now compose almost half of the modern Northeast Honshu forearc basements and continue north into Hokkaido.

The counterclockwise rotation of NE Honshu has been ascribed to the opening of the Japan Sea on the basis of paleomagnetic data. The formation of grabens initiated at around 23-21 Ma, nearly the same time that basalts began erupting in the Japan Sea. Opening of the Japan Sea ceased at about 13.5 Ma, the tectonic stress field changed from extension to intermediate, and characteristics of volcanism changed from rifting volcanism to island-arc volcanism. In the final stage of the Japan Sea opening, numbers of Kuroko VMS (or volcanogenic massive sulfide) deposits are formed on the seafloor. The island-arc stage of NE Honshu can be divided into four phases: submarine volcanism, late Miocene caldera-forming phase, Pliocene caldera-forming phase and compressional volcanic arc. In the caldera-forming phases, felsic volcanism was concentrated in the structural high of the central mountainous ranges, and nearly eighty piston-cylinder type calderas were formed under a condition of neutral to weak compressional stress fields. Present Quaternary volcanoes are divided into four volcanic zones.

High-magnesian andesite produced by two-stage magma mixing at Ebisumori of Hachimantai, northern Honshu, Japan

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High-magnesian andesite, containing MgO up to 8 wt%, occurs at Ebisumori of Hachimantai, northern Honshu, Japan. The rocks disequilibrium features imply that phenocryst minerals are derived from three magmas. Chemical compositions and zoning profiles are accounted for by two-stage magma mixing: the first mixing occurs between aphyric basalt magma and differentiated olivine basalt magma; the second stage mixing occurs between the resultant of the first stage mixing and andesite magma that is similar to the andesite from the contiguous stratocone. Mass balance of phenocryst minerals shows that endmember compositions are ca. 51.5 wt% SiO₂ and 10.5 wt% MgO for the mafic endmember and 58.5 wt% SiO₂ for the felsic endmember of the second stage mixing. Mineralogical aspects of the first stage mixing endmember indicate the similarity of endmember composition with basalt from nearby volcanoes. The counterpart in the first stage mixing is crystal-free magnesian basalt.

Computations of the phase equilibrium of similar basalts from nearby volcanoes with MELTS and COMAGMAT and by comparing results with phase equilibrium experiments by Takagi et al. (2005) showed the olivine basalt endmember of the first stage as hydrous and situated at a depth of lower pressure than 2 kb. Two-pyroxene thermometer estimates are 1050°C for the pyroxenes derived from the felsic endmember of the second stage mixing, and 1180°C for groundmass. Crystallization temperatures of 1170–1230°C are estimated for minerals from the mafic endmember of second stage mixing by phase equilibrium computation using MELTS. These similar temperature estimates between groundmass and the mafic endmember imply achievement of a thermal equilibrium between endmembers preceding crystallization.

The magma plumbing system of the eastern Hachimantai is analogized by a recent volcanic event, involving lateral dike intrusion toward a pressure source. The encounter of a laterally migrated basalt dike and an andesite magma chamber triggered the magma mixing that produced high-magnesian andesite. The model can account for the relation between the petrological model and distribution of volcanic rocks. Unlike boninite suites, the presence of mantle-derived primary andesite can not be proved in that region because magma mixing of basalt and andesite can account for production of the high-magnesian andesite. Infrequency of such mixing-derived high-magnesian andesite stems from the particularity of the high-magnesian basalt endmember, suggested by the rareness of high-magnesian basalt in northern Honshu.

Petrologic significance of magmatic enclaves on the origin of Hakusan volcanic rocks, central Japan

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Lavas of Quaternary Hakusan Volcano, grown during Kagamuro (0.43-0.32 Ma) and later (Ko-Hakusan, 0.14-0.06 Ma; Shin-Hakusan plus Uguisu-daira, <0.03 Ma) stages, contain small amounts (probably <1 vol. %) of basaltic to andesitic enclaves. The enclaves and their host lavas carry plagioclase, orthopyroxene, amphibole, opaque minerals, ±olivine with spinel inclusion, ±clinopyroxene, ±biotite and ±quartz as phenocrysts. The enclaves generally have coarser-grained and more vesiculated groundmass compared with their host lavas. We have analyzed 4 enclaves and 4 lavas from the Kagamuro volcanics, and 8 enclaves and 14 lavas from the later volcanics on major and trace elements using X-ray fluorescence techniques. Among those the least silicic enclave contains ~52 % SiO₂, ~6.5 % MgO and ~70 ppm Ni. The Kagamuro enclaves are estimated to have ~130 ppm Zr, ~21 ppm Y, ~550 ppm Sr, ~25 Sr/Y and ~6 Zr/Y at 55 % SiO₂, while the later enclaves ~180 ppm Zr, ~19 ppm Y, ~900 ppm Sr, ~45 Sr/Y and ~9 Zr/Y at the same SiO₂ content. Similarly the Kagamuro host lavas tend to be lower in Zr, Sr, Sr/Y and Zr/Y and higher in Y than the later lavas. All the Kagamuro enclaves and their host lavas plot in the island arc andesite-dacite-rhyolite (ADR) field, while the later ones mostly in the adakite field in the Sr/Y-Y diagram of Defant et al. (1991, J. Petrology, 32).

The enclaves change in geochemical characteristics in concert with their hosts, suggesting that the enclaves had some magmatic consanguinity with their hosts, being an observation against a lower crustal melting model for the origin of the Hakusan magmas because such a basalt magma as represented by the least silicic enclave mentioned above is unlikely to have been derived from the lower crust. In addition, the increase in Zr/Y ratio from the Kagamuro volcanics to the later volcanics is not in favor of the lower crustal melting model where the ratio should decrease with time because (1) $D_{Zr} < D_Y < 1$ and (2) later-formed magmas are expected to be produced by greater degrees of partial melting. The observed Sr/Y-Y relations suggest that Hakusan magma-genesis changed from an island arc ADR type to an adakite type between 0.32 Ma and 0.14 Ma. The subducted Philippine Sea plate seems to have started melting beneath the area following the eruption of adakitic rocks from Bishamon-dake (0.36-0.28 Ma) about 20 km to the south of Hakusan Volcano.

Origin of garnet crystals in calc-alkaline volcanic rocks from the Setouchi volcanic belt, Japan

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Calc-alkaline dacites from the Setouchi volcanic belt contain garnet crystals that are classified petrographically and chemically into two types: type-I and type-M. Type-M garnets are characterized by acicular sillimanite inclusions or dissolution textures, and may be accompanied by xenolith fragments. They exhibit extensive compositional zoning with an increase in MgO/FeO and decrease in MnO content toward the margin. These petrographical and compositional features are identical to those of garnets from metamorphic xenoliths entrained in the Setouchi volcanic rocks, suggesting a xenocrystic origin for the type-M garnets. In contrast, type-I garnets lack sillimanite inclusions and have different rim compositions from the type-M garnets. TEM (Transmission Electron Microscope) analysis has revealed the presence of minute glass inclusions in the type-I garnets, which indicate conclusively that these garnets grew in the presence of a melt. Type-I garnets have oscillatory zoning characterized by an antipathetic variation between FeO and MgO. This zoning was most likely caused by magma heterogeneity within magma batch. Differences in rim compositions between the two types of garnets, and the presence of reaction rims indicate that the xenocrystic type-M garnets were incorporated into the magma after phenocrystic type-I garnet became unstable due to decompression during magma ascent.

Origin of orthopyroxenite in the Horoman peridotite complex, Japan: A natural example of products after partial melting of heterogeneous mantle materials.

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Orthopyroxenite often occurs in orogenic peridotites massifs. Orthopyroxenite is characterized by rich in SiO₂ component compared with typical peridotites such as harzburgite and lherzolite. Origin of orthopyroxenite is still in debate. Yaxley and Green (1998) experimentally examined interaction between SiO₂-rich partial melts of eclogite and peridotite using a sandwiching layer of basalt and peridotite compositions as starting materials at upper mantle P-T conditions. They reported that opx-rich layer (orthopyroxenite) was formed between the two layers. However, field observations on partial melting of such a heterogeneous mantle materials are scarce so far.

The Horoman Peridotite Complex, Hokkaido, northern Japan, consists of peridotites with minor amounts of mafic rocks (e.g. Niida, 1984). Orthopyroxenites rarely occur between peridotites and mafic rocks mainly consisting of plagioclase and clinopyroxene. The mafic rocks belong to GB I or Type I of Shiotani and Niida (1997) and Takazawa et al. (1999), and are characterized by high TiO₂ contents. Takazawa et al. (1999) interpreted that Type I mafic layer was of garnet clinopyroxenite origin formed as cumulates at upper mantle conditions. Thus Type I mafic layer would ascend with surrounding peridotites from upper mantle conditions. It is interesting to note that the Type I mafic layer is expected to be melted during upwelling of the complex based on P-T trajectory of the Horoman peridotites (Ozawa, 2004). In this case, it is highly possible that orthopyroxenite forms due to interaction between partial melts of the Type I mafic layer and surrounding peridotites. Actually, the relationship between orthopyroxenite and other rocks in Horoman complex are very similar to those in experiments of Yaxley and Green (1998). In the contexts above, we examine petrology and geochemistry of orthopyroxenites in the Horoman complex, and discuss their origin as a natural example of products after partial melting of heterogeneous mantle materials.

Orthopyroxenes in orthopyroxenites are high in both Al₂O₃ and Cr₂O₃ contents compared to those in the host peridotites. Chondrite-normalized REE patterns of orthopyroxenes in the orthopyroxenites are higher in LREE than those in the host peridotites. Petrologic and geochemical signatures of orthopyroxenites can be explained by interaction between peridotites and SiO₂-rich melts having slightly LREE-enriched patterns, that are compatible with partial melts of LREE-depleted Type I mafic layers.

Melt Inclusions from the Higashi-Izu Monogenetic Volcano group

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The Higashi-Izu Monogenetic Volcanic Group (HMGV) comprises nearly 100 vents dispersed throughout the northeastern Izu Peninsula and offshore. The location of HMGV vents is controlled by the regional stress field of the Izu Peninsula, with volcanism occurring along northwest-southeast trending lineaments. Takatsukayama and Sukumoyama scoria cones represent two contemporary vents formed early in the magmatic history of the HMGV (ca. 125ka), which is still active today. Olivine-hosted melt inclusions were examined from these vents to constrain the composition of parental magmas at the initiation of HMGV volcanism.

Sukumoyama and the majority of Takatsukayama melt inclusions (n=100) are high-Al (15-19 wt. % Al₂O₃) basalts that exhibit strong calc-alkaline trends, consistent with all previously reported HMGV whole rock compositions. Melt inclusions in olivine phenocrysts provide samples of the host magma at an early stage of its evolution, and thus can approach parental compositions free from the fractional crystallization and crustal contamination apparent in HMGV whole rock compositions. This is evident in lower SiO₂ and higher MgO contents (44-55 wt.% SiO₂, 6-12 wt.% MgO) of the inclusions compared to host rock compositions (49-60 wt.% SiO₂, 3-9 wt.% MgO). Sukumoyama melt inclusions have a smaller compositional range than Takatsukayama inclusions, and cluster towards more primitive compositions. Major element trends for most melt inclusion compositions can be explained by limited fractional crystallization of olivine +/- plagioclase. However, at similar MgO and SiO₂ contents, Sukumoyama inclusions are more depleted in some incompatible elements, most notably Na₂O, K₂O, P₂O₅, Cl and H₂O, suggesting a relative depletion of fluid-mobile elements in their source region compared to Takatsukayama melts.

A small but significant population of Takatsukayama melt inclusions (n=14) are not high Al-basalts (11-14 wt. % Al₂O₃). These inclusions are at the higher range of SiO₂ content, and have significantly higher TiO₂ contents compared to the high-Al basalts (1.3-2.1 wt.% versus 0.8-1.1 wt.% TiO₂ respectively), as well as lower FeO, CaO and Na₂O and higher MgO, K₂O, P₂O₅ and Cl at the same SiO₂ content. Fractionation of high Al, low Si plagioclase, found as phenocrysts in the scoria, could account for some of these features. An alternative explanation is melting of a greater proportion of plagioclase, and lower proportion of a volatile and Ti-rich phase, such as amphibole or mica, in the mantle source to produce the high-Al basaltic suite.

Variation in mineralogy and mineral isochron age of ultramafic to mafic xenoliths from the NE Japan Arc.

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Xenoliths of ultramafic to mafic igneous cumulates included in Cenozoic basaltic to andesitic volcanic rocks from NE Japan are the fragments of continental crust. Mineral chemistry indicates that the xenoliths with abundant primary amphibole were formed from arc magma, characterized by high An content of plagioclase. While those with minor or no amphibole were formed from oceanic tholeiite magma, having plagioclase with low An. Internal mineral isochron ages were determined for some xenoliths in Rb-Sr and Sm-Nd systems. Ages for amphibole-poor type from the Ichinomegata Volcano are in the range from 462 to 504 Ma, with SrIs of 0.70330 - 0.70347. Those for the amphibole-rich type are in the range of 223 - 253 Ma with higher SrIs of 0.70425 - 0.70430. These xenoliths may represent trapped oceanic lower crust, and underplated magmatic lower crust of continental arc, respectively. Ages of 28 - 32 and 58 - 61 Ma are obtained for amphibole-poor gabbroic xenoliths and 54 - 66 Ma for amphibole-rich ones from the Atsumi area (Miocene volcanics). Both are characterized by high NdIs (0.51286 - 0.51293) and low SrIs (0.70323 - 0.70329) similar with basaltic rocks produced in the back-arc area of NE Japan after the opening of the Japan Sea basin (<15 Ma). MORB-source mantle should have existed beneath the eastern margin of Asia at least in the late Cretaceous.

Petrology and geochemistry of Quaternary Oginosen monogenic volcano, eastern part of Southwest Japan

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Mt. Oginosen, on the eastern part of volcanic front of Southwest Japan arc, is composed of twenty monogenic volcanoes. Alkali basalt magmas have erupted subsequent to sub-alkali basalt and calc-alkali andesite magmas from Oginosen.

The genetic conditions and compositions of primary magmas were estimated using olivine maximum fractionation model: the alkali basalt magmas formed under conditions of about 16 - 25 kbar and about 1300 - 1420°C, and have been differentiated by separation of about 5 - 15 percent olivine; while the sub-alkali basalt magma formed at about > 30 kbar and about 1490°C, and have been differentiated by separation about 22 percent olivine. The degree of partial melting of the source mantle peridotite was estimated using the estimated Fo content of olivine in equilibrium with primary basalt magma and olivine-spinel pair trend: 5 - 13 percent for the alkali basalts and 1 percent for the sub-alkali basalt, respectively.

The estimated trace element compositions of primary basalt magmas indicate that the alkali basalts are within-plate type and that their sources were enriched in incompatible elements. The sub-alkali basalt is island arc type and the magma source was depleted in LIL element and Nb than the alkali basalt magma sources. Lower crustal xenoliths and xenocrysts are recognized in the alkali basalts, suggesting that the andesite magmas could have been derived by crustal assimilation. However, the results of examination using the Zr/Y-Y relations do not support a model of andesite genesis by interaction of the basalt magmas with the lower crust. The andesites, high in Sr/Y ratio (41 - 64) and low in Y content (14 - 18 ppm), have geochemical characteristics suggesting that they were produced by about 5 - 30 percent melting of oceanic slab leaving garnet residue. They are adakites according to Defant and Drummond (1990).

The geochemical data combined with the stratigraphy (Furuyama et al., 1993) suggests that upwelling mantle yielded the alkali basalt magmas and triggered the Oginosen volcanic activity. The generation of andesites and basalts may have been strongly controlled by adiabatic melting by induced convection (Furukawa, 1993) above the subducted Philippine Sea plate. This particular condition and low temperature seem to have been responsible for the origin of magmas having diverse geochemical signatures.

Petrology of the Hijikai pluton, Okayama Prefecture, Southwest Japan

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The late-Cretaceous Hijikai pluton (7 km x 6 km) is a representative zoned pluton in the San'yō Zone, southwest Japan. This consists of tonalite, granodiorite, hornblende-biotite granite and biotite granite, concentrically zoned with this order from the core towards the margin. The former three rock-types are gradational each other, whereas, the biotite granite is intruded into the hornblende-biotite granite. The major and trace element variations for all of the rock-types indicate that they had been formed through a magmatic differentiation (Taga *et al.*, 2004). Chemical compositions of major minerals were determined by EPMA envisaged to estimate the emplacement and crystallization conditions. Plagioclase ranges from An78 to An29 in the tonalite, An87-An20 in the granodiorite, An56-An7 those in the hornblende-biotite granite, and An52-An2 in the biotite granite. Therefore, plagioclase seems to become more Ab-rich with advance of crystallization, although the most An-rich plagioclase (An87) is found in the granodiorite. Alkali feldspar in the biotite granite is of Or89-Or98 and those in another three rock-types are of Or81-Or94. Orthopyroxene in the tonalite is of Fs47 homogeneously and Fs45-Fs49 in the granodiorite. Clinopyroxene in the tonalite is salite, whereas those in both of the granodiorite and hornblende-biotite granite are salite and augite. Amphiboles are all of ferrohornblende with Mg/(Mg+Fe) of 0.42-0.52. Si content of biotite on the 23(O) bases is 5.4-5.5 in the biotite granite, and 5.5-6.0 in another rock-types. Mg/(Mg+Fe+Mn) ratio increases with Si content. The amphibole crystallized at the pressure of 0.24 GPa estimated by the hornblende geobarometer (Schmidt, 1992).

Various fluid-rock interaction and tourmalinization in the Sanbagawa high-P/T metamorphic rocks, central Shikoku, Japan.

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Various metasomatic rocks, such as tourmaline-rich and micaceous schists have been found from the high-P/T Sanbagawa metamorphic belt, central Shikoku, SW Japan. The Sanbagawa schist in the Niihama area is tectonostratigraphically represented by Besshi nappe and structurally overlying Ojyoin nappe. The mineral zones of Besshi nappe is cut by fault of nappe boundary. Serpentinite bodies are widely distributed around the nappe boundary. Part of serpentinites and lithologic-boundary between pelitic schist and mafic rock received various metasomatism, such as tourmalinization. The mafic-ultramafic complex body in Uchiyoke area is one of the best examples of Sanbagawa metasomatic alteration, with several phases of developed metasomatism. Widespread high-pressure metasomatism ensued, involving tourmalinization in serpentinite-alteration zone, formation of chlorite, talc and actinolite rocks, and mica formation in the mafic rocks. Tourmaline-rich rocks in chlorite schist were altered to an usual boron-rich composition, reflecting infiltration of highly boron, chemically reactive externally derived fluid. The modal abundance of tourmaline is up to 80 %, and they are just tourmalinites. REE (rare earth element) distribution pattern of the tourmalinites and chlorite schists are LREE-enriched (La/Yb=6.1-26.3) and similar to pelitic schist's pattern (La/Yb=9.3-20.1). Ratios of La/Yb of Serpentinite and mafic schist (La/Yb=0.4-2.8) are obviously lower than these of tourmalinites and chlorite schist. Micaceous schists were also altered to an usual K-rich composition, reflecting infiltration of K-rich fluid. In order that mica may replaced an amphibole and chlorite preferentially, the increase of the amount of K+Al and decrease of these of Mg+Fe are accepted. The stage of B-rich fluid infiltration is earlier than these of K-rich fluid, judging from a mineral texture and inclusions. Tourmaline of Sanbagawa schist belongs to the schörl-dravite solid-solution series. The tourmaline has the zonal structure which shows formation condition. The change of X_{Mg} in the common pelitic tourmaline increases from the core to rim. However, rich-layer's tourmaline has no X_{Mg} and/or X_{Mg} reverse zoning structure. These tourmaline suggests that external fluid supply B to the formation of tourmaline rather than the tourmaline grew using ordinal B content from clay mineral. Based on geologic, petrographic and geochemical data, the infiltration of large volumes of B-rich fluid may have been focused along lithological boundaries, shear zones and serpentinites around the Ojyoin and Besshi nappe boundary during the high-P/T Sanbagawa metamorphism. B-rich fluids must have been derived from external system. The character of these fluids is similar with that of the components added to arc volcanism.

High-temperature sublimate minerals from Iwodake volcano, Satsuma-Iwojima, Kyusyu, Southwestern Japan.

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"Volcanic sublimates" are solids or minerals which precipitate directly from the gas phase by vapor deposition processes, including those formed after gas-air mixing. They often deposit around the mouth of a fumarole. High-temperature volcanic sublimates, so-called "molybdenum blue", are enriched in trace elements such as Mo, Pb, Sn, Zn, Bi, As, and W. Formations of molybdenum blue are exemplified by Iwodake volcano (the Satsuma-Iwojima, Japan), Kudriavy volcano (the Iturup Island), Merapi volcano (central Java, Indonesia) and Santiaguito volcano (Guatemala), all of which are located in Island arcs or continental margins. Molybdenum blues from Iwodake volcano, were characterized by X-ray powder diffraction, X-ray micro-diffraction, Raman micro-scattering and electron microprobe analyses. The identified minerals are molybdenite, sphalerite, tugarinovite (MoO₃), molybdate (MoO₄), hematite, halite, sylite, anglesite (PbSO₄), wulfenite (PbMoO₄), quartz, tridymite and cristobalite. This identification illustrates the first occurrences of tugarinovite and molybdate in Japan. Occurrences of these two minerals are observed in Kudriavy volcano, too, and their coexistence is considered to be characteristic of high-temperature volcanic sublimates. Moreover, the present molybdenite and sphalerite are exceedingly rich in Re (up to 7700 ppm) and In (up to 1.69 wt%), respectively, distinguished readily from those of a different origin (e.g. skarn deposits, hydrothermal veins and porphyry copper deposits) by chemical composition. Their enrichments may originate from far-reaching effects due to dense concentration of Re and In elements steadily developed in subduction zones. Although the difference in the host rock arises between the Iwodake (rhyolite) and the Kudriavy (basaltic andesite) volcanoes, with minor deviations F and Cl contents in the former volcanic gases are roughly parallel to those in the latter one: HCl and HF contents in the high-temperature volcanic gases are 0.2-1.0 mol% and 0.01-0.1 mol%, respectively. Resultantly comparison of the sublimate minerals occurring in these two volcanoes emphasizes a general similarity between their high-temperature volcanic sublimates.

Migmatite as a "Seal" of Magmatic Fluid in Tanohata Thermal Aureole, NE Japan

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A distinct difference is observed in oxygen isotopic compositions of migmatites and normal metasedimentary rocks in a thermal aureole of Tanohata plutonic complex, Kitakami Mountains, NE Japan. The Tanohata complex is one of the Cretaceous plutonic rocks in the mountains, and has adakitic geochemistry and magnetite series mineralogy. The complex intruded and thermally metamorphosed the Jurassic accretionary sedimentary pile, forming a thermal aureole comprising 4 mineral zones (biotite, cordierite, cordierite-K feldspar and garnet-cordierite zones. in the order of increasing temperatures). The estimated temperatures are 700-750°C in garnet-cordierite zone, and 560-700°C in cordierite-K feldspar zone. at pressures of 200-250MPa. Detailed field survey has shown that the high-temperature mineral zones, namely, cordierite-K feldspar and garnet-cordierite zones, develop in widths 5 to 10 times larger in the roof pendant area than in the flank of the complex. The observation suggests that the heat transport were very effective in the roof pendant area: the influx of high-temperature magmatic fluid from solidifying granitoid can be a possible mechanism. To investigate the effect of magmatic fluid, a bulk rock oxygen isotopic study was carried out for plutonic and metamorphic rocks of the Tanohata area. The whole rock isotopic ratios range $\delta^{18}O(SMOW, \text{‰}) = 14.5-22.0$ in micaceous slates and massive hornfels of the biotite to cordierite-K feldspar zones, and generally increase with their SiO₂ contents. The isotopic ratios are distinctly higher than those of Tanohata granitoid ($\delta^{18}O = 7.8-8.7\text{‰}$). Metasediments of the garnet-cordierite zone are gneissose hornfels and banded migmatite. The isotopic ratios range $\delta^{18}O = 11.9-12.4\text{‰}$ and do not show clear relation with SiO₂ contents. A local difference of 2.6‰ is observed between large-scale felsic leucosome ($\delta^{18}O = 11.9\text{‰}$) and host gneissose hornfels ($\delta^{18}O = 14.5\text{‰}$). The observed differences probably indicate an incorporation of isotopically light fluid in the partial melting of metasedimentary rocks of the garnet-cordierite zone; the fluid is concentrated in the melt phase and its isotopic effect is limited to residual solid rock. The observed isotopic distinction further suggests that the partial melt can be a "seal" to the invasion of magmatic fluid into the rest of metasedimentary aureole. The effective heat transport in the roof pendant area may be due to convective fluid flow within the metasedimentary cover that is independent from magmatic fluid system.

Chemical evolution of ferrocolumbite and their paragenesis with ixiolites from the Ishikawa-yama granitic pegmatites, Fukushima, Japan

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Chemical evolution of ferrocolumbite from the Ishikawa-yama granitic pegmatites, Fukushima, Japan, has been revealed by electron microprobe analysis. Three discernible trends in compositional variations in ferrocolumbite have been observed: (1) a homogeneous crystal trend, with low Ta/(Ta+Nb); (2) a trend with oscillatory zoning related to Ta and Nb; (3) a trend with patchy zoning related to Fe and Mn. The compositional trend varies from Nb-rich ferrocolumbite to Ta-rich ferrocolumbite, following the magmatic process, and constantly shifts toward Mn-rich ferrocolumbite through topotaxy producing the patchy zoning. These fractionations in ferrocolumbite from granites of the Japanese island arc differ from those observed in beryl pegmatites of the continents. Paragenesis of ferrocolumbite (ordered columbite) with ixiolite (disordered columbite) has been examined by electron microprobe and X-ray diffraction analyses of their single crystals. Ferrocolumbite were found in a feldspar-quartz matrix and observed paragenetic on crystals of microcline and albite. Backscattered electron (BSE) images reveal faint patchy parts in dark zones between which planar bright zones were inserted. The typical formulae of the dark and bright zones derived from electron microprobe analyses are $(\text{Fe}_{0.81}\text{Mn}_{0.21})(\text{Nb}_{0.57}\text{Ta}_{0.37}\text{Ti}_{0.07})_2\text{O}_6$ and $(\text{Fe}_{0.60}\text{Mn}_{0.40})(\text{Nb}_{0.54}\text{Ta}_{0.41}\text{Ti}_{0.05})_2\text{O}_6$ respectively, and the bright zones have higher Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios than the dark zones. Single-crystal X-ray structure refinements prove that the crystal of the dark zone is identified as ferrocolumbite, whereas the crystals of bright zone can be indexed by ixiolite. The structure refinements of ferrocolumbite by the present and other studies (Wenger et al. 1991, Wenger and Armbruster 1991) indicate that the ixiolite structure can exist only in the middle compositions of four endmembers in the columbite quadrilateral diagram (Černý 1989, 1992). Furthermore a thorough examination of the refined structures disclose that distortions of octahedral sites in ixiolites are intermediate between those of octahedral A and B ones in ferrocolumbite on the plots of quadratic elongations for octahedra (Robinson et al. 1971) against average cation-O bonding distances. Textural and crystal-chemical relations between ferrocolumbite and ixiolite indicate that ixiolite is a product of an oriented intergrowth (epitaxy) on the associated ferrocolumbite from hydrothermal fluids relatively enriched in Mn and Ta. A $\text{Ba}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ perovskite with the disordered distribution of Mn^{2+} and Nb^{5+} among the octahedral sites is synthesized at 200 °C (Liu et al. 2005). It should be concluded from the present paragenesis of microcline with ixiolite and the synthesis of disordered perovskite (Liu et al. 2005) that ixiolite crystallizes from the hydrothermal fluids below 200 °C.

Zircon crystallization age and protolith history of the metavulcanites and metagranites of the Ollo de Sapo Domain in central Spain. Implications for the Neoproterozoic to Early-Paleozoic evolution of Iberia

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Dating the pre-Middle Ordovician metavulcanites and metagranites of the Ollo de Sapo Domain has, historically, been difficult because of the small compositional variation, the effects of the Variscan orogeny and, as revealed in this paper, the unusually high fraction of inherited zircon components. The first reliable zircon data indicate that the Ollo de Sapo volcanism spanned 495 ± 5 Ma to 483 ± 3 Ma, and it was followed by the intrusion of high-level granites from 483 ± 3 Ma to 474 ± 4 Ma. In both metavulcanites and metagranites no less than 70-80% of zircon grains are either totally Precambrian or contain a Precambrian core overgrown by a Cambro-Ordovician rim. About 80-90% of inherited zircons are Early Ediacaran (602-614 Ma) and derived from calc-alkaline intermediate to felsic igneous rocks generated at the end of the Pan-African arc-continent collision. In the Villadepera region, located to the west, both the metagranites and metavulcanites also contained Mesoproterozoic zircons (ca. 3.0-3.2 Ga) which, ultimately, originated in the West African Craton. In the Hiendelaencina region, located to the east, both the metagranites and metavulcanites lack Mesoproterozoic zircons, but they have two different inherited zircon populations, one Cryogenian (650-700 Ma) and the other Tonian (850-900 Ma), which suggest older-than-Ediacaran additional island arc components. The different proportion of source components and the marked variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ suggest that the across-arc polarity of the remnants of the Pan-African arc of Iberia trended east-west (respect to the current coordinates) during Cambro-Ordovician times, and that the passive margin was situated to the west.

Serpentinities of the Motagua fault zone, Guatemala: A mineralogical assessment

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The Motagua Fault Zone (MFZ) of Guatemala is interpreted as the active plate boundary between the North American and Caribbean plates with accumulated displacement of $\sim 10^3$ km. Belts of serpentinite mélange are exposed on both sides of the MFZ, and these mélanges contain tectonic inclusions of high-pressure, low-temperature (HP/LT) rocks, including jadeite, eclogite and various metabasites. The belts represent collisional emplacement of subduction channel assemblages. Ar-Ar ages from white micas of ~ 120 Ma from HP/LT rocks, including abundant lawsonite eclogite, south of the fault are significantly older than the ~ 70 Ma ages of similar rocks, but no lawsonite eclogite, from north of the fault. The juxtaposition of mélanges of different Ar-Ar age across a strike-slip fault is odd, and a robust interpretation has not been determined. A mineralogical study of numerous serpentinite samples from both sides of the MFZ is underway to assess their metamorphic processing, diversity and origin. Most serpentinite is sheared and recrystallized to antigorite schist whether from north or south of the fault. Less-tectonized samples with relict textures and minerals are few; most commonly they have affinity with harzburgite (containing relict exsolved opx with few discrete cpx grains), followed by lherzolite (both relict opx and cpx) and rarely dunite (no relict pyroxene but common chromite). Relict cpx contains up to ~ 8 wt% Al_2O_3 , suggesting high-T equilibration/formation. Antigorite predominates in all samples with much less, if any, lizardite, and chrysotile is only found in very-late veins. Magnetite is common; chromite less so; Mn-ilmenite, talc, and chlorite are not uncommon; and olivine, brucite and andradite are rare. Carbonates include both magnesite and dolomite; calcite and silica are secondary. Early results on sulfides shows pentlandite, mackinawite, heazlewoodite and millerite, which suggests low-T re-equilibration and possible influence from late-stage fluids. Rare awaruite and Cu-awaruite are present. The preponderance of antigorite in serpentinite supports the interpretation that these rocks are products of hydration in or immediately above a subduction channel. Serpentinite from north of the MFZ commonly contains magnesite which suggests higher levels of CO_2 in the serpentinizing fluids and may result from the distinct ~ 70 Ma event. The samples from the south more commonly contain lizardite with antigorite which is consistent with colder, and perhaps even wetter, conditions that produced lawsonite eclogites during the ~ 120 Ma event. The combination of interpreted original lithologies, mineralogies and mineral chemistries are most consistent with origin from a complex mantle-wedge peridotite assemblage.

Tourmaline in the Álamo complex (Central Iberian Zone, Spain): evidence for boron recycling in the continental crust and petrogenetic implications

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Tourmaline-rich rocks are widespread minor lithologies within the Schist-Greywacke complex (SGC) in the Central Iberian Zone (CIIZ), particularly in the so-called Álamo complex. In this complex, low-grade metamorphic rocks alternate with aniforms composed by leucogranites and anatectic complexes. Tourmaline concentrations occur in stratiform tourmalinites, psammo-pelitic metasediments, breccias, gneisses, migmatites, peraluminous leucogranites, pegmatites and quartz veins. Combined petrographic, chemical and isotopic data document a multistaged development of tourmaline. Overall, tourmaline composition can be described within the schorl-dravite-foitite-Mg-foitite quadrilateral. It belongs to the alkali-group with variable $\text{Fe}/(\text{Fe} + \text{Mg})$ and $\text{X}/(\text{X} + \text{Na})$ ratios, from 0.43 to 0.84 and 0.25 to 0.55, respectively, where X represents vacancies in the X-site. Based on field and petrographic criteria, two groups of tourmalinites can be distinguished: (i) early tourmalinites affected by the Variscan deformation and metamorphism; and (ii) later tourmalinites related to the emplacement of Variscan leucogranites. Textural and geochemical data are consistent with a psammopelitic parentage for the protolith of the tourmalinites. The generation of leucogranites is attributed to mid-crustal partial melting under an extensional regime. Two distinct facies can be defined in granitic rocks of the Álamo complex: (i) two-mica granites, including biotite + muscovite + plagioclase + K-feldspar + quartz $\pm$ tourmaline $\pm$ Al silicates, characterized by relatively high $(\text{FeO} + \text{MgO} + \text{TiO}_2)$; and (ii) tourmaline granites (up to 5% vol.), with the assemblage muscovite + tourmaline + albite + K-feldspar + quartz $\pm$ garnet $\pm$ biotite, and low $(\text{FeO} + \text{MgO} + \text{TiO}_2)$. Biotite falls in the syderophillite field ($\text{Al}^{\text{IV}} > 2.6$ apfu), with $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.55-0.95$, and $\text{Ti} < 0.24$ apfu. Primary muscovite has $\text{Na}/(\text{Na} + \text{K}) > 0.06$, and Ti up to 0.10 apfu. Garnet is relatively rich in Mn (24.08-34.75 mol% Sp). The boron budget during Variscan orogeny is thought to stem from: (i) early (Cadomian?) tourmalinites caused by a B-metasomatism induced by tourmaline-bearing nearby granites and orthogneisses as potential candidates to represent the source of boron; and/or (ii) infiltration of boron-rich aqueous fluids into the midcrustal zone during continental collision. Boron was removed from the rocks via solution in aqueous fluids released by dewatering and devolatilization reactions during prograde metamorphism. The occurrence of tourmaline in a variety of rocks denotes a significant crustal recycling of boron, perhaps from Cadomian to Variscan orogeny, what may have been important for the genesis and evolution of granitic magmas in the CIIZ.

Significance of elevated contents of $\square\text{Si}_4\text{O}_8$ and $\text{AlAl}_3\text{SiO}_8$ end-members in black clouded plagioclase from the Lac Saint-Jean anorthosite: Evidence for oxidation-induced postmagmatic exsolution of Fe-Ti oxide inclusions from plagioclase

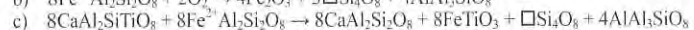
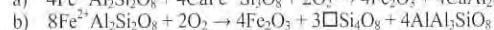
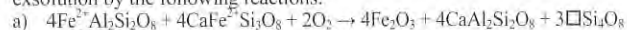
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Large anorthosite massifs have plagioclase phenocrysts that are black and clouded by myriads of minute Fe-Ti oxide crystals. Single crystals of such black plagioclase from the Lac Saint-Jean Proterozoic massif-type anorthosite in Québec (Canada) were studied to explain the simultaneous existence of oriented acicular crystals of hematite and hemo-ilmenite, fine unidentified Fe-Ti dust, and the unusual presence of the $\square\text{Si}_4\text{O}_8$ and $\text{AlAl}_3\text{SiO}_8$ end-members in the plagioclase. Our previous EMPA analyses of single-crystals of plagioclase from this intrusion suggest that these fine oxides and compositional end-members are products of exsolution by the following reactions:



If our exsolution model is true, the initial bulk composition of the crystals should have no $\square\text{Si}_4\text{O}_8$ or $\text{AlAl}_3\text{SiO}_8$. To verify our hypothesis, we conducted bulk XRF analyses of the single-crystal specimens from which we removed the numerous inclusions of other minerals such as clinopyroxene, amphibole, mica and occasional large grains of ilmenite or magnetite that are texturally-different from the fine acicular oxides and dust that we believe result from the exsolution reactions. This purification was done by meticulous examination and selection under the microscope of thin slices of the plagioclase crystals. Also removed were the granulated boundaries between crystals and fractures that have suffered late albitization. Our preliminary results show that the initial bulk composition has no significant $\square\text{Si}_4\text{O}_8$ content. The molar ratio of $\square\text{Si}_4\text{O}_8$ to $\text{AlAl}_3\text{SiO}_8$ is approximately 3:4 in the large single crystals; smaller crystals have fairly steep ratios. We believe that in the presence of oxygenated fluids, reactions a) and b) occurred rapidly and simultaneously to produce large amounts of fine oxide dust. This rapid and combined reaction led to a steep slope in excess of 0.75 in the $\square\text{Si}_4\text{O}_8$ vs. $\text{AlAl}_3\text{SiO}_8$ diagram. In contrast, with lesser concentrations of oxygenated fluids, longer reactions times gave rise to oxides via a two-step reaction model, by which reaction a) first yielded high initial concentrations of $\square\text{Si}_4\text{O}_8$ at low values of $\text{AlAl}_3\text{SiO}_8$, followed by further production of $\square\text{Si}_4\text{O}_8$ and $\text{AlAl}_3\text{SiO}_8$ from reaction b) to yield a slope of 0.75 in the diagram. In the case of reaction c), the slope in the diagram would be even less than 0.75.

O20-01

Melt migration processes in the mantle and their geochemical consequences: a review based on evidence from ophiolites

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Deep-seated processes related to melt generation beneath oceanic spreading centers are poorly constrained by direct observation. The variability in ocean ridge and back-arc basalts composition call for complex mixing, crystallization and melt-rock interaction processes during melt migration but the interpretation of these indirect data remains ambiguous. The aim of this talk is to review direct field and petrological constraints relevant to this problem; it is based on evidence from several ophiolites including Oman, Trinity and Bay of Island.

The analysis of the distribution and composition of hundreds of former melt conduits exposed in Oman peridotites was used to map the thermal structure of asthenospheric diapirs and of their surrounding lithospheric mantle. The temperature field is mirrored in petrological characters sensitive to the degree of fractional crystallization (cotectic assemblages and compatible element contents). The distribution of the geochemical characteristics diagnostic of the fertility of the source and of the degree of decompression melting are, however, randomly distributed and quite variable from one conduit to the others. This indicates that melt migration does not homogenize efficiently the incremental melt fractions and that their extraction from their zone of production is a stochastic process.

Another conclusion concerns the geochemical impact of melt-rock interaction during migration. In dry systems, melt rock interaction is restricted to very high temperatures; as soon as cracks form, which is observed to occur just below solidus conditions, the melt is chemically insulated from its host peridotite. In fluid-rich systems, melt rock/interaction can have major and spectacular effects, like the formation of granitic melts, down to much lower temperatures.

High temperature melt/rock interaction can have dramatic effects on the composition of the peridotite on rather large distances off porous flow channels (up to ten times the channel thickness); the interaction is generally modal close to the channel (i.e. the mineral proportions change together with mineral composition) but becomes entirely cryptic further away from it. Both cases of re-fertilization and de-fertilization in incompatible elements are observed depending on the relative composition of the melt and of the host peridotite. The formation of dunitic channels is not restricted to interaction with MORB-like melts but can concern a wide variety of melt compositions - provided they are undersaturated in silica relative to the peridotite - even in a single ophiolite. Such interactions influence the composition of the melt itself, although in an extent that remains hard to quantify.

O20-02

Contrasting upper crustal structures revealed by deep ocean crust drilling — insights into shallow magma plumbing systems beneath intermediate versus superfast spreading ridges

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ODP Hole 1256D, drilled by ODP Leg 206 and IODP-Expeditions 309 and 312, is situated on 15-Ma oceanic crust formed at the superfast (220 mm/yr) spread East Pacific Rise on Cocos plate off Costa Rica. Hole 1256D penetrated the entire upper oceanic crust from 250-m thick sediments, 811-m thick extrusives (including the Transition Zone) and a thin (346 m) sheeted dike complex and drilled 105 m into the upper gabbro.

The extrusive rocks are dominantly sheet flows with minor intervening pillows. The Transition Zone and the Sheeted Dikes are marked by the presence of brecciated basalt cut by numerous fine veins and cataclastic stringers, and thin glassy to aphanitic dikelets in-situ fragmented into hyaloclastite. Intimate association of brecciation-dike intrusion-hydrothermal fluid circulation increases downhole in frequency. The massive hosts are aphyric and non-vesicular holocrystalline or doleritic basalts. The lower portion of the sheeted dikes are altered and locally recrystallized to Granoblastic Dikes. Gabbroic rocks range from gabbro to oxide gabbro, opx-bearing gabbro, gabbro-norite and quartz diorite.

Hole 504B is the deepest drill hole that penetrated 1815 m into 6.9-Ma oceanic basement formed at Cocos-Nazca Spreading Center, asymmetrically spread at 36 mm/yr to the south and 30 mm/yr to the north. The 506 m-thick pillow-dominated extrusive rocks are gradually replaced by subvertical dikes and changes into 100% sheeted dikes > 1056 m in thickness. Seismic layer 2/3 boundary lies 1200 m in depth within the sheeted dikes and is associated with gradual change in porosity and alteration, but not a lithological transition from sheeted dikes to gabbro.

Lithostatic and magmatic pressure estimates show that the pillow-dominant extrusives and the lower extrusive/intrusive ratio for 504B crust result in a lower level of neutral buoyancy (LNB) of uprising magma, which favors the intrusion of dikes at this level in the upper crust. In contrast, the dense sheet flow-dominant 1256D crust has LNB at very shallow levels, which are favorable for eruption rather than dike intrusion throughout most part of the upper crust except the less dense uppermost extrusives. This resulted in the higher extrusive/intrusive ratio for the 1256D crust. After passage of dikes, fractures were left behind which hosted the hydrothermal circulation.

O20-03

A preliminary result of an oceanic lithosphere drilling: IODP Expedition 304 and 305 at the Atlantis Massif, the Mid-Atlantic Ridge 30°N

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Hole U1309D was penetrated to 1415.5 mbsf on the oceanic lithosphere with 75% recovery during IODP expeditions 304 and 305 at the Atlantis Massif, Mid-Atlantic Ridge 30°N. The aims of the cruises was to characterize variations in rock type, structure, and alteration with depth at this massif, to obtain core of essentially fresh, in situ peridotite, and to investigate the formation mechanism of oceanic core complex.

A total of 1043m of mafic and ultramafic rock was recovered from Hole U1309D. More than 95 vol% of the hole is made up of gabbroic rocks and 0.3 % is serpentinized ultramafic rock. Several diabase sheets of variable thickness (0.01 - 10 m) with chilled margins compose 2.9% of the volume. The most abundant rock types are medium-grained to pegmatitic gabbros and gabbro-norites (56%). Both grain size and modal composition can vary strongly on a dm-scale, and commonly include minor quantities of olivine (rarely exceeding 10%), Fe-Ti-oxides, and/or orthopyroxene. Intercalated with these gabbros are medium-grained olivine gabbros (28%). The troctolitic gabbro are continuously grade into troctolite, and a rarely recovered olivine-rich troctolite with more than 70% olivine (5.4 vol% of the samples). Oxide gabbro defined by the occurrence of more than 2% modal Fe-Ti-oxide minerals is recovered 7.7 vol% of the rocks, and the Fe-Ti-oxides occur as heterogeneously distributed patches or seams. The oxide gabbros can occur as discrete dikelets crosscutting other lithologies, or display strong enrichment in ductile deformation zones. There are two separate and distinct sequences of these lithologies of several hundred meters thickness comprising of Hole U1309D. These lithologies also show a variable range of alterations correlated with/without the depth. Moreover, the contact relationships of these lithologies suggests that even only gabbroic rocks provide a wide range of aspects with variable mineral proportions, which may reflect variety of physical processes.

O20-04

Magmatic processes in the deep oceanic crust triggered by water: Experimental constraint

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Recent observations in ophiolites and in the recent oceanic crust showed that hydrous fluids may interact with the just frozen, still very hot lithosphere triggering partial melting processes which may produce distinct late-stage modification or which may even result in the formation of special rock types. In some cases it is evidenced that the water-rich fluids are seawater-derived, thus suggesting a model that hydrothermal circulation at fast-spreading ridge operates much deeper than previously known. Moreover, it has been suggested that this type of hydrothermal circulation at very high temperatures even has the potential to reach the sub-MOHO level causing interaction between seawater and harzburgite at magmatic temperatures. In order to understand the magmatic processes/reactions behind these interactions, we started different series of experiments in specially designed internally heated pressure vessels enabling the control of oxygen fugacity and the rapid quenching of the experimental runs.

(1) Water-saturated partial melting of natural oceanic gabbros between 900 and 1000°C at 200 MPa produces a SiO₂-enriched melt and a characteristic residual paragenesis consisting of An-enriched plagioclase, orthopyroxene and pargasitic amphibole. The experimentally features can also be observed in many typical oceanic gabbros suggesting that the hydrous partial melting of gabbros by hydrothermal activity is a common process within the oceanic crust.

(2) Crystallization experiments in a gabbroic system shows that at pressures > 100 MPa under high water activities olivine and clinopyroxene crystallize first, while the stability of plagioclase is suppressed. This demonstrates that wet MORB-type magmas have the potential to form "wehrlitic" parageneses by the accumulation of early crystallized olivine and clinopyroxene. Thus, typical late wehrlitic intrusions within the oceanic crust (e.g., in the Oman ophiolite) can be regarded as products of hydrous tholeiitic melts.

(3) Water-saturated partial melting of harzburgite at shallow pressures starts at 1060°C leading to melts showing the characteristics of typical "High-Ca boninites". They are highly depleted in incompatible trace elements showing extremely high Ca/Na ratios. A potential fractionation of such melts would lead to highly depleted gabbro-norites with An contents of plagioclase generally above 90 mol%. Thus, such cumulates correspond well to those "depleted gabbro-norite" sometimes found as late intrusions in the oceanic crust. The residual minerals left behind after the experimental partial melting correspond to typical dunitic assemblages.

Magma processes beneath fast-spreading ridges: constraints from petrological evidence in gabbroic unit of the Oman ophiolite

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There is a controversial subject where gabbros were crystallized in oceanic crust. Large magma chamber models (Pallister and Hopson, 1981; Smewing, 1981) are now abandoned, however, two different models which are called as "gabbro glacier model" and "sheeted sill model" (Coogan et al., 2002a) are proposed. Gabbro glacier model requires all melts that are added to crust to pass through melt lens (Quick and Denlinger, 1993; Coogan et al., 2002a, 2002b). While sheeted sill models require most melts to have undergone significant crystallization within the lower crust prior to be fed to the melt lens (Kelemen et al., 1997; Kelemen and Aharonov, 1998). Besides, Boudier et al. (1996) proposed an intermediate model. In this paper we discuss for magmatic process beneath fast-spreading ridges based on petrological evidence in the gabbroic unit of the Oman ophiolite.

We have examined vertical mineral compositional profiles in the gabbroic unit from three areas in the northern Oman ophiolite, Wadi Fizh, Wadi Thuqbah, and Wadi Hilti to Sudum areas. These areas correspond to segment margin, center and intermediate in segment structure, respectively (Miyashita et al., 2003; Adachi and Miyashita, 2003). We found that the mineral compositions of olivine, plagioclase and clinopyroxene in the gabbroic unit vary depending on the stratigraphic positions. That is, these mineral compositions tend to evolve upward stratigraphic position, indicating that systematic fractional crystallization occurred within the gabbroic unit. However, some of upper gabbros in Wadi Fizh area (segment margin) have similar or more primitive compositions than the underlying layered gabbros. It suggests that primitive melts without little fractionation could be fed to the melt lens at the segment boundary, in good agreement with bulk rock compositional change of sheeted dike complex (Miyashita et al., 2003). Furthermore, Na₂O contents of clinopyroxenes in upper gabbro and sheeted dike complex (phenocryst) are systematically lower than that in layered gabbro at given Mg# in each studied area, while TiO₂ contents of these rocks show a similar trend. Because partition coefficients for Na₂O between clinopyroxene and basaltic melt decrease greatly with decreasing pressures, the difference in Na₂O contents of clinopyroxenes suggests that the upper gabbro and sheeted dike complex were crystallized at the lower pressure conditions than layered gabbros. So that layered gabbro and upper gabbro crystallized at lower crust and axial melt lens, respectively. Thus, several lines of evidence support a sheeted sill model.

Kilo meter-scaled highly refractory zone found in the mantle section of the northern Oman ophiolite (Fizh block): implications for remelting of oceanic lithospheric mantle

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Spatial chemical variation in the mantle section of the northern Fizh block in the Oman ophiolite is studied to understand formation and evolution of oceanic lithospheric mantle. We have analyzed minerals for major element compositions by EPMA in 278 harzburgites collected from an area of 25 x 15 km² and 101 samples for whole rock chemistry by XRF and ICP-MS.

The Fo content of olivine ranges in narrow range from 90 to 92 but Cr# [=100°Cr/(Cr+Al)] ratio of spinel widely ranges from 24.2 to 77.6. We plotted spinel Cr# on the map of northern Fizh block and found that the harzburgites with spinel Cr# more than 70 linearly distribute in the western side of NW-SE oriented shear zone in the Fizh mantle section. It is also confirmed that abundances of whole rock HREE are lowest in the western side of shear zone.

Variations of middle REE (Nd, Sm, Eu) against Yb for whole rocks can be separated into two positive trends that are parallel each other. First group contains spinel with Cr# <60 while the other group contains spinel with Cr# >60. The former indicates residual trend after partial melting of upwelling asthenospheric mantle beneath mid-ocean ridge while the latter may have created by fluid flux-assisted remelting of residual peridotite resulted in the depletion in Yb and enrichment in L-MREE. Abundance of LREE in whole rocks is highest in the northwestern region near basal thrust and decrease toward the Moho. It may indicate that the LREE-enriched fluid migrated from the ophiolite base into the mantle section.

On the basis of above observations we propose that the mantle section of the northern Fizh block evolved through two stages. First, asthenospheric mantle ascent and melted beneath mid-ocean ridge forming a residual mantle column with more depleted peridotite on the top. Second, during oceanic thrusting of the ophiolite, LREE-enriched fluid was derived by dehydration of metamorphic sole and flew into the mantle section through shear zone. Migration of fluid reduced solidus temperature of residual harzburgite and caused remelting of residual peridotite forming spinel with Cr# more than 60. Moreover, the reaction with LREE-enriched fluid produced LREE-enriched patterns in peridotites. Near the Moho, small amount of trapped melt caused refertilization of uppermost mantle.

High magnesian diopsidite dykes in the Oman Ophiolite: evidence for high temperature hydrothermal circulation in the oceanic mantle.

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Mafic and ultramafic dykes and veins are frequent features in the mantle section of the Oman ophiolite. They are generally the result of the crystallization of common silicate liquid like MORB or andesitic melts. From place to place a specific kind of dyke, made mainly of highly magnesian diopside and which textural, mineralogical and chemical characteristics do not match a purely magmatic origin outcrops. These features are not infrequent in the omanese peridotites but as their field aspect presents confusing similarities with totally altered gabbro dyke, they were previously not sampled and studied.

Most of the samples are composed by almost pure magnesian diopside (0.94<Xmg<1), mainly devoid of all minor (Ti, Al and Cr being frequently below detection limits) and trace elements. Some of them contain also a substantial proportion of pure anorthite (An% up to 99%), minor amounts of forsterite (Fo>95%) or traces of andradite. The mineralogical assemblages and fibrous textures, that are generally observed in skarns developing in contact metamorphic halos, and the commonly observed euhedral diopsides and/or andradites inside of serpentine holes or carbonate veins suggest a metamorphic growth in a matrix of serpentine and/or carbonates.

The distribution of this kind of dyke at the scale of the Oman ophiolite is not random, the higher abundance being observed in the vicinity of former asthenospheric diapirs. The relationships between the diopsidite dykes and the surrounding peridotite are ambiguous, ranging from sharp or faulted to gradational with progressive replacement of the mantle mineral with metamorphic pyroxene and/or olivine. On the field, dioritic to quartz-dioritic dykes or intrusion are frequently present in the proximity (few tens to few hundreds of meter) of the diopsidite dykes.

These diopsidite dykes may be interpreted as the result of very high temperature (up to 1000°C) hydrothermal circulations in the upper mantle and its interaction with melt issued from the partial melting of peridotites at that depth which induce successive stages of serpentinization and prograde metamorphism of the serpentinized mantle. The observed lithologies and chemical data confirm the idea of McCollom and Shook (Journal of Geophysical research, vol 103, 1998) who proposed that anhydrous minerals like plagioclase and pyroxene may crystallize from very high temperature liquids, intermediate between silicate melts and supercritical water. Our data confirm also previous hypotheses suggesting that there is no clear cut between magmatic and hydrothermal lithologies.

Fertile peridotites from the Isabela Ophiolite: fragments of the lower part of a Cretaceous oceanic lithosphere

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The Isabela Ophiolite is an elongated N-S-oriented Cretaceous mid-ocean ridge (MOR)-derived oceanic lithosphere exposed along the eastern margin of north Luzon. It is mainly composed of the mantle-peridotite section varying from massive and layered pyroxene-rich harzburgites and lherzolites to massive and layered harzburgites. Dunites occur as concordant layers in the stratified peridotites, or as dike-like bodies cross cutting the peridotite foliation showing replacive nature. Crustal lithologies such as gabbros, dike complex and pillow lavas are exposed in the central and northern part of the ophiolite body.

Petrological and geochemical study of the mantle peridotites suggests a continuous section from fertile lherzolites to residual harzburgites and dunites. The most fertile among the peridotites are exposed in Dinapigui Point, the southern tip of the Isabela Ophiolite. Dinapigui Point lherzolites are rich in coarse-grained 2 pyroxenes (ex. clinopyroxene >15 modal %) with porphyroclastic texture suggesting a primary nature. Chromian spinel also shows relatively coarse grains with strong association with the pyroxenes. Petrography suggests that these peridotites have undergone very low degrees of partial melting and could have originated near the source region of MOR basalts or in the deeper part of the oceanic lithosphere. The presence of pargasitic amphibole is consistent with this hypothesis. Peridotites with deep derivation (ex. from continental lithosphere) have pargasitic amphiboles as an accessory mineral.

Geochemistry of the Dinapigui Point lherzolites further strengthens the deep near-source derivation model. Isotope ratios of Sr and εNd from primary clinopyroxenes overlap with the field of MOR basalts. This strongly implies that the peridotite body is more likely related to MOR basalt generation, reaffirming the earlier MOR classification of the ophiolite. Among the Isabela Ophiolite peridotites, the Dinapigui Point lherzolites have the highest rare earth elements (REE) composition, which means they are the most fertile ultramafic rocks in this ophiolite. Composition systematically decreases towards the more depleted peridotites. The REE pattern exemplifies typical MOR signature and does not show any indication of refertilization. Chromian spinel, a very good indicator of partial melting, strongly suggests that only a small amount of melt have been extracted from the Dinapigui Point lherzolites. The very low chromium number (Cr# <0.1) is among the lowest values documented for oceanic peridotites. In the diagram spinel Cr# versus magnesium number (Mg#), the Dinapigui Point lherzolites plots just outside the lower end of the field of abyssal peridotites defined by Dick and Bullen (1989).

Hydrous metasomatic overprinting in mantle section of the Isabela ophiolite, Philippines

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In subduction zone, H₂O-rich fluids/melts released from subducted lithosphere interact extensively with the overlying mantle as they percolate upward through it. Direct petrographical evidence for hydrous metasomatism in the mantle is scarce and is limited in sub-arc xenoliths (e.g., Blatter & Carmichael, 1998, *Geology* 26, 1035-; McInnes et al., 2001, *EPSL* 188, 169-). Here we report amphibole-bearing orthopyroxenite veins (Amph-OPXnite hereafter) in mantle section of the Isabela ophiolite, the Northeastern Luzon region (Philippines) as hydrous metasomatic overprinting of oceanic lithosphere in response to a switch in tectonic setting from a mid-ocean ridge to a convergent margin.

The Isabela ophiolite is located along the northeastern portions of the Philippine Mobile Belt extending for 90 km. Peridotites, massive and layered gabbros, dike complexes, pillow basalts and chert are not sequentially distributed in the area (e.g., Andal et al., 2005, *IA* 14, 272-). Peridotites are mainly lherzolite to clinopyroxene-rich harzburgite having granular to porphyroclastic texture with minor amounts of harzburgite, dunite and pyroxenite (Andal et al., 2005). Several chromitites occur as pod shape in a relatively thick dunite lens (Morishita et al., 2006, *IA* 15, 84-). Recently Andal et al. (2005) concluded that the Isabela ophiolite is of a slow-spreading ocean ridge origin.

Amph-OPXnites occur as veins (a few meter thick) including a lot of peridotite clasts. Major and trace elements compositions of orthopyroxene in the Amph-OPXnites are apparently different from those of orthopyroxene porphyroclasts in the host. Coarse-grained amphibole (pargasitic to tremolitic compositions) is abundant in the middle of the vein and line to make a sublayer parallel to the direction of vein. The Amph-OPXnite partly consists of very fine-grained minerals of orthopyroxene and olivine with small amount of amphibole and spinel. Olivine in fine-grained matrix (10-100 μ m in size), which mainly consists of fine-grained olivine and orthopyroxene (low-Al & Ca) with small amount of amphibole, is rich in Fe component and Ni content. Petrology and geochemistry of the Amph-OPXnite are similar to those in hydrous metasomatized peridotite xenoliths in arc setting (Papua New Guinea) (McInnes et al., 2001). We concluded that the Amph-OPXnites were formed by interaction with peridotite and SiO₂-rich hydrous fluids/melts possibly derived from a subducting slab just before obduction of the ophiolite.

High-pressure mafic layers of gabbroic origin embedded in mantle-derived orogenic peridotite: the Horoman peridotite and other examples

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Orogenic peridotite masses contain layers or lenses of mafic rocks, typically concordant to the primary structure of the host peridotite. Origin of these mafic layers and the origin of the layered structure of the mafic ultramafic complex have been an important subject of petrology and tectonics of the upper mantle. Although these layers were all once equilibrated in the upper mantle, at high-temperature and high-pressure granulite- or eclogite-facies conditions, a distinctive genetic type of mafic rocks of primarily low-pressure gabbroic origin has been identified and is referred to as the Type II (Kornprobst et al., 1990). They are characterized by high Mg#, high Al, low Ti and Na, lower HREE, and positive Eu and Sr anomalies for whole rock composition and some contain kyanite or corundum, depending upon their equilibration conditions. The type II mafic rocks have been identified in other orogenic peridotite such as Horoman (Takazawa, et al., 1999) and Ronda (Morishita and Arai, 2001). Obata et al. (2006) presented a simple method of identifying this type of mafic rocks utilizing whole-rock major element compositions. We review and demonstrate the power of this method for the case of a well-characterized Japanese orogenic lherzolite massif, the Horoman peridotite. By reviewing other orogenic peridotite world-wide (Beni Bousera, Ronda, Czech and Austrian Moldanubian, etc.), we emphasize a universal association of the high-pressure metagabbros (Type II) and real high-pressure cumulate rocks occurring within the same masses of peridotite and emphasize tectonic significance for such association.

Multiple vein/dike-related alteration, metasomatism and thermal metamorphism of the oceanic lower crust at IODP Site U1309, Mid-Atlantic Ridge

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The drilling of Hole 1309D during IODP Expedition 304/305 recovered relatively fresh gabbroic rocks below 350 mbsf. These rocks are not affected by pervasive alteration and therefore provide a good opportunity for studying pure dike/vein-related transformation processes of in-situ oceanic lower crust at a slow-spreading ridge (Mid-Atlantic Ridge). A common observation in the present core is that alteration halos, from millimeters to decimeters wide, have developed in host gabbros along late gabbroic dikes or amphibole/chlorite veins, and olivine-rich hosts show a zonal pattern of alteration halo with systematic change of mineralogy. The zoned halos commonly consist of three zones: Corona Zone, Talc Zone and Psd-Tremolite Zone toward the dike/vein. These zones are respectively characterized by tremolite and chlorite showing a coronitic rim around primary olivine next to plagioclase, by talc replacing olivine, and by tremolite pseudomorphs after olivine (complete decomposition of olivine) associated with coronitic chlorite around plagioclase. All the secondary minerals appear in increasing amounts toward the intrusion, although talc is restricted to the Talc Zone. In the Psd-Tremolite Zone, green hornblende commonly occurs cutting coronitic chlorite. The zoned halos cut brown hornblende trails replacing clinopyroxene, and are cut themselves by clay or clay-carbonate veins. From textural relations, serpentinization looks to be posterior to the formation of the zoned halos. Mineral assemblages indicate greenschist to amphibolite facies conditions for the formation of the zoned halos. The crosscutting relationships of veining represent an alteration sequence under conditions of the upper amphibolite to sub-greenschist facies in association with monotonous cooling of the gabbroic complex. However, the formation of green hornblende cutting chlorite in the Psd-Tremolite Zone suggests an increase in temperature, i.e., thermal metamorphism. Furthermore, the two kinds of alteration products in the zoned halos, tremolite + chlorite and talc, require metasomatic agents of different H₂O and SiO₂ activity. From the present lines of evidence, it is concluded that the zoned halos were caused by intrusions evolving from early aqueous fluids to late higher-temperature siliceous melts, which passed across the lower crust through common pathways yielded by brittle deformation.

Evidence for primitive magmatism at segment-end on ultraslow spreading ridges: A case study from the Atlantis II Fracture Zone, Southwest Indian Ridge

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Spreading rate and position on a ridge segment, i.e. whether at mid-point or edge of a segment, have been thought as important parameters for magmatism along mid-ocean ridges. Thus, segment-ends on ultraslow spreading ridges have been believed as the most inactive areas of magmatism in the global mid-ocean ridge system. Atlantis II Fracture Zone (AIIFZ), 57°E of the Southwest Indian Ridge (SWIR), is well known as one of the typical areas of such an extreme situation. At the Atlantis Bank, a wave-cut terrace on the eastern transverse ridge of AIIFZ, 1.5-km Hole 735B was drilled through lower gabbroic crust, however no primitive cumulate was found. A compositional break was observed between the most magnesian olivine (Fo86) from the gabbros and mantle residual olivine ($\geq$ Fo90-89 in general), Fe/Mg partitioning between olivine and melt is virtually independent of pressure, temperature and composition of system, so magnesian olivine must be present somewhere if mantle melts were present at this part of SWIR. At the eastern slope of AIIFZ, during SHINKAI dive (#643 and #649), we observed an exposure showing continuous upward transition from mantle peridotite to layered gabbro. However, there is still a break in olivine composition between Fo91-90 in the mantle peridotites and Fo72-71 of the layered gabbros. Two explanations have been proposed for the missing of primitive cumulates: (1) mantle melts were focused to mid-point of the segment and only evolved melts were supplied toward segment-end by lateral migration; (2) the primitive cumulates crystallized within a cold thermal boundary layer in the mantle. Fortunately, during SHINKAI dive (#646) at the eastern slope of AIIFZ, we found a primitive troctolite xenolith in dolerite, which is exposed above mantle peridotites. The troctolite is composed of olivine (Fo90-89) and plagioclase (An86-83). Chromian spinel (Mg# = 0.77-0.63, Cr# = 0.26-0.43) contained in composition between spinels in mantle peridotites and those from gabbros, dolerites and basalts sampled in this area. Cotectic crystallization of olivine and plagioclase indicates the pressure conditions of $\leq$ 7-8 kbar, and we have no more constraint for the original depth of the xenolith. However, the thermal boundary layer within the mantle is more plausible because of no substantial outcrop of gabbros between the dolerite and mantle peridotite along the diving track. In conclusion, we found evidence for primary mantle melt at the ridge segment offset on ultraslow SWIR.

Dunite-Wehrlite-Olivine Clinopyroxenite Series Rocks from the North Fiji Basin as Deep-Seated Rocks from the Backarc Basin

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Dunite, wehrlite, and olivine clinopyroxenite were recovered by dredging from the North Fiji Basin, one of the active backarc basins in the southwest Pacific. These rocks are commonly observed in ophiolite suite, but are very rare, as compared with residual peridotite, from the oceanic floor. Ultramafic rocks have been rarely reported from the backarc basin. Thus wehrlite series rocks from the North Fiji Basin are precious samples because the backarc basin is one of the candidates for tectonic setting of ophiolite genesis.

The wehrlite series rocks were dredged from the Central Hill, which is a topographic high lying in the nearby north of Fiji Transform Fault, by the 2004 cruise on the JAPAN-SOPAC co-operative deep-sea mineral resources study program supported by JICA and JOGMEC. Fo value of olivine in wehrlite and olivine clinopyroxenite is variable from 88.2 to 78.9, showing their plotting off the olivine spinel mantle array, which is a residual spinel peridotite field. Chromian spinel is highly variable in chemistry. Cr# [=Cr/(Cr+Al)] and Mg# [=Mg/(Mg+Fe²⁺)] are variable from 0.41 to 0.85 and 0.15 to 0.50, respectively, in chromian spinel. TiO₂ content and Fe³⁺# [=Fe³⁺/(Cr+Al+Fe³⁺)] of chromian spinel are also variable, from 0.06 to 1.67 wt% and from 0.03 to 0.37, respectively. Clinopyroxene is depleted in REE, especially in LREE.

Wehrlites and olivine clinopyroxenites from the North Fiji Basin are possibly of cumulus origin. The high Cr# character of chromian spinel indicates their equilibration with a certain high-degree partial melt produced by a high-degree partial melting. And the high Fe³⁺# and low TiO₂ content of chromian spinel indicate a linkage to arc-related basalts. The Fiji Platform is interpreted as a remnant of an island arc that was active before formation of the North Fiji Basin, and the Central Hill could be separated from the Fiji Platform by a motion of the Fiji Transform Fault. The genesis of the wehrlite series rocks obtained from the Central Hill is possibly related to a magmatic activity of the old Fiji Platform. This chemical character of chromian spinel and REE patterns of clinopyroxene in wehrlite and olivine clinopyroxenite are similar to those of the late-intrusive wehrlites from the Oman ophiolite. This similarity might support an assumption that the late-intrusive plutonic rocks of the ophiolite were formed at an arc setting.

A speculation on thermal history of forearc peridotites in the Mariana arc-trench system

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In the Mariana forearc area, a large number of seamounts composed mainly of serpentinized peridotites are widely distributed westwards within the region of 50-120 km from the trench axis. To understand the thermal history of peridotites, we examined the peridotites recovered from Conical Seamount during ODP Leg 125 (1989) and from South Chamorro Seamount during ODP Leg 195 (2001). Modal analyses of peridotites indicate that harzburgite is predominant, dunite is subordinate, and lherzolite is rare. Rock types, whole rock compositions, and spinel chemistry indicate that these peridotites are the products of moderate degree (15-30 %) of partial melting in the lherzolitic source mantle, which is comparable with those of on-land ophiolite of island-arc origin.

Olivines of serpentinized peridotites are always homogeneous in Fe/Mg except for the parts being in contact with spinels, and have 89-92 forsterite contents. Spinel has remarkable zonal structures of decrease of X_{Mg} (=Mg/(Mg+Fe)) from core to rim. Incomplete exchange of Mg-Fe²⁺ in both olivine and spinel provides useful information on the thermal histories of the host rocks. Based on the method of Ozawa (1984), cooling rates were estimated from the relationship between the grain size of spinel and temperature calculated from the chemical compositions of the core of a spinel grain and of olivine far from it. The calculated temperatures of the peridotites from both seamounts by using the olivine-spinel geothermometer decrease monotonically with decrease of grain size of spinel, suggesting that the forearc peridotites have cooled gradually from about 800°C to 600°C; the cooling rate can be estimated at 10⁻⁴ to 10⁻² °C /yr. This cooling history of forearc peridotites may be explained by the cooling of wedge mantle by subducting cold slab at the initial stage of subduction of the Pacific plate beneath the Philippine Sea Plate at about 45 Ma. The cooling rates of forearc peridotites estimated here are in good agreement with those of peridotites from on-land ophiolites in Japan provided by Ozawa (1984). It is highly probable that the on-land peridotites originated from island arc also have experienced the cooling due to subduction of cold slab at the initiation of subduction.

Petrological structure of the uppermost mantle beneath a mid-ocean ridge: an example from Wadi Rajmi, northern Oman ophiolite

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Vertical petrological structure of the oceanic uppermost mantle has been little known because of poor sampling for deep seated rocks from the present-day ocean floor. Mantle section of ophiolite provides unrivaled opportunity of studying the upper mantle materials beneath mid-ocean ridges (e.g., Nicolas, 1989). We conducted detailed petrological investigations on the uppermost mantle section along Wadi Rajmi of the northern Oman ophiolite. The upper mantle peridotite (harzburgite) was examined for approximately 4 km thickness downsection from the uppermost mantle just beneath the Moho transition zone. The Oman ophiolite possibly has a complicated history, i.e. a switch of tectonic setting from mid-ocean ridge to island arc (e.g. Arai et al., 2006), and discordant dunite and surrounding peridotite, which may have been related with the island-arc tectonic setting, were excluded for our examination.

The uppermost section is composed of harzburgites with or without clinopyroxene, of which orthopyroxene amounts increase almost systematically downward, from 10 to 30 volume % on average. The mineral chemical properties are rather constant in these harzburgites. Olivine is around Fo₉₁, and the Cr# (= Cr/(Cr + Al) atomic ratio) is around 0.5-0.6. Clinopyroxene is depleted in LREE, and its REE patterns are almost the same for all harzburgites examined. The harzburgites are similar to the most depleted abyssal harzburgite in mineral chemistry.

The variations of modal composition decoupled with the mineral chemistry in harzburgite can be explained by later chemical homogenization of a harzburgite mass stratified by olivine/orthopyroxene ratio beneath the mid-ocean ridge. Diapirically uprising MORB source mantle is expected to be partially melted in such a way that the degree of partial melting increases upward. The modally stratified harzburgite mass was subsequently invaded by a chemically homogeneous MORB, which was roughly in equilibrium with harzburgitic mineral assemblage and did not alter the modal compositions. The harzburgites were, however, homogenized only in mineral chemistry through the interaction with the chemically homogeneous MORB melt. The melt was formed by mixing of incremental primary melts in equilibrium with various harzburgites (e.g. Johnson et al., 1990).

"Late intrusive rocks" in the Oman ophiolite as a peridotite/melt reaction product

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Relatively young plutonic rocks named "late-intrusive rocks" are characteristics of the crustal section of the Oman ophiolite. The late-intrusive rocks are important materials for interpretation of the ophiolite genesis including modification of the oceanic crust. However, the process for the late-intrusive rock formation has not been fully discussed to date.

In the lowermost crustal section of Wadi Hilti, Salahi block, the northern Oman ophiolite, the late-intrusive rocks (dunite) are exposed, enclosing blocks of mantle peridotite (harzburgite). Strikes and dips of foliation of the harzburgite are variable from one block to another. Plagioclase-bearing harzburgite was observed at margins of some harzburgite blocks.

Orthopyroxene of the harzburgite is finer in size at the margin of some blocks than in the core, and shows the texture suggesting replacement by olivine. It decreases in volume from the core (20%) to the margin (10%) of the blocks. The plagioclase-bearing harzburgite also contains coarse clinopyroxene grains.

In the harzburgite blocks NiO content of the olivine core varies from 0.4 wt% at the core to 0.39 - 0.28 wt% at the rim although Fo content is almost the same (Fo=91). Rare earth elements patterns of clinopyroxene in the dunite are convex upward, showing slight depletion of light REEs ((La/Sm)_N = 0.071). The calculated melt in equilibrium with this clinopyroxene shows general depletion of rare earth elements as compared with generally flat REE patterns of MORB.

Petrographic characteristics and mineral chemistry indicate that the harzburgite blocks were captured from the mantle section upward by the melt formed the late-intrusive rocks, and the mantle/melt reaction, that is, the crystallization of melt combined with the incongruent dissolution of the orthopyroxene in harzburgite, occurred. It is most probable that the late-intrusive rocks were formed by this mantle/melt interaction. Plagioclase and clinopyroxene in the harzburgite were formed by crystallization of the melt infiltrated into the peridotite blocks. The depletion of REEs of the melt involved in formation of the late-intrusive rocks relative to MORB possibly indicates that the parental melt was formed by remelting of residual peridotite at arc setting. The xeno-blocks of mantle peridotite possibly retain information about conditions of formation of the parental magma.

The Tacloban Ophiolite Complex: A petrological and geochemical characterization of a supra-subduction zone basement complex in central Philippines

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The Tacloban Ophiolite Complex (TOC) represents the basement complex of northeastern Leyte, Central Philippines. Its mantle section is composed primarily of harzburgites and the crustal section is made up of isotropic gabbros, sheeted dike complex and volcanic sequences. Cherts, siliceous mudstones and siltstones cap the ophiolite. Uranium-lead isotopic dating on zircons separated from a gabbro sample yield an Early Cretaceous isotopic ages of formation for the TOC, much older than the previously reported whole rock K-Ar derived Eocene ages of two gabbros and basalt samples. Petrographic analysis of crustal rocks show pl-px and px-pl crystallization orders suggesting environments analogous to those prevailing in modern mid-oceanic ridges (MOR) and supra-subduction zone (SSZ) settings. The harzburgites yield spinels with XCr (Cr/(Al+Cr)) ranging from 0.47 to 0.52, which are transitional to those found in mantle rocks collected from both modern MOR and SSZ environments. The crustal rocks are mostly subalkaline and follow the tholeiitic trend. Plots of these rocks in Harker-type diagrams suggest that they could be related by magmatic affinities. However, fractional crystallization modeling indicates that there could have been several different magmatic sources for these rocks. Intersecting multi-element spectra (normalized to primitive mantle values) of the rocks supports this contention. Moreover, the rocks exhibit contrasting multi-element patterns. Some rocks, on one hand, show clear negative anomalies in Ti and Nb typical of SSZ-related magmas. On the other hand, other samples exhibit relatively flat patterns that dip toward Th similar to those noted in MOR magmas. Field, petrological and geochemical data suggest that the TOC represents a fragment of an Early Cretaceous oceanic crust probably formed along an intermediate- to fast-spreading center in an SSZ-related basin. This oceanic basin could have been a part of the proto-Philippine Sea Plate. Cretaceous ophiolite and ophiolitic rocks underlie most of the islands in Central Philippines. The morphology and structure of these complexes resemble oceanic crust formed along intermediate- to fast-spreading ridges. Moreover, geochemical data from these basement complexes indicate that they could have been derived from SSZ-related basins. Age constraints do not support a Philippine Sea Plate origin for these ophiolites. Alternatively, the aforementioned similarities strongly suggest that the complexes represent exhumed fragments derived from a single SSZ-related basin dated to Cretaceous, which could have been the proto-Philippine Sea Plate.

Geochemistry of Clinopyroxene in Peridotites from the Nukabira Complex, northern Japan: Residues of Multi-Stage Melting

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Trace-element compositions of clinopyroxene in peridotite are quite useful to estimate partial melting degree and to understanding partial melting processes of an upper mantle material. We report the clinopyroxene geochemistries in peridotites from the Nukabira complex, and discuss multi-melting events of their formation process. The Nukabira complex in the Kamuikotan zone, Hokkaido, Japan, is mainly composed of mantle-derived peridotites with wide compositional variations. Lherzolite (e.g., C# of spinel= 0.18-0.34) and depleted harzburgite (e.g., Cr# = 0.4-0.7) are predominant lithologies, and dunite (e.g., Cr# = 0.35-0.85) is often observed within them. The clinopyroxene geochemical compositions of the peridotites were determined by using LA-ICP-MS. Chondrite-normalized rare earth element (REE) patterns of clinopyroxene in the lherzolites are characterized by strong depletion of light-REE (LREE) and middle-REE (MREE) relative to high heavy-REE (HREE) (e.g., (Nd/Yb)_N = chondrite normalized value < 0.004, Yb_N = 2.7-6.1). One lherzolite sample, however, has exceptionally high LREE/HREE ratio of clinopyroxene (e.g., (Ce/Yb)_N = 0.02-0.06, Yb_N = 5.3). The clinopyroxene REE patterns in the depleted harzburgites are "spoon-shaped" being high in MREE and LREE and low in HREE abundances (e.g., (Nd/Yb)_N < 0.09, Yb_N = 1.0-1.7). The dunites tend to be similar in clinopyroxene compositions to surrounding peridotites. The geochemical variations of the lherzolite can be ascribed not only to the difference of melting degree but also to conditions on melting, such as polybaric melting (melting in garnet peridotite stability field prior to in spinel peridotite stability field). To reproduce the clinopyroxene REE patterns, the lherzolite needed 0-15% melting in the garnet-stability field, based on the modeling of perfect fractional melting of MORB source mantle. The harzburgite may be residue of further melting of the lherzolite. The clinopyroxene geochemistry, however, indicates that the harzburgite was produced by a melting process different from the lherzolite forming one variations. The melting assisted by LREE-rich hydrous fluid is more preferable to explain the harzburgite features and origin. The differences in melting process were due to transition of tectonic setting from MOR to supra-subduction zone for the Nukabira peridotite. The lherzolites probably correspond to residual material survived the melting at the supra-subduction zone and indicating an older environment.

Geochemical and petrological features of fine-grained peridotite xenoliths from Avacha volcano, the southern Kamchatka

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Peridotite xenoliths have been reported from many localities, although strongly deformed ones, for example, mylonites, are rare. Recently, fine-grained peridotite xenoliths are reported from some arc settings, including Avacha volcano, which located at the southern Kamchatka arc. Among the Avacha peridotite, the fine-grained peridotite accounts for only about 15 % of all. Color of the fine-grained peridotite is paler than the coarse-grained one, and olivine grains are quite fine (down to < 50 μm). Most of primary spinel grains have been stretched and elongated to form aggregates of very fine grains. Modal proportions of minerals are not recognized because of their fine grain size, but we guess that almost of all are spinel harzburgite to dunite. We found composite xenoliths of fine-grained and coarse-grained peridotites with sharp contacts across which the change of grain size is drastic from the coarse-grained to fine-grained parts. Olivine in the fine-grained part contains abundant minute fluid and glass inclusions, and sometimes sulfide grains.

Avacha peridotite xenoliths suffered metasomatic enrichment of SiO₂ and contain secondary orthopyroxene replacing olivine. The secondary orthopyroxene, especially forming radial aggregate, is frequently observed sometimes with hornblende and clinopyroxene. Some fine-grained peridotites have higher Fo content of olivine relative to coarse-grained ones (92.7 and 91.7, respectively), although Cr# (= Cr/(Cr+Al) atomic ratio) of spinel is almost the same. There is no obvious difference in REE concentrations of whole-rock peridotite between the coarse-grained and fine-grained peridotites. However, to be interesting, the composite xenoliths of coarse-grained and fine-grained peridotite demonstrate LREE-enriched patterns, which are peculiar to the composite xenoliths. Influx of H₂O-rich fluid possibly played a role in the genesis of the fine-grained peridotite, which may represent a kind of conduit for melt and/or fluid beneath the sub-arc mantle. The origin of the fine-grained peridotite may be complicated, and further works would be needed.

Trace-element mineral chemistry of peridotite xenoliths, Green Knobs

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We examined peridotite xenoliths from Green Knobs, New Mexico, USA, which are famous for containing various amounts of secondary hydrous minerals. We conducted in-situ trace-element analyses on all phases present in the xenoliths to discuss the geochemical interactions between the peridotite and involved fluids.

The mineral assemblages of the samples we examined are as follows:

N53GN Olivine + Opx + Cpx + spinel ± hornblende ± sulfide,

N106GN Olivine + Opx + Cpx + spinel + chlorite + pyrope ± hornblende ± sulfide ± ilmenite,

N156GN Opx + Cpx + hornblende ± spinel ± sulfide and

N23GN Olivine + Opx + Cpx + chlorite + Na-tremolite + Ti-clinohumite ± sulfide.

The degree of hydration increases from N53GN (almost anhydrous) to N23GN. In N53GN almost all grains of Cpx and Opx are associated with spinel, and some olivine grains have exsolution lamellae. N106GN contains garnet between Cpx and spinel, and hornblende (pale green in thin section) around the grain boundary of Cpx. N156GN has hornblende veinlets cutting other anhydrous silicate minerals. N23GN is characterized by Na-tremolite and Ti-clinohumite, which are around chlorite, and Cpx forms symplectite with other minerals (e.g., hornblende and opaque). Cleavable olivines were recognized in N23GN. We used electron microprobe for major-element analysis of minerals and an excimer laser (193nm; ArF) coupled to a quadrupole inductively coupled plasma mass spectrometry (LA-ICP-MS) for *in-situ* measurement of trace elements in minerals at Kanazawa University. The Opx grains are MREE-depleted and HREE-enriched. In N23GN, Opx is very poor in Al₂O₃ (1wt%) and in REEs (< detection limits). Cpx grains in N53GN are LREE-depleted and HREE-enriched. With an increase of the amount of hydrous minerals, Cpx tends to be enriched in LREE, Sr and Ba and depleted in HREE. Sr and Ba were detected at the lamellae in olivine of N53GN. Sr and Ba were similarly detected in the cleavage part of cleavable olivine in N23GN. LREE contents of amphibole are higher than those of Cpx. REEs were not detected in Ti-clinohumite and chlorite. Al-rich Opx associated with spinel in N53GN are MREE-depleted and HREE-enriched, being similar in REE pattern to Pyrope in N106GN. Same of Opx are breakdown products of garnet. LREE, Sr and Ba contents of Cpx increase with an increase of the degree of hydration, possibly indicating the rocks have been enriched with these elements with a progress of hydration.

Petrological Feature of Mantle Xenoliths From Bir Ali Area, Yemen: An Implication For Mantle Processes Related to The Rifted Continental Margin.

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Ultramafic and mafic xenoliths were collected from Pliocene-Quaternary basalts in the Shabwa Governorate (Bir Ali area) southern Yemen. More than 100 mantle xenoliths were selected for this study in order to examine the upper mantle processes related to continental rifting. These samples show a great variety of rock types (anhydrous and hydrous lherzolite, spinel harzburgite, pyroxenites, dunite, cpx-rich lherzolite, wehrlite, granulite, and banded plagioclase peridotite). The spinel peridotites are various in texture from protogranular to mosaic equigranular. Fo content of olivine and Cr# of spinel in the studied spinel peridotites vary continuously from 91 to 87 and 0.36 to 0.06, respectively. Dunite and wehrlite to cpx-rich lherzolite display the lowest Fo contents. The cpx-rich lherzolite is characteristic of the Bir Ali peridotite xenolith suite. It contains lower Fo content of olivine than ordinary lherzolite at given Cr#s of spinel. Its clinopyroxene is higher in TiO₂ content than ordinary lherzolite. In addition, the cpx-rich lherzolite and wehrlite display evidence of late crystallization of clinopyroxene. This strongly indicates metasomatic addition of clinopyroxene to ordinary lherzolite for genesis of cpx-rich lherzolite. Furthermore, the cpx-rich lherzolite to wehrlite have lower temperature than ordinary lherzolite. These data suggest that the upper most part of lithospheric mantle beneath Yemen is composed of anomalous peridotite. This peridotite was possibly produced by magmatic underplating at the incipient stage of continental rifting.

Carbonaceous materials in wedge mantle: A case study of the Horoman Peridotite Complex, Hokkaido, NE Japan

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Voluminous carbonaceous materials (CM) derived from subducted oceanic slab have been supplied to the wedge mantle, but the behavior of this materials is not clear. We here report the types and occurrences of these CMs and stable carbon isotopes of bulk rocks and minerals from plagioclase lherzolite (Pl-Lz), spinel lherzolite (Sp-Lz) and harzburgite (Hz) of the lower zone of the Horoman Peridotite Complex. We then discuss the origin of the peridotite mass, based on constraints imposed by the carbonaceous materials.

(1) **EPMA compositional mapping** (a) Some CM inclusions in olivine from Sp-Lz contain Cl, S, B, and N. However, CM along grain boundaries does not contain B and N. (b) Opx from Sp-Lz contains CM inclusions containing Cl and S, and olivine from Hz has CM inclusions with Cl, N and S.

(2) **Pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) analyses at 600°C** Aromatic chlorine compounds were detected in Pl-Lz, Sp-Lz and Hz bulk rocks, but not within the minerals. This suggests that the aromatic chlorine compounds occur along crystal boundaries. Aliphatic hydrocarbons such as n-C₈₋₁₃ alkanes and alkenes were detected in Pl-Lz bulk rock, Cpx, Opx and Ol, and also in Opx from Hz, but were not detected in the rock Sp-Lz or its constituent minerals.

(3) **$\delta^{13}\text{C}$ values** : [non-carbonate carbon (TOC) in pl-Lz]: bulk rock: -24.4‰, Ol: -27.7‰, Cpx: -17.7‰, Opx: -26.7‰, [carbonate carbon (CC) in bulk Pl-Lz]: -14.6‰, [TOC in Sp-Lz]: bulk rock: -23.4‰, Ol: -23.7‰, Cpx: -26.0‰, Opx: -27.7‰, [CC in bulk Sp-Lz]: -6.7‰, [TOC in Hz]: bulk rock: -21.2‰, Ol: -25.7‰, Opx: -26.7‰, [CC in bulk Hz]: -5.9‰.

Based on combined Py-GC/MS analysis and $\delta^{13}\text{C}$ values, the CMs in the minerals were originally derived from sediments of the subducted slab. This suggests that porphyroclasts of Ol, Cpx and Opx formed under mantle wedge conditions, although the source material might be MORB. $\delta^{13}\text{C}$ values suggest that in the Horoman Peridotite Complex, carbon from subducted slab sediments was mixed with original mantle carbon during the mantle wedge stage. Consequently, the wedge mantle may be modified by fluids derived from the subducted slab.

Sulfide minerals in the Horoman and Nikanbetsu complexes, Hokkaido, Japan

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The study of sulfide minerals from mantle-derived rocks is significant for better understanding of upper mantle processes. During the last 40 years, sulfides in mantle peridotites have been well-studied using various techniques such as Re-Os isotope and investigation of closely-related platinum group elements. These sulfides generally record lower temperatures than those in associated refractory silicate minerals. If the sulfide assemblages and their chemical compositions, aided by available phase diagram(s), are determined, the crystallization P-T conditions of the host mantle rock can be deduced. In Japan, little attention has been paid to these minerals in peridotites. This study provides a preliminary mineralogical and chemical data of some identified sulfides from the Horoman and Nikanbetsu peridotite complexes of the Hidaka metamorphic belt, Hokkaido, northern Japan.

The Horoman peridotite complex mainly consists of lherzolite, harzburgite, and dunite. Identified sulfide minerals in lherzolite and harzburgite are pentlandite (pn), heazlewoodite (hz) and native copper (Cu), which occur in the Cu-Fe-Ni-S system. The minerals are present as single grains. The pn-hz and hz-Cu associations are predominant. The Fe/Ni atomic ratio of pentlandite is about 1.0. Heazlewoodite contains up to 1.5 atom.% Fe. The Nikanbetsu complex is comprised of mostly plagioclase lherzolite that hosts pn, Cu, troilite (tro), and chalcopyrite (cp). Some unidentified minerals of Fe-Ni-Cu-S system are also present. As similar to Horoman complex, the minerals also occur as single grains. The typical mineral assemblages are pn-tro, pn-Cu and pn-cp. The Fe/Ni atomic ratio of pentlandite is between 1.6 and 2.0.

In both complexes, all the minerals occur in interstitial spaces of silicate minerals, possibly pyroxene, olivine, etc. Sulfide bleb, rounded sulfide(s) initially trapped as melt inclusion in silicate phenocrysts, was not found. In the investigated polished sections, the grain size of the interstitial minerals is 20-400 µm; the amount of both sulfides and Cu is <0.1 volume %. The identified minerals and their textural features and mineral assemblages suggest that they precipitated (soon) after the crystallization of silicate phases. According to the phase relations of Fe-Ni-S system, the textural relations of the co-precipitated pn and hz and their chemical compositions indicate that the crystallization temperature of the pn-hz assemblage from the Horoman complex was at least above 500°C.

Effect of H₂O and fO₂ on the phase equilibria in a primitive basaltic system

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We present crystallization experiments on a basaltic composition from the Southwest Indian Ridge (SWIR) with the aim of determining the effect of water and oxygen fugacity on the phase equilibria. Both parameters affect significantly the stabilities and compositions of the phases in the system. The comparison of the experimental results with natural oceanic gabbros from Leg 176 (SWIR) will help to constrain magmatic processes occurring in the oceanic crust.

To investigate the effect of water, we performed crystallization experiments at pressures of 100, 200 and 500 MPa in a temperature range of 940 to 1220°C using four different water contents. Depending on the water activity, the oxygen fugacity varied between 1 and 4 log units above the quartz-fayalite-magnetite (QFM) buffer.

The addition of water to the dry system shifts the solidus to lower temperatures by more than 250°C and increases the amount of melt drastically. For instance, at 1100°C and 200 MPa, the melt fraction increases from 12.5% at a water content of 1.6 wt% to 96.3% at a water content of 5 wt% in the melt. The compositions of the experimental phases show also a strong effect of water. Plagioclase is shifted to higher anorthite contents; olivine and clinopyroxene show generally higher MgO/FeO ratios with added water, but this could also be related to the increasing oxygen fugacity with water. Moreover, water affects the slope of the stability curves of individual minerals and with it the crystallization sequence. At pressures >100 MPa, plagioclase crystallizes before clinopyroxene at low water contents (<3 wt%), but after clinopyroxene at H₂O in the melt >3 wt%. Finally, water affects the partitioning of certain elements between minerals and melts, e.g., the Ca partitioning between olivine and melt.

To determine the effect of oxygen fugacity on the phase relations two sets of experiments at 200 MPa under reducing conditions were conducted, the first set at QFM+2 (QFM+2 to -1, depending on the aH₂O), the second set at QFM (QFM+0 to -3, depending on the aH₂O). The oxygen fugacity controls the Fe²⁺/Fe³⁺ ratio and thus influences the composition and stability of all iron bearing phases and with it affects the crystallization sequence.

The experimental results combined with the analyses of minerals of natural rocks from SWIR will be used to constrain the prevailing conditions occurring during differentiation (T, P, aH₂O and fO₂).

Carbonate Bodies in the Ophiolitic Ultramafic Rocks, Where They Came From?S. Alaabed¹

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Ultramafic rocks of ophiolites are dominated by tectonite peridotites namely harzburgites and lherzolites with dunite lenses and lesser pyroxenite dikes. Granitic dikes may also prevail in some places especially close to the transition zone. Carbonate occurrences within the ultramafic rocks are not coherent with peridotite diversity. As in the northern Semail ophiolite, however, they are distributed more or less all over the mantle sequence, and more pronounced at the base of the sequence. They primarily occur as veins and fillings along fractures and fault zones. Magnesite and dolomite are found to be the most common minerals in the carbonate veins of northern Semail ophiolite. High to low temperature alteration, rock compression and squeezing related solution, and infiltrating meteoric water are hypotheses that have been suggested for the origin of the carbonate occurrences in the mantle sequence. Field and petrography observations have shown remarks and proofs of water invasion and hydration/weathering of the ultramafic country rocks. Combination these with other lines of evidence, including chemical analysis, have suggested that these carbonate veins and fillings might have mainly been originated by seawater weathering during emplacement process of the Semail ophiolite.

O21-01

Heavy trace elements in presolar silicon carbide grains: Isotopic and elemental signatures

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Noble gases (Kr, Xe) that show the signature of the s-process of nucleosynthesis contained in meteoritic SiC grains were instrumental in identifying these grains as of presolar origin. Starting with the case of Ba, the signature of the s-process has been identified in a variety of other (non-gaseous) elements. Detailed analyses of single presolar grains have turned out to be possible for the more abundant of these (Sr, Zr, Mo, Ru, Ba). These allow detailed comparison with expectations for the main component of s-process nucleosynthesis produced in asymptotic giant branch (AGB) stars. We have obtained new data for Ba in single grains by the NanoSIMS, as well as data by ICP-MS for the whole mass region from Sr to Hf in "bulk samples" (aggregates of many grains). While molecular and isotopic interferences are a problem in the latter multi-element technique, the signature of the s-process has been clearly identified for many elements, especially in the region of the Rare Earth Elements. The more refractory REE occur in relative abundances consistent with expected production ratios. Relative to these the more volatile REE Yb, S, and Eu are deficient providing a record of condensation processes around the parent stars. We are currently exploring various types of photo-electron spectroscopy such as Nano-ESCA and XANES as methods for non-destructively identifying grains with high trace element content for further single grain isotopic analysis by mass spectrometric (destructive) means.

O21-02

Metamorphic conditions of unequilibrated chondrites

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Anhydrous unequilibrated chondrites are classified into petrologic types 3.0-3.9. Chondrites of types 3.0 and 3.1 are further divided into 3.00 to 3.15 from the Cr distribution in olivine [1]. Recently, Kimura et al. [2] found that the characteristic features of Fe-Ni metal in ordinary and CO chondrites are highly sensitive to thermal metamorphism, and are consistent with the classification system proposed by [2]. Here we discuss the metamorphic conditions of unequilibrated chondrites, estimated from Fe-Ni metal and spinel group minerals.

We studied Fe-Ni metal in unequilibrated H, L, LL, CO and CV chondrites, and spinel group minerals in LL chondrites. Fe-Ni metal in chondrules from Semarkona (LL3.00) shows a fine-grained plessitic intergrowth, whereas those in the other chondrites commonly show a coarser intergrowth of kamacite and high Ni metal. Isolated metal grains in type 3.00-3.15 chondrites are enriched both in Ni and Co, although in the other chondrites, kamacite always has a higher Co content than Ni-rich metal, regardless of its occurrence. The abundance and grain size of spinel group minerals increase with petrologic type. The compositional variation of spinel group minerals systematically becomes narrower from types 3.0-3.3 to 3.9.

The composition and plessitic intergrowth of Semarkona metal are evidently distinct from those of higher petrologic type chondrites. Alexander et al. [4] suggested that Semarkona did not experience temperatures >250°C. Metal in the other chondrites was modified by metamorphism. The intergrowth of kamacite and Ni-rich metal in chondrules of type 3.05-3.2 chondrites gives temperatures of 350-500°C, by the method of [3]. On the other hand, LL chondrites of types 3.5-3.9 show higher metamorphic temperatures, 440-650 °C, from spinel group minerals. Unequilibrated chondrites experienced thermal metamorphism, to various degrees, reflecting petrologic type. A number of petrologic features (Cr in olivine [2], spinel composition and abundance, and metal composition and texture) form a consistent set of sensitive gages for low levels of thermal metamorphism in unequilibrated chondrites.

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O21-03

Silicate darkening in CK chondrites: A possible indicator of shock on a heated parent body

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CK chondrites differ from other types of carbonaceous chondrites in that most of them have been thermally metamorphosed to yield petrologic type 4-6. A striking feature of the CK chondrites is that their matrices show a dark, dusty appearance (silicate darkening), when their thin sections are observed in transmitted light. The true cause for the silicate darkening has long been unknown. A recent study of the Kobe CK4 chondrite (Tomeoka et al., 2001) revealed that unusual "vesicular olivine" is the principal cause of the silicate darkening. We undertook a detailed survey of three other CK4-5 chondrites, Karoonda (CK4), ALH85002 (CK4) and Y693 (CK5) in order to examine whether vesicular olivine is also the cause for their silicate darkening and, if so, to determine how vesicular olivine was formed.

Karoonda, ALH85002 and Y693 show high degrees of silicate darkening. Backscattered electron images of highly dark regions in the matrices of the three chondrites show that vesicular olivine fills interstices of nonvesicular olivine crystals, exhibiting a complex network of veinlets (5-20 µm wide). The vesicular olivines contain numerous small vesicles (<0.1-3 µm in diameter) and spherical grains (<0.1-5 µm) of magnetite and pentlandite as well as anhedral grains of plagioclase, low-Ca and high Ca pyroxenes. There is a tendency for a region having a higher volume proportion of vesicular olivine to exhibit a darker appearance in transmitted light. From these results, we conclude that vesicular olivine is the principal cause of the silicate darkening in the CK chondrites.

The internal texture of the vesicular olivine closely resembles those of local melts produced in the matrices of shocked carbonaceous chondrites (Tomeoka et al., 1999; Kiriya et al., 2001). However, the CK chondrites exhibit light shock effects (mainly moderate undulatory extinction in olivine) that are consistent with shock stage S2, which is too low to account for shock-induced melting. We suggest that the vesicular olivine was produced by shock at the state where the meteorite was heated to a high temperature. The results of recent shock experiments on Allende preheated to 600-800°C (Kiriya et al., 2000) indicated that vesicular melts are indeed produced in the matrix at peak pressures of 20-25 GPa. The results suggest that the vesicular olivine was produced in a region (or regions) of the parent body where it was heated to a temperature ≥600°C and shocked at a pressure ≤25 GPa.

O21-04

Hydrothermal alteration experiments of enstatite under various pH, temperature and run duration conditions: Implications for aqueous alteration of carbonaceous chondrites

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Most chondrites of petrologic type 1-3 contain various amounts of phyllosilicates that were probably formed by aqueous alteration on their parent bodies. Enstatite is one of the major constituent minerals in the chondrites and has been more preferentially replaced by phyllosilicates than other major primary silicates. Phyllosilicate mineralogy differs among different types of chondrite. For example, serpentine occurs in CM chondrites, saponite occurs in CV chondrites, and both serpentine and saponite occur in CI chondrites. The differences may have resulted from different aqueous alteration conditions on their parent bodies. In order to explore this possibility, we conducted hydrothermal alteration experiments of enstatite with aqueous solutions of various pHs (pH 0-14) at 100-300 °C for 24-336 hrs, using a hydrothermal apparatus. Recovered samples were studied using XRD, SEM-EDS and TEM-EDS. Our goals were to compare alteration products with those in the chondrites and to provide constraints on aqueous alteration conditions of the chondrite parent bodies.

The results of our experiments revealed that alteration products of enstatite differ greatly with varying pH of the aqueous solutions. No significant alteration reactions occurred under acidic conditions (pH 0, 6). At 300 °C for ≥168 hrs, serpentine formed under neutral to alkaline conditions (pH 7, 12), and serpentine and saponite formed under highly alkaline conditions (pH 13, 14). In the latter case, serpentine and saponite formed unit cell-scale coherent intergrowths, which resemble those in CI chondrites. Alteration products also differ with varying temperature and run duration. Under highly alkaline conditions (pH 13, 14), saponite has a tendency to form at relatively higher temperature and for longer run duration than serpentine.

These results indicate that alteration reaction of enstatite is strongly dependent on aqueous alteration conditions, especially pH, and phyllosilicate mineralogy produced by alteration of enstatite in chondrites may serve as a sensitive indicator of pH conditions on their parent bodies. We suggest that CM chondrites, in which enstatite has been replaced by serpentine, have experienced aqueous alteration under neutral to alkaline conditions, and CV chondrites, in which enstatite has been replaced by saponite, have experienced aqueous alteration under more alkaline conditions than CM chondrites. We also suggest that CI chondrites, which contain coherent intergrowths of serpentine and saponite, have experienced aqueous alteration under alkaline conditions.

Mineralogical and noble-gas isotopic signatures of thermally metamorphosed hydrous carbonaceous chondrites

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Many hydrous carbonaceous chondrites have been heated to higher temperature after extensive aqueous alteration [e.g., 1], which caused evaporation loss of highly volatile elements and dehydration of hydrous minerals. A combined study on mineralogy and noble gas isotopes was carried out on many CM chondrites, in order to establish classification scheme for the degree of heating of CM chondrites based on matrix mineralogy, to see heating effects on presolar grain abundances based on primordial noble gas concentration in two thermally metamorphosed CM chondrites, and to obtain some constraints on the timing of heating of CM chondrites based on concentrations of radiogenic noble gases.

Synchrotron X-ray diffraction analysis indicates that CM matrix can be classified into four heating stages based on the degree of thermal decomposition of hydrous minerals [2]: Stage I is unheated or very weakly heated samples (< 300°C) that consists of hydrous phases such as serpentine and tochilinite, stage II is weakly heated samples (< 500°C) that consist mostly of amorphous silicates formed from decomposed phyllosilicates, stage III is moderately heated samples (< 700°C) that consist of poorly crystallized olivine, and stage IV is strongly heated samples (> 700°C) that consist of crystalline olivine and low-Ca pyroxene.

Matrices of CM chondrites contain large amounts of trapped noble gases. The abundance of noble gases is expected to reflect the degree of heating. To obtain accurate changes of abundances of presolar grains during heating of CM chondrite parent bodies, chemical treatment was performed on a 0.7g chip of a stage-II sample Y-86695 and a 1.1g chip of a stage IV sample Y-86720, using a high-yield procedure developed by Huss and Lewis [3]. The results of noble gas analysis indicate that presolar SiC is much more stable during heating than presolar diamonds. Next question is when the heating occurred. In addition to the depletion of trapped noble gases, radiogenic noble gases, not only short-half-life decay products such as ¹³⁶Xe but also long-half-life decay products such as ⁴⁰Ar, are apparently depleted in heated samples relative to Murray. The degree of depletion is in accordance with increasing heating stage. This suggests that the heating events, which caused the loss of ⁴⁰Ar, occurred relatively later in the meteorite history.

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O21-06

Heating effects on the matrix of experimentally shocked Murchison CM chondrite: Comparison to micrometeorites

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Micrometeorites have been significantly altered or melted by heating, which has been mainly ascribed to aerodynamic drag during atmospheric entry. However, if a major fraction of micrometeorites are produced by impacts on porous asteroids, they may have experienced shock heating before contact with the earth's atmosphere.

Our TEM study of the matrix of Murchison CM chondrite experimentally shocked at pressures 10-49 GPa shows that its mineralogy and texture change dramatically, mainly due to shock heating, with the progressive shock pressures. Tochilinite is completely decomposed to an amorphous material at 10 GPa. Fe-Mg serpentine is partially decomposed and decreases in amount with increasing pressure from 10 to 30 GPa and is completely decomposed at 36 GPa. At 49 GPa, the matrix is extensively melted and consists mostly of aggregates of equigranular grains of Fe-rich olivine and less abundant low-Ca pyroxene embedded in Si-rich glass.

Previous TEM studies show that unmelted, fine-grained micrometeorites can be classified into three types, olivine-rich, pyroxene-rich and phyllosilicate-rich (e.g., Nakamura et al. 2001). Phyllosilicate-rich micrometeorites can be subdivided into two types, serpentine-rich and smectite-rich. Serpentine-rich micrometeorites contain Fe-rich serpentine that is similar to cronstedtite in CM chondrites. However, tochilinite coexisting with serpentine in CM chondrites has not been found in any of the micrometeorites. Our study shows that tochilinite is completely decomposed by post-shock heating even at 10 GPa. This suggests that tochilinite preferentially breaks down at the time of dust production by impacts on CM parent bodies. Thus, the serpentine-rich micrometeorites may be CM chondrite fragments that were shocked at pressures lower than 36 GPa. In olivine-rich micrometeorites, olivine typically occurs as aggregates of equigranular, rounded to subhedral grains (e.g., Greshake et al. 1998; Nakamura et al. 2001). A Si-rich amorphous material, which is commonly intermixed with fine-grained magnetite and Fe-sulfide, fills interspaces between the olivine grains. These characteristics are very similar to those of the Murchison matrix shocked at 49 GPa. We suggest that micrometeorites derived from porous asteroids are likely to go through both shock and atmospheric-entry heating processes.

O21-07

Infrared absorption spectroscopy of chondrules from Allende (CV)

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Introduction: Astronomical infrared spectroscopy gives us information about the composition of dust in circumstellar disks around young stellar objects (YSO), which are similar to our own young Solar System.

An important step in the evolution of our Solar System was the formation of chondrules, spherical objects crystallized from rapidly cooled silicate melt droplets.

To find out if there are signs for chondrule-like materials in astronomical infrared spectra, we measured infrared spectra of the bulk composition of 11 chondrules from the Allende CV chondrite for comparison purposes.

Techniques: Chondrules separated from a gently crushed Allende sample were characterized, and representative pieces ground with an agate mortar to a sub-micron powder. About 1 mg of powdered material was mixed with KBr-powder and pressed to pellets using an evacuated pellet press at 10 tons/cm².

The pellets were dried for three days at 100 °C to avoid bands of absorbed water. Infrared transmission/absorption spectra were obtained using a Perkin Elmer SpectrumOne workbench (Natural History Museum London), at a spectral resolution of 4 cm⁻¹.

Astronomical spectra were provided by Roy van Boekel (Amsterdam) and obtained using the ESO telescope. Here, the data is discussed for the 8 – 13 µm range, the atmospheric window for ground-based astronomical observations.

Results and Discussion: Most of the chondrules were Porphyritic Olivine Chondrules (PO). With the exception of a Porphyritic Pyroxene chondrule (PP), all spectra show a characteristic strong olivine band at ~11.3 µm. Also in all spectra a usually rounded feature occurs between 10 and 10.5 µm. This is probably owing to the interference of a strong olivine feature and the band of amorphous mesostasis. A weaker feature at ~9.4 µm reflects the pyroxene contents. The relative intensity of the two strongest bands varies strongly, with in 8 spectra the 11.3 µm feature being the strongest band, and the 10 µm feature in the other 3 cases.

Preliminary comparison with spectra of YSO shows features of spectra of two Porphyritic Olivine and Pyroxene chondrules (POP) with significant pyroxene features at 9.4 µm, and strong 10 µm and 11.3 µm features similar to the spectra of two Herbig AE stars, HD 142527 (~1 My old) and HD 104237 (~2 My).

This is, however, a simplified picture of the situation, the astronomical spectra probably represent a mixture of several components. Future work will focus on the calculation of complex mixtures with additional types of components (e.g. matrix or CAI).

O21-08

Unusual matrix mineralogy and texture in the Ningqiang carbonaceous chondrite: Evidence for parent-body processes

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Ningqiang is an anomalous CV3 chondrite containing low abundances of Ca-Al-rich inclusions (CAIs) (~1.0 vol%) and refractory lithophile elements (Rubin, 1988). Our previous study revealed that most CAIs in Ningqiang contain abundant nepheline and show evidence of extensive alteration. In order to find a clue to the anomalous characteristics and possibly unique alteration history of Ningqiang, we undertook a detailed mineralogical and petrographic study of its matrix, using a scanning electron microscope and an electron probe microanalyzer.

The matrix of Ningqiang consists mainly of fine grains of Fe-rich olivine, having an overall texture similar to the matrices of most CV3 chondrites. However, our observations reveal that the matrix has unusual characteristics that have not been reported from any CV3 chondrites. The matrix of Ningqiang can be divided into two regions: one consists mainly of very fine, equidimensional grains (<1 µm in size) of relatively Fe-poor olivine (Fa49.9±2.1), and the other consists mainly of coarse, irregularly shaped grains (2-20 µm) of relatively Fe-rich olivine (Fa52.9±1.8). These two regions (Fe-poor and Fe-rich) are intermixed on scales of 10-100 µm. In the Fe-poor regions, nepheline occurs pervasively as fine grains (<0.1 to 5 µm in size), whereas in the Fe-rich regions, nepheline is rare but Fe sulfide and magnetite occur much more abundantly as fine grains (<0.1 to 10 µm). The bulk composition of the matrix, obtained by using a defocused (10 µm-diameter) beam, is similar to mean CV3 matrix for most elements. However, Na and Al are significantly higher (3.6 and 1.8 by factor, respectively). Plots of the analyses of the Fe-poor regions in terms of Na vs. Al show an apparent correlation of the two elements with a slope of approximately Na/Al=1 (in atomic proportion), which suggests that Na and Al can be mainly explained by nepheline (Na₂Al₂Si₂O₈).

The results suggest that the matrix of Ningqiang has been formed by mixing of materials derived from two different reservoirs in the meteorite parent body. In the Fe-poor reservoir, a reaction to form nepheline (Na-metasomatism) probably occurred, whereas in the Fe-rich reservoir, no such reaction occurred but Fe-enrichment of olivines (Fe-metasomatism) occurred presumably due to thermal metamorphism. These imply that the Ningqiang parent body was heterogeneous in distribution of both materials and alteration conditions. The mixing of the materials from the two reservoirs may be analogous to some sedimentary processes that occur in terrestrial environments.

Petrography and mineralogy of a unique spherical CAI in the Murchison(CM2) meteorite

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Calcium-aluminum-rich inclusions(CAIs) from chondritic meteorites are widely considered to represent the first materials that formed in the solar nebula.

I discovered for the first time a unique spherical CAI(Ca-Al-rich Inclusion), which consist of spinel, diopside, calcite, and PCP in the Murchison (CM2) meteorite. Its size is approximately 1.5mm and this is large when comparing with the size of chondrules in the all chondrites. Its shape is like chondrules, but fusion organization which is characteristic of chondrules is denied by absence of the glass and mesostasis. The unique spherical CAI never melts after the formation. Bulk composition is similar to Ca-Al-rich chondrules discovered in ordinary chondrites, or CAI of CV carbonaceous chondrite.

Comparison with normal CAI, its may be generated from different formation processes. The inside of the unique spherical CAI, spinel, diopside, calcite and PCP coexist each other. Replacement is not seen. Therefore, the unique CAI is thought to be mixture of high temperature condensation minerals and low temperature materials as well as PCP in the early solar nebula.

Composition analysis of the Wild-2 samples collected by Stardust

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On Jan. 2, 2004 NASA's Stardust spacecraft flew through the coma of comet Wild-2, capturing dust in low-density silica aerogel that was delivered to Earth on Jan. 15, 2006. Wild-2 is a short-period comet, believed to have originated in the Kuiper Belt. Thus, analysis of Wild-2 dust provides the first opportunity to probe conditions in the Kuiper Belt during dust formation and compare them with conditions in the asteroid belt, as inferred from primitive meteorites. The Stardust Composition Preliminary Examination Team is employing a variety of instruments in laboratories on 4 continents to examine these samples. X-Ray Microprobes (XRM), with analysis spots ranging from 10 µm to 200 nm, have been employed to perform chemical analyses of terminal particles and map element distribution in 2- and 3-dimensions along tracks in slices and keystones. The inherent limitation on *in-situ* analysis is the escape of fluorescence x-rays, but elements as light as Mg can be detected at the maximum depth reached by 10 µm Wild-2 grains. Some XRM can also perform bonding state characterization by X-Ray Absorption Near-Edge Structure (XANES) spectroscopy and/or x-ray diffraction, identifying mineral hosts of the elements. A proton probe has been used to map element distributions by Proton Induced X-ray Emission (PIXE), Rutherford backscatter spectroscopy and forward scattering ion spectroscopy (which can extend the sensitivity down to H). After the XRM or PIXE analysis particles will be extracted and ultramicrotome slices will be prepared for XRM and TEM analyses. SEM-EDX and TOF-SIMS will be used to characterize extracted particles. The C and N contents will be measured by EELS and Nuclear Microprobe. There are four specific objectives during the composition Preliminary Examination, to determine:

1. if all terminal particles are similar in composition or if they group into distinct compositional types that can be recognized (e.g., by optical characteristics),
2. if the composition of the terminal particle is representative of the particle as it entered the aerogel or if fragments or volatiles were deposited along the track,
3. the mean chemical composition of the Wild-2 dust, comparing this to other types of extraterrestrial materials, and
4. the element associations with mineralogy – testing nebula models.

The preliminary examination will be completed by July 15, 2006, and the results will be described.

Mineralogy of the comet Wild2 nucleus samples returned by the Stardust mission

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The Stardust spacecraft sampled the coma of comet P/Wild 2 in January 2004. The sample return capsule of the Stardust spacecraft was subsequently recovered in northern Utah on January 15, 2006, and was delivered to the new Stardust Curation Laboratory at the Johnson Space Center two days later. Within the first week we began the harvesting of aerogel cells, and the comet nucleus samples they contain for detailed analysis. This talk will present the results from the mineralogical and petrological analyses that will have been performed by meeting time. Numerous electron beam analyses (SEM, STEM, EELS, EBSD, microprobe), XRD, and spectroscopic analyses have been made from harvested grains, as well as microtomed slices and potted butts. The basic goals of the Mineralogy/Petrology subgroup of the Preliminary Examination Team are as follows. (1) Determine comet nucleus mineralogy and petrology. (2) Assess the variability of the samples. (3) Recognize the IDPs that should have been captured along with the cometary grains. (4) Discover how the samples were altered by the collection process. We can expect to be surprised.

Optical spectroscopy of Stardust samples

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The Stardust spacecraft collected dust samples of the Kuiper belt comet 81P Wild-2 in aerogel and returned them to Earth January 15, 2006. Preliminary examination (PE) of the collected dust includes teams focused on mineralogy, chemical composition, isotopic measurements, organic analysis, cratering and spectroscopic properties. The main PE science goals are to provide an initial characterization of the returned samples with an emphasis on the capture process and its effects on the samples, a comparison of Stardust samples to other meteoritic materials, and the abundance of presolar materials in the Stardust samples. The science objectives of the Spectroscopy team are to obtain spectroscopic data on Stardust particles through infrared (IR), UV/Vis and Raman measurements of particles in aerogel, extracted particles, keystones, and microtome thin sections. These data will be used to answer fundamental science questions about the nature of the samples, but will also serve as preliminary mineralogical data to guide follow-on measurements that will be performed in the other preliminary examination teams.

The IR characteristics of Stardust particles are measured to determine: 1) the nature of the indigenous 3.4 µm organic feature, is it detected and can it be differentiated/deconvolved from the contaminated aerogel? How does it compare to features observed in interplanetary dust particles (IDPs) and to astronomical measurements of comets and interstellar dust? 2) the shape and fine structure within the 10 µm silicate feature. Overlap with the strong Si-O stretching vibration from the aerogel complicates this analysis, but we hope to determine if the feature is dominated by amorphous silicates such as those observed in IDPs and comets and whether or not crystalline silicates (e.g. olivine, pyroxene, clays) are present, 3) the presence of secondary (alteration) phases. Deep Impact results suggest that IR observations of Stardust particles should be evaluated for the presence of hydrated materials (water bands at 3 and 6 µm) and carbonates (6.8 µm and other resonances) and 4) the detection of crystalline features in the far-IR (20-100 µm region where crystalline silicates and other minerals have strong bands that can be used both for phase analysis and phase chemistry. It has been demonstrated that these far-IR measurements can be obtained *in situ* on particles in aerogel keystones.

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The Hayabusa (MUSES-C) spacecraft, which was designed to acquire sample from the surface of an asteroid and return to Earth, was in close proximity to the near-Earth asteroid 25143 Itokawa (1998 SF36) in September through November 2005. During rendezvous with the asteroid, a telescopic imaging camera (AMICA), a near-infrared spectrometer (NIRS), a laser ranging instrument (LIDAR), and an X-ray fluorescence spectrometer (XRS) had observed the surface of Itokawa. We present a nature of Itokawa, and scientific results obtained from the observation by Hayabusa spacecraft.

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Enstatite chondrites (ECs) are one of the most reduced meteorite groups. ECs record complicated thermal history resulted from extensive shock heating in addition to the thermal metamorphism that is predominant in ordinary chondrites. Noble gas composition of ECs is also characteristic: in some ECs primordial gas is enriched in ³⁶Ar relative to ¹³²Xe, compared to another primordial noble gas (P1 gas) contained commonly in chondrites. The ³⁶Ar/¹³²Xe ratio in most chondrites is within the range of 30-70, while the ³⁶Ar/¹³²Xe ratio in ECs is up to 3000. The noble gas with high ³⁶Ar/¹³²Xe ratio in ECs is called "subsolar gas," with an implication of the link with the solar gas (³⁶Ar/¹³²Xe ~ 10⁴). However, the ²⁰Ne/¹³²Xe of subsolar gas is 10⁻⁴ times lower than that of solar wind and comparable to P1 gas, suggesting of elemental fractionation from solar-type gas.

In a comprehensive study, we have measured noble gases, for 15 EC with a stepped heating method and for 6 ECs with a laser microprobe extraction method. Based on elemental abundances, we assort ECs into two groups: "subsolar-containing" and "subsolar-free" ECs. In some subsolar-containing ECs, solar-like Xe isotope signature is observed. The elemental ratios and Xe isotopes released from subsolar-containing ECs are suggestive of the solar wind origin. The concentration of P1 gas in subsolar-free ECs correlates with their petrologic types, suggesting that P1 gas has been incorporated with parental materials of the ECs prior to metamorphism. In contrast, the subsolar gas abundance correlates neither with chemical subclass nor petrologic type. The release temperature of subsolar gas is around 1400-1600°C, higher than that of P1 gas (800-1200°C).

Laser microprobe analyses revealed that the subsolar gas is concentrated in some porphyritic pyroxene chondrules of subsolar-containing ECs, but not in any chondrule of subsolar-free ECs. One of the possible explanations is that chondrule precursor material trapped solar-type noble gases and lost some part of noble gases, preferentially light isotopes, during the chondrule formation. The subsolar gas is not common even in ECs, which suggests that gas-rich chondrules were distributed heterogeneously in the EC parent body formation region of the solar nebula. EC parent bodies might have formed from parental material different in noble gas compositions, and experienced impact shock heating and thermal metamorphism in different degrees.

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Introduction: Presolar silicates have been found in interplanetary dust particles and chondrites. The abundances of presolar silicates vary among clomical groups as well as petrologic types. The variation may correspond to the processes and in the early solar nebula and in parent body. Among the CO chondrites, the abundances of presolar silicates in Yamato-81025 (CO3.0) and ALHA77307 (CO3.0) are estimated to be 30 - 50 ppm. In this study we report presolar silicates survey in Kainsaz (CO3.1). Kainsaz is a petrologic type 3.1 CO chondrite and experienced thermal metamorphism in the chondrite parent body relative to the case of CO3.0 chondrites.

Experimental: Petrography and mineralogy were studied using FE-SEM (JEOL JSM-7000F) equipped with energy dispersive X-ray spectrometer (Oxford INCA). Isotope imaging was conducted by the isotope microscope (Cameca ims-1270 + SCAPS (2-D ion detector)) in HokuDai to obtain isotope images of ¹⁶O, ¹⁷O, ¹⁸O, ²⁷Al, and ²⁸Si. The selection criterion for isotopically anomalous presolar grain candidates is that the isotopic composition is 2σ away from 3σ ellipse of the distribution of the isotopically normal matrix materials. The matrix-normalized abundance is calculated assuming the grains are 0.3 μm in diameter that is an average size of presolar silicates reported to date.

Results and Discussion: Total area of ~27,000 μm² was analyzed in matrix of Kainsaz and one presolar candidate grain was found from oxygen isotopic ratio images. The grain was estimated to be silicate mineral by electron microprobe but could not be completely identified because of the small size of the grain. The matrix-normalized abundance of presolar silicate in Kainsaz is estimated to be ~3 ppm. Comparing the abundance of the presolar silicates among Y-81025, ALHA77307 and Kainsaz, CO3 chondrites, the abundance of presolar silicates in Kainsaz is clearly lower than those reported in CO3.0 chondrites. The lower abundance in Kainsaz may be due to destruction of silicate grains by thermal metamorphism in the parent body.

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Primitive meteorites contain diverse assemblages of organic compounds, including a minor population of soluble organic molecules and a dominant insoluble phase with similarities to terrestrial kerogen. Isotopic and structural studies of meteoritic organics suggests that some fraction of this material formed in a very low temperature environment, such as a protosolar cold molecular cloud or the outer reaches of the solar nebula. The organic compounds in meteorites have experienced variable degrees of secondary processing in the solar nebula and hydrothermal alteration in meteorite parent bodies. Although hundreds of organic compounds have been identified in meteorites, there is still considerable uncertainty in the original state of the organic matter prior to incorporation in the meteorite parent bodies.

Tagish Lake is a unique carbonaceous chondrite which shares some mineralogical and chemical similarities to CI and CM chondrites but is distinct from both. Because much of the Tagish Lake meteorite was collected within days of its fall and kept in an exceptionally clean state, it presents a unique opportunity to study the microscale distributions of organic compounds. Organic globules (100-500nm) are found distributed throughout the Tagish Lake matrix. These globules are commonly found to exhibit enrichments in ¹⁵N, demonstrating that they are indigenous to the meteorite. Here we present results of a coordinated study of submicrometer organic globules in the Tagish Lake meteorite using a field emission scanning-transmission electron microscopy (STEM) equipped with a thin window energy-dispersive X-ray (EDX) spectrometer and C and N isotopic measurements with a NanoSIMS 50L ion microprobe. Spectrum images containing a high count-rate EDX spectrum in each pixel are obtained with the STEM, and enable the determination of quantitative element abundances in addition to displaying the spatial distribution of major and minor elements with nanometer spatial resolution.

Fragments of the carbonate-poor lithology from a pristine sample of Tagish Lake were studied. The samples were embedded in elemental S and sliced with a diamond ultramicrotome, in order to avoid any possibility of contamination with organic epoxy.

We identified dozens of organic globules, distributed randomly throughout the matrix of the meteorite. All four of the globules subjected to isotopic measurement so far were found to be ¹⁵N-rich, with values ranging from +400 to +600 ‰. The globules were easily distinguished in energy-filtered STEM images, and electron energy loss spectroscopy will be used to determine N and C bonding states.

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Primitive meteorites contain presolar grains that predate the formation of our solar system. Recently presolar silicate grains were identified in IDPs and in primitive carbonaceous and ordinary chondrites. In enstatite chondrites, presolar carbonaceous and oxide grains have been reported, but no presolar silicate grains have been identified. Here we report the first finding of presolar silicates from in three primitive Enstatite (EH3) chondrites, Yamato(Y)-691, Allan Hills (ALHA)81189, and Sahara(SAH) 97072.

Mineralogical and petrographical characterization of matrices was conducted using SEM-EDS and FESEM-EDS. Presolar grains were surveyed by isotopograph using an isotope microscope system.

The total analyzed areas of oxygen isotopographs are about 61,000, 58,000 and 30,000 micrometer squares for Y-691, ALHA81189 and SAH 97072. 3 and 9 presolar silicates were identified for Y-691 and ALHA81189, respectively, whereas no presolar silicates were identified for SAH 97072. Presolar carbonaceous grains were also identified by carbon isotopographs: 10 grains from areas of about 63,000 micrometer squares for Y-691; 6 from about 61,000 for ALHA81189; and 2 from about 32,000 for SAH 97072. Matrix-normalized abundances of presolar silicate grains were calculated to be about 4, 14 and under 3ppm for Y-691, ALHA81189 and SAH 97072, respectively, assuming the mean grain size to be 0.3 micrometer in diameter. In the same calculation method, presolar carbonaceous grains were calculated to be about 14, 9 and 6ppm for Y-691, ALHA81189 and SAH 97072, respectively.

The smaller abundance in SAH 97072 may be due to decomposition of the presolar carbonaceous grains by thermal metamorphism in the parent body. The abundance of presolar silicates is the highest in ALHA81189 and continues to Y-691, SAH 97072. The lowest abundance for SAH 97072 is the same case of carbonaceous grains. These results support that metamorphic degree is highest in SAH 97072 among the three EH3 chondrites. The abundance of presolar silicates is much smaller in EH3 chondrites than in primitive carbonaceous chondrites. The small abundance in EH3 chondrites suggests that parts of the presolar silicate grains of EH3 chondrites have been decomposed by the mild thermal metamorphism in the parent body or in the solar nebula. The abundance of presolar silicate grains (14ppm) of ALHA81189 is probably a minimum estimate of the original abundance for EH3 chondrite formation area in the solar nebula. The oxygen isotopic compositions of presolar silicates show that the most grains (~80%) belong to group 1. The rest grains belong to group 4.

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Chondrules are mm-sized silicate spherules which are included in primitive meteorites. They were crystallized from levitated melt droplets in the early solar nebula some 4.6 billion years ago. Although the previous experimental data all showed that the formation process of chondrule was slow at near the equilibrium condition by slow cooling (1000 K/hour), our experimental results by levitation method show the faster process (100 K/s).

A gas jet levitator has been employed and solidification process was precisely observed by optical and by pyrometrical in-situ observation systems. The effect of heterogeneous nucleation was investigated by active seeding using small, micrometer size particles.

Mg₂SiO₄ (forsterite) melts did crystallize with and without seeding but larger supercooling ($\Delta T > 1000$ K) was required for the nucleation without seeding. Without seeding, the MgSiO₃ (enstatite) melt droplets did not nucleate at all and thus only glass spherules formed during cooling. Even with active seeding, a sufficiently large supercooling (220 K $< \Delta T < 900$ K) was needed to promote the nucleation. At a lower supercooling ($\Delta T < 220$ K), levitated melts did not nucleate in spite of contact with seed particles.

The present levitation data clearly demonstrates that crystallization of chondrule melts takes place in less than 10 seconds at a supercooling of approximately 700–1000 K for forsterite chondrules and of 650–860 K for enstatite chondrules. Outside these experimental conditions, the texture of chondrules could not be realized. And the crystallization temperature of chondrules shows that chondrules formed always from hypercooled melt droplets (about $\Delta T > 500$ K). The hypercooling temperature is defined as the enthalpy of crystallization divided by the specific heat of the liquid. In hypercooled melts, faceted crystals, like the ones present in porphyritic textures, can be formed because the hypercooled melt acts as a heat sink for the absorption of the latent heat of crystallization.

The necessity of seeding for the crystallization of enstatite melts implies that the melt droplets in the early solar nebula have been collided with particles such as cosmic dusts. The present crystallization experiments using levitation methods point out that the chondrule crystallization could have been completed within a few seconds in the hypercooled melt. These results strongly support the currently postulated hypothesis for chondrule formation by flash heating followed by rapid cooling of the melt droplets.

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Most meteorites are subjected to shock metamorphism in some degrees. Estimation of the degree of shock is important in order to know the evolution processes in a planet and also of the solar system. Uchizono *et al.* (1999) found by shock experiments that the apparent strains of olivine crystals, being obtained from broadening of each reflection in an x-ray diffraction pattern, have a proportional correlation to shock pressures loaded on it. Their result suggests that the apparent strain can be used as a quantitative index of shock pressures at which shock metamorphism occurred. However, the cause of the apparent strain is not well known. In this study, we observed small olivine crystals by a transmitted electron microscope (TEM) of which apparent strains are estimated by an x-ray method using a Gandolphi camera.

The apparent strains of 14 single crystals of olivine, less than 100 μm in size, were determined and range from 0.075 % to 0.250 %. Selected 4 samples from the 14 crystals, denominated as 1, 2, 3 and 4, were observed by TEM together with a San Carlos olivine as a standard. The apparent strains of samples 1, 2, 3 and 4 are 0.075, 0.164, 0.170, and 0.250 %, respectively. The samples are fabricated into 200 nm thick by a focused ion beam (FIB) method for TEM observations.

The San Carlos olivine shows homogeneous contrast with no textures under bright and dark field conditions, suggesting even surface of a sample and no or very few damages due to fabrication by a FIB method. Dislocation densities in samples 1, 2, 3, and 4 were measured in dark field images using 002, 06-2, 02-1 and 002 diffractions, respectively, at which samples do not agree with the extinction conditions. The dislocation densities of samples 1, 2 and 3 were calculated by dividing the number of dislocations by the area of samples, and that of sample 4 were calculated by dividing the total length of dislocations by the volume, because dislocations of sample 4 are connected to each other. The dislocation densities obtained are 2×10^8 , 32×10^8 , 26×10^8 and $208 \times 10^8 \text{ cm}^{-2}$ for samples 1, 2, 3 and 4, respectively. The results show a linear correlation between apparent strains and common logarithms of dislocation densities of samples and suggest that the apparent strain obtained by an x-ray method corresponds to the density of dislocations observed by TEM.

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Tagish Lake is an unusual type 2 carbonaceous chondrite which bears similarities to both C1 and CM chondrites (e.g., Zolensky *et al.*, 2002). Its high proportion of fine-grained matrix and high carbon and water contents suggest a close relationship to C1 chondrites, but the presence of chondrules makes it bear a resemblance to CM chondrites. Most of chondrules in Tagish Lake are surrounded by thick, fine-grained rims. Chondrules with fine-grained rims are common in most of type 2 and 3 chondrites. It has been controversial whether the rims formed by accretion of dust onto chondrules in the solar nebula or by processes that occurred on the meteorite parent bodies. Here, we present the results of mineralogical and petrological study of fine-grained rims surrounding chondrules. A thin section of Tagish Lake (~72 μm^2 area) was studied using a scanning electron microscope and an electron probe microanalyzer.

The matrix of Tagish Lake consists mainly of fine grains (<1-20 μm in diameter) of phyllosilicates, Fe-Ni sulfides, carbonates, magnetite and olivine. We found 53 chondrules and coarse-grained aggregates (which are treated as chondrules) (100-1000 μm in diameter) set in the matrix. Individual chondrules have cores of forsterite and/or enstatite grains (10-100 μm in size) surrounded by 5 to 220 nm thick, fine-grained rims. The rims consist mainly of phyllosilicates and minor amounts of Fe-Ni sulfides and are distinctly less porous than the surrounding matrix. There is much textural evidence that the rims were formed partially by replacing the cores. We also found 22 fine-grained clasts (50-130 μm), which are generally round to oval in shape. The clasts are closely similar in texture and mineralogy to the rims. Broad-beam WDS analyses indicate that the rims and the clasts have similar compositions, whereas the matrix is significantly more enriched in Mg.

We suggest that most chondrules in Tagish Lake have been replaced by phyllosilicates preferentially from the surface toward the center of each chondrule, thus forming phyllosilicate-rich rims. Relatively large chondrules retain unreplaced olivine and pyroxene in their interiors, which we now see as cores. Small chondrules ($\leq 130 \mu\text{m}$ in diameter) may have been completely replaced by phyllosilicates, remaining as the rounded to oval-shaped, fine-grained clasts. Alternatively, the clasts may be cross sections of chondrule rims that were cut outside of the cores.

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The KLE98300 EH3 chondrite includes large numbers of graphite grains associated with Fe-Ni metal. Such graphite grains are considered to be products of parent body metamorphism [1]. We have initiated a mineralogical, carbon- and nitrogen-isotopic, and chemical study of graphite and the bulk meteorite. This study should provide information on parent body processes of enstatite chondrite parent bodies. Here we report the results of noble gases and nitrogen analyses of the bulk meteorite sample by stepped pyrolysis (500, 900, 1200, and 1700°C).

Elemental ratios of $^{40}\text{Ar}/^{132}\text{Xe}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ in the 1200 and 1700°C fractions are lower than those of subsolar-gases, characteristic for E4-6 chondrites [2] and even below those of Q-gases contained in carbonaceous and ordinary chondrites [3]. Xe isotopic ratios in these fractions are close to those of Q-gases [3], but not to those of subsolar-gases [2]. The low elemental ratios and Xe-Q like isotopic ratios suggest the presence of sub-Q gases [4], which are characteristic for E3 chondrites and are believed to originate from fractionation of Q-gases [4]. The nitrogen concentration (281ppm) and $\delta^{15}\text{N}$ value (-12.2‰) are in the ranges of E4-6 chondrites (100-100ppm and -47.4 to +0.6‰; [5]). Nitrogen release pattern showed two characteristics: (1) isotopically lighter nitrogen is released in the higher temperature fractions (>1200°C) and (2) an enormous proportion of nitrogen (70%) is released in these fractions. These two characteristics are seen also in E4-6 chondrites [5].

To conclude, trapped noble gas signatures of KLE98300 are different from those of E4-6 chondrites. This is consistent with previous results [4]. Patzer and Schultz [4] suggested distinct evolutionary paths for E3 and E4-6 chondrites prior to parent body metamorphism. On the other hand, there appears to be no difference between nitrogen signatures of KLE98300 and of E4-6 chondrites. This suggests that nitrogen-bearing minerals in E3 and E4-6 chondrites emerged from the same nitrogen reservoirs.

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Micrometeorites account for 90% of extraterrestrial materials accreting to the Earth and may have contributed to the evolution of pre-biotic organic matter on the early Earth. However, natures of organic compounds in micrometeorites are poorly known. In this study, some Antarctic Micrometeorites (AMMs) were studied non-destructively by infrared (IR) microspectroscopy for characterizing organic and hydrous components in these particles. These characters of organic and hydrous components in AMMs were compared with those in carbonaceous chondrites.

Micrometeorites/candidates separated from glacial sands were hand-picked under a microscope with a simple criteria that the unmelted particles have dark grey-to-black colors and irregular shapes. These particles were then analyzed using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDX) to select particles with Si:Mg:Fe ratio of 1:1:1 (chondritic composition) approximately. These particles were pressed between two Al foils and after removing the upper Al foil, the particles were analyzed by IR microspectroscopy using the transmission-reflection method.

The IR spectra of these AMMs showed IR absorption peaks of OH (molecular water) at 3400 cm^{-1} , aliphatic carbonaceous components at 2960 cm^{-1} for CH_3 and 2925 and 2860 cm^{-1} for CH_2 and Si-O of silicates at 1200 cm^{-1} . By using peak height ratios of CH_3/CH_2 (2960 $\text{cm}^{-1}/2925 \text{ cm}^{-1}$) and OH/CH_2 (3400 $\text{cm}^{-1}/2925 \text{ cm}^{-1}$), aliphatic and hydrous component characters of AMMs can be quantitatively investigated. The CH_3/CH_2 and OH/CH_2 ratios of AMMs are ranging 0.6~0.9 and 1~3, respectively. These ratios of AMMs are smaller than those of carbonaceous chondrites. Aliphatics in AMMs might have relatively longer aliphatic CH_2 chains than those in carbonaceous chondrites. AMMs have lower abundance of hydrous components than carbonaceous chondrites.

In order to study the effects of heating on these CH_3/CH_2 and OH/CH_2 ratios, a AMM was heated in atmosphere at temperatures from room temperature (RT) to 600°C and observed *in-situ* under the IR microscope. The OH peak at 3400 cm^{-1} disappeared at 400°C, while 2960 cm^{-1} (CH_3) and 2925 cm^{-1} (CH_2) peaks disappeared at 300°C. The peak height ratio of CH_3/CH_2 remained mostly unchanged from RT to 210°C and increased from 210°C to 300°C. The OH/CH_2 ratio decreased from RT to 210°C and then increased greatly from 210°C to 300°C. These thermal changes of aliphatic and hydrous components can explain variations in CH_3/CH_2 and OH/CH_2 ratios of AMMs and also a part of those on carbonaceous chondrites.

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A major fraction of interplanetary dust particles are thought to be produced by impacts on mutual collisions of asteroids. Recent shock-recovery experiments (Tomeoka et al., 2003) revealed that the application of shock to a hydrated chondrite reduces it to minute particles through a much broader range of pressures than for an anhydrous chondrite. The shock heating must cause dehydration of hydrous minerals and increase in gas volume, and as a result, generates great expansive force on pressure release. The results, therefore, suggest that hydrated asteroids will produce dust particles during collisions at a much higher rate than anhydrous asteroids.

In order to better understand the dust formation mechanism, we performed shock experiments of hydrous serpentine powder using a vertical propellant gun. The experiments have been conducted in an open system, in which the target sample is not confined within a container. The samples were shocked in two experiments at impact pressures 4.9 GPa (Shot 1) and 7.9 GPa (Shot 2). Aerogel capture cells were set above the target assembly to collect ejected particles. Recovered samples were studied using an optical microscope, a SEM-EDS and an EPMA-WDS.

SEM observations reveal that part of the material recovered from Shot 2 has numerous vesicles (0.1-1 μm in diameter), exhibiting a typical texture of shock melted materials. WDS analyses show that its analytical totals are distinctly higher than those of the starting material (88.9 vs. 82.4 wt% on average), indicating that the material has been significantly dehydrated. Based on measurements of a track length and a diameter of each particle captured inside the aerogel cells, we found that the velocities of a major proportion of particles in Shot 2 were significantly higher than those of Shot 1.

The amount of post-shock heat in porous material is known to be much larger than in nonporous material (e.g., Bauer, 1979). Our results revealed that dehydration and partial melting of serpentine powder occur with shock at an impact pressure 7.9 GPa. From the pulse-heating experiments of a serpentine-rich meteorite (Toppani et al., 2001), the material was probably heated to >1350°C. Shock at 7.9 GPa is in the range of shock stage S2 (Stöffler et al., 1991), which is regarded to be far too low to produce shock melts. The results, therefore, suggest that the degree of heating in shock on porous asteroids is much higher than those estimated from the conventional shock experiments.

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Changes of properties of constituent minerals by heavy shock-metamorphism are not well known, although shock-induced high pressure minerals are frequently described. Then, in this study, we investigated the properties of constituent minerals in the strongly shocked Sahara 98222 L6 chondrite, 4×5×0.5 cm in size, which is classified as S6 of Stöffler et al. (1991).

After cutting the sample into five pieces, polished thin sections (PTs) were prepared for each piece. Chemical compositions of minerals were analyzed by an electron-probe microanalyser (EPMA). Equilibration temperatures were determined for ortho- and clinopyroxenes by a method of Lindsley (1983). X-ray powder diffraction patterns of olivine, plagioclase and plagioclase glass were obtained with tiny grains of 50-100 μm in size by a Gandolfi camera. Apparent strains of each olivine crystal were determined based on broadening of reflections in an x-ray pattern. Formation temperature of well-crystallized plagioclase was determined by using the relation diagram between the $\Delta 131$ parameter and synthesis temperature of plagioclase by Smith (1972), after correcting for the influence of K by Kroll & Ribbe (1980).

Recrystallization and staining of olivine and plagioclase glass, which are characteristics of S6, were observed. However, the maximum value of apparent strains of olivine is determined to be 0.16 %, which corresponds to that of S3 on the relation diagram between apparent strain and shock pressure by Yoshida (2001). The result suggests that the meteorite has been thermally annealed after shock.

Chemical compositions of olivine are $\text{Fo}_{75.1-77.7}\text{Fa}_{22.3-24.9}$ and homogeneous in each grain. Chemical compositions of pyroxenes are $\text{En}_{75.7-79.1}\text{Fs}_{19.3-23.5}\text{Wo}_{1.0-1.7}$ and $\text{En}_{46.9-50.3}\text{Fs}_{7.0-9.0}\text{Wo}_{4.1-9.3}$. Plagioclase and plagioclase glass show compositions in the range of $\text{Ab}_{90.6-12.6}\text{An}_{79.5-85.0}\text{Or}_{4.4-9.5}$, which spread a little toward Ab-poor side on the Or-An diagram compared to weakly shocked L6 chondrites.

Temperatures obtained from adjacent ortho- and clinopyroxenes were 760-850 and 1190-1260 °C, respectively. The discrepancy of temperatures between ortho- and clinopyroxenes suggests that the both pyroxenes were not in equilibrium after shock. Crystallization temperatures of plagioclase are obtained as 660 and 700 °C, which are near to the temperatures obtained from orthopyroxene compositions. From the above results, following thermal histories were estimated: (1) more than 1260 °C, being suggested by clinopyroxene, was attained by shock heating and plagioclase melted, (2) the meteorite was cooled rapidly after shock to about 700 °C and cooled slowly below 700 °C, at which plagioclase crystallized. The slow cooling below 700 °C may have occurred by deposition of the meteorite on a parent body.

P21-08

In-situ micro-FTIR study of thermal changes of organics in carbonaceous chondrites – Behavior of aliphatic hydrocarbons and effects of minerals –Y. Kebukawa^{1,2}, S. Nakashima¹, and M. E. Zolensky³¹Department of Earth and Space Science, Osaka University, Osaka, 560-0043, Japan²Department of Earth and Planetary Science, Tokyo Institute of Technology, Tokyo 152-8551, Japan

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Carbonaceous chondrites are known to contain generally a few wt. % of carbon. Its majority is in the form of macromolecular organic compounds. Although they have been extensively studied by various geochemical methods, their thermal stabilities and changes remain unsolved. Therefore thermal behavior of chondritic macromolecular organic matter was studied here by means of in-situ heating infrared (IR) microspectroscopy. These were compared with those of simple aliphatic hydrocarbonaceous compounds with and without a representative phyllosilicate mineral (antigorite) to investigate effects of the mineral matrix.

Step heating experiments from room temperature to 500-600°C of chondritic organics revealed that thermal behavior is different between [CI (Orgueil, Ivuna, Alais) + Tagish Lake (carbonate-poor)] and [CM (Murchison, Murray) + Tagish Lake (carbonate-rich)].

Step heating behavior of model aliphatic substances (octadecane, octadecanol and stearic acid) without antigorite showed general decrease of most of the peaks with constant CH₃/CH₂ ratio. This volatilization of aliphatic molecules was prevented by the presence of antigorite. Heating of these simple compounds with antigorite showed a decrease in CH₃/CH₂ ratio at lower temperatures (<~100-200 °C) and its increase at higher temperatures (>~100-200 °C). These reactions might correspond to oxidation and thermal cracking, respectively. The mineral appeared to increase changes in the CH₃/CH₂ ratio possibly by catalyzing the above reactions of organics.

Kinetic isothermal heating experiments indicate that decrease of aliphatic C–H in carbonaceous chondrites can be well fitted by a combination of two first order reactions. The faster reaction has a very low activation energy around 0-10 kJ/mol, while the slower reaction has a low activation energy around 20-30 kJ/mol, which is much smaller than typical oxidation and cracking reactions of aliphatics, due possibly to catalytic effects of mineral matrix.

The same type of kinetic experiments on simple aliphatic substances revealed the similarities of C–H decrease rates and activation energies of stearic acid in the presence of antigorite to those of chondritic aliphatics. Macromolecular organics in carbonaceous chondrites thus showed similar thermal behavior to aliphatic carboxylic acid in the presence of a phyllosilicate.

P21-10

Possible maximum size of porphyritic chondrules in the shock-wave heating modelS. Yasuda¹ and T. Nakamoto²¹Pure and Applied Sciences, Tsukuba University, Tsukuba, Ibaraki, 305-8571, Japan

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Chondrules are thought to have formed through some flash heating events in the early solar nebula. In shock wave heating model, one of the most plausible models for chondrule formation, temperature distribution in the dust particle can be inhomogeneous because the gas frictional heating works only on the upstream side of the particle.

Kato *et al.* (2006) have shown that when the particle is partially molten and a liquid mantle is present on a solid core, the stripping of the liquid surface due to the gas flow can take place. But the temperature distribution in the particle and the temperature dependence of the viscosity were not considered in their study. Porphyritic chondrules (PC) are thought to have experienced the temperature 200K or more below (*T*_{min}=1700K) the liquidus temperature (*T*_{liq}=1900K) (Cohen *et al.* 2000). The viscosity of material below the *T*_{liq} is usually high, and it may be difficult to strip off a highly viscous liquid surface from the particle. So the stripping of the liquid surface may not take place in the case of PC. In this study, we first obtain the temperature and viscosity distributions in the dust particles by solving a three-dimensional heat conduction equation. Then, we discuss the stripping of the liquid surface from the particle and the possible size of PC.

We can see that the temperature distribution in the dust particle is generally inhomogeneous. Then we examine whether the stripping of the liquid surface occurs or not considering viscosity as a function of temperature. One of the necessary conditions for stripping is the low viscosity part should move relative to the high viscosity part while high and low viscosity parts coexist. According to our estimation, we can find that when the temperature does not reach enough temperature (*T*_c), which is higher than *T*_{min}, the stripping can hardly occur. On the other hand, it is necessary for the precursor dust particle to experience the temperature between the *T*_{min} and *T*_c to form PC remaining size of dust. Thus, the possible maximum size of the PC should be the maximum radius that satisfies this condition. Using our temperature distribution results, the possible size of the PC is found to be about 40nm. This critical radius is larger than those of natural PC. Thus, at least in terms of PC sizes, the shock-wave heating model is consistent with observations.

P21-09

A new constraint on the formation of compound chondrulesM. Uesugi¹ and T. Akaki²¹Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198 Japan

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Chondrules are igneous submillimeter-sized spherical objects found in the most primitive class of meteorites, chondrites. Compound chondrules, which consist of two or more chondrules fused together, are important key for the formation process of chondrules, because they clearly indicate that the chondrules those have different melting degree could exist very close distance at the time of chondrule formation. The origin of the difference of melting degree would have important information for the environment of chondrule formation processes. There are several possibilities for the origin, such as difference of liquidus temperature, rapid cooling, and small scale of heating in solar nebula.

We investigated a compound chondrule in ALH-77011(L3), which shows that the primary chondrule, which retains its spherical shape, is radial pyroxene and the secondary, which loses its spherical shape by sticking on primary, is porphyritic olivine chondrule. We analyzed the bulk chemical composition of constituent chondrules in compound chondrules by EPMA, and then calculated the liquidus temperature of those chondrules using MELTS. The calculated liquidus temperature is 1741 K for secondary chondrule and 1655 K for primary chondrule. Thus, secondary chondrule have liquids temperature ~90 K higher than that of primary chondrule. This result indicates that the constituent chondrules of compound had different temperature, at least 90 K at the time of their collision. If the heating in the solar nebula melted both of the constituent chondrules at the same time, their melting degree should depend on their liquidus temperature. However, the example shows that the melting degree of constituent chondrules in compound do not depend on their liquidus temperature. Thus the heating would melted only secondary chondrule at the time of chondrule formation.

This result indicates very small scale of chondrule formation process, especially heating. This can be very strong restriction on the chondrule formation models.

O22-01

The quiet revolution in lunar science: Lunar meteorites, global remote sensing and the magma ocean hypothesis

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One of the most important insights in planetary science was the recognition by John Wood and others that feldspathic fragments in Apollo 11 soil indicated the existence of a global differentiation event that came to be known as the Lunar Magma Ocean. Subsequent study of lunar samples supported this insight in many ways, including the presence of large cumulate anorthosites, complementary Eu anomalies in the anorthosites and mare basalts indicating the participation of the sources of these rocks in a large differentiation event, and the uniformity of the KREEP (potassium, rare earth element, phosphorus) component that seems to represent the residual liquid of the differentiation event. Global remote sensing both supported the magma ocean, but also provide new observations that in some ways seemed to render it incomplete. In support of the magma ocean, measurements of surface abundance of iron show that vast regions of the lunar farside are extremely iron poor, consistent with the presence of abundant anorthosite. However, the Moon exhibits great lateral heterogeneity, to the extent that the Moon has recently been divided into three "terranes" that Wieczorek and others have argued have had quite distinct histories. The lunar nearside shows a distinct excess of Th and REE indicating the presence of abundant KREEP material. Much of the rest of the Moon is feldspathic, except for the large South Pole-Aitken basin that shows an enrichment in iron and mafic minerals. This lateral heterogeneity is outside a one-dimensional differentiation model. However, while the original magma ocean concept was one-dimensional, later work by Hess and Parmentier showed that late crystallizing ilmenite-rich cumulates are gravitationally unstable leading to convective overturn. Thus the magma ocean hypothesis requires major reworking of the entire mantle, and perhaps the crust. Geophysical models by Parmentier, Zhong and Zuber, and others show that large-scale lateral differentiation driven by the gravitational instability is feasible. Thus the magma ocean can accommodate the remote sensing observations. Like the remote sensing, lunar meteorites both support and complicate the magma ocean view. The KREEP-poor meteorites, presumably from the lunar farside, are feldspathic, supporting the anorthosite enrichment of the crust. But the mineral associations in the feldspathic meteorites indicate a significant component of magnesium olivine in the anorthosites, utterly unexpected in late-crystallizing anorthosites. Remote sensing and lunar meteorites have not overturned the lunar magma ocean, but challenge us to clarify how this general process operated in detail.

O22-02

SELENE - A pathfinder for new era of lunar exploration

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SELENE (SElenological and ENgineering Explorer) is the first Japanese large-scaled lunar explorer which will be launched in summer of 2007. Currently (as of Mar. 2006), SELENE is under profiling test for lunar environment, preparing for the next-year's launch.

SELENE has 14 instruments on board, such as X-ray spectrometer and terrain camera, magnetometer, and plasma imager. And SELENE also has Hi-Vision camera for publication use on board. This is the first time in the world that brings Hi-Vision camera to the moon.

SELENE has mainly three objectives:

- 1) To clarify birth of the moon and clinch the theory of lunar birth (especially confirm "Giant-Impact" hypothesis).
- 2) To reveal lunar evolution history and global geology.
- 3) To investigate lunar resources and environment for future manned lunar exploration.

In this lecture, I state on the current situation of SELENE development and explain significance of exploration in comparison with other exploration of America, India and China.

affiliations.) No illustrations, photographs, tables or references are permitted. The title should be in bold uppercase, used only at the beginning of the title and proper names as appropriate, and lowercase letters. Leave one blank line after the title, and then write the names of the authors (initials followed by the family name) in the upper and lowercase letters. Underline the name of the communicating author who gives the presentation. The addresses of each author should be given on the next line linked to the names by superscript numbers. The e-mail address of the communicating author should be given. After a further blank line, the abstract itself should be inserted. All the text must be written in single spacing.

O22-03

Lunar Imager / Spectro Meter (LISM) for the SELENE Project

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An imaging and spectral profiling instrument will be loaded on SELENE launched in 2007. The instrument is called LISM (Lunar Imager / SpectroMeter). LISM will provide us much higher spatial resolution, wavelength resolution and signal to noise ratio than that of past lunar missions. LISM consists of three sub-systems: Terrain Camera (TC), Multi-band Imager (MI) and Spectral Profiler (SP). The main purpose of TC is to take high spatial resolution images with high S/N and stereo-pair images for DEM. MI is expected to take multi-band images with higher spatial resolution in visible to near infrared range. The main role of SP is to make accurate global and regional mineral/rock type maps of the Moon. We are also developing softwares for the analyses of data provided by the LISM along with a study of characteristics of mineral reflectance spectra. LISM will provide fundamental data for studies on many significant themes of lunar sciences.

O22-04

Mg-number mapping of mare serenitatis with a hyper-spectral telescope

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Mg-number ($Mg\# = \text{atomic Mg} / (\text{Mg} + \text{Fe})$) is an important factor when analyzing lunar rocks and interpreting the subsurface structure of the moon. $Mg\#$ variation shifts the wavelength of the absorption spectra of ferrous iron with their peaks at around 1000 nm and 2000 nm. The shift had, however, not been detected by remote sensing because it is limited to a very small range. In order to detect this slight shift, ground-based observations of the moon were carried out with Advanced Lunar Imaging Spectrometer (ALIS) (Saiki et al., 2004) which is a kind of Hyper-spectral Telescope. The location of the observation was Science City at the peak of Mt. Haleakala, Maui, Hawaii, USA. The dates of observation were August 15 - 26, 2005 and December 12 - 18, 2005. The obtained image cubes of the moon were processed by the following steps; (1) dark and flat field correction, (2) normalization of all mare spectra with the same standard highland spectrum, (3) baseline correction with line which starts from 700 nm and ends at 1050 nm. Comparing the resultant spectra, we detected the slight shift of the absorption bands. The absorption-peak map of Mare Serenitatis has been made. Most of the absorption peaks range from 970 nm to 980 nm. In addition to $Mg\#$ variation, there are two major factors shifting the wavelength of absorption spectrum of ferrous iron; space weathering and calcium in pyroxene. When the both can be regarded as constant in some limited area, the shift can be interpreted as $Mg\#$ change and the absorption-peak map can be regarded as $Mg\#$ map of the area. Kodama (2003) classified mare deposits of Mare Serenitatis into 7 groups; Sr1, Sr2, Sr3A, Sr3B, Sr4, Sr5, and DMM (dark mantle material), using Clementine UV/VIS multi-spectral data including FeO and TiO₂ content based on Lucey (2000). The Sr3A, Sr3B, and Sr4, containing more Fe-rich pyroxene than other deposits, appear to have wide $Mg\#$ range.

Can orbital data distinguish Mg-rich crustal rocks from Mg-rich basalt cumulates?

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To search for the not-yet-sampled Mg-rich mafic cumulate rocks complementary to the anorthosite generated from the postulated global magma ocean has been one of the major objectives in the past lunar orbital missions such as Clementine and Lunar Prospector, and will be in the future SELENE mission. However, there are some warnings in search for such Mg-rich rocks utilizing the orbital data, because there are varieties for the Mg-rich rocks in the petrologic and mineralogical view points. The Mg-rich rocks in the Apollo samples and lunar meteorites are not Mg-rich mafic cumulates derived from the global magma ocean, but from Mg-rich magma intruded into the anorthositic crust during the post-magma ocean magmatism. In addition, there is another Mg-rich rock, which is an olivine cumulate at the depth of relatively thick mare basalt flow. All of the three are expected to have similar major-element composition, modal mineralogy and mineral composition. While the mafic cumulate from the magma ocean should be deep seated probably in the mantle, the other two occur in the shallow crust or somewhere near the surface. Since it has been generally assumed that there are apparent discrepancies in Mg# [=Mg/(Mg+Fe) atomic ratio] between the Mg-rich intruded rocks and Fe-rich mare basalts, it is expected that the two can be easily distinguished from each other on the basis of Mg#. However, it is not the case for the ancient, pre-Imbrium (so-called cryptomare) basalts, generally buried underneath the anorthositic surface regolith. The cryptomare basalts from Apollo 14 site exhibit Mg-rich compositions comparable to that the Mg-rich intruded rocks, and lack the Fe-enrichment trend typical of the young, post-Imbrium mare basalts. They consist of differentiated basalt units with Mg-rich olivine cumulate and Al, K-enriched basalts without the enrichment of iron. This makes difficult to distinguish the Mg-rich intrusion from the Mg-rich mare basalt. Thus, we should be careful in identifying Mg-rich lithologies based on the orbital spectral data. We must establish appropriate criteria in defining the rock types, such as major element abundances other than Fe and Mg, trace element abundances, thickness and depth of the basalt flow, and geologic setting.

Na-Ca-bearing planetary minerals and preparation of lunar simulants for lunar bases

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Major rock forming minerals in differentiated planets, Moon, and asteroids are pyroxenes, olivines and plagioclases. Andesitic materials produced from segregation of partial melts and residues from the primitive chondritic source materials of the solar system, consists of diopside and albite. Residues of partial melts from carbonaceous source material is known as ureilites. Crystal fractionation products from a thin magma ocean on a large differentiated asteroids such as 4 Vesta show a unique trend from magnesian orthopyroxene, low-Ca pigeonite to high-Ca, high-Fe pigeonites with crystallization of calcic plagioclase in later stage. If the partial melts of the chondritic source materials form the magma ocean (Vesta), 1/10th of sodium have to be lost to produce eucritic, calcic plagioclases. Then, albite-diopside assemblage is converted to magnesian pyroxene and calcic plagioclase. Lunar highland materials are characterized by magnesian and ferroan anorthosites with high An values. Basaltic materials such as lunar and Martian mare basalts were produced by partial melting in depth by accumulation of heat from long lived radiogenic isotopes. Earth minerals are quite complex because of the presence of water, ocean and atmosphere. Because of the repeated igneous activities, many terrestrial plagioclases are enriched in Na and K.

The high Na abundance in plagioclase is a problem, when we try to make lunar simulants for lunar highland materials. One candidate site for construction of a lunar base in a proposed future manned lunar mission, is lunar farside or rims of craters at the south pole area. Remote sensing data suggest that the estimated concentrations of Th and FeO on the farside of the Moon are very low. Such materials were not recovered by the Apollo and Luna missions, but were recovered from the Oman desert as lunar meteorites. Dhofar 489 contains magnesian anorthosites with An₉₆. It has been difficult to find high-Ca plagioclase in large quantities on Earth, particularly in Japan. If space agriculture is planned in the base, we have to produce soil simulants. Biologists assume that the presence of organic materials and microorganisms is essential in the terrestrial soil, but it is not recommended for bacteria to go out of the base on the moon. The fossil sea water called brine in the Chiba Kazusa formation, contains fulvic acid, which show biological stimulation effect. If the fulvic acid convert plagioclase into clay minerals and release Ca ion, such organic materials are better than living organism to help growing plants.

Experimental partitioning of Cr³⁺ and Sc³⁺ into olivine: Mechanisms and implications

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Olivine (Mg, Fe)Si₂O₄ does not, by stoichiometry, accept cations such as Sc³⁺ or Cr³⁺. However, the partition coefficients of Sc and Cr between olivine and liquid are significant — 0.2-1.0. We have measured Cr³⁺ partition coefficients of near unity and have grown olivines with nearly 3 wt.% Sc₂O₃. Therefore, there must be a simple means of charge balancing 3+ ions in a crystal structure that was obviously not designed to receive other than 2+ ions on the olivine M sites. The simplest explanation is that two 3+ ions enter the olivine structure by displacing three 2+ ions and creating an M site vacancy.

Even this explanation has difficulties. For minor elements in our experiments (~1 wt.%) the odds of a minor element 3+ ion finding a second 3+ for charge balance are of the order of 100:1 against. Because of the reducing conditions of our experiments, Fe³⁺ will not suffice; and Al³⁺ is not in sufficient quantity in olivine for charge balance. Therefore, Cr or Sc must, in effect, charge balance itself.

For true trace elements, the problem is compounded many times. For an ion at the 10 ppm level the chances of finding a second (for example) Sc ion is ~10⁵:1 against. Of course, any other 3+ ion would suffice but comparisons between percent level doping experiments and trace level partitioning indicate that Henry's law is obeyed. This implies that the same substitution mechanism occurs at both the percent and tens of ppm levels.

There are two simple solutions to this problem: (i) The electrical conductivity of olivine is such that charge balance need not be "local." This requires substantial domains within the olivine crystal in electrical contact by migration of vacancies or electronic defects. (ii) The 3+ cation brings along its own charge-balancing ion because it existed as a dimer in the silicate liquid.

Olivine is not a true insulator but is actually a p-type semiconductor. Even so, electrical communication by this means is unlikely over the tens or hundreds of unit cells that would be required for charge balance to be "local." Therefore, we cautiously favor the idea that melt speciation is the means by which 3+ ions enter the olivine structure. Possibly this model might be tested by *in situ* XAFS measurements or by molecular dynamical calculations.

Pyroxenes in Martian meteorites as petrogenetic indicators

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Pyroxenes in Martian meteorites are important recorders of petrogenetic processes. Understanding the details of pyroxene major and minor element compositional variations can provide important insights into those processes. A combination of careful petrographic analysis of natural samples and experimental crystallization studies can lead to better understanding of the processes that gave rise to these samples on Mars. In addition, experimentally determined major, minor and trace element partition coefficients are important for using natural pyroxenes to estimate the compositions of the melts from which they crystallized and the oxidation conditions that prevailed during crystallization.

We will report on minor element (Al, Ti, Cr) zoning in nakhlite pyroxenes and in synthetic pyroxenes that we have grown for the purposes of determining pyroxene/melt partition coefficients for Sr and REE. The natural pyroxenes have patchy Al zoning that, by analogy with our experimental pyroxenes, we interpret as sector zoning. The irregular patchy nature of the zoning is probably the result of the vagaries of growth kinetics and local environment during crystal growth. More slowly cooled nakhlites have the most distinct bimodal zoning, with one mode having Al₂O₃ around 0.5-0.6 wt%, and the other around 0.9 %. Average Al content increases with increasing cooling rate. This feature is puzzling, since the cumulus pyroxenes were almost certainly present at the time of eruption. Al and Ti are strongly correlated, but Cr is completely decoupled from those elements.

The synthetic pyroxenes are distinctly sector zoned in Al and Ti, and the sector-to-sector variation in Al within a single crystal has important effects on trace element partition coefficients. Trivalent REE are strongly correlated with Al, while divalent elements (Sr, Eu²⁺) show a significantly weaker correlation. For example, as the Al₂O₃ content varies from 0.3 to 0.6 wt % from one sector to another, D(Gd) increases by ~80% while D(Sr) and D(Eu) only increase by 20-30% at oxygen fugacities near 1W. The different Al dependency of D for trivalent REE vs. divalent Eu and Sr considerably complicates the calibration of the Eu oxybarometer.

Mineralogy of nakhlite Martian meteorites: Implications for their relative burial depths

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Nakhlites are Martian cumulate rocks mainly composed of augite with variable amounts of olivine and groundmass (mesostasis). Currently seven samples are known: Nakhla (Nak), Governador Valadares (GV), Lafayette (Laf), NWA817, Y000593 (Y), NWA998 and MIL03346 (MIL). All the nakhlites show a similar unbrecciated cumulate texture, and their identical crystallization and exposure ages suggest that they originated from the same igneous body on Mars and were ejected by the same impact event. It is important to study difference of their mineralogy to reconstruct the igneous body from which nakhlites originated. Augite grains in all nakhlites have a nearly identical core composition ($\text{En}_{39}\text{Fs}_{22}\text{Wo}_{39}$) and have thin Fe-rich rims. These Fe-rich rims are zoned to Ca-poor pyroxene compositions and the degree of chemical zoning varies from one sample to another. NWA998 has the most Mg-rich edge composition. The edge composition becomes more Fe-rich in the order of Laf, Nak/GV, Y and NWA817. Unlike other samples, the Fe-rich edge of MIL augite is zoned to the hedenbergite composition. Olivine grains in all samples except Laf and NWA998 show extensive chemical zoning whose degree is clearly related to the chemical zoning of pyroxenes. MIL and NWA817 have the widest compositional ranges (Fa_{54-93}). Y has a slightly narrower compositional range of Fa_{58-85} . Nak and GV have even narrower ranges (Fa_{58-72}). In contrast to these samples, olivines in Laf and NWA998 are homogeneous (Fa_{66-67} and Fa_{61-62} , respectively). Such chemical zoning (Fa and Ca) can be used to quantitatively estimate their cooling rates (burial depths) because it was clearly formed by interaction with the intercumulus melt. The obtained burial depths are 1-2 m for NWA817, 4 m for MIL, 7 m for Y, ~10 m for Nak and GV, and >30 m for Laf and NWA998. This order is clearly related to the degree of pyroxene chemical zoning. The abundance and mineralogy of nakhlite groundmass are also consistent with this order. In Nak, GV and Laf, the groundmass abundance is about 7-8%. Y and NWA998 have a slightly higher abundance (10%), while NWA817 and MIL have much higher abundance (20-24%). The groundmass texture is also related to its abundance. The groundmass of Nak, GV, Laf and Y is mainly composed of feldspar laths. In contrast, NWA817 and MIL have glassy mesostasis without feldspar crystals. In NWA998, feldspar is a large blocky crystal with clear twinning, suggesting that it is even deeper than Laf.

Crystallization experiments for nakhlite martian meteorites

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Nakhlite meteorites consist mainly of augites and are igneous cumulates which were crystallized at 1.3 billion years ago on Mars. We are mineralogically and petrologically studying two independent nakhlites (Yamato nakhlites and MIL 03346 nakhlite) recently recovered from Antarctica, and have estimated their primary melt compositions and their crystallization sequences (Imae et al., 2005; Imae and Ikeda, 2005). The estimated melt compositions for the two nakhlites are similar, but not identical to each other.

Using some possible primary melt compositions, we have been carrying out isothermal and cooling experiments for nakhlite magma in order to clarify the crystallization processes (Imae, 2004). Here we summarize the series of our experiments, compare the textures and the compositional variations in run products of cooling experiments with those in nakhlites, and discuss the crystallization process in detail.

The isothermal experiments show that the liquidus temperature is 1140 °C, where titanomagnetite and augite ($\text{En}_{45}\text{Fs}_{18}\text{Wo}_{37}$) co-crystallize. We find that an experiment with a cooling rate of 4.2 °C/h under the near QFM condition at 1 bar, is closely similar in textures and composition to the most rapidly cooled nakhlite, MIL 03346. The occurrences of phenocrystic augites and dendritic olivine in groundmass glass are the same between the two. Especially, the composition of phenocrystic augites are very similar between the two; core augites are $\text{En}_{40}\text{Fs}_{20}\text{Wo}_{40}$, inner rim augites are ferroan with $\text{mg}\# = 66-44$, and outer rim augites are hedenburgitic.

In summary, the present experiments suggest that our estimation of the primary melt composition, the oxygen fugacity and the cooling rate for nakhlites are appropriate for the formational environment of nakhlites.

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Guinier-Preston exsolutions in extraterrestrial orthopyroxene

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Pyroxenes undergo exsolutions and cation ordering upon cooling in igneous rocks. As the cooling rate is commonly too fast to achieve equilibrium, pyroxenes show often stranded microstructures. The development of Ca-rich exsolution platelets in orthopyroxene from one to a few unit-cells in width - the so-called Guinier-Preston (GP) zones - is one such consequence of disequilibrium. GP zones were previously interpreted to possess $Pbc2_1$ symmetry and to consist of two half-unit cell layers with Wo0 and Wo50 [1].

To unravel the structure of GP zones we have studied orthopyroxene from the Johnstown achondrite and a lunar troctolite (76535) [1, 2], using transmission electron microscopy (TEM). The Johnstown orthopyroxene contains GP zones parallel to (100) apparently a single unit cell in width (18 Å), whereas the lunar orthopyroxene is penetrated by GP zones up to 3 unit cells in width. Electron diffraction patterns taken along the crystallographic axes of Johnstown and lunar host orthopyroxenes show absences of reflections that are fully compatible with the expected space group $Pbca$.

However, the electron diffraction patterns taken from host regions containing GP zones reveal a violation of the a - and b -glide, compatible with the monoclinic space group $P2_1/c$ [2]. High resolution TEM taken along the c -axis of Johnstown and lunar orthopyroxenes show that the GP zones are fully coherent with the orthopyroxene lattice. To test the hypothesis of Ca ordering in GP zones [1], high-resolution TEM (HRTEM) have been numerically simulated. The calculations suggest that Ca ordering in sublayers of the unit cell would result in intensity variations in HRTEM images. As these intensity variations are not visible, it seems to be more likely that Ca is homogeneously distributed in GP zones. In summary, our TEM study shows that GP zones are metrically orthorhombic but possess monoclinic symmetry. The symmetry reduction is due to homogenous Ca enrichment in GP zones, leading to a local distortion of the lattice.

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Lonsdaleite, doubt on the existence in meteorites

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Hexagonal diamond, a polymorph of diamond with the wurtzite structure, was first reported by Bundy and Kasper (1967) in their high-pressure experiments using well-crystallized graphite. Hanneman et al. (1967) first found the hexagonal diamond in nature from the Canyon Diablo iron meteorite. Frondel and Marvin (1967) proposed lonsdaleite as the mineralogical designation for the hexagonal polymorph of diamond. After that, lonsdaleite was also reported from ureilites, being meteorites characteristically containing diamond. However, the properties of lonsdaleite from meteorites are not well known because of its low abundance in meteorites. In all reports except Hanneman et al. (1967), even evidence of lonsdaleite has not been presented in the form that we can check on.

Recently, Yagi et al. (1992) carried out high-pressure *in situ* x-ray diffraction analyses and found that a high-pressure phase, of which x-ray diffraction profiles were well explained by the hexagonal diamond structure, was unquenchable upon release of pressure. In the experiments carried out by Bundy and Kasper (1967), it is also noticeable that the retrieved hexagonal diamond was always accompanied by cubic diamond. These experimental results throw a doubt on the existence of lonsdaleite in meteorites. Then, the purpose of this study is to inspect meteorites for the existence of lonsdaleite by obtaining precise x-ray diffraction patterns of carbon materials from ureilites.

X-ray powder diffraction patterns were obtained of more than 120 carbon-rich grains of about 100 µm in size from 10 Antarctic ureilites by using a Gandolfi camera. The carbon-rich grains are composed of well-crystallized graphite or a mixture of graphite and diamond with a small amount of compressed graphite, which has a little smaller basal spacing than normal graphite. Exact lonsdaleite was not found in this study and a lonsdaleite-like mineral was found only in some grains from Y-74130. The lonsdaleite-like mineral shows a broad reflection at 63.7° (2θ Cr Kα) which markedly tails toward the high-angle side. The overlapped pattern of the reflection and the diamond 111 reflection is very similar to the overlapped reflections from lonsdaleite and diamond shown as the evidence of lonsdaleite by Hanneman et al. (1967). Because of tailing of the reflection and the lack of other reflections suggesting lonsdaleite, the lonsdaleite-like mineral in ureilites is thought to have a disordered stacking of carbon sheets in its structure. The results of this study strongly suggest that lonsdaleite, being a hexagonal polymorph of diamond, may not exist in meteorites.

Fe-enrichment vs. Si-enrichment trends in two samples from the Moon

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Major silicate minerals in breccia clasts from the lunar meteorite NWA 773 show a range of compositions that can be explained by extreme Fe-enrichment during magmatic differentiation. Clasts in Apollo sample 15405 have also been interpreted as resulting from igneous differentiation (Ryder, 1976, EPSL v. 29, 255-268), though in this sample silica-rich clasts have mafic silicates with intermediate Mg/(Mg+Fe). This study reviews the evidence for magmatic differentiation in these rocks and speculates on the controls of magmatic trends on the Moon.

NWA 773 is composed of two rock-types: an olivine cumulate gabbro and a heterolithic breccia (Fagan et al., 2003, MaPS v. 38, 529-554). Major phases in the olivine gabbro include olivine (Fo₆₅), pigeonite (Wo₁₁En₆₅), augite (Wo₃₈En₅₀) and plagioclase, with minor K,Ba-feldspar, ilmenite, troilite and Ca-phosphates. Co-magmatic clasts in the breccia consist of gabbros, FeO-rich lithic clasts and symplectites. Pyroxene exhibits a continuous variation in Mg/(Fe+Mg) in these lithologies from ~0.75 to 0.05. Likewise, pyroxene Ti/(Cr+Ti) shows a continuous variation from ~0.2 to 1.0. Olivine records only a part of the Fe-enrichment trend, with a gap in the occurrence of olivine between ~Fo₃₅ to Fo₁₅. Silica and K,Ba-feldspar occur in some, but not all, clasts with fayalitic olivine. Some of the FeO-rich clasts have symplectic intergrowths of fayalite, hedenbergite, and silica or a non-stoichiometric silica-rich phase.

Reported results (Ryder, 1976) from Apollo sample 15405 show a range in augite and pigeonite compositions from Mg/(Mg+Fe) as high as 0.8 in basaltic clasts to values near 0.3 in granitic clasts. The main difference between the NWA 773 and 15405 trends is the timing of free silica relative to Fe-enrichment in mafic silicates and is comparable to tholeiitic and calc-alkaline trends on Earth.

One controlling factor in the terrestrial systems is hypothesized to be oxygen fugacity. In high-f(O₂) systems, Fe precipitates in oxide minerals, driving the residual liquid to more SiO₂-rich compositions with relatively small changes in silicate mineral Mg/(Mg+Fe). In low-f(O₂) systems, Fe speciates in mafic silicates, resulting in a broad shift in silicate Mg/(Mg+Fe) with minor variation in silica during differentiation.

Oxygen fugacity is a possible control in lunar magmatic systems, but may drive magmatic crystallization in opposite directions to those observed on Earth. With the lower f(O₂) of the Moon, Fe can be displaced from the silicate assemblage by precipitation as Fe-metal or Fe-sulfides.

P22-02

Development and Comparison of two types of Telescopic Imaging Spectrometer for the Moon

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Two types of imaging spectrometer had been developed and examined. This presentation introduces and compares them. One telescope is Advanced Lunar Imaging Spectrometer (ALIS) and another is Tunable Liquid-crystal Telescope (TLT). They apply different dispersive elements. ALIS uses PGP (Prism-Grating-Prism) devices covering 380 – 1700 nm. It is a Cassegrain telescope equipped with two spectrometers; Visible (VIS) one and Near Infrared (NIR) one. Each spectrometer is composed of an imaging sensor and a PGP unit named "ImSpector" made by Specim Corporation. The spectrometers capture "1-line spatial information" x "wavelength information" image at one shot. Line images are assembled by scanning an image on a slit of the spectrometer using a rotating mirror. TLT is a multi-band telescope using a tunable liquid-crystal filter covering 650 - 1100 nm. It is a refracting telescope (Vixen, ED80S) equipped with a cooling CCD camera (Apogee, U260) and a tunable liquid-crystal filter (Cambridge Res. Inc., NIR-07). Each telescope has its own merits and demerits. The merits of ALIS are (1) simultaneity of acquisitions of hundreds of bands at each sampling point and (2) perfect spatial coincidence among the bands. The demerits of ALIS are (1) difficulty in flat field correction because mainly of wavelength-shift called smile effect, (2) difficulty in photometric measurement of stars caused by scanning system, and (3) perfect tracking requirement for correct geometry of objects. The merits of TLT are (1) simultaneity of acquisitions of all pixels on each mono-band image and (2) facility in flat field correction. The demerits of TLT are (1) sub-pixel discordance in reconstruction of spectrum for one specific point and (2) difficulty in temperature control for the stability of the liquid crystal. Making the most of their advantages, ground-based observations of the moon were carried out. ALIS was used to detect the shift of the wavelength of Fe 2+ absorption band at around 1000 nm and TLT was used to gain a lunar absolute radiance and reflectance. Both observations were carried out at the same period by ALIS users group. The location of the observations was Science City at the peak of Mt. Haleakala, Maui, Hawaii, USA. The dates of observation were August 15 – 26, 2005 and December 12 – 18, 2005. Mees Solar Observatory at Hawaii University and Okano Laboratory at Tohoku University provided us peripheral facilities. Results will be presented separately by Mr. Okuno and Ms. Saito at the same session as this presentation.

P22-03

The estimation of the lunar absolute radiance and reflectance by ground-based observation using a tunable liquid-crystal filter

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Although the Moon is our nearest neighbor, few studies about the lunar reflectance had been carried out. The lunar reflectance allows us to compare directly reflectance spectra of planetary materials with spacecraft data. McEwen (1996) derived the visible photometric function for the entire moon by utilizing the images taken by SSI onboard Galileo. The improved version (McEwen, 1998) was applied to the photometric normalization of lunar images from Clementine UVVIS camera. Although the images have a resolution of 100m per pixel, the values of reflectance appears to be too blight because of its calibration method. Recently the latest photometric models for 32 bands were reported by Robotic Lunar Observatory (ROLO) project (Kieffer 2005). However, the digital numbers of the reflectance images are not open to public. To gain a lunar absolute radiance and reflectance, the multi-band images of the lunar surface and those of some standard stars had been acquired. The location of the observation was Science City at the peak of Mt. Haleakala, Maui, Hawaii, USA. The dates of observation were August 15 – 26, 2005 and December 12 – 18, 2005. The images at five bands; 650, 750, 900, 950, and 1000 nm, had obtained. These images were obtained with a cooling CCD camera (Apogee, U260) mounted on a telescope (Vixen, ED80S) equipped with a tunable liquid-crystal filter (Cambridge Res. Inc., NIR-07). The absolute radiance was derived from the lunar multi-band images by following steps; (1) dark and flat-field correction, (2) atmospheric correction, (3) photometric correction, and (4) radiance calibration. To obtain extra-atmospheric intensity in the atmospheric correction, Langley plot (Langley, 1881) was applied. To remove the effects of observation geometry on the brightness of the moon caused by phase and libration, the photometric functions of Brown University (1995) and Yokota et al. (1998) were applied. In the radiometric calibration, Vega (Alfa Lyra) images of our observation and spacecraft data of Vega (Bohlin and Gilliland, 2004) are used for radiance standards. The lunar reflectance was calculated using the radiance images after photometric correction and the solar radiance estimated from the Plank's law of black body radiation. The resultant reflectance of the moon is about 0.6 times that of Clementine UVVIS images. On our poster the near-side images of the lunar absolute radiance and reflectance and the histogram of the reflectance will be presented.

P22-04

Mineralogy and chemical compositions of several eucrites: Implication for impact processing of the HED parent body

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Eucrites are basalts or gabbro probably made up the outer crust of the HED parent body, which may have been asteroid 4Vesta. Mesosiderites are polymict breccias composed of roughly equal proportions of metal and silicates, the latter of which is similar to HED meteorites. The genetic relationships between these meteorite groups are not clear. Mesosiderites may have formed by impact mixing of large metallic core fragments with the surface of a parent body similar to the HED parent body. The textures and isotopic ages of HED meteorites suggest that the parent body experienced a heavy meteorite bombardment ~4.1-3.5 Gyr ago. The nature of projectile materials that caused the meteorite bombardment is poorly known. To better understand the nature of projectile materials and genetic relationships between HED meteorites and mesosiderites, we performed a mineralogical and geochemical study of several brecciated and unbrecciated eucrites. ALH76005 is a polymict eucrite composed of a variety eucrite clasts, mineral fragments, and dark impact melt clasts. This meteorite contains grains of FeNi-metal in the clastic matrix, derived from projectiles. EET92023 and Dho 007 (EET/Dho) are coarse-grained cumulate eucrites formed in a crust of the parent body. Unlike monomict eucrites, EET/Dho contain a significant amount of FeNi-metals. The siderophile elements are highly enriched, and could have been introduced by impact events. The mineralogy of pyroxenes and FeNi metals suggest that EET/Dho have experienced a two stage thermal history: rapid cooling at high temperatures (~1000°C) and slow cooling at lower temperatures (<700°C), similar to those of mesosiderites. The siderophile abundance patterns suggest that Dho/EET and ALH76005 are related to mesosiderites. It appears that HED meteorites and mesosiderites form a continuum with respect to the abundances of FeNi metals. After large cratering events, thermal histories of individual meteorites vary significantly, considering the diversity in sizes and temperatures of the components in metal-rich and metal-poor regions. The large cratering events would explain a variety of breccia types, thermal histories, and the abundance patterns of siderophile elements.

O23-01

Evaporation and condensation kinetics for minerals and silicate melt

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At low pressures in the early solar nebula and circumstellar environments, condensation and evaporation are the fundamental phase change, which are responsible for chemical fractionation and in particular mass-dependent isotopic fractionation. The processes are kinetic that take place at the surface of condensed materials, of which kinetic parameters are obtained only by experiments. These processes are also affected by diffusion of species concerned within the condensed phase and the ambient gas, and vacuum evaporation is the only exception where the role of ambient gas can be neglected. Evaporation experiments have been extensively carried out in this decade and evaporation coefficients and kinetic isotopic fractionation factors have been obtained for minerals and silicate melts, which were applied to estimate the formation histories of dusts and chondritic components such as CAIs and chondrules (e.g., Nagahara and Ozawa, 2005).

Evaporation coefficient is the ratio of number of atoms evaporated against theoretical value estimated from the kinetic theory of gas. Experiments have been done mostly for forsterite and silicate melt, and Mg is the most extensively studied element. The evaporation coefficient of Mg is a function of temperature for forsterite and silicate melt, and it is anisotropic for olivine (including pure forsterite), which shows temperature dependence. The temperature dependence has a kink on the Arrhenius plot (Matsumoto et al., this volume). These results indicate the role of surface roughness on the evaporation coefficient, which has been pointed out by Young et al. (1998) as the role of breaking bond.

Mass dependent isotopic fractionation is kinetic distribution coefficient between the condensed phase and gas, which corresponds to the Rayleigh fractionation factor (square root of two masses) if there is no kinetic barrier. Experimentally determined isotopic fractionation factors are, however, closer to unity than the theoretical value for all the elements studied for forsterite and silicate melts, which means the presence of kinetic barrier. We have also shown anisotropy for Mg isotopic fractionation from forsterite, which is well understood by considering the difference in vibrational frequencies of two masses (Tachibana et al., this volume). Contrary to evaporation, condensation is hard to experimentally perform, and we have scarce kinetic data. Only one systematic data available is Fe metal, which is close to unity for a range of supersaturation (Ikeda et al., 2005) with small pressure dependence.

In summary, the origin of kinetic barrier for evaporation and condensation is now getting understood.

O23-02

Evaporation anisotropy of olivine

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Evaporation, which plays an important role in chemical and isotope fractionation at low pressures, is a surface reaction, and its kinetics is affected by surface conditions, such as roughness and density and orientation of dislocation outcrops. Recent experimental studies [e.g., Nagahara and Ozawa, 1999; 2000] have revealed anisotropy on evaporation kinetics for forsterite and Fe-Mg olivine, which includes those in the evaporation rate and surface microstructures. In order for better understanding the evaporation process, we carried out experiments in a wider range of temperature and discuss evaporation mode from temperature dependence of evaporation rates and surface microstructures.

Experiments were carried out in a vacuum heating chamber. Starting materials are single crystals of Fe-Mg natural olivine (Fo-90) and synthetic forsterite, which are cut into crystallographically oriented rectangular parallelepipeds. The experimental temperature in the present and our previous studies ranged from 1300 to 1600 °C for Fe-Mg olivine and from 1500 to 1750 °C for forsterite. Surface microstructures of experimental residues were observed with FE-SEM, and average evaporation rates are obtained by sample size and weight loss.

Fe-Mg olivine evaporates at larger evaporation rates with smaller anisotropy than forsterite does. The evaporation rate is (001)>(100)>(010) at temperatures above ~1500°C, which is consistent with forsterite in the same temperature range, whereas (001)>(010)>(100) below ~1500°C. This crossover between (100) and (010) at about 1500°C is attributed to enhancement of evaporation from (100) surface at higher temperatures due to a change in evaporation kinetics. STM observation on (010) surface shows that the surface is smooth with steps throughout the experimental temperature range, suggesting a common evaporation kinetics and nearly constant activation energy. FE-SEM observations on the (100) surface suggest that the surface is rough above ~1500°C and smooth below the temperature with appearance of many macro steps around dislocation outcrops. The crossover of the evaporation rate between (100) and (010) would be induced by roughening transition at around 1500°C for (100).

O23-03

Evaporation of forsterite in vacuum: anisotropy in rates and Mg isotopic fractionation

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Evaporation of condensed materials at low pressures plays important roles in chemical and isotopic fractionations in protoplanetary disks or in circumstellar environments. We have studied anisotropy of isotopic fractionation of Mg during evaporation of forsterite (Mg₂SiO₄) in vacuum. Ion-microprobe depth profiling of forsterite evaporated at 1500-1700°C in vacuum showed that the isotopic fractionation was limited near the evaporating surface and that the Mg isotopic zoning profiles are notably differ along the a-, b-, and c-axes, which can be attributed to anisotropy in self-diffusion coefficient of Mg (D_{Mg}) and an isotopic fractionation factor for evaporation of Mg (β). The D_{Mg} and β were obtained from zoning profiles by applying the diffusion-controlled isotopic fractionation model of Wang et al. (1999). The D_{Mg} is largest and smallest along the a- and c-axes, respectively. The activation energy of 560-670 kJ/mol indicates that Mg diffusion at 1500-1700°C occurred in the intrinsic diffusion regime.

The β along all the crystallographic orientations is closer to unity than that expected from the kinetic theory of gases, a square root of the inverse mass ratio of evaporating gas species containing different isotopes. Although the predicted β should be constant irrespective of crystallographic orientations, we found that β depends both on crystallographic orientations and on temperature. The β seems to be largest and smallest along the c- and b-axis, respectively, especially at higher temperatures.

We propose that the isotopic fractionation factor for kinetic evaporation can be expressed by the ratio between detachment rates of isotopes, which depend on vibrational frequencies between an adatom and a surface atom (or atomic cluster). If the vibration mode with a maximum frequency is responsible for detachment of adatoms, the isotopic fractionation factor can be expressed by the inverse ratio of reduced mass of the vibrating system. If we assume an adsorbed Mg isotope vibrates with a surface O atom or a SiO₄ tetrahedra, β corresponds to the range of the β obtained in this study and in previous studies. Anisotropy may also be explained by the difference of the surface atom (or atomic cluster) vibrating with Mg: the surface O atom may be the dominant species vibrating with Mg at the (010) surface with the largest bond density.

We relate such surface processes to the evaporation rate in vacuum, which is usually expressed only by the velocity of gas species detaching from the evaporating surface.

O23-04

Condensation experiments of metallic iron and accompanied isotopic mass fractionation.

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High temperature processes, such as evaporation and condensation, played an important role in the evolution of materials in the early solar nebula. So far, many experimental studies of evaporation and accompanied isotopic mass fractionation have been carried out. Although a limited number of experimental studies have been made on isotopic mass fractionation by condensation, isotopic mass fractionation caused by condensation of forsterite [1] differs from those expected from evaporation kinetics. Thus, we performed condensation experiments of metallic iron to understand isotopic mass fractionation by condensation.

Condensation experiments were performed using an evaporation-condensation furnace in vacuum. Metallic iron (180-320 mg) placed on the bottom of an alumina (or mullite) tube (5 mm in inner diameter and 180 mm long) was evaporated at 1350-1390°C for 2-8 hrs (evaporated mass: 2-10 mg). Metallic iron condensed along the cooler tube wall with a temperature gradient (~40 to ~180 mm from the bottom). Condensation products were observed and analyzed by an SEM/EDX system. Various morphologies of condensed metallic iron grains were observed as a function of condensation temperature. At high temperatures (above 1200°C), iron grains shapes were mainly close to cubes or rectangular parallelepipeds. At the temperatures from 1000°C to 1200°C, whiskers were mainly observed. At low temperatures (below 1000°C), the shapes were irregular or too small to be identified. The size of the condensed iron (< a few tens micron) in the present experiments is smaller than those in CH chondrites, which may be formed by condensation.

The isotopic compositions of Fe (⁵⁴Fe/⁵⁶Fe) in condensed iron grains were obtained using a SIMS. Isotopic mass fractionation was observed as a function of the condensation temperature. The degree of isotopic mass fractionation increases with decreasing the condensation temperature. This can be explained by the heavy isotope fractionated in the condensates from the gas phase. The present results are consistent with those of [1] while inconsistent with the isotopic mass fractionation simply expected from the Hertz-Knudsen equation. It should be noted that heavy isotopes are fractionated in a condensed phase by condensation for materials with different chemical bonds, metallic in the present experiments and ionic in [1]. Condensation coefficient in the Hertz-Knudsen equation may be dependent on the mass of atoms attached on the solid surface.

[1] Ueda et al. (1991) EPSL, 107, 138-147.

Non-Mass dependent oxygen isotopic fractionation of silicate grains during grain formation in various environments

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Oxygen isotopic compositions formed by non-mass dependent fractionation processes have been widely observed in calcium-aluminum rich inclusions (CAIs) and chondrules produced in the early solar nebula. So far, only photodissociation has been known to produce non-mass dependent oxygen isotopic fractionation. Therefore, the reason for the oxygen isotopic compositions of CAIs and chondrules has been discussed based on an ultraviolet photodissociation process of carbon monoxide in solar nebula¹.

Recently, we found that electrical discharge can produce non-mass dependent oxygen isotopic fractionation in refractory oxide grains^{2,3}. Presolar silicate materials, which are an important reservoir of oxygen in the early solar nebula, are believed to have been produced in high-temperature regions prior to the formation of the solar nebula. Our results may provide another possible path, caused by the processing of presolar silicate materials and leading to the non-mass dependent oxygen isotopic fractionation of CAIs and chondrules.

Silicate and iron oxide particles were produced from the gas phase in the Condensation Flow Apparatus between newly installed electrodes at the middle of the gas stream with a gap that could be set between 1-3 mm apart^{4,5}. An electrical discharge is made between the electrodes powered by a Tesla coil. Silane and/or pentacarbonyl iron were introduced into the apparatus together with an atmosphere dominated by hydrogen or helium mixed with oxygen or nitrous oxide. The total pressure was controlled to be either ~90 or 40 Torr. Smoke particles are produced and deposited on the each surface between the high-voltage and grounded electrodes.

The samples were sent to the University of California, San Diego for isotopic analysis. As a result, silica was shown to be non-mass dependently fractionated with positive values of up to 2.3 in $\Delta^{17}\text{O}$ when produced in an electrical discharge using oxygen gas. Nitrous oxide gas produced no fractionation. These experiments are still progressing. We will present temperature and gas species dependences for the observed fractionation processes combined with infrared spectra and transmission electron microscope observations.

[1] e.g., Yurimoto, H. & Kuramoto, K., *Science* 305 (2004) 1763. [2] Nuth, J.A., Kimura, Y., Thieme, M.H. & Chakraborty, S., *Proc. LPSC 37th* (2006) #1077. [3] Chakraborty, S., Thieme, M.H., Kimura, Y. & Nuth, J.A., *Proc. LPSC 37th* (2006) #1389. [4] Nelson, R., Thieme, M., Nuth, J., & Donn, B., *Proc. LPSC 19th* (1989) 559. [5] Nuth, J. A., Rietmeijer, F. J. M., & Hill, H. G. M., *Meteoritics & Planetary Science*, 37 (2002) 1579.

O23-06

Nickel isotopes in meteorites: Evidence for live ⁶⁰Fe and distinct Ni isotope reservoirs in the early Solar System

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With a half-life of 1.49 Myr, the ⁶⁰Fe-⁶⁰Ni decay scheme is well suited for dating events that occurred in the first 10 Myr of the Solar System. Further, Ni possesses two neutron-rich isotopes, ⁶²Ni and ⁶⁴Ni, considered to be produced through nuclear statistical equilibrium processes in neutron-rich supernova ejecta. Anomalous compositions of neutron-rich isotopes from iron group elements have been documented in normal and FUN calcium-aluminum-rich inclusions (CAIs) as well as in primitive and differentiated meteorites.

We measured the Ni isotope composition of seven iron meteorites (IIAB, IIICD, IIAB, IAB and IC), the carbonaceous chondrites Murchison and the terrestrial basalt BHVO-1 by MC-ICPMS. The analyses of the BHVO-1 terrestrial basalt and Murchison yielded $\delta^{60}\text{Ni}^*$ of $0.0008 \pm 0.0074\%$ and $0.0000 \pm 0.0071\%$, respectively, identical to the terrestrial standard solution. In contrast, all iron meteorites analyzed in this study show resolvable ⁶⁰Ni deficits ranging from $\delta^{60}\text{Ni}^*$ of $-0.0279 \pm 0.0107\%$ to $-0.0111 \pm 0.0065\%$. The Murchison carbonaceous chondrite has resolvable excesses in $\delta^{62}\text{Ni}$ and $\delta^{64}\text{Ni}$ of $0.0357 \pm 0.0103\%$ and $0.1030 \pm 0.0330\%$ relative to Earth. Irons meteorites are characterized by rather uniform deficits in $\delta^{62}\text{Ni}$ and $\delta^{64}\text{Ni}$ of $-0.0407 \pm 0.0223\%$ and $-0.1040 \pm 0.0279\%$.

The ⁶⁰Ni deficits observed in iron meteorites are consistent with Fe/Ni fractionation during the lifespan of ⁶⁰Fe. We infer that such deficits record the timing of primary Fe/Ni fractionation from a chondritic source reservoir leading to core segregation on differentiated asteroids. Using ⁵⁶Fe/⁵⁸Ni ratios estimated for the liquid core compositions, we calculate initial ⁶⁰Fe/⁵⁶Fe of $1.48 \pm 0.87 \times 10^{-6}$ for IIAB metals and $1.09 \pm 0.14 \times 10^{-6}$ for IAB metals, at the time of core formation. Assuming an initial ⁶⁰Fe/⁵⁶Fe of ca. 1×10^{-6} at the time of CAI formation, core formation on the IIAB and IIIB iron parent bodies occurred as early as 0.19 (+0.31, -0.27) and 0.86 (+1.91, -1.00) Myr prior to the CAI-forming event, respectively.

Together with previously published Ni data for Allende CAIs, our study demonstrates the presence of at least four distinct Ni isotope reservoirs in the early Solar System. While CAIs exhibit $\delta^{62}\text{Ni}$ and $\delta^{64}\text{Ni}$ excesses compared to Earth, iron meteorites are characterized by relatively uniform deficits. Moreover, Carbonaceous chondrites show resolvable $\delta^{62}\text{Ni}$ and $\delta^{64}\text{Ni}$ excesses, but of lesser magnitude to that observed in CAIs. Iron meteorite parent bodies thus accreted from precursor material isotopically distinct from that of carbonaceous chondrites and Earth. These results provide important constraints regarding the genetic relations between early Solar System planetesimals and demonstrates the presence of large scale Ni isotopic heterogeneity within the accretion disc.

O23-07

Origin and evolution of oxygen isotopic compositions of the solar system

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The oxygen isotopic variations among planets, chondrite and achondrite asteroids, and meteoritic components (refractory inclusions, chondrules, and matrix) provide key constraints for understanding the origin and evolution of our protoplanetary disk. Oxygen isotopic composition of the Sun is unknown but probably ¹⁶O-rich. Oxygen isotopic variations in solar system materials are far larger than observed for other elements, and do not reflect nucleosynthetic processes in stars. Instead they result from processes in the parent molecular cloud and the protoplanetary disk. On a three-oxygen isotope diagram ($\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$) compositions of the Earth, Moon, Mars, and most achondrites plot along mass-dependent fractionation slopes of $\sim 1/2$, whereas those of chondrules and refractory inclusions plot along mass-independent fractionation slope of ~ 1 and show a large range of $\Delta^{17}\text{O}$ (-35% to $+5\%$). These mass-independent variations in oxygen isotope compositions of chondritic components most likely resulted from mixing of ¹⁶O-rich and ¹⁶O-poor solids and gas during thermal processing of dust in the protoplanetary disk. Based on the astronomical observations of star-forming regions, theoretical models of the protoplanetary disk evolution, and meteoritic data, mass-independent fractionation of oxygen isotopes recorded by meteorites has recently been attributed to isotopic self-shielding during the ultra-violet (UV) photolysis of CO in an initially ¹⁶O-rich ($\Delta^{17}\text{O} \sim -25\%$) protoplanetary disk or parent molecular cloud. According to these models, the UV photolysis preferentially dissociates C¹⁷O and C¹⁸O in certain zones of the protoplanetary disk or the parent molecular cloud. If this process occurs in the stability field of water ice, the released atomic ¹⁷O and ¹⁸O are incorporated into water ice, while the residual CO gas becomes enriched in ¹⁶O. Subsequent enhancement of ¹⁶O-depleted water ice relative to ¹⁶O-enriched CO gas in the midplane of the protoplanetary disk outside the snow line, followed by radial migration of icy bodies towards the proto-Sun and their evaporation can potentially result in generation of an ¹⁶O-poor gas. The ¹⁶O-poor gas can be delivered to the inner solar system by astrophysical mechanisms. Correlated study of oxygen isotope compositions and ²⁰⁷Pb-²⁰⁶Pb absolute and ²⁶Al-²⁶Mg relative ages of chondrules and refractory inclusions in primitive (unaltered) chondrites suggest that the inner solar system was ¹⁶O-rich when refractory inclusions formed, but less than 0.8 Ma later, gas in the inner solar nebula became ¹⁶O-poor and this state appears to have persisted at least 1-2 Myr later, possibly until dissipation of the solar nebula.

O23-08

Time interval of formation for a type B2 CAI.

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Calcium, aluminum-rich inclusions (CAIs) consist of high temperature minerals in the solar nebula; i.e., spinel, melilite, fassaite and anorthite. CAIs show the oldest age in the solar system [1] and formed over a short time interval [2]. The initial value of (²⁶Al/²⁷Al)₀ of many CAIs is typically $\sim 5 \times 10^{-5}$, but smaller values have often been reported [3]. The variation corresponds to formation interval if ²⁶Al distributes homogeneously in the solar system, and is inconsistent to the brief formation interval of CAIs. Here we report a CAI consisting of minerals with and without live-²⁶Al. Because heterogeneous O-isotopic distribution among minerals in the CAI indicates that the CAI have experienced multiple melting events in the solar nebula [4, 5], the variation of ²⁶Al shows CAI forming thermal process continued several Myrs in the early solar system. This time scale overlaps with chondrule formation in the early solar system.

We analyzed Mg-isotopic compositions of individual minerals in the type B2 CAI from the Vigarano meteorite using a CAMECA ims 1270 SIMS instrument. Melilite, spinel and fassaite had ²⁶Mg excesses of 5.2 ± 1.0 , 5.1 ± 0.7 and 4.2 ± 0.5 times 10^{-3} for the initial values, respectively. This result indicates that these minerals had formed in the very early age of the solar system. In contrast, anorthite grains have no clear ²⁶Mg excesses ($-0.4 \pm 3.5 \times 10^{-6}$) indicating at least 2.6 Myr late formation after other mineral crystallization in the CAI. The abrupt O-isotope change within a single crystal of anorthite [5] indicates that the anorthite is crystallized in liquid and diffusive migration of Mg in anorthite after crystallization cannot erase the ²⁶Mg excesses even if anorthite originally had similar ²⁶Mg excesses like other minerals of the CAI. Therefore, the absence of clear ²⁶Mg excesses in the anorthite is not due to secondary disturbance but primary at crystallization. These results suggest that formation process of the CAI had continued during ~ 2.6 Myr.

[1] Amelin Y. et al. (2002) *Science* 297, 1678-1683. [2] Bizzarro et al. (2004) *Science* 331, 275-278. [3] MacPherson et al. (1995) *Meteoritics*, 30, 365-386. [4] Yoshitake M. et al. (2005) *GCA* 69, 2663-2674. [5] Nagashima K. et al. (2004) *Chondrites and the Protoplanetary Disk* conf. 153-154.

Oxygen and Al-Mg isotopic compositions of a barred olivine chondrule from NWA1152 C3-ungrouped chondrite.

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With the discovery of the existence of ¹⁶O-rich reservoir in the chondrule formation region (e.g., Kobayashi et al., 2004), the oxygen isotopes evolution among the CAIs and chondrules are controversial; contemporaneous formation of chondrules and CAIs, that is, not only from ¹⁶O-rich to ¹⁶O-poor but also from ¹⁶O-poor to ¹⁶O-rich (e.g. Itoh and Yurimoto, 2003), especially that of chondrule forming region is unclear. In this study, we report the petrography, high precision oxygen and Al-Mg isotopic compositions in the barred olivine chondrule from NWA1152 C3-ungrouped chondrite, in order to estimate the oxygen isotopes evolution between CAIs and chondrules in the early solar system. The C1m chondrule in a barred olivine chondrule (~1.5mm across) surrounded by porphyritic igneous rim (~200µm in width). The barred olivine chondrule consists of platy olivine crystals (Fo₉₀) and blocky subhedral spinel grains (Mg-sp) embedded in a mostly subhedral large crystalline Al-rich diopsides (Di) and mesostasis. The igneous rim mainly consists of pigeonite phenocrysts embedding euhedral olivine crystals and Fe-Ni metals.

The oxygen isotopic compositions of the barred olivine part are distributed around SMOW value ($\delta^{17,18}\text{O}_{\text{SMOW}} = -0\text{‰}$), while the igneous rim of pigeonite and olivine crystals are slightly enriched in ¹⁶O ($\delta^{17,18}\text{O}_{\text{SMOW}} = -5$ to -12‰) relative to the barred olivine part.

The Al-Mg isotopic compositions of spinel, olivine, Al-rich diopside and rim of pigeonite grains were measured. The spinel only shows the clear excesses of ²⁶Mg isotope ($(^{26}\text{Al}/^{27}\text{Al})_0 = 1 \times 10^{-5}$).

The oxygen isotope disequilibrium between the core and igneous rim suggests that the formation process of C1m results from the multiple heating. Based on the chemical composition and oxygen isotopic compositions in igneous rim that is enriched in ¹⁶O relative to that of core, these results suggest that the ¹⁶O-rich Si-rich gas reservoir exists in the chondrule formation region. This might be caused by the fluctuation of oxygen isotopic compositions in the solar nebula (Itoh and Yurimoto, 2003).

The ²⁶Mg* distribution among core minerals suggests that formation of this chondrule started at least ~2Myr after CAI formation having the canonical values and continued several Myrs. After the barred olivine chondrule formation, the igneous rim was formed in the ¹⁶O-enriched nebular environment. This suggests that ¹⁶O-rich reservoir existed in the chondrule formation region at several Myrs after the CAI formation.

Crystallization experiment of amorphous silicates with the CI chondritic composition

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The authors performed heating experiments of amorphous silicates with the CI chondritic composition for analogue of cosmic dust in circumstellar environment around oxygen-rich young star. Two kinds of the starting amorphous silicate samples were synthesized by the Sol-Gel method; one contains all iron as divalent (Fe/Si = 0.90) and the other contains iron (Fe/Si = 0.39), where the rest of iron forms FeS and not included in the amorphous silicate. The infrared (IR) spectrum of the amorphous sample showed two broad absorption peaks at 10- and 20-µm bands, which were attributed to the Si-O stretching and O-Si-O bending vibrations, respectively. The amorphous samples were heated to investigate temperature and time dependences of crystallization. In the IR spectra, the absorption peaks of olivine grew gradually with increasing heating duration at a constant temperature or increasing temperature for a constant duration. The amorphous silicate with the lower iron content crystallized more rapidly than that with the higher iron content. Mg-rich, nearly endmember, olivine crystallized in the early stage of the crystallization from the iron-contained amorphous silicate and iron content of olivine increased gradually. The authors performed an IR spectral fit of the heated samples and estimated the degree of crystallization quantitatively. Using this parameter, crystallization process could be formulated using the Johnson-Mehl-Avrami equation.

Diamond formation in interstellar clouds and parent bodies of carbonaceous chondrites

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We performed experiments simulating the formation of organic materials by UV irradiation of the ices in a molecular cloud and the processing of organic materials in a diffuse cloud to investigate the possible role of these processes in diamond formation. TEM observation of molecular cloud organics shows the existence of diamond precursors. Further UV-irradiated molecular cloud organics, diffuse-cloud organics analogs, clearly reveals diamond crystals, demonstrating that diamond precursors nucleated by UV irradiation in the molecular cloud could easily grow into nanodiamonds around 5 nm in a diffuse cloud within 10⁵ years.

Interstellar organic grains undergo heating and partial evaporation upon formation of the solar nebula. These grains grew by aggregation into planetesimals and then into meteorite parent bodies. To investigate these processes, we performed experiments simulating aqueous alteration and subsequent thermal metamorphism for parent bodies of C-chondrites. Aqueously-altered molecular-cloud organics analog showed a halo electron diffraction pattern suggesting an amorphous structure. While, heated samples after aqueous alteration contain both graphite and diamond crystals. This indicates that the aqueous alteration and subsequent thermal metamorphism of molecular-cloud organics produces diamond by a presently unknown mechanism.

Although numerous models have been proposed for the formation of presolar nanodiamonds found in chondrites, it remains unclear how these diamonds formed. In particular, no model has satisfactorily explained the large abundance of diamond as compared to SiC and graphite and the carbon isotope ratio found. If we assume that diamonds can form in interstellar clouds and/or on the parent bodies of C-chondrites as demonstrated in the present study, then all features could be explained reasonably. Several types of presolar nanodiamonds have been reported, suggesting that diamonds could originate from many sources. The results of the present experiments support two possible diamond formation sites: interstellar clouds and parent bodies of C-chondrites.

Origin of olivines in Type I chondrules

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It is generally inferred that chondrules formed about 4.56 billion years ago within 5 AU from the proto-Sun as solidified melt droplets freely floating in space by melting of fine-grained solid precursor materials, and that during these melting events chondrules behaved as closed systems, both chemically and isotopically; i.e., the observed range in chondrule bulk chemistry and modal mineralogy was entirely inherited from solid precursor materials that experienced melting to various degrees followed by igneous crystallization. Shock-wave heating is currently considered to be the most plausible chondrule-forming mechanism. Our petrologic survey of Type I chondrules in the CV carbonaceous chondrite revealed the presence of olivine-rich aggregates showing granoblastic textures and composed of coarse-grained forsteritic olivines and Fe,Ni-metal nodules. Such textures are easily recognizable in optical microscope using transmitted cross-polarized light, but can be missed if studied only in backscattered electron images using scanning electron microscope. In two dimensions, the aggregates consist of polygonal, misoriented, olivine grains showing triple junctions with interfacial angles around ~120°. In some of these aggregates, olivine-olivine and olivine-metal grain boundaries are dry, i.e., lack any layer of glassy mesostasis. In lithic clast-bearing, Type I chondrules with high abundance of glassy mesostasis, some of the olivine-olivine grain boundaries in lithic clasts are separated by thin layers of glass (i.e., wet), whereas others remain dry. Olivine grains with wet contacts have rounded outlines, indicating dissolution in chondrule glass. The aggregates are surrounded by shells of low-Ca pyroxene and glassy mesostasis, commonly observed in Type I chondrules in ordinary and carbonaceous chondrites, and by fine-grained, matrix-like rims. Formation of the granoblastic textures requires sintering and prolonged, high-temperature (>1000°C) annealing – conditions which are not expected in the solar nebula during chondrule formation, but could have been achieved on parent bodies of olivine-rich differentiated meteorites e.g., ureilites and brachinites. We conclude that the lithic fragments in CV chondrules are relict grains resulting from fragmentation of unidentified differentiated planetesimals. Magnesian Type I chondrules are thus complex objects composed of an inherited component, mainly forsteritic olivine and (Fe,Ni)-metal, originated from olivine-dominated (dunite-like) mantle material of earlier generations of differentiated planetesimals, and an igneous component equilibrated with nebular gas – glass, low-Ca pyroxene, high-Ca pyroxene, and silica phase. This implies that Type I chondrules are not as pristine as conventionally viewed; they consist of nebular and asteroidal materials and must have postdated accretion and differentiation of some early generation planetesimals.

Shock-Wave Heating Model for Chondrule Formation: Relation between External Shapes of Molten Droplets and Non-spherical Chondrules

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Chondrules are millimeter-sized, spherical-shaped grains universally contained in chondritic meteorites. They are considered to have formed from chondrule precursor dust particles; they were heated and melted through flash heating events in the solar nebula and cooled again to solidify in a short period of time. The shock-wave heating model is considered to be one of the most plausible models for chondrule formation. In this model, shock waves cause a high-velocity rarefied gas flow around chondrule precursor dust particles. If dust particles have asymmetrical shapes, they would begin to rotate in the gas flow. Therefore, it can be considered that rotating molten dust particles are exposed to the high-velocity gas flow. The external shapes of molten droplets deform due to the effects of the gas drag force and the dust rotation. The deformation of molten droplets might reflect chondrule shapes. In fact, three-dimensional measurement of chondrule shapes shows that most of them has deformation of some degree. However, it has not been well investigated how the rotating molten droplets deform in the high-velocity gas flow.

The purpose of this study is to investigate the deformation of rotating molten droplets exposed to the gas flow. We perform the three-dimensional hydrodynamic simulations of molten droplets. We take into account not only the gas frictional force acting onto the molten droplets but also the dust rotation. As the first step for elucidating the origin of chondrule shapes, we consider relatively low-viscous fluid as molten droplets in this study. We found that the dust rotation plays an important role to bring about the diversity of chondrule shapes; droplet shape changes from oblate to prolate as the rotation becomes faster. We also analytically derived the three-dimensional shapes of the droplets (linear solution) and confirmed that results of hydrodynamic simulations well match with the linear solution when the rotation speed is not so large. In cases of more rapid rotation, our numerical simulations indicate more largely deformed prolate shapes. The sequence of the shape change as rotation speed increases well matches with the chondrule data. These results indicate that the shock-wave heating model has a strong possibility to explain not only the thermal evolution of the precursor dust particles but also the external shapes of chondrules.

O23-14

Compound Chondrule Formation in Shock-Wave Heating Model

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Chondrules are 0.1-1 mm-sized spherical silicate objects in chondritic meteorites. It is considered that chondrules were formed in the protoplanetary disk through melting. Since the temperature of the protoplanetary disk is not high enough to melt silicate material, some transient heating processes should be present to form chondrules. Though the chondrule forming heating process has not been revealed yet, it is thought that the shock-wave heating mechanism is a promising model.

Compound chondrules, which consist of two independent chondrules, are present in chondrites. A number ratio of them to single chondrules is about 5 %. Compound chondrules are thought to be formed by collision of two molten particles. Previous work on the compound chondrule formation, especially based on the shock-wave heating model, is very limited. In this study, we examine the formation process of compound chondrules in detail in the framework of the shock-wave heating model. To collide two particles and coalesce together, some physical quantities should meet appropriate conditions. For example, the number of collisions should be larger than a certain value, and the collision velocity should be smaller than a certain value so that the particles would not be destructed.

First, we considered processes by which the particle number density in the post-shock region is enhanced. Dust particles entering to the shocked region could be destructed mechanically by the gas ram pressure in the post-shock region. And partially molten part of the particle would be stripped off. Moreover, the collisional destruction between particles could happen. Those processes generally produce many dust particles, which we call here secondary particles. Then, the number density is enhanced locally.

Second, we examined the collision velocity. It was noted that the relative velocity among secondary particles and between the initial and secondary particles could be small enough. Then, it is expected that the collisions between those particles could form compound chondrules without leading to destruction.

Phenomena introduced above are complicated in general. So, it is not easy to precisely estimate the probability of compound chondrule formation, but it is possible to evaluate its order of magnitude value based on the shock-wave heating model. According to our estimation, it seems likely that the compound chondrules can be formed in the shock-wave heating model.

O23-15

Experimental investigation of wetting textures in the Fe-Ni-S system; Application to Bencubbin-like (CB) meteorites

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Some metal globules in Bencubbin-like meteorites display peculiar metal-sulfide assemblages (e.g., Newsom and Drake, 1979, GCA, 43:689-707, their Fig. 4). To better understand the textural relationships of sulfide phases with (Fe,Ni) metal, we carried out an experimental study aimed at: (i) characterizing the wetting behavior of a small fraction of (Fe,Ni,S) liquid in a polycrystalline aggregate of (Fe,Ni); and (ii) quantifying the kinetics of textural equilibration of the sulfide phase when a partially molten Fe-Ni-S system is cooled below the eutectic temperature.

The wetting experiments were conducted at 0.1 MPa and $T = 950\text{--}1250^\circ\text{C}$, in the Fe-S, Ni-S and $(\text{Fe}_{90}\text{Ni}_{10})\text{-S}$ systems. The starting mixtures of metal and FeS were adjusted in order to yield 10 vol. % of sulfide liquid at the temperatures of the experiments. Equilibrium textures were observed for run durations of 24 hrs. At 1100°C , the dihedral angles θ_{SMM} at the junction of the sulfide phase with two metal grains were measured to be 29° in the Fe-S system, 27° in the $(\text{Fe}_{90}\text{Ni}_{10})\text{-S}$ system, and 11° in the Ni-S system. These low values of θ_{SMM} indicate that a small volume fraction of sulfide liquid dispersed in polycrystalline metal should form an interconnected network along grain edges. The effect of T was investigated in the Fe-S system from 1025 to 1250°C and was found to be negligible, within the error of measurements ($\pm 2^\circ$).

In the kinetic experiments, samples were first equilibrated at 1100°C for 24 hrs, then rapidly cooled below the eutectic temperature (980°C), and finally held at 950°C for variable durations of 4 to 100 hrs. Upon solidification, the dihedral angle increased from 29° to 89° , leading to rapid textural changes such as a decrease of the surface/volume ratio of sulfide pockets at grain edges.

By comparison to the experiments, we conclude that the metal-sulfide assemblages observed in Bencubbin-like meteorites can be interpreted as equilibrium textures of a sulfide liquid within polycrystalline aggregates of metal. Sulfide pockets show evidence of moderate subsolidus textural reequilibration. From the kinetic experiments, these assemblages should have been maintained at high temperature for durations in the order of a few days. These constraints are compatible with a genetic model based on shock for the Bencubbin-like meteorites (Kallemeyn et al., 1978, GCA, 42:507-515.)

O23-16

Magnetic alignment of enstatite and forsterite detected by weak field of a horseshoe magnet and determination of field structure in young stellar objects

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Magnetic alignments of minerals are believed to occur only for particles which possess spontaneous magnetic moments at present. We report significant rotational oscillation due to anisotropy of paramagnetic susceptibility $(\Delta\chi)_{\text{PARA}}$ for large single crystals of forsterite and enstatite at a weak field of 200 G produced by a horseshoe magnet; magnetic oscillations of ordinary oxide minerals without spontaneous moments at this field intensity do not appear in previous literatures. Similar efficiency of magneto-rotation due to $(\Delta\chi)_{\text{PARA}}$ is expected for most of the rock forming minerals, which usually possess comparable amount of $(\Delta\chi)_{\text{PARA}}$ caused mainly by the Fe ions. Precise $(\Delta\chi)_{\text{PARA}}\text{-}T$ relationships were obtained from the period of oscillation at temperatures between $T = 300\text{--}100\text{ K}$. Possibility of new types of magnetic effects on ordinary rock forming minerals in various cosmic and terrestrial conditions may be considered based on the measured $(\Delta\chi)_{\text{PARA}}$ values. One of such possibility is concerned with the mechanism of dust alignment due to magnetic field in planetary formation region. Magnetic field is one of the major factors which control stellar and planetary formation; circumstellar field is estimated by light polarization due to dust alignment. The mechanism of alignment is an open question as yet. Therefore, field intensity to achieve alignment B_s was measured in the present work for micron-sized enstatite and forsterite; these minerals were recently identified as the major materials of dust particles in planetary formation regions. An apparatus using He gas as dispersing medium was capable in reproducing dust alignment in a temperature range of $T = 300\text{ K}$ and 10 K , because He gas is a unique medium that can disperse grain and remain as a fluid at low temperatures. The above temperature range is comparable to that estimated for the circumstellar region. B_s of enstatite reduced from 1200 to 210 G when temperature decreased from $T = 298\text{ K}$ to 88 K. Magnetic alignment of solid particles without spontaneous moments were not achieved at such low field previously. This occurred because $(\Delta\chi)_{\text{PARA}}$ is proportional to the reciprocal of T following a Curie law; this temperature dependence was confirmed from the above measurements. Partial alignment large enough to cause observable polarization is expected for the YSO conditions according to measured $B_s\text{-}T$ relationship and a paleomagnetic data on meteorites; the lower limit of field intensity of planetary formation region is estimated to be about $B = 1\text{ G}$ from remnant magnetization of primitive meteorites.

P23-01

Fe-Mg interdiffusion in olivine at 1 atm and in vacuum: temperature dependence and anisotropyH. Kawasaki¹, S. Tamada¹, S. Tachibana¹, H. Nagahara¹, K. Ozawa¹, and N. Matsumoto¹¹Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Tokyo, 113-0033, Japan
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Diffusivity of ions in minerals can be used to incorporate time into studies of various geological processes such as thermal and deformation histories of rocks and minerals. Numerous previous studies have determined an Fe-Mg interdiffusion coefficient ($D_{\text{Fe-Mg}}$) in olivine, one of the major rock-forming minerals, and have discussed diffusion mechanisms of divalent cations in olivine. Here we present new experimental data on Fe-Mg interdiffusion in olivine at 1 atm in the temperature range of 1400-1600°C using the diffusion couple technique.

Single crystals of synthetic forsterite and San Carlos olivine (Fo_{91} and Fo_{80}) were aligned along the a-, b-, or c-axis and tied with platinum wire as a diffusion couple. The diffusion couples were annealed at a desired temperature for 26-73 hours in a one-atmosphere gas-mixing furnace at a controlled oxygen fugacity (f_{O_2}). The Fe-Mg diffusion profile was obtained with EPMA, and $D_{\text{Fe-Mg}}$ was determined by the Boltzman-Matano analysis.

We found little compositional dependence of $D_{\text{Fe-Mg}}$ within the compositional range of Fo_{100} - Fo_{89} . The obtained $D_{\text{Fe-Mg}}$ shows anisotropy within all the temperature range at f_{O_2} of $10^{-7.5}$ bar; $D_{\text{Fe-Mg}}$ is largest (or smallest) along the c- (or a-) axis. A similar anisotropy of $D_{\text{Fe-Mg}}$ was obtained in vacuum evaporation experiments of olivine at 1400°C by Ozawa and Nagahara (2000), but the degree of anisotropy of $D_{\text{Fe-Mg}}$ in vacuum is greater than that at 1 atm. $D_{\text{Fe-Mg}}$ along the c-axis in vacuum (Ozawa and Nagahara, 2000) is ~3 times larger than that obtained at 1 atm in this study. This seems to be consistent with the results by Düffels et al. (2004) although the f_{O_2} dependence should be taken into account.

The activation energy of $D_{\text{Fe-Mg}}$ for Fo_{95} was ~210, ~290, and ~290 kJ/mol along the a-, b- and c-axis, respectively, which is consistent with those obtained at lower temperatures (e.g., Chakraborty et al., 1997), implying that Fe-Mg interdiffusion mechanisms at 1400-1600°C are the same as that at lower temperatures. If the Fe-Mg interdiffusion at temperatures below 1300°C is controlled by the presence of impurities in olivine (e.g., Chakraborty et al., 1997), diffusion at temperatures above 1400°C may also occur in the extrinsic diffusion regime.

We compare $D_{\text{Fe-Mg}}$ in this study with those obtained in vacuum evaporation experiments of olivine at temperatures (Nagahara and Ozawa, 2000; Matsumoto et al., this volume) and discuss the diffusion mechanisms of Fe and Mg in olivine at 1 atm and in vacuum.

P23-02

Volatile signatures and geochemical characteristics of impact melt products from the Lake Bosumtwi impact structure, Ghana, W. Africa, and Ivory Coast tektitesB. Kreher-Hartmann¹, F. Langenhorst¹, A. Deutsch², U. Bläß¹, K. Heide¹¹Institute of Geoscience, Friedrich-Schiller-Universität Jena, Burgweg 11, D-07749 Jena, Germany
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The Lake Bosumtwi Impact structure in Ghana, West Africa, is a young (1.07 Ma), excellently preserved crater and one of only four known craters associated with a tektite strewn field. In context with the International Continental Drilling Projects (ICDP) this large crater (10.5 km in diameter) had been drilled in 2004. In connection to Bosumtwi there are glasses from three different localities known. (1) Ivory Coast (IVC) tektites, (2) microtektites from a strewn field in the Atlantic Ocean, and (3) impact glasses from suevites outside the crater.

The drill cores contain mainly brecciated meta-sediments such as carbonaceous greywackes, carbon-rich phyllites, and argillaceous schists to slates. The breccias document a low grade of shock metamorphism. Particles of impact glasses and diaplectic glasses are very rare. Outside the crater rim, however, various impact glasses occur in suevites. For the present study, we are using such glass-rich suevites and IVC tektites (courtesy of MPI Heidelberg/ Germany). For characterisation of the glasses we have employed optical and electron microscopy, thermogravimetry coupled with mass spectrometry (DEGAS - Directly coupled Evolved Gas Analyzing System) and analytical energy-filtered TEM techniques. The goals of this study are to (i) determine the precursor rocks to the impact melt products and (ii) constrain the cooling history of impact glasses.

Under the microscope three different types of glasses have been detected in the suevites: (1) Coesite bearing diaplectic quartz glasses (2) mineral glasses with fluidal textures and (3) heterogeneous ("mixed") glass splinters which are rich in bubbles and contain striae. The DEGAS analytics show the release of low amounts of water indicating the presence of clay minerals as lining around the bubbles. Furthermore traces of CO_2/CO , SO_2 and H_2 (ordered according to decreasing contents) have been detected. Contrary to that the Ivory Coast tektites are totally degassed.

The TEM studies on bubble-rich glasses show noticeable heterogeneities in the distribution of Al and Si, and glass - glass-exsolutions in a SiO_2 -rich matrix occur. This observations point to low cooling rates at the glass transition temperature. The exsolved glass spherules show very high Al_2O_3 -contents (up to 56 wt%). The best explanation for the high total Al_2O_3 -contents (about 22 wt%) in some glasses is that staurolite-bearing mica schist are one prominent precursor lithology. Such rocks occur as clasts in the suevites.

P23-03

High Sensitive Ion Imaging System using Direct Combination of Stacked-type Solid-State Imager and Microchannel Plate

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Imaging system for ions and electrons of keV energy level is useful for instruments for surface analysis. Recently, a direct imaging system capable for charged particles has been proposed. This system is suitable for precise isotopic imaging for long accumulation time with slow readout. In this study, an ion imaging system operated in both high sensitive and high precision modes has been developed using a combination of stacked-type solid-state imager (SCAPS) and microchannel plate (MCP).

The SCAPS is an integral-type 2D detector with 576 x 600 independent pixels that have several advantages including direct detection for charged particles, low dark current, wide dynamic range, no insensitive period, and high fill factor. In order to detect single incoming ions, a MCP is settled in front of SCAPS device to amplify the incident ion signal. A noteworthy feature of new system is that the MCP device is removable from the SCAPS and re-mountable onto the SCAPS in vacuum. This mechanism enables to switch the system from high sensitive, high speed mode to conventional high precision mode and vice versa.

The vacuum chamber of this system is composed of MCP movement unit, SCAPS cooling unit with liquid nitrogen, multipin-mini-electronic feedthrough specially ordered for the SCAPS package and electrical driving circuit. New electronic system is applied that composed of voltage supply, pulse generator and readout circuit. We use PXI-bus unit for this system fully controlled by LabVIEW (National Instrument) software. Using this electronic control system we expect that more flexible systemic change could be enabled and that optimization of analysis could be much easier than ever before.

Capabilities of single ion detection of this system were evaluated using a sector-type stigmatic secondary ion mass spectrometer (ims-1270, CAMECA). The secondary ion intensity during the experiment was adjusted to 100 ions per one image frame. This condition avoids multiple ion incidences into the same channel of MCP for an accumulation time of one SCAPS frame. The load voltages for MCP were changed from -900V to -1100V in order to control the MCP gain.

The detected ion counts become saturated over the voltages of about 1kV. The saturated level is about 60 ions per frame. This value is about 60% of incident ion numbers. Because the open area ratio of the MCP is 58%, the saturated level shows that this system accurately detected the single incident ions.

O24-01

Sequestration of Cu from mineral sources by type II methanotrophs

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Subsurface microbial communities are intimately associated with the rocks and minerals that comprise their habitat. This interaction has profound implications for the weathering rates of minerals that serve as a source of terminal electron acceptors, nutrients, or trace metals for microorganisms. An emerging example of this type of microbe-mineral association is the intimate relationship between Cu availability in the environment and methanotroph ecology and metabolism. We are currently investigating the relationships among Cu-bearing mineral phases, methanotroph selection, and methane oxidation rates in soil environments. Here we present new insights into acquisition strategies by methanotrophic bacteria to sequester copper from minerals and the relationship between soil mineralogy and the distribution of methanotrophs in the subsurface. Specifically, we investigated the extracellular Cu-binding molecule, methanobactin, produced by the type II methanotroph, *Methylosinus trichosporium* OB3b, and its ability to mobilize Cu from tropical oxisols and primary silicates. 24-hour batch dissolution experiments demonstrate that methanobactin readily acquires copper from soils at methanobactin:Cu ratios of 1:1 and 5:1. Sequential extraction data of these soils suggest that Cu is associated with the silicate, organic, and oxide fractions. Steady-state Cu concentrations from batch experiments correlate to the more available, though less concentrated, oxide and organic fractions. Methanobactin also increased the release of Cu from feldspar (anorthoclase; CuO = 10 ppm) compared to controls, but at minimal levels in comparison to soils with more available Cu. This suggests that Cu-associated with silicates in the presence of air and methane may not support substantial methane oxidation. Methanotroph populations associated with the investigated oxisols were also characterized and reveal that methanobactins may, in fact, be very broadly present in nature. *Methylosinus sporium* sp. NRVK was isolated from shallow depth in a Panamanian oxisol and characterized using 16S rDNA clone libraries. This organism produces a new methanobactin very similar to methanobactins from *M. trichosporium* OB3b and *Methylococcus capsulatus* based on spectra from Negative ion MALDI-TOF mass spectrum data. Although we lack structural detail for the NR3K methanobactin molecule, its MW is 1218 Da and it has similar Cu-binding characteristics to the *Methylococcus capsulatus* OB3b methanobactin. The size and superficial function of the two molecules are very similar, suggesting that methanobactins might have some structural and functional consistency. Given this, identifying other methanobactins in nature and linking their presence to methanotroph activity is the next critical step in determining what regulates methane-oxidation rate in nature.

O24-02

The role of bacteria in secondary gold formation

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The role of bacteria on the mobility of gold has been examined under controlled conditions in order to understand the origin of secondary gold deposition, and the effect of complex organic/inorganic reactions on the morphology of gold particles. Growth of an *Acidithiobacillus thiooxidans* on media containing thiosulfate and gold thiosulfate as their source of energy decreased the pH of the culture medium from pH 5.4 to 1.9 and increased the Eh from 0.3 to between 0.5-0.6 Volts. The gold was stable in the bacterial systems until sulfur oxidation was complete, then the bacteria precipitated fine-grained colloidal gold (5-10 nm) inside the bacterial cells and µm-scale crystalline gold in the bulk fluid phase. Sulfate reducing bacteria, which utilise oxidized sulfur species as their terminal electron acceptor, were able to precipitate gold from gold thiosulfate. The gold precipitated intracellularly as nm-scale colloids, and extracellularly, as nm-scale colloids within biogenic FeS(s), µm-scale spherical aggregates of gold and µm-scale, octahedral gold. In chemical control experiments, gold was not precipitated under similar experimental conditions and duration. The reaction between filamentous cyanobacteria (i.e., *Plectonema boryanum* UTEX 485) and aqueous gold-chloride killed the cultures instantly and resulted in quantitative precipitation of crystalline octahedral (111) gold. The particle size of the gold was directly proportional to temperature, ranging from 1.5 µm at 25°C to 10 µm at 100°C. Real-time absorption spectroscopy (XAS) experiments have demonstrated that the reduction mechanism of gold(III)-chloride to elemental gold by cyanobacteria involves the formation of intermediate Au(I) species as gold(I)-sulfide. Addition of gold(I) thiosulfate complex to *Plectonema boryanum* at 25°C resulted in the division of the filamentous cyanobacteria into individual cells. Precipitation of gold occurred as fine grained (≤10 nm) gold nanoparticles within the cells and in association with membrane vesicles released by the cyanobacteria. At elevated temperatures, 60 to 200°C, cubic nanoparticles (~25 nm) of gold precipitated on the cell surfaces. TEM-EDS indicated Au:S ratios close to 3:1, and XPS showed that the sulfur was present dominantly as reduced species. XPS indicates the presence of Au⁰ along with dominant peaks positioned between gold (I) and gold (III) that may represent organically-bound Au in the interior of the cells. Under abiotic conditions, the gold chloride and gold thiosulfate complexes were stable for one month at 25°C; nanoparticles of gold were precipitated in the blank experiments at 60 to 200°C.

O24-03

Cyanobacterial calcite nucleation: driven by photosynthesis or mediated by cell surfaces?

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Cyanobacteria of the genera *Synechococcus* are abundant in the world ocean from 50° south to 70° north and play a significant role in metal sorption. Although cyanobacterial picoplankton are often the dominant phytoplankton in terms of biomass, a limited number of studies have examined their influence on the biogeochemical cycling in aquatic systems. Recent studies indicate that Gram-negative picocyanobacteria also play an important role in calcite precipitation in oligotrophic lakes. However, the detailed steps of the precipitation on the cell surface remain unclear.

In presented studies we investigated the mechanisms of calcite nucleation on the surface of *Synechococcus* strain PCC 7942. On the one hand the influence of photosynthesis and active ion exchange processes across the cell membrane on calcite nucleation and growth. On the other hand, experiments were performed in order to clarify the role of cell surfaces.

We performed long-term precipitation experiments at a constant CO₂ levels under different metabolic conditions: with ongoing photosynthesis, with blocked photosystem II and without photosynthesis. The surface properties of two picocyanobacteria strains were examined by measurements of zeta potential, potentiometric titration, and infrared spectroscopy (IR). Furthermore, in-situ and in-vivo atomic force microscopy experiments were carried out for cell surfaces observations during calcite nucleation.

Our experimental results clearly demonstrated that photosynthesis does not directly influence the nucleation process of calcite on cell surfaces of *Synechococcus* PCC 7942 of CO₂ supply is sufficient. Thus, nucleation is a passive process mediated by surface of the cells, which offer preferential sites for nucleation. We observed a change of the bacteria surface charge due to calcium adsorption. This fast adsorption process was followed by the reversible formation of protuberance at the cell surfaces. The Ca-adsorption on the cell surface is likely to be a first step of the nucleation process. The dominant functional groups of bacterial surface are carboxyl, amide, phosphate, hydroxyl, and carbohydrate related moieties. Modeling results and IR spectra are consistent with the presence of five distinct surface sites on the bacterial surface with pK_a's values 4.35, 5.24, 6.88, 9.1 and 10.00 with a total concentration of 7.78x10⁻⁴ mol g⁻¹. The carboxylic and phosphate groups together dominate the surface sites and calcium cations can therefore be easily attracted. On the other hand, the presence of amine groups on the cell surface influences the carbonate anions. Both reactions are important in the nucleation of calcite on the cell and may be key processes for the calcite precipitation in lakes.

O24-04

Microbial Colonization and Weathering of Carbonates in Deep Subsurface Settings

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The classic model for karst landscape evolution is based on the chemical dissolution of carbonate rocks in both shallow and deep settings, whereby numerous geomorphic features develop (such as caves and subterranean conduit drainage systems). The karstification processes are almost entirely based on abiotic chemical and hydrologic controls, while biological controls have typically been considered too complicated to stimulate study.

The Edwards Aquifer, a karstified aquifer in Central Texas (USA), is an important freshwater resource for nearly two million people. The eastern aquifer boundary is marked by a transition to saline, anaerobic to disaerobic, hydrogen sulfide-rich (up to 500 ppm) "bad-water" (BW). Down-hole video logs of uncased BW wells (depths from 100 - 800 m) reveal a complex network of fractures, solution pockets, and caves, but also white filamentous and colloidal biomass in the water column and thick biofilms on the rocks. Previous geochemical and hydrogeological work in the BW delineated some chemical attributes, but virtually nothing is known about the BW microbiology and the potential role of microbes to geochemical and geological processes.

Although there is regional geochemical variability, the BW wells are predominately supersaturated with respect to calcite (SI = +0.1 to +1.4), but undersaturated with respect to gypsum (SI = -0.2 to -1.2). *In situ* microcosms (sterile and non-sterile) consisting of calcite chips were deployed in four BW wells (150-220 m depth) for three months to test for rock dissolution due to microbial colonization. In two of the study wells that modeled supersaturated with respect to calcite (and representing geochemical end-members), non-sterile chips lost ~3-5x as much weight as the sterile microcosms; the surfaces were heavily weathered and dissolution pits were associated with a variety of microbial cell morphologies. Moreover, despite the waters being undersaturated with respect to gypsum, gypsum occurred in some biofilms. These results indicate that the chip surfaces were not in equilibrium with the surrounding aquifer waters and that microbial metabolism locally mediated both calcite dissolution and gypsum precipitation.

Presently, the relationship of microbes to carbonate weathering in these deep BW settings is inferred from the geochemical and experimental studies; genetic characterization of the microbial communities is underway to identify dominant guilds. Preliminary results indicate that *Epsilomproteobacteria* are present, suspected to be microaerophilic sulfur-oxidizers. This study provides insight into the unique, energy-rich microbial BW habitat and the potential role of microbes in deep subsurface carbonate weathering and karstification.

Clays and bacteria carry important role to release Hg from small scale Au mine near Lake Victoria, Tanzania

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Pollution of Hg has attracted much attention in Au mines at North America, Africa, and South America, because Minamata-diseases are still increasing in the 21st century. Mercury fragments influence on not only human but also air and soil environments including natural microbial systems. Studies on bacterial mineralization have received much attention as well. However, only few studies have been conducted on the Au mine in relation to the long-term bioremediation study. In this study, mineralogical properties of clay minerals, goethite, quartz, and calcite associated with heavy metals, such as Fe, Au, Ag, Hg, Ba, Sb, and Pb from the small scale Au mine, Geita, near Lake Victoria, Tanzania, have been studied using electron micro techniques. The lateritic reddish mud samples were collected from 7 locations of Hg panning ponds whereas air dusts were collected from 35 locations from Dar Es Salaam to Geita for about 1000 km away. Both the wet mud and air dust samples are mainly composed of clay minerals (smectite, halloysite, kaolinite), calcite, and goethite, associated with ppm ordered Hg on the surface or in the structures. Observation of FE-TEM electron microscopy and elemental distribution maps revealed that the clay particles, calcite grains, and bacterial colonies contain relatively high Hg and Fe on the surface and/or in the structures, indicating Hg pollution release from the panning ponds in the Au mine after heating treatment of Au-Hg amalgam. Volatilization of Hg carry to the air dusts associated with dried fine clays at all over the land in Tanzania. The highest Hg content in the dust was about 8 ppm in Muguli, Southern parts of Lake Victoria. The soils near Hg panning pond contains relatively high Hg as 1.5 ppm in Nyaruyeye. The results suggest that biodegradation of heavy metals by microorganisms is one of the primary ways by which heavy metals are eliminated from contaminated sites. The finding of heavy metals-degrading bacteria and clay minerals in the Au mine may have a significant effect on the weathering processes during the long term bioremediation.

Geomicrobiological factors controlling uranium mobility in natural systems

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Understanding of the behavior of uranium (U) in the environment is essential not only for the protection of aquifers from U contamination but also for the prediction of the fate of U and other actinides disposed of in deep geological settings. It had been long believed that the redox chemistry of U can be simply predicted by thermodynamics, and that the development of a low redox potential is a sufficient condition for U reduction. Recent studies, however, demonstrated that the redox transformations of U are controlled by kinetic factors, which are tremendously influenced by microbial activity. Although abiological U oxidation proceeds efficiently under oxygenic conditions, abiological reduction of U is inhibited by the formation of negatively charged U(VI)-CO₃ complexes, which prevail in nature. Phylogenetically diverse microorganisms are capable of enzymatically reducing U(VI)-CO₃ complexes to form U(IV)-bearing minerals such as uraninite (UO₂). The only abiological pathway currently known for the reduction of U(VI)-CO₃ complexes involves the Fe(II) monohydroxo surface complex $\equiv \text{Fe}^{\text{II}}\text{OFe}^{\text{II}}\text{OH}^0$, which is formed by the adsorption of aqueous Fe(II) onto the surface of Fe(III)-oxide minerals. The Fe(II) monohydroxo surface complex is mainly produced by microbial reduction of Fe(III) in natural systems. Thus, U(VI) reduction is controlled, at least in part, by microbial activity in direct and indirect manners. Several mechanisms of U oxidation under non-oxygenic conditions were recently revealed by laboratory and field studies. U(IV) is abiologically oxidized by Fe(III) and Mn(IV) oxides. Microbial nitrate reduction to molecular nitrogen, which occurs after the depletion of O₂, produces nitrogen intermediates including nitrite (NO₂⁻), nitrous oxide (NO) and nitric oxide (N₂O). Although the nitrogen intermediates oxidize U(IV), poorly crystalline Fe(III)-oxide minerals produced from the oxidation of aqueous Fe(II) species by the nitrogen intermediates more efficiently oxidize U(IV) than the nitrogen intermediates alone. Remarkably, the formation of Ca-U(VI)-CO₃ complexes due to the increased level(s) of Ca²⁺ and/or HCO₃⁻ leads to the re-oxidation of bioreduced U(IV) under reducing conditions. These geomicrobiological factors pose challenges to manipulate and/or predict the mobility and fate of U in the complexity and heterogeneity of environmental settings.

Rare earth element patterns as biomineralization probes

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The influence of microbial activity on mineral formation has been studied from a chemical, mineralogical and microbiological point of view in present-day aquatic systems. However, it is still not easy to extend the information gained from such environments to ancient geological formations because of post-depositional transformations. For example, the origin of banded iron-formations (BIF) has been interpreted as being the direct or indirect product of biological activity or resulting from hydrothermal activity. Therefore, there is a need to obtain more evidence with the help of different geochemical tools to ascertain the role of bacteria in BIF formation or in any other geological samples.

In this study, we propose the use of rare-earth element (REE) distribution patterns as probes of bacterial presence in natural minerals based on sorption studies of REE onto bacteria under laboratory conditions and on determination of REE abundances in bacteria-bearing natural samples. In laboratory experiments, adsorption of REE onto *Bacillus subtilis*, *Escherichia coli*, *Alcaligenes faecalis*, *Shewanella putrefaciens* and *Pseudomonas fluorescens* was studied. The distribution coefficients of REE between the bacterial cell surface and water showed a pattern with a prominent enrichment of heavy REE and a maximum around Sm. These characteristics can be well explained by surface complexation of REE with various binding sites on the bacterial surfaces and also by X-ray absorption studies on the local structure of REE sorbed onto bacteria.

In a natural aquifer, similar REE patterns were also observed in modern natural microbial biofilms containing *Gallionella ferruginea* and *Leptothrix* sp. found in Budo pond in Higashi-Hiroshima. In addition, the HREE enrichment was also observed in Fe oxyhydroxide precipitates found in association with neutrophilic iron-oxidizing bacteria when compared with Fe oxyhydroxides formed inorganically by precipitation. These results strongly suggest that microbial activity appears to modify the REE patterns of natural iron oxide minerals and that the REE patterns can be used as probes of bacterial activity in pure bacterial suspensions, natural biofilms and natural iron oxide minerals formed as a result of microbial activity. Some REE patterns of BIF in the Hamersley Province in northwestern Australia also show similar REE features, suggesting the potential role of bacteria in the formation of some banded iron-formations.

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Redox transformations at the mineral-microbe interface; mechanisms, environmental impact and biotechnological applications

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The microbial reduction of metals has attracted recent interest as these transformations can play crucial roles in the cycling of both inorganic and organic species in a range of environments and, if harnessed, may offer the basis of a wide range of innovative biotechnological processes. These include the bioremediation of metal contaminated land and water, the oxidation of xenobiotics under anaerobic conditions, metal recovery in combination with the formation of novel biocatalysts, and even the generation of electricity from sediments. Under certain conditions, however, microbial metal reduction can also mobilise toxic metals with potentially calamitous effects on human health. Rapid advances over the last decade have resulted in a detailed understanding of some of these transformations at a molecular level, with added impetus expected from the imminent availability of complete genome sequences for key metal-reducing bacteria, in combination with genomic and proteomic tools.

Focusing on "dissimilatory" processes, I will discuss recent advances in the understanding of the mechanism of Fe(III) reduction in the subsurface, and the impact of this biotransformation on sediment biogeochemistry. In particular, I will focus on the impact of Fe(III)-reducing bacteria on the solubility of key radionuclides of environmental concern (uranium, plutonium, neptunium and technetium), and also toxic metals/metalloids such as arsenic. The former will include a detailed discussion on recent research into the full redox cycle of uranium and technetium, with reference to enzymatic and indirect (e.g. Fe(II)-mediated) transformations. The latter will focus on the impact of microbial As(V) respiration on arsenic solubility in SE Asian aquifers, with an update on the application of stable isotope probing techniques to identify the active microbial fraction responsible for mobilizing soluble As(III). The biotechnological application of Fe(III)-reducing bacteria for the generation of commercially useful bionanomaterials will also be discussed, alongside their use in ex situ remediation of water contaminated with inorganic and organic contaminants.

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The interaction of actinides with microorganisms has been extensively studied because of the potential for using these organisms to remediate contaminated waste streams and groundwater. However, the mechanisms of microorganisms actinides are poorly understood. We have been conducting basic on microbial actinides in order to the environmental behavior of actinides under relevant conditions.

Effect of desferrioxamine B (DFO) on the sorption of Pu(IV), Th(IV) and Eu(III) (analog for Am(III)) on *Pseudomonas fluorescens* was studied. In the presence of DFO the sorption of Pu(IV), Th(IV) and Eu(III) on the cells increased with a decrease in pH from 7 to 4. In contrast, without DFO most of Pu(IV), Th(IV) and Eu(III) were precipitated from solution. Adsorption of DFO on the cells was negligible in the solution with and without metals. Adsorption of Pu(IV), Th(IV) and Eu(III) on *P. fluorescens* cells decreased in the order Eu(III) > Th(IV) > Pu(IV), which corresponds to increasing stability constant of the DFO complexes. These results indicate that Th(IV), Pu(IV) and Eu(III) dissociate when in contact with cells, after which the metals are adsorbed.

Mechanism of uranium(VI) mineralization by the yeast *Saccharomyces cerevisiae* was examined by batch experiment at pH 3.2. FESEM-EDS, TEM, and visible diffuse reflectance spectrometry revealed the formation of H-autunite, $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ on the yeast cells. Thermodynamic calculations suggest that the chemical compositions of the solutions were undersaturated with respect to H-autunite, but were supersaturated with ten-times more U(VI) and P than were actually observed. Apparently, the sorbed U(VI) on the cell surfaces reacts with P released from the yeast to form H-autunite by local saturation. These findings indicate that the yeast's cell surfaces, rather than the bulk solution, offer the specific conditions for this geochemical process.

We studied the effect of Eu(III) on the degradation of malic acid by *P. fluorescens*. Its breakdown depended upon the ratio of Eu(III) to malic acid-concentrations; the higher the ratio, the less malic acid was degraded. These results suggest that Eu(III) retards the degradation of malic acid, and the effect can be masked through its complexation with malic acid. The degradation of malic acid resulted in the accumulation of unidentified metabolites which were associated with Eu(III). One of the metabolites was identified as pyruvic acid by ESI-MS.

These findings suggests that bacterial adsorption, mineralization and degradation affect environmental behavior of actinides.

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Redox transformation of heavy metals and radionuclides influences the migration of contaminants in subsurface sedimentary environments. Dissimilatory metal reducing bacteria catalyze the reduction of many valence transformations by poorly understood mechanisms. These organisms produce electrically conductive appendages, which we call bacterial nanowires, in direct response to electron acceptor limitation. Nanowires produced by *S. oneidensis* strain MR-1, which served as our primary model organism, are functionalized by decaheme cytochromes MtrC and OmcA that are distributed along the length of the nanowires. Mutants deficient in MtrC and OmcA produce nanowires that were poorly conductive as determined by Scanning Tunneling Microscopy (STM). These mutants also differed from the wild type in their inability to reduce solid phase iron oxides, poor power production in a mediator-less microbial fuel cell, and failure to form complex biofilms at air-liquid interfaces. Nanowires were also produced by other bacteria, including the oxygenic, phototrophic cyanobacterium *Synechocystis* PCC6803. These results demonstrate that electrically conductive nanowires are not restricted to metal reducing bacteria and may be common throughout the bacterial world where they serve as structures for efficient electron transfer and energy distribution.

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In surface and subsurface aqueous environments native microbial communities are a primary control on the mobility and distribution of trace elements in both the solution and mineral phases. Processes mediated by microbial metabolic activities and cell surfaces in these environments are integral to understanding the remediation of trace elements in modern systems and leave distinct diagenetic signatures preserved in ancient rocks. Ferric iron oxides and oxyhydroxides are ubiquitous in surficial environments where they often control the cycling of heavy metals and have a profound influence on the geochemical distribution of sulfur, carbon and phosphorus. It is well established that the use of Fe(III) as a terminal electron acceptor by dissimilatory iron reducing bacteria (DIRB), causes the reductive dissolution of iron oxide minerals leading to the release of Fe²⁺ and the oxidation of organic matter. Because of their biological reactivity, iron oxides have been extensively studied, in particular due to their ability to sorb a wide variety of anions and cations and to act as the primary redox buffering mineral phase in many soil and sediment environments.

To this end we use a suite of electrochemical and spectroscopic techniques to determine metal speciation in the environment and in laboratory bacterial incubation experiments under reducing conditions. Our preliminary results suggest that Pb in the sediment porewaters occurs predominantly as very stable organic complexes. One implication of a strongly complexed Pb reservoir is that it may be less susceptible to participation in many biogeochemical processes that would generally remove it from the environment. For example, complexed Pb may not be reactive towards particles settling from a water column and would therefore exhibit an enhanced residence time with respect to free Pb. This also has important implications to studies using Pb as a geochronometer in which the mobility of Pb is assumed to be minimal and for the toxicity of Pb in the environment. Some of our recent work suggests that the organic ligands responsible for Pb complexation may issue from sediments. We have conducted experimental work suggestive that bacterial populations in the sediments produce ligands during respiration. In summary, the distribution of heavy metal contaminants in near-surface geologic settings maybe controlled to a large extent by exogenous ligands with the ability to stabilize dissolved metals against particle scavenging.

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Because of their high surface area-to-volume ratio and sorptive capacity, microcrystalline iron oxides have gained attention in the development of novel remediation technologies. Biogenic iron oxides (BIOS) are those formed as a result of microbial iron oxidation. They may be more chemically and structurally stable than synthetic forms, due to the presence of organic residues and stabilizing ions such as silicates and phosphates. Abundant iron oxide precipitates were found associated with a fresh-water spring located in Deep River, Ontario, Canada. Electron microscopy (EM) and energy dispersive X-ray spectroscopy revealed a predominantly amorphous mineral phase, rich in iron, silicon and various light elements. EM also confirmed the presence of twisted stalks and filamentous microbial sheaths similar in appearance to those of the iron-oxidizing bacteria, *Gallionella* spp. and *Leptothrix* spp., suggesting that the iron oxides were biological in origin. The Deep River BIOS contained 400 ppm Fe per gram of dried sediment, as measured by inductively-coupled plasma optical emission spectroscopy. X-ray diffraction yielded several peaks corresponding to some minor-phase quartz and potassium feldspar, as well as two broad reflections centered at approximately 1.5 and 2.5 angstrom (characteristic of the iron oxide mineral, 2-line ferrihydrite). Experiments were conducted to determine how readily the BIOS could be utilized as terminal electron acceptor by dissimilatory iron-reducing bacteria (DIRB). Cultures of the facultative anaerobe *Shewanella putrefaciens* CN32 were inoculated into a chemically defined medium inside an anaerobic chamber (under 100% nitrogen atmosphere). BIOS (at an approximate concentration of 4mM total Fe) were included in the medium. Cultures were enumerated by viable plate counts and Fe(II) quantified using the ferrozine colourimetric assay as the cultures aged. In all cases, the concentration of Fe(II) increased to a maximum (approximately 40% of the total Fe added to the medium) within the first 2 to 4 days following inoculation and remained at this level thereafter. Cultures remained viable, but cell numbers did not increase significantly over the same period, suggesting that reduction of the BIOS was sufficient to maintain cellular metabolism and reproduction, but insufficient for net growth of the culture. Growth of this organism under identical conditions, but using synthetic 2-line ferrihydrite indicated maximum reduction values of 40-60% of the total available iron, suggesting that BIOS may not be as easily reducible as synthetic forms of iron oxide. BIOS may therefore represent a more favourable form of iron oxide for use in future remediation strategies.

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Iron (hydr)oxides such as ferrihydrite exert a dominant influence on arsenic retention within soils and sediments. Under anaerobic conditions, the reductive transformation of ferrihydrite, or other ferric (hydr)oxides, may release arsenic to the aqueous phase. However, reductive biomineralization may limit the release of arsenic, and promote arsenic sequestration, through its incorporation in (or on) secondary solids. Rather than promoting arsenic mobilization, Fe(II) reduction of ferrihydrite by the iron reducing bacterium *Shewanella putrefaciens* in a packed mineral column under advective flow resulted in arsenic sequestration. Various secondary sinks may retain arsenic, but, we observe a strong correlation between arsenic retention and dissolved Fe(II), suggesting the formation of an Fe(II)-As(III) precipitate. In order to decipher the mechanism by which arsenic is retained upon ferrihydrite reductive dissolution and transformation, we examined a biologically produced precipitate using a host of spectroscopic and microscopic techniques. We completed these investigations with synthetic analogs in which varying concentrations of Fe(II) and As(III) were reacted at multiple pH values to define conditions conducive to the formation of the solid phase (potential 'reduced' sink of arsenic).

Synthetic precipitates resulting from the reaction of Fe(II) and As(III) have a nearly one to one stoichiometric elemental ratio. X-ray absorption spectroscopic (XAS) analysis of synthetic Fe(II)-As(III) suggests, on the basis of local coordination environments, that the Fe(II)-As(III) solid consists of brucite [Mg(OH)₂] like Fe(OH)₂ sheets with As(III) in double-corner and edge-sharing coordination to Fe octahedra. X-ray diffraction spectra, obtained both from conventional and synchrotron X-ray sources, further supports the formation of a sheet-like precipitate. Morphological and lattice features of the Fe(II)-As(III) precipitate, imaged using transmission and scanning electron microscopy, confirm a sheet structure of aged Fe(II)-As(III) solids.

Contrary to the current paradigm of arsenic release under anaerobic conditions, elevation of dissolved Fe(II) concentrations, typically through bioreduction of Fe(III), may stabilize arsenic relative to its transport. The formation of an Fe(II)-As(III) phase would necessitate high level of Fe(II) through intense Fe(III) reduction. Intense Fe(III) reduction requires the presence of a highly bioavailable Fe (hydr)oxide such as ferrihydrite, high organic carbon content, circumneutral pH, and warm temperature (near 25 °C). Thus, soils in tropical regions undergoing seasonal redox cycling (flooding and drying) would be likely candidates for internal cycling of arsenic within oxidized and reduced solids.

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The iron respiring bacteria like *Shewanella* spp. has been showed to transform, in lab-experiments, lepidocrocite in extra-cellular iron (II)-bearing minerals such as magnetite or green rust (GR). GRs are layered Fe(II-III) hydroxides that consist of positively charged iron hydroxyl layers and interlayers containing anions and water. In the natural environment, the GR, identified during the last decade has been called fougérite (IMA 2003-057). On the other hand, magnetite is an inverse spinel mineral, that consists of Fe(II) in octahedral sites and Fe(III) in both tetrahedral and octahedral coordination.

Due to their great reactivity with several pollutants (CrVI, NO₃⁻, HgII...), GRs are potential candidates for remediation process in polluted hydromorphic soils. Therefore, the control of GR production by bacteria represents an interesting challenge from a fundamental and applied point of view. However, the significance of microbially mediated pathways of GRs *versus* magnetite formation is poorly known.

Therefore, our research aims at a better understanding of the processes that determine the formation of GR and magnetite under biological conditions which would enable us to get an insight on the implication of bacterial cells on these minerals precipitation. The iron oxide reduction kinetic was previously suggested as the main factor controlling the biomineralization pathways. However, the factors controlling this kinetic are not well established. Several conditions were tested to identify the relevant factor(s). Neither the presence of electron shuttles, nor the bacterial growth phase, control the biomineralization processes. In addition, we showed that the (*E*_h/pH) Pourbaix diagram can not be used to forecast unambiguously the nature of the mineral formed. One the other hand, the confocal microscopy analyses reveal a significant effect of the ratio [bacteria]/[lepidocrocite] on the structure of the aggregates which is strongly linked to the biomineralization pathways, GR *versus* magnetite.

This study showed that the "biogenic" mineral nature can be controlled by playing on the [cell]/[lepidocrocite] ratio. Moreover, it brings new insight of the parameters controlling Fe(III) biomineralization in iron respiring bacteria culture.

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Iron can undergo transformations of oxidation and reduction in environmental systems. For instance, dissolved Fe(II) is oxidized and usually precipitates as an iron oxyhydroxide when it is transported or diffuses from an anoxic to an oxic environment. This occurs commonly, for instance at seeps, in soils, or in the upper layer of sediments. In such systems, the presence of bacteria is ubiquitous, and it has been debated to which extent they could affect the processes of oxidation and precipitation. Two major categories of biotic mechanisms have been identified: metabolic mechanisms, throughout which bacteria actively design strategies interacting with the oxidation and the precipitation of iron; and passive processes, whereby the bacterial cells merely offer their reactive surfaces towards their aquatic surroundings, and adsorb dissolved ferrous ions, crystals nuclei or crystals in growth. It has been suggested that bacteria catalyze the oxidation and hydrolysis of Fe(II) through both passive and active mechanisms, and that their surface act as nucleation surfaces for the precipitation of nanometric particles. Our research is designed to address these hypotheses for both types of passive and active mechanisms, in general, and also in the specific context of an iron seep in Brittany (pH ≈ 6).

Our approach consists in a laboratory study coupled with a field study. In the laboratory study, we have previously shown that the properties of iron-oxides can be affected by the presence of bacterial cells, and we have quantitatively measured how Fe(II) ions adsorb on the surface of *Bacillus subtilis*. We are now assessing the role of the presence of bacteria on the kinetics of oxidation of Fe(II) in controlled conditions of pH, temperature, oxygen concentration and conductivity. *Bacillus subtilis* and *Pseudomonas aeruginosa*, a Gram-positive and a Gram-negative species respectively, were selected for this study. Our first results indicate that Fe(II) sorption onto bacterial cells retards and limits the extent of the oxidation of iron. In the field study, we have sampled iron precipitates throughout the year at a natural iron seep, and observed their properties by SEM. *Leptothrix ochracea* was a dominant species, but stalks characteristic of *Gallionella ferruginea* were also observed. Along with these observations, the spatial and temporal variability of the microbial communities is currently being analyzed by sequencing the 16S rRNA gene. We are also planning to extend the laboratory kinetic experiments to natural bacterial suspensions sampled at the iron seep.

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We have used several advanced transmission electron microscopy techniques to study the physical, chemical and magnetic properties of intracellular ferrimagnetic magnetite (Fe₃O₄) and greigite (Fe₃S₄) crystals in magnetotactic bacteria. The structures, orientations and morphologies of the magnetosomes were identified using electron diffraction, high-resolution electron microscopy and high-angle annular dark field electron tomography. Their compositions were studied using energy-selected imaging. Off-axis electron holography was used to record magnetic induction maps of the cells.

Iron sulfide-containing, rod-shaped cells were collected from salt marshes. Each cell contained multiple chains of greigite magnetosomes, which had random shapes and orientations. Many of the greigite crystals appeared to be only weakly magnetic, presumably because their magnetic induction direction was almost parallel to that of the electron beam. The disordered three-dimensional arrangement of the crystals resulted in the magnetic field in the chain following a meandering path between adjacent crystals. Nevertheless, the magnetosomes were observed to collectively comprise a permanent magnetic dipole moment that is sufficient for magnetotaxis.

Magnetite-producing cocci were collected from lakes and streams. A cell type containing two double chains of magnetite magnetosomes was studied in detail. Within the double chains, the [111] axes of most crystals were approximately parallel to the chain axis. In contrast, the crystallographic directions perpendicular to the chain axis were randomly distributed. Each chain was therefore analogous to beads on a string, in which biological control appeared to be stricter in setting the [111] magnetocrystalline easy axis of the crystals to be parallel to the chain axis than in constraining their orientation about this direction. The magnetic signal was dominated by inter-particle interactions and by the shapes of the individual crystals.

The magnetic microstructures of chains and clusters of magnetite crystals in *Magnetospirillum gryphiswaldense* and its genetically engineered mutants were studied. Wild-type cells contained single chains of cubooctahedral magnetite crystals that were uniformly magnetized along the length of the chain. Mutant Δ magJ cells lacked a magnetosome-associated protein that was apparently responsible for assembling the magnetosomes into chains. The magnetite crystals then occurred in clusters in each cell, producing a wide variety of magnetic microstructures, including vortex states with no net magnetic moment. Other mutant cells contained chains of small (~30 nm), irregularly-shaped crystals, many of which were superparamagnetic at room temperature. These observations highlight the delicate balance between crystal size, shape, orientation and chain configuration that determines whether such cells are able to respond to an external magnetic field.

Pyrite surface alteration as effect of microbial activity and crystallographic orientation

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The relevance of microbial mineral leaching processes afforded great environmental and experimental research efforts in the past. As part of these studies, a wide variety of minerals leached by pure and mixed cultures of Bacteria and Archaea were experimentally examined.

The project presented here aims to enhance our understanding of effects of parameters such as pH, temperature, incubation time, varied metabolism, direct or indirect leaching effects, and crystallographic orientation (anisotropy) on microbial leaching of pyrite surfaces. Systematic assessment of highly characterized surfaces before and after exposure to the microbial cultures may result in quantification of the leaching processes. This will lead us to determine whether varied crystallographic orientation results in varied surface leaching features. The long-term goals of the study are to establish means that allow the controlled manipulation of pyrite and other metal sulfide surfaces.

We devise microbial leaching experiments on pyrite surfaces of different orientation, including {100}, {111} and {210}. The experiments are performed using four strains of mesophilic Bacteria and four thermophilic Archaea.

Epifluorescence microscopy observations show, that some microbial strains attach to the mineral surface whereas others remain planktonic in the liquid growth medium. Systematic studies addressing the effect of time are accomplished in time spans between one day and six weeks. Cell attachment commences after few days attaining a surface cell density that remains stable after approximately two weeks. Scanning Electron Microscopy (SEM) studies have shown that leaching effects become visible within few days of incubation. Surface alteration produces structures such as channels, inverse pyramids following crystallographic orientation, rectangular or round pits in the 10s to 100s μm size range. Epifluorescence microscopy and SEM analysis have shown that surface alteration as result of microbial activity occurs first at weaknesses in the surface, such as micro-scratches and possibly at crystallographic defects. Leaching occurs due to microbial activity, which results in lowering pH-values from 2.5 in the growth medium to approximately 1.5 in local micro-environments. To test whether microbial activity has a direct bearing on surface alteration, or whether abiotic acid leaching produces similar results, we accomplished experiments using sulfuric acid (three different concentrations). After etching (three time steps) the resulting features resembled what was observed after microbially mediated etching, however, qualitative variety of alteration features proved to be greater with microbial influence (e.g. inverted pyramids) and the effects appear much more pronounced, suggesting that microbial activity has a distinct influence on surface alteration in this system.

P24-01

Hydrocarbon-Degrading Bacteria and Paraffin from the Nakhodka Oil Spill-Polluted Seashores in the Sea of Japan After 9 Years of Bioremediation

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The biodegradation of hydrocarbons by microorganisms is one of the primary ways by which oil spill is eliminated from contaminated sites. Russian tanker the *Nakhodka* had spilled heavy oil into the Sea of Japan on January 2, 1997. This paper describes the weathering of hydrocarbon-degrading bacteria (genus *Pseudomonas*) and crystallized organic compounds from the *Nakhodka* oil spill-polluted seashores after nine years. Upon the slow evaporation of the *Nakhodka* oil spill during the 9-year weathering, the dendritic crystal growth of paraffin (a mixture of alkanes) occurred in the oil crust under the natural conditions. The X-ray studies suggest that the ridges formed in certain crystallographic directions on crystals of normal alkanes are related to the shearing which occurs when molecular chains undergo tilting. Heavy metals were obtained in original heavy oil samples of three seashores in the Sea of Japan. Results indicated that Si, S, Ti, Cr, Ni, Cu, and Zn were predominantly indigenous to the *Nakhodka* oil spill, whereas these heavy metals and S were not present after 9 years of weathering. Our data also have a significant insight into how these metals in the *Nakhodka* oil spill affect the biodegradation of heavy oil during the 9-year bioremediation, thereby giving more fruitful information for such kinds of oil spills. In contrast, these results also provided information that the *Nakhodka* oil spill resulted in not only organic pollutants (i.e., hydrocarbons) but also heavy metal pollutants (i.e., Cr) along the coastal areas of Sea of Japan.

Anaerobic reverse side of the oil crust contained numerous coccus typed bacteria associated with halite. The finding of hydrocarbon-degrading bacteria and paraffin wax in the oil crust may have a significant effect on the weathering processes of the *Nakhodka* oil spill during the 9-year bioremediation.

P24-02

Elemental behavior during the corrosion process of *sekishu* roof-tile glaze affected with *Lecidea* s.lat. sp.

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The elemental behavior during the corrosion process of *sekishu* roof-tile glaze affected with *Lecidea* s.lat. sp. (crustose lichen) has been investigated by means of optical microscope, fluorescent microscope, electron probe microanalyzer (EPMA), field emission scanning electron microscopy (FE-SEM) equipped with EDS detector and high-resolution transmission electron microscopy (HRTEM). The Japanese *sekishu* roof tiles have the reddish brown opaque glaze on their surfaces, which is consisted with alkali feldspar-type amorphous glass recrystallized under a high temperature condition ($\sim 1200^\circ\text{C}$). A large amount of lead is artificially added to the glaze as a decreasing agent of melting temperature on its manufacturing process. The growth of *Lecidea* sp. was observed widespread on the glaze surface of aged tiles (about 20 years old). Representative roof tile specimens with lichen thalli were embedded with epoxy-resin after dehydrated in ethanol and infiltrated with a gradational ethanol/resin series, and standard petrographic thin sections were prepared. The resultant thin sections cleared the $<20\mu\text{m}$ depth corrosion occurring on the lichen-glaze interface. Each corrosion pit were filled with fungal hyphae showing an increased blue fluorescence of DAPI under UV light. The elemental line profile and two-dimensional mapping by EPMA did not demonstrate the significant trends of mass transport of elements. However, further sensitive elemental mapping performed with FE-SEM under a low accelerating potential voltage (15.0 kV) detected concentrations of iron and titanium to the lichen-glaze interface correlated with a carbon behavior, suggesting possibility of biomineralization. Although abundant nanometer scale vermicular minerals (crystalline) were observed around the lichen-glaze interface, it was likely that they were not results of biomineralization because of their spatial distributions. It may be concluded from those investigations that *Lecidea* sp. plays a protective role against the weathering of roof-tile glaze through the concentrations of metal ions.

P24-03

Degradation of Tetrachloroethene by Several Co-metabolism Substrates in Groundwater

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Since 1940s, chlorohydrocarbon, as an organic solvent, has been widely employed as a degreasing solvent in modern industry. Because of inappropriate disposal of sewage and the leaking, chlorohydrocarbon has become the commonest contaminants in groundwater, and tetrachloroethene (PCE) is one of the main contaminants arousing environmental problem. As a persistent organic compound, PCE is listed as one of the priority contaminants under control by the USEPA, which is believed to be "carcinogenic, teratogenic and mutagenesis". Because PCE is widely detected in groundwater as drinking water resource, it has become a world-wide major issue and also an area that has attracted great interests of scientists.

Since the natural attenuation rate of PCE is slow, PCE is biodegraded by reductive dechlorination with co-metabolism substrate under anaerobic conditions. By inoculating sludge from an anaerobic pool, a biodegradation test of PCE is conducted in the anaerobic condition. In the test, several substrates, including methanol, ethanol, formate, acetate, lactate and glucose, are conducive to the conversion from PCE to TCE and DCEs.

The results show the microbe can be cultivated well under the anaerobic circumstances of mixture of sewage (sludge) and soil with the index of COD after eleven days. With six different co-metabolism substrates, i.e. methanol, ethanol, formate, acetate, lactate and glucose, and the condition of increasing PCE concentration, the cultured anaerobic microbes are acclimated. For six substrates, the activity of microbe is stronger when the last three substrates, including acetate, lactate and glucose, are co-metabolism substrates of microbe acclimation. The acclimated anaerobic microbe can be used to degrade PCE. Six substrates and PCE are added to six glass bottles respectively. The theoretical value of added PCE is $324\mu\text{g/L}$ (1951.8nmol/L). The experiment lasts 9 days. The results show PCE is reduced and dechlorinated to TCE and DCEs with the six substrates. The fitting curves of degradation of PCE at the six substrates are accord with one order kinetics equation. The sequence of the reaction rate constant is $K_{\text{acetate}} > K_{\text{glucose}} > K_{\text{lactate}} > K_{\text{ethanol}} > K_{\text{formate}} > K_{\text{methanol}}$, which shows that the degradation rate of PCE is the fastest when acetate as co-metabolism substrate under this experiment condition, so acetate is a best co-metabolism substrate whose reaction rate constant is 0.6632d^{-1} .

Anaerobic Biodegradation of Tetrachloroethylene with Acetic Acid as Cometabolism Substrate

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PCE is widely used as solvents, dry cleaning, and de-greasing agents. As a result of long-standing solvent disposal malpractice, PCE is among the most ubiquitous chlorinated compounds found in groundwater. Some researchers found that TCE, DCEs, VC and ETH in the soil that contaminated by PCE, but the dechlorination rate was quite slow under natural conditions. Efforts have been undertaken during recent years to decontaminate polluted environments by physical method, chemical methods or biological degradation to less toxic products. Compared to the physical and chemical treatment technologies, biological technology may be more advantageous for its low cost and high contaminant destruction rate.

In this experiment, PCE dechlorination with acetate acid as co-cometabolism substrate was studied. It is difficult to get the aquifer deposit that contaminated by PCE, so the microorganism was cultured in the laboratory. The anaerobic sludge of a meat plant is chosen as inoculum to soil, which is from a garden to incubate microorganism. Some compounds will be formed when mineral react with groundwater, so groundwater was added to supply inorganic mineral and trace elements. When the microorganism was active enough, PCE (the concentration is from low to high) was added to start acclimation experiment. After the microorganism in the microcosm can adapt PCE of 120 µg/L, the degradation of PCE was studied.

The degradation results show that PCE can be biodegraded to TCE and DCEs. After 11 days, the removal efficient of PCE exceed to 90%. The reaction rate is relatively high with acetate acid as co-metabolism substrate. The reaction rate constant is 0.2342d⁻¹ and the half life is 2.95days, while in natural groundwater, half life of PCE is 108 days. Acetic acid is a suitable electron donor to supply carbon to dechlorinate PCE to TCE, and further to DCEs. At the end of the experiment, 20.4% of PCE was transformed to TCE, and 4.1% of PCE was transformed to DCEs. When the acclimation experiment was done with the microorganism cultured in the laboratory, there was a lag period of 20 days, while the degradation experiment was done with the microorganism acclimated, the lag period is only 1 day. Acetate acid exists naturally in the environment and during the organic matters fermentation period, some acetate acid can be obtained. In this experiment, a small quantity of acetate acid can meet PCE dechlorination. From the view of practical application and economics, this research has some advantage and prospect.

New insight into the nucleation and growth mechanism of nacreous aragonite in pearl oyster

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The mechanism of polymorph switching between calcite and aragonite in the mollusk shells is one of the most attracting topics in the researches of biomineralization. For instance, several molecular-biological studies to seek macromolecules responsible for the switching have been performed, by extracting them from nacre that mainly consists of aragonite platelets and protein-polysaccharide organic layers. However, conclusive evidence has not been obtained yet.

If we assume that the aragonite platelets are connected together with "mineral bridges" penetrating the intercalated organic layers and the polymorph is inherited from the underlying platelet via the bridges, the selection of the polymorph is originated in the first nucleation site of nacre that is the interface with the outer prismatic layer. Therefore, we have investigated in detail the initial nacre in pearl oyster (*Pinctada fucata*) mainly by using electron microscopic techniques.

It is known that the initial nacre is formed on a thick organic matrix that covers calcite crystals of the prismatic layer. The surface of the trench between the calcite prisms was firstly covered with the organic matrix and then the trench is filled with the initial nacre. Electron Back-Scattered Diffraction (EBSD) analysis revealed that this initial nacre is already aragonite and the c-axis is oriented perpendicularly to the shell surface, as seen in the aragonite platelets. Furthermore, it was found that the nucleation site of the mineral is at the edge of a dimple structure formed on the surface of the organic matrix. This region was taken using the Focused Ion Beam (FIB) technique and examined by TEM. An intricate boundary between fine aragonite crystals and organic matrix was observed.

Analysis of Pebble Surfaces Coated with Biogenic Manganese Oxides

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Pebbles coated with a thin black layer are found in the Kikukawa river system, Shizuoka, Japan. This river system drains strongly-acidified water from tea plantations. It has been reported that the coatings are manganese oxides and deposited by Mn(II)-oxidizing microorganisms. Manganese oxide coatings are actively forming over submerged pebbles on the streambed of the river. We will report characterization of the biogenic manganese oxide coatings on the pebble surfaces.

Submerged pebbles and boulders with black coatings were collected from the Kikukawa River. Micrographs, X-ray spectra and elemental maps of the surface and cross-section of the pebble were taken by scanning electron microscope (SEM) with an energy-dispersive X-ray spectrometer. Black coatings on the boulders were scraped off and used for powder X-ray diffraction (XRD) measurement. A thin section of the surface was cut from a pebble sample for surface analysis by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS).

A wrinkled structure of the coating on the pebble surface was observed by SEM. The X-ray spectra and elemental mapping of the cross-section clearly demonstrated the deposition of manganese oxide on the pebble surface. The thickness of the manganese oxide layer was estimated to be about 5-20 µm. The XRD pattern of the manganese oxide coatings was typical of phyllosilicate with a 10 Å d-spacing (poorly-crystallized buserite). After heating at 110 °C for 3 hours, the 10 Å diffraction line contracted to 8.8 Å due to the loss of interlayer water. The X-ray photoelectron spectra of the pebble surface suggested that the coating is a mixture of manganese and iron oxides, silicate minerals and carbonaceous materials. The Mn 2p_{3/2} binding energy of the coating was consistent with that of MnO₂. The C and N 1s binding energies and N/C atomic ratio were comparable to those of the fungus sample isolated from the streambed pebbles, suggesting that the carbonaceous materials are due to the remains of Mn(II)-oxidizing microorganisms. Depth profiling of the pebble surface by SIMS (analyzing depth of up to several hundred nanometers) showed increasing and decreasing secondary ion intensities of Mn and Si, respectively, with sputtering time, indicating that the surface of manganese oxide coating contains silicate mineral particles. In addition, the depth profile of Mn showed an oscillating pattern with a repeat period of several tens of nanometers which might be attributable to seasonal fluctuation in manganese oxide formation by Mn(II)-oxidizing microorganisms.

Rate enhancement of kaolinite dissolution by interaction with proteins released from bacterial cells

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Dissolution experiments of kaolinite(KG-1) in bacterial system containing *Pseudomonas fluorescens* were carried out to evaluate the effects of bacteria on the dissolution rates. Similar dissolution experiments using organic system containing protein (albumin) were also carried out to confirm the factors affecting the dissolution rates of kaolinite in bacterial system. The dissolution experiments were performed using batch reactors containing 0.2 g of kaolinite and 100 ml of 10 mM NaCl solution at 25°C for up to 30 days. Results of the experiments indicated that the bacteria have strong rate-enhancement effects on the dissolution of kaolinite depending on their concentrations. The dissolution rates were increased successively approximately 10 times with increasing bacterial amounts from 10⁵ to 10⁹ cells/ml relative to the abiotic systems. For organic system containing protein, it was found that protein increased greatly the dissolution rate of kaolinite. Chemical analyses of organic molecules in solutions of bacterial system revealed that significant amounts of protein was released from the bacterial cells with small amounts of polysaccharide. Thus, the rate-enhancement in bacterial system may be caused by interaction of bacterial protein with the kaolinite surface. It is well known that protein molecules have functional group such as carboxyl (X-COOH) and amino (X-NH₂) groups in their structural units of amino acids. FITEQL analysis of the protein indicated that carboxyl groups play an important roles on the kaolinite dissolution as reactive sites.

Structural change of non-crystalline biogenic silica of diatoms by heat treatment

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Diatoms are plankton of unicellular whose cell walls (frustules) made of silica and organic materials. So, diatom is interested in the fields of bio-mineralization and material science.

In this study, nano-structure of diatom frustules was investigated by means of X-ray diffraction measurements and micro FTIR spectroscopy. Obtained X-ray diffraction profile of diatoms shows only a broad peak around $2\theta = 20^\circ$ (Cu-K α). This may indicate that diatoms were composed by non-crystalline SiO₂ materials. Its relatively high intensity of small angle scattering suggests that the basic structure of this non-crystalline matter is similar to silica gels. SiO₂ gels have primary structures of 10–100 nm scale. Therefore, it is possible that micro structure of diatoms have similar structural units with 10–100 nm scale and pores with similar scale. The IR spectrum of diatoms shows a clear Si-OH stretching band at $\nu = 949\text{ cm}^{-1}$ as well as the strong Si-O stretching band at $\nu = 1000\text{--}1250\text{ cm}^{-1}$. These features are consistent with the results of X-ray measurement. Further, the relative absorbance of Si-O-Si band at $\nu = 750\text{--}900\text{ cm}^{-1}$ for diatom is smaller than those of the fully polymerized SiO₂ materials such as quartz and silica glass. These facts may indicate that network structure of SiO₄ tetrahedra of silica based non-crystalline materials for diatom includes some Si-OH bonds and large scale pores. The IR spectrum shows also C-N-H combination band ($\nu = 1534\text{ cm}^{-1}$), C=O stretching and H-O-H bending bands ($\nu = 1674\text{ cm}^{-1}$), and C-H stretching band ($\nu = 2935\text{ cm}^{-1}$). These bands suggest the non-crystalline silica of diatom frustules unites with the hydroxyl residue of amino acid.

The structural evolution of these silica base frustules by heat treatment up to 1150°C was also investigated by means of IR spectroscopy. By the heat treatment up to 400°C, diatom lose organic materials, OH and Si-OH bond. This may indicate the polymerization of SiO₄ tetrahedra advanced by dehydration of frustules. Heat treated diatoms shows more sharp Si-O stretching band in IR spectra than non-treated one. This suggests that heat treated diatoms have SiO₄ tetrahedra with relatively small distortions in its basic structure.

Precipitation of calcium carbonate polymorphs effectuated through catalytic decomposition of urea in solutions of calcium salts

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Precipitation processes of carbonate particles of different size, shape, and surface properties have been intensively investigated due to their importance in geo- and biosciences, and in numerous industrial applications. This study describes and discusses a conceptually new method for the precipitation of calcium carbonate polymorphs, effectuated through catalytic decomposition of urea at elevated temperatures and by using *Canavalia ensiformis* urease enzyme at ambient conditions in solutions of calcium salts. It was found that the formation of different polymorphs of calcium carbonate at elevated temperatures was affected mostly by agitation and by the mixing procedures of reacting solutions. This study has also confirmed that the enzyme macromolecules are important in the development of calcite faces and, as such, they exert significant influence on calcite morphology.

Texture of aragonite in nacre: the potential of different diffraction techniques

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Nacre in molluscs consists of subparallel aragonite platelets flattened on (001). Depending on the species and/or the location of nacre within the shell, the perfection of alignment of platelets varies. The texture ranges between an assemblage of platelets almost parallel along all three axes to textures with only c^* parallel. The study of the alignment of platelets allows us to establish or rule out phylogenetic relationships between recent and fossil molluscan taxa and to gain other valuable information. Three techniques have been used to examine preferred orientation of aragonite platelets in the nacre of molluscs, (i) X-ray texture diffractometry (on a modified powder diffractometer), (ii) oblique-texture X-ray photographs (on a precession camera), and (iii) EBSD. All of them yield some identical results, but there also are some differences.

The area irradiated on the diffractometer is at least several mm² in size; the data collected have good counting statistics, but they average out variations on a smaller scale. Also, bent shells may be difficult or impossible to examine. Two pole figures are needed, one for the [001]* axis and one for an axis perpendicular to it, typically [100]*. There is a non-overlapping 002 for the first. However, 200 is the weaker component in a doublet with 102, so other diffractions have to be monitored and the data merged numerically. With Cu radiation, the peaks are recorded at medium angles, and the results characterize a thin layer near the shell's surface.

Oblique-texture photographs represent a finer area, the collimated beam is less than 0.5mm in diameter; a photograph along the c^* axis is a check for randomness (or lack thereof) of [100] axes. Most diffractions arise by transmission, so unwanted shell layers must be removed. Lateral variation in a fragment can be monitored, and the tilt of c^* with respect to vector N can be measured with precision.

Electron backscatter diffraction provides the most local information of the three techniques. The resolution of EBSD is much lower than 1 micron, and the orientation of each nacreous platelet is determined independently. Data are collected from an area around 0.0Xmm², and only platelets on the polished surface generate diffraction patterns.

Even though all diffraction techniques used (X-ray texture diffractometry, oblique-texture X-ray diffraction, EBSD) provide information about the texture in a nacreous layer, each represents a different volume of nacre, and a proper one should be selected according to the nature of the problem studied.

Fossilized Chemoautotrophic Microorganism in Artificial Drilled Holes at the Suiyo Submarine Hydrothermal Field, Izu-Bonin Arc, Western Pacific, Japan

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The active hydrothermal field of the Suiyo Seamount, Izu-Bonin Arc, Western Pacific, Japan, was drilled during 2001 to 2002. Drilled holes were cased and active biological activities, including Archaea-type sulfate-reducing bacteria, were found insides of casing pipes when the hydrothermal fluids discharge through the artificial casing pipes.

Artificial pipes were filled with chemical precipitates, including fossilized microorganism. These were sampled by ROV *Hyperdolphin* during September of 2005. Analyses of organic carbon concentrations and their stable isotope compositions were performed, in addition to FE-SEM observations.

It is found through the course of this study that chemical precipitates include up to 0.6wt% organic carbon, surprisingly comparable to the modern marine sediments. The $\delta^{13}\text{C}$ value of organic matter was -27.7‰ . It is also found through the FE-SEM observation that the fossilized microbes together with amorphous Fe-S compounds were covered by amorphous silica. These findings suggest that (1) microbial activities in the artificial casing pipes were extremely high and (2) drilling action made unique environment (such as no competition to other microbes, or availability of H₂ from H₂O decomposition) and that is suitable for activity of many chemoautotrophic microorganisms in the submarine hydrothermal environments.

Crystallographic direction of coccolith elements of the marine alga *Braarudosphaera* and its fossil group, *Discoaster* spp.

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Selected area electron diffraction (SEAD), high-resolution transmission electron microscopic and scanning electron microscopic analyses of coccoliths, the exoskeleton of certain unicellular algae (the coccolithophores), were performed to determine crystal habits of two types of nannolith elements, *Braarudosphaera bigelowii* and *Discoaster* spp.. Determination of crystallographic direction of elements were used as overgrown method of Okazaki and Inoue (1976) [1]. *Braarudosphaera bigelowii* has pentagonal segment which conjugated five trapezoidal elements.

A form of individual *Braarudosphaera* is dodecahedron which combined the twelve pentagonal segment. The trapezoidal face of the element conformed with cleavage face of calcite (104). However, two types of *Braarudosphaera* existed in this study. The one type of contact face of each element is vertical to trapezoidal face and the other type is oblique (like a screw propeller.)

A Neogene *Discoaster* specimen is composed of a form like the frame of spread umbrella in which bent leg (called "ray") radially combined. There are mainly the five-rayed and six-rayed types and the latter type has two kinds of tip shapes, the linear tip type (*Discoaster brouweri*) and the Y character tip type (*Discoaster variabilis*). Each ray seems to be respectively the single crystal. Moreover, the [001] direction of a ray is identical on the five ray type and six ray type and its direction is perpendicular to the tangent plane of the central area of *Discoaster* spp.. Therefore, each base part of rays is almost perpendicularly elongated for the [001]. Each ray is being joined together in the plane which is parallel for [001].

On the other hand, Paleogene *Discoaster* specimens. (*Discoaster barbadiensis* and *Discoaster saipanensis*) have many rays further than the Neogene species. Elongated direction of base part of rays are similar to the Neogene type, but Paleogene type rays are turned to right or left for the tip. Consequently crystal growth mechanism of Neogene type and Paleogene type may be different.

[1] Okazaki, K. and Inoue, S. *Development, Growth and Differentiation* 18:1976, 413,434

In-situ X-ray reflectivity study of the mica-fulvic acid interface in aqueous solutions containing barium and mercury

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Most minerals are covered by organic matter in natural systems at Earth's surface and as a result the reactivity of the coated surfaces may be substantially different from that of pristine surfaces. To assess the effect of organic coatings on metal ion sorption, we performed *in-situ* X-ray reflectivity measurements of the interface between muscovite mica and fulvic acid solutions with and without dissolved metals (Ba^{2+} and Hg^{2+}) using synchrotron radiation (Advanced Photon Source; BESSRC 11-ID-D). Resonant Anomalous X-ray Reflectivity (RAXR) measurements were applied to determine the ion-specific electron-density profiles of dissolved mercury. We built structural models of the metal ions and organic molecules adsorbed on the mica surface, and used the models to interpret sorption mechanisms. Experiments were conducted with ASTM-VI grade muscovite in the presence or absence of 100 ppm Elliott Soil Fulvic Acid II (IHSS). Divalent cations were added from solutions of 5 mM BaCl_2 at pH 5.5 (pH 3-4 with fulvic acid) and 1 mM $\text{Hg}(\text{NO}_3)_2$ at pH 2.

The interfacial electron-density profiles of the mica in Ba^{2+} - or Hg^{2+} -containing solutions without fulvic acid show two discrete peaks corresponding to ions positioned over both the ditrigonal cavity and the basal oxygen plane of the mica surface. The results suggest that Ba^{2+} adsorbed largely in the ditrigonal site in amounts that compensate the surface charge deficiency of the mica. In contrast, only small amounts of Hg^{2+} adsorbed due to the competition between Hg^{2+} and H_3O^+ at the lower pH. In the BaCl_2 -fulvic acid solution, the electron-density peaks nearest the surface match those in the BaCl_2 solution implying that the fulvic acid had little effect on the sorption of Ba^{2+} . A broader peak of lower electron-density is positioned farther from the surface and is interpreted as a fulvic acid layer with a thickness of approximately 6 Å. This model suggests that Ba^{2+} acts dominantly as a bridging cation between the mica surface and fulvic acid. In the $\text{Hg}(\text{NO}_3)_2$ -fulvic acid solution, the discrete surface peaks were replaced by a single broad peak with a gentle tailing slope extending approximately 20 Å away from the mica surface. This pattern implies that Hg^{2+} is incorporated into the fulvic acid resulting in a thicker coating of organic material with an overall higher electron-density. Electrostatic repulsion between the mica surface and the negatively-charged functional groups in the fulvic acid is probably diminished by positive Hg ions embedded in the fulvic structure.

Morphology and chemistry of placer gold from Chaliyar River, southern India

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The Nilambur Valley region, southwestern India, has been known for its gold potential since early 20th century. Placer gold has been mined from the Chaliyar River which is the major river draining the Nilambur region. In this study, the morphology, surface texture and chemical composition of gold grains in stream sediments from the Chaliyar have been examined by SEM, SEM-EDS and EPMA. Precambrian crystalline rocks together with pegmatites and quartz veins are the dominant basement rocks in the Chaliyar drainage region. A thick laterite develops over the crystalline rocks around the gold mining area. The placer samples were collected at seven sites along the stream in the upper reaches of the Chaliyar. Gold grains were obtained by panning and hand-picking from the placer samples.

The placer gold grains show sub-rounded shapes with ellipsoidal, flattened, elongated or folded outlines. Their size ranges from 0.1 to 1 mm. The gold grains show various corrosion textures such as etch pits and chemical corrosion cavities. Some of the cavities are filled with fine clay. The EDS spectra show that the clays are lateritic clays with organic matter consisting of O, Al, Si, Fe and C. Fine plant roots are also found in some cavities and on the grains. These gold grains are considered to have undergone chemical corrosion in lateritic weathering front near the placer sites.

The electron microprobe data show that many gold grains are characterized by outer or marginal growths of high purity gold (>97 wt% Au) with varying degree of silver-enriched core (97-81 wt% Au; 3-19 wt% Ag). Some grains are homogeneous pure gold with exceedingly high Au content (>98 wt%). From morphological and chemical characteristics, it is inferred that the placer gold grains underwent chemical refinement by selective extraction of Ag and reprecipitation of Au from primary gold under the influence of organic acids in the weathering front.

Changes in secondary structures of dissolved polypeptides with pH, salts and temperature as analyzed by attenuated total reflection infrared spectroscopy (ATR-IR)

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Proteins are essential materials for life. However, little is known about the environment where proteins were formed in the chemical evolution. Proteins are the chains of 20 amino acids bound by peptide linkages, which are folded into well-ordered three dimensional structures resulting in many functions. To examine the origin of life, it is necessary to elucidate the environments where proteins been produced and evolved in the early earth.

Deep-sea hydrothermal systems are considered to be one of candidate environments for the chemical evolution. Several peptides not more than 6-8 amino acids have been synthesized simulating these environments. However, 3-dimensional protein structures have not yet been obtained. In order to study formation mechanisms of 3-dimensional proteins, it is first necessary to investigate effects of dissolved ionic species, temperature and minerals on the structures of proteins.

In this study, to establish the methodology for studying these effects on protein structures, changes of secondary structures of polypeptides/proteins have been measured by using attenuated total reflection infrared spectroscopy (ATR-IR). Changes of the secondary structures (alpha helix and random coil) of poly-L-glutamic acid sodium salt were studied mainly by the amide bands (1630 and 1550cm⁻¹) during pH change, adding of salts and heating. The IR amide bands changed by these operations. Based on these results, favorable pH, salt and temperature environments for well-ordered polypeptides will be discussed. The effects of mineral surfaces will also be examined.

Characteristics of black and reddish brown microbial mats in spring water

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Layered black and reddish brown microbial mats are formed in spring water under Fe-rich condition at the Onma Formation, in Kanazawa, Ishikawa prefecture, Japan which is mainly composed of sandstone deposited at shallow sea in the early Pleistocene. The microbial mats are evaluated characteristics of mineralogy, chemistry, microbiology and micro morphology using with optical microscope, ED-XRF, XRD, AAS, SEM-EDX and TEM. The characteristics of spring water indicated pH 6.8 - 7.0, Eh 160 mV, EC 120 - 136 μ S/cm and DO 5.1 - 7.1 mg/l, under neutrality and micro aerobic conditions. The spring water contains mainly total Fe (9.0 ppm) and Mn²⁺ (1.0 ppm). The layered microbial mats on the surface are covered in reddish brown materials showing high concentration of Fe (82.4 wt%) and Mn (8.9 wt%), associated with traces of Si, P, S, K and Ca by ED-XRF analyses. XRD results of the mats show the broad diffraction pattern suggesting presence of amorphous materials, such as iron hydroxides. Furthermore, optical microscope and SEM-EDX observations revealed that existence of rods-shaped bacteria and Fe spherical particle in the reddish brown layers. On the other hand, the black layers show high concentration of Mn (28.4 wt%) with contains of Fe (65.4 wt%), and associated with traces of Si, P, K and Ca, identified as birnessite reflections at 7.5, 3.7 and 2.4 Å. Moreover, many bacteria exist in the substance which makes mainly Mn minerals in the black layers. Formation of Fe hydroxides is more superior to Mn minerals in this spring water. These results indicated the relation between Fe and Mn bio-minerals formation in spring water, suggesting the history of geo-, aqua-, and bio-systems in each layer.

Effect of trivalent actinides on the degradation of malic acid by *Pseudomonas fluorescens*

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The transuranic elements, such as Am(III) and Cm(III), are highly toxic because they emit high-energy α particles and have long half-lives. To estimate their long-term environmental behavior, we need to elucidate degradation of actinide-organic complexes by microorganisms.

We studied the biodegradation of Eu(III)-malic acid complexes by *Pseudomonas fluorescens*. Malic acid is ubiquitous in the environment and is one of the microbial metabolites that is part of the tricarboxylic acid (TCA) cycle. Europium(III) is a good analogue for Am(III) and Cm(III). To investigate the effect of Eu(III) on the degradation of malic acid by *P. fluorescens*, we compared the degradation behavior of Eu(III)-malic acid complexes to that of Fe(III)- and Al(III)-malic acid complexes.

In the medium containing 1 mM malic acid and 0-0.5 mM Fe(III), malic acid was degraded completely. In the medium containing 1 mM malic acid and 0.05-0.5 mM Al(III), malic acid was degraded until the concentration of malic acid became equal to that of Al(III), indicating that Al(III)-malic acid complex with 1:1 molar ratio was recalcitrant to biodegradation. In the medium containing 1 mM malic acid and 0.05-0.5 mM Eu(III), degradation of malic acid was not observed. The effect of metals on degradation of malic acid was in the order of Fe(III) < Al(III) < Eu(III). The stability constants of 1:1 Fe(III)-, Al(III)-, and Eu(III)-malic acid complexes are 7.1, 4.6, and 4.9, respectively. These results indicate that degradability of malic acid does not depend on the stability constants of metal-malic acid complexes.

We found that 10 mM malic acid was degraded in the presence of 0.05 and 0.1 mM Eu(III) but 1 mM malic acid was not degraded in the presence of 0.05 and 0.1 mM Eu(III). The degradation rate of malic acid increased with a decreasing ratio of Eu(III) to malic acid.

The shell nacre of *Sinohyolipsis schlegeli* recorded water environmental factor

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Sinohyolipsis schlegeli inhabit in the freshwater in Biwako Lake, Siga, and Kasumigaura Lake, Ibaraki, Japan, since 1931. Recently, pearls are produced in both lakes. The shells are able to separate two sections, such as vertical prismatic structure and horizontal nacreous structure. Pearl is a carbonate mineral grain in nacreous structure formed from mantle. Main component of bivalves shell is CaCO₃. Furthermore *Sinohyolipsis schlegeli* have not only ability of pearl producing but also ability of water quality purification. Distribution of metal elements of Mg and Sr are correlated with water temperature in which mother shell lives (Masuda, 1986). In this study, we intend that the detection of environmental change recorded in the shell nacre of *Sinohyolipsis schlegeli*. The shell cultivated at the regulating pondage of Kanazawa University, Japan for 1 year, from December 2004 to December 2005. The 5 months aging shell (sample A) and 1 year aging shell (sample B) were compared. Water quality (pH, Eh, EC, DO, WT) and dissolved ions of regulating pondage were measured periodically. The shell structures were cut at vertical section to nacre layer for observation by optical microscope, SEM-EDX and EPMA. The water quality of regulating pondage indicated that there are correlations between pH and seasonal changing of water temperature. Furthermore the result of EPMA analysis of shell nacre presented three Mn layers attend to shell growth within 1 year. The high Mn content layers are correlated with Ca content in the water of regulating pondage. The shell nacre recorded the history of aqua- and bio-systems in each layer. Shell will certainly play an important role in future ecosystems as bioremediation of pollution of a water system.

Radioactive biofilm in Tamagawa Hot Springs at Akita prefecture

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Tamagawa Hot Springs at Akita prefecture is famous of radioactive hot springs in Japan, produced 'Hokutolite' contains Ba, Pb, Sr, and trace of radium (Ra). Although Tamagawa hot springs have been studied about Hokutolite by many researchers, only a few studies have focused on the microbiological point of view. In this study, accumulation of radioactive ²²⁶Ra to biofilm collected from Tamagawa hot springs is considered through optical microscopy, SEM and TEM observation. Reddish biofilm on the hot spring water has high radioactivity. ²²⁶Ra content in the biofilm is higher than the hot spring water (2.26 Bq/g in the microbial mats, whereas 0.06 Bq/g in the hot spring water). The characteristics of hot spring water show pH 1.3, Eh 267 mV, EC 28.7 mS/cm, DO 2.8 mg/l, and water temperature 55.3°C, indicating extremely strong acidic and reducing condition. The elemental composition of biofilm was analyzed by ED-XRF, showing mainly S (55 wt%), As (30 wt%), and traces of Pb, Ba, Ca, Si, and Fe. The XRD profile of biofilm included sharp diffraction peaks at 7.69 Å, 4.31 Å, and 4.28 Å. This diffraction peak come near gypsum (7.63 Å, 3.07 Å, 3.07 Å), and other diffraction peaks are tridymite, and barite. However those diffraction are very low intensity, and there are no diffraction of minerals contains As and S. Therefore this biofilm is mainly amorphous materials. TEM and SEM equipped with EDS observation and analyses revealed bacterial biomineralization processes of amorphous materials (As-S) and relationships ²²⁶Ra and amorphous materials (As-S).

Biominingalization of Magnetite Nanoparticles by Fermentative Processes

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Anaerobic Fe(III)-reducing bacteria precipitate or transform the crystalline or amorphous iron oxides into crystalline Fe phases such as magnetite, siderite, vivianite, iron sulfide, and green rust. The objective of this study is to examine biominingalization of magnetite by fermentation processes. The reductive biotransformation of a akaganeite (β -FeOOH) by two Fe(III)-reducing bacteria, *Thermoanaerobacter ethanolicus* (TOR-39) and *Shewanella saccharophila* (HN-41), was investigated under anaerobic fermentation processes at circumneutral pH (pH = 7 – 8). The two Fe(III)-reducing bacteria are capable of producing extracellular magnetite using akaganeite as a magnetite precursor. No exogenous electron carrier substance (i.e., anthraquinone disulfonate) or reducing agent (i.e., cysteine) was added to the anaerobic medium. By comparison of iron minerals formed by *Shewanella saccharophila* at 25°C and *Thermoanaerobacter ethanolicus* at 65°C using akaganeite, it was shown that *Shewanella saccharophila* formed 2 ~ 3 nm-sized magnetite (Fe_3O_4) particles at 25°C within 10 days, whereas *Thermoanaerobacter ethanolicus* formed mainly 30 ~ 200 nm-sized magnetite particles at 60°C within 3 days. Unlike mostly superparamagnetic magnetite (< 5 nm) produced by HN-41 at 25°C, the thermophilic Fe(III)-reducing bacteria, TOR-39, produced mainly well-formed single-domain magnetite (>35 nm) at 60°C. These results suggest that microbially facilitated formation of the magnetite nanoparticles by fermentation processes at near ambient temperatures may influence the biogeochemical cycles of carbon and metals in subsurface environments. And extracellular production of magnetite nanoparticles at near ambient temperatures may expand the possible use of specialized ferromagnetic nanoparticles.

Effect of Several Kinds of Mineral Dusts to the Growth of Silicate Bacteria S35

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From the analysis of the chemical composition of six kinds of mineral dusts and the changes of pH value, glucose (GLU), electrolyte and Mn, Si, Fe after the dusts acted with silicate bacteria S35. Compared the chemical compositions and physical properties of dusts on silicate bacteria S35. And then through SEM analysis, studied the bacterial form and interface action status in the course of action between dusts and bacteria. The results show that all kinds of mineral dusts have different degree effects on experiment bacteria. So we can say that the effect of mineral dusts to silicate bacteria have correlation with dust's chemical compositions and physical properties.

From the experimental results, we can get some conclusions as following:

(1) After mineral dust acted with silicate bacteria S35, the macroelement of Ca, Mg, N, K and the trace elements of Mn, Si, Fe had differently been increased in culture liquids relative to dusts controls without bacteria. Among them, Si of DJ-4# and Mg of DJ-20# had most obvious increment that expressed silicate bacteria have some stimulative to their dissolution.

(2) GLU wastage and pH values of silicate bacteria S35 had different degree been increased after acted with all kinds of dusts relative to normal controls, especially DJ-4# and DJ-20# are more obvious.

(3) SEM analysis shows that, the thalli of silicate bacteria have obviously changed after acted with DJ-4# dusts, bacterial autolyzing degree increased, thalli have distorted and their surfaces had become dry rot and lose water badly. This is mainly because that a great of Ca and Si have been dissolved out from dusts (CaSiO_3) in the culture liquid.

(4) Thalli of silicate bacteria had seriously transformed and become silk shape and intervened mutually to "bacterial net". The abundant dissolution of Mg should be responsible for it.

The growth effect researches of mineral dust to silicate bacteria and the other bacteria about the surface electricity, shape, elementary characteristic etc. still need further experiment.

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Origin and genesis of phosphate and related minerals from Senbutsu-do Cave, Fukuoka Prefecture, southwest Japan

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As cave system is chemically and physically stable, it is regarded uniform for most mineralogenesis unlike magmatic or metamorphic process. In spite of this simplicity, Hill and Forti (1997) reported 255 species all the world over. This implies cave minerals are strongly related to microbiological activity. Previous studies of cave minerals were rather focused within a realm of descriptive, further approach including water chemistry is necessary to elucidate the origin and genesis of cave minerals geochemically.

Senbutsu-do Cave is a limestone cave over 700 m known length in Hirao-dai Plateau, southwest Japan. It is located adjacent to boundary of Paleozoic Limestone and late Paleozoic to early Mesozoic metamorphic rocks. These older rocks have been raised and metamorphosed by Mesozoic granodiorite. Hereinafter the cave formation, sedimentation of Aso-4 pyroclastic deposits occurred inside at about 90 ka.

Several mounds of bat guano up to 0.3 meters height are recognized on the floor of a small hall. Surface of the guano is crumbly about several millimeters in size, dark-grey to black in color and wet. Samples for mineral identification and chemical analysis were collected both vertically within the guano mound and horizontally between the guano and the limestone wall. The concentration of K and Ca ions in pore and/or absorbed water of guanoic sediments was calculated by analysis of extracts from guano into ion-exchanged water.

Vertical changes in mineral species from amorphous silica, quartz and ill-crystallized leucophosphate were observed while changes in pH were 6.0 to 2.3. Horizontal changes of mineral species from variscite, taranakite, hydroxylapatite and calcite were also observed. The pH of guano sediments was 2.2 on the guano side to 6.2 on the limestone wall side. The solubility of variscite in water is lower than that of hydroxylapatite in the pH range 2.3 to 5.0. On the contrary, the solubilities for two minerals are reversed at pH around 7. The distribution variation of phosphate minerals depends mainly on pH and partly increasing content of Ca ion from the guano to the limestone wall in the cave. Distribution of phosphate minerals is elucidated on the basis of water chemistry. Only 32 cave mineral species were reported from Japan (Kashima and Hisatomi, 2002), detailed study for origin and genesis of these from geochemical viewpoint is further needed.

A new way for evaluation of lake water quality: mineralogical study of fish otoliths

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The otoliths of carps (*Cyprinus carpio*), from the Baiyangdian Lake of Hebei province, the Miyun Reservoir of Beijing Municipality, and the Lianhuanhu Lake of Heilongjiang province, China, were studied with optical microscope, SEM, EMPA, TL, Atomic Active Analyses and LA-ICP-MS. Two types of nanometer-scaled aragonite were found with granular and prismatic crystal forms, which might be related with environmental temperature. The granular aragonite was formed under relatively higher water temperature whereas the prismatic was formed under cooler water. The thermoluminescent parameters of the otoliths from Baiyangdian and Miyun are quite different, reflecting the geochemical characteristics of the two waters. The experimental result indicates that the shapes of the thermoluminescence curves obtained from the otoliths samples of the two waters are similar, but the peak point temperature values (T), the thermoluminescence intensities (I), the integral intensities (S) and the half width (W) of the fish otoliths from the Baiyangdian Lake are greater than those from the Miyun reservoir. According to the investigations, the contaminative degree and eutrophication in the water of the Baiyangdian Lake is heavier than that of the Miyun reservoir, so the thermoluminescence parameters of the fish otoliths are quite sensitive to contaminated and non-contaminated waters, and they can be regarded as important marks of the degree of the contaminated water. The analyses reveals that most of the trace elements are greatly enriched in otoliths than in waters, and the chemistry of the otoliths is good mark for water's chemistry. The LA-ICP-MS profile analyses from the core, mantle to the rim of otoliths can reflect the variation of the water chemistry. A correlation of the otoliths of the carps from the waters around Beijing in China with those from Australia suggests that the sizes of the otoliths are positively related with the lengths of the carp bodies, but their correlation coefficients are quite different. In the past two or three decades, quite a few achievements have been made in the research of fish otoliths, however, the study on thermoluminescence characteristics of the fish otoliths and relationship of nanometer-scaled aragonite crystal form with water temperature have not been reported in public. The results may lead to the establishment of biominingalogical method for evaluation and dynamical monitoring of lake water quality. This study is financially supported by the National Natural Science Foundation of China (Grant No. 40473044).

O25-01

The role of near-surface alteration at the fluid-mineral interface: evolving views on the mechanisms of dissolution.

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Mineral dissolution has been studied for well over a century now, and still there is no unanimity on the exact mechanism(s) controlling the dissolution process, in particular with respect to primary metal cation silicates. One of the key aspects to the dissolution process of these minerals is non-stoichiometric dissolution that is linked to the formation of an altered near-surface zone that is chemically and structurally different from the unaltered bulk mineral. Early on, it was suggested that laboratory-measured dissolution kinetics characterized by parabolic rate vs. time relations could be attributed to diffusional mass transfer through this layer.

However, starting in the sixties, a few workers such as Lagache (1965) challenged the widely accepted diffusion-limited kinetic theory by proposing that parabolic kinetics were the result of an increase in the concentration of released components to the fluid, and that dissolution was really controlled by surface chemical reactions. Integrating surface reaction control with non-stoichiometric dissolution and the formation of altered layers required the development of the so called 'leached layer' theory. It is based on the premise of preferential (faster) release of certain cations from the mineral structure, leaving behind a relict structure (leached layer) that is amorphous and chemically distinct from the bulk mineral. Its thickness can range up to several hundreds of nm, and is dependent on the properties of both the solution (pH, temperature, composition) and the mineral (composition, structure). The preferential loss of cations is coupled to the preferential uptake of H^+ from solution (to ensure electroneutrality) via an interdiffusion process. The leached layer theory effectively proposes two simultaneous mechanisms, retreat of the fluid-leached layer interface by surface reaction, and propagation of the leached layer into the bulk mineral by diffusion; when these two processes attain the same rate, the leached layer stops growing in thickness.

However, several recent studies, based on nano-scale chemical cartography, have demonstrated that the chemical gradients between the altered zone (i.e. leached layer) and the bulk mineral are almost atomically sharp, and are spatially coincident with an atomically sharp amorphous-crystalline transition. Such sharp boundaries are incompatible with a diffusional process, and rather point to a dissolution-precipitation mechanism occurring in a thin film at the interface (a theory proposed, but never proven, almost 40 years ago by Taylor and O'Neil, 1967). A selected set of nano-scale data supporting this new concept will be presented by R. Hellmann in this keynote lecture.

O25-02

NANOKIN: a geochemical computer model for dissolution, nucleation and growth of minerals in aqueous solutions

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In order to take into account the initial stages of formation of mineral nanoparticles in water-rock interaction models, we have developed a theoretical approach of nucleation, growth and ageing processes, relevant for precipitation in solution. It is based on the classical nucleation theory, on a size-dependent (algebraic) growth law allowing growth, resorption and ripening of particles simultaneously, and on conservation laws akin to a thermodynamically closed system.

The model yields a set of highly non-linear coupled equations, which, aside from the initial conditions, are functions of only three irreducible dimensionless parameters. We find that the formation of the new phase obeys a generic scenario, involving mainly three stages: a phase of pure nucleation during which the supersaturation decreases, a plateau characterized by a quasi-equilibrium between nucleation and (positive) growth on the one hand, and resorption on the other hand, and an ageing stage ending with a single particle in thermodynamic equilibrium with its surrounding medium. During the plateau regime, very complex dynamical effects take place, which may be disentangled thanks to the full knowledge of the particle population obtained by our approach.

The resulting geochemical model called NANOKIN is applied to the formation of silicate phases, and particularly kaolinite-type minerals, from aqueous solutions resulting from rock alteration processes. The nanoparticle formation results from oversaturation states in solutions and is simulated versus time in terms of populations of particles appearing successively, surviving and growing or disappearing depending on the evolution of the resulting saturation state of the solution with respect to the corresponding mineral phase: the geochemical code allows to take into account the feed-back effect of precipitation on the composition of the aqueous phase.

References:

- C. Noguera, B. Fritz, A. Clément, A. Baronnet: "Nucleation, growth and ageing scenarios in closed systems I: a unified mathematical framework for precipitation, condensation and crystallization", submitted

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O25-03

Simulated water attack modeled for silica

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The attack of silica by a water molecule was modeled with molecular orbital calculations to clarify the hydrolysis and dissolution of silica, using the Gaussian 03 software at both the B3LYP/3-21G* and B3LYP/6-311G(2d,p) basis set levels. A relatively large hydrogen clad model of silica, $Si_4O_{10}(OH)_4$, was used to represent the bulk structure of silica. The atomic positions of the water molecule, and those of the target $SiO_3(OH)$ moiety of the model, were varied in mimicking the surface reaction whereas the positions of the remaining $Si_3O_3(OH)_3$ atoms were frozen throughout the geometry optimization. The reactant (the adsorption state), the transition state and the reaction product (hydrolysis) were successfully geometry optimized at B3LYP/6-311G(2d,p) level. The transition state was verified by calculating it both from the local maximum geometry and from the combination of the reactant and product states, which converged exactly to the same configuration.

The total energy of the product is lower than that of the reactant by 15.1 kJ/mol (3.6 kcal/mol), indicating that the hydrolysis state is more stable than the adsorption state. The energy of the transition state is 138.5 kJ/mol (33.1 kcal/mol) higher than that of the reactant, which is consistent with values found by earlier workers.

Movie frames of the structural changes, including electron density deformation maps near the transition state, were generated. As the water molecule approached the model structure, the Si_1 atom became 5-coordinated with the addition of O_w to the coordination sphere of the atom. In addition, one of the H atoms of the water molecule concomitantly bonds to the bridging O_{br} atom bonded to Si_1 , resulting in a weakening of the Si_1-O_{br} bonded interaction and an ultimate cleavage of this SiO bond. The key step is the hopping of the H atom from the water oxygen to the domain of lone-pair electron density of the bridging oxygen, resulting in the formation of two silanol groups. The end result is a mechanism for H enrichment of earth materials.

O25-04

Predicting mineral phases formed at low temperatures

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This paper discusses the formation of minerals at low temperatures where the formation rate is extremely slow for some stable phases. At high temperatures we can thermodynamically predict what kind of mineral precipitates from a solution if we know the composition of the solution, temperature and pressure. The reason why we can predict the mineral formed at high temperatures is that the formation rate is fast and that the factor we should consider is thermodynamic stability. On the other hand, at low temperatures we have difficulties in predicting a formation mineral only from thermodynamic stability. This is because the thermodynamically stable phase often precipitates extremely slowly so that no traceable amount of the stable phase is formed at low temperatures. Instead, a meta-stable phase is formed at low temperatures. This meta-stable phase precipitates fast compared with the stable phase. This meta-stable phase is often a disordered phase such as amorphous or clay. This is because the disordered phase has high entropy, and a phase with high entropy precipitates fast. The precipitation rate is proportional to $\exp(S/k)$, where S is the entropy of the mineral and k is the Boltzmann constant. On the basis of this equation, we propose the method to predict the formation of minerals at low temperatures. As an application of this theory, we discuss the simultaneous precipitation of crystalline and amorphous phases with the same chemical composition. This phenomenon is observed in the precipitation of calcium carbon dioxide. When a solution is super-saturated with amorphous and crystalline phases, both amorphous and crystalline phases precipitate simultaneously and the concentration in the solution decreases rapidly until the solution is unsaturated with the amorphous phase. The amount of the crystalline phase, however, is so small that we can hardly detect the crystalline phase. Next, the system reaches a steady state where the concentration in the solution does not change. The solution is super-saturated for the crystalline phase but unsaturated for the amorphous phase, so the crystalline phase is precipitating but the amorphous phase is dissolving. The concentration of the solution is adjusted so that the precipitation rate of crystalline phase is as same as the dissolution rate of amorphous phase. Finally, all the amorphous phase has dissolved and the concentration in the solution starts to decrease again until the concentration reaches equilibrium with the crystalline phase.

Natural weathering processes and surface textures of pyroxenes and amphiboles

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Etch pits and related features (e.g., denticulated margins) are ubiquitous on naturally weathered pyroxenes (single- and double-chain silicates). Natural weathering of chain silicates corrodes them in a crystallographically controlled manner, resulting in etch pits on the surface of the mineral and eventually denticulated margins. Most denticles originate at fractures (often marked by preserved early-formed weathering products), but others can form without fractures, along arrays of laterally adjacent dislocations. The range of corrosion morphologies is identical between pyroxenes and amphiboles, and within each group across a range of diverse compositions. The surface morphology of weathered pyroxenes can be strongly influenced by the distribution of more- and less-weathering-resistant volumes of pyroxene (e.g., exsolution lamellae). Natural weathering mechanisms of pyroxenes appear to more closely resemble corrosion mechanisms at extremely low pHs than corrosion mechanisms in dissolution experiments carried out at pH conditions similar to those of natural weathering.

Weathered pyroxenes and amphiboles at numerous locations and in a wide variety of weathering environments exhibit the same types and ranges of weathering morphologies, despite differences in parent material, geomorphic history, vegetation, land use, presence/absence of secondary-minerals, and geochemical differences that result in formation of very different weathering products. Inferences about textural relationships between reactant pyroxenes and their phyllosilicate weathering products are strongly dependent on sample preparation methods.

Chain silicates appear to weather by a single ubiquitous mechanism; environmental factors appear not to vary sufficiently among sites to produce different surface textures. The dimensions of corrosion textures vary systematically with the duration and intensity of weathering in natural weathering profiles; however, dimensional differences are variations on a single theme of etching morphology. This textural conservatism may be characteristic of interface-limited reactions. Chain-silicates weather by the same (rate-determining) mechanism, and produce similar textures, in a wide variety of environments, allowing textures to be used as a basis for quantitative comparisons between different profiles (e.g., hornblende etching as a tool for relative-age, soil-development, and paleoclimate studies in glacial landscapes).

Mechanisms of feldspar dissolution in the tropics

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Abstract

Chemical weathering of granite under tropical conditions can produce up to 40m of laterite. Feldspar dissolution is a key process in laterisation. In order to develop a mechanistic understanding of feldspar weathering under such conditions, we have conducted detailed investigations involving mineralogical, geochemical and micro-structural characteristics of weathering profiles, including the underlying unweathered granitic rocks, at two locations in Malaysia. In the Cheras muscovite granite, samples were obtained from a 33m recently exposed cut surface. In the Rawang biotite granite, samples were obtained from a 15m recently cut surface and 15m deep drill holes. Feldspar dissolution and clay mineral development were examined using SEM, XRD and XRF. It was found that the dissolution of feldspars almost all occurs over a 1 to 2m thick zone at the weathering front between rock and laterite. Plagioclase breaks down first. Scanning electron microscope observations show that in alkali feldspars dissolution of albitic perthite lamellae occurs first, initially at misfit dislocations. At an advanced stage, the albite lamellae dissolve completely and the K-feldspar grains collapse. Remaining orthoclase or microcline persists through a considerable thickness, about 2 to 5m of the overlying laterite. The first main product of feldspar weathering is halloysite (the hydrated form of kaolinite). Kaolinite develops in the upper (i.e. older) part of the sections. In the localities studied, with gentle, rolling topography, the rock-laterite front and the halloysite-kaolinite front follow the topography of the land surface.

Relation of redox-sensitive elements in Precambrian paleosols to atmospheric oxygen evolution

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Iron, Mn and Ce are redox sensitive elements and require different oxidation levels to get into a higher state. We can expect variations in ratios of these three elements remaining in paleosols (ancient soils formed by weathering) with respect to parent rocks as a consequence of changing atmospheric oxygen concentration with time. This point has made us examine the relation of Fe, Mn and Ce in 2.8 to 1.7 Ga old paleosols to atmospheric oxygen evolution. Because the abundance of Ce in rocks is much lower than those of Fe and Mn, we used two different methods to estimate the ratios of these three redox-sensitive elements remaining in paleosols relative to their parent rocks. Fe²⁺ and Mn²⁺ are soluble and, it can be assumed, they leave the weathering profile whereas Fe³⁺ and Mn³⁺ remain in the profile. The retention fractions of Fe and Mn were calculated from their concentrations in the paleosols (literature data) considering compaction of the paleosols. On the other hand, the remaining ratios of Ce were calculated based on the concentrations of Ce in rhabdophane, REE phosphate, in the paleosols. Ce³⁺ is oxidized to form cerianite (Ce⁴⁺O₂) under oxic conditions whereas it remains as Ce³⁺ to form rhabdophane under anoxic conditions. The Fe retention increased almost linearly with time from around 2.6 Ga and reached 1 (i.e., complete retention) at around 2.1 Ga. The Mn retention also increased almost linearly with time and reached 1 at around 1.7 Ga. The increase of the Mn retention is characterized by less steep slope than that of Fe, which is well explained by a slower oxidation rate of Mn²⁺ than Fe²⁺. The Ce³⁺/La ratio in rhabdophane decreased almost linearly with time and reached 0 at around 1.7 Ga. The slope during the time period is almost the same as that of the Mn retention although the sign is reverse. The variations of the remaining ratios of Fe, Mn and Ce described above suggest that the atmospheric oxygen increased in the time period of 2.6 to 1.7 Ga. This is consistent with the geologic record of $\delta^{13}\text{C}$ excursion and $\Delta^{33}\text{S}$.

Linking a microscopic approach to macroscopic observations for ion adsorption on mineral surfaces

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Mineral surfaces are relevant for the description and understanding of the behavior of ionic substances in the environment via adsorption/desorption processes and/or via dissolution/precipitation reaction. In most cases the reactions are surface controlled. Modern spectroscopy has led to increased insight in the structure of chemicals as they are adsorbed on mineral surfaces. The challenge is to link this molecular information together with information on the structure of the mineral surface to the macroscopic pH dependent ion adsorption process. The Multi Site Ion Complexation (MUSIC) model allows linking the structure of the mineral surface to the reaction with strong acid or bases, by estimating *a priori* proton binding constants for various types of reactive surface groups. Other ions may react with the surface via a ligand exchange reaction. In this case, part of the ligands of the adsorbing ion is 'in' the surface and part is more oriented towards the solution. For modeling it is essential to distribute the charge of the adsorbing ion over two electrostatic planes. The value of the Charge Distribution (CD) needed in the model can be linked to the structure of the adsorbing complex using the Brown bond valence approach. This approach requires knowledge of the interatomic distances. These distances can in principle be derived from EXAFS spectroscopy and/or from quantum chemical calculations. For several surface species, we will compare the predicted CD values with CD values derived from interpreting macroscopic adsorption data and also with CD values that result from using a simple Pauling bond valence approach. In some cases the experimental results show some bias with the microscopic CD values. The possible reason for this discrepancy will be discussed.

In environmental systems metal(hydr)oxides are also interacting with large natural organic molecules like humic and fulvic acids. These interactions should be incorporated in surface complexation models. These larger organic molecules have many ligands per molecule, which makes the number of possible species huge. Recently a breakthrough in our understanding of the complicated adsorption process for such type of molecules has been obtained (Langmuir 2006 22:389-397). The theoretical background of this process will be discussed and some examples of its application will be given.

Simultaneous inner- and outer-sphere As(V) adsorption on iron and aluminum oxide surfaces

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Adsorption of toxic elements onto mineral surfaces reduces their bioavailability and potential for transport. A fundamental understanding of adsorption processes is desired in order to predict the fate of contaminants in complex systems and to generalize about the behavior of these elements in the environment. The adsorption of arsenate (AsO_4^{3-}) at pH 5 on the (012) surfaces of corundum and hematite was studied using resonant anomalous X-ray reflectivity (RAXR). Two distinct sorbed arsenate species were observed in roughly equal proportions: an inner-sphere species consistent with a bridging bidentate complex, and an outer-sphere species, presumably adsorbed via hydrogen bonding. The relative fraction of arsenate adsorbed in the outer-sphere complex was generally independent of the arsenate concentration in solution. These results suggest that outer-sphere arsenate adsorption may be a significant sequestration mechanism that has been largely overlooked in past studies and whose impacts on the fate and bioavailability of arsenic need further evaluation.

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Elucidation of geochemical reactions at the water-mineral interface on a molecular level by time resolved laser fluorescence spectroscopy with Cm(III)

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For the long-term performance assessment of nuclear waste repositories, knowledge on the interactions of actinide ions with mineral surfaces is imperative. Present representation of such processes is based on bulk distribution coefficients. Future representation will need to reflect a deeper process oriented description, reflecting the future expectation level on the state-of-the-art, i.e. predictive process based geochemical modeling.

The mobility of released radionuclides is strongly dependent on the sorption and desorption processes at mineral surfaces. Because of the reductive conditions in the environment of a waste repository in deep geologic formations, heavy metal ions are present in their low oxidation state. Actinides dominate the radiotoxic inventory over the main part of the time span of concern. Americium occurs in the trivalent state, in the case of plutonium this is also expected under strongly reducing conditions. Due to the excellent spectroscopic properties, Cm(III) is chosen as a chemical representative for the trivalent actinides. It has a high fluorescence yield, a favourable fluorescence decay behaviour and thus allows speciation studies in the nanomolar concentration range by time resolved laser fluorescence spectroscopy (TRLFS). This can also be used for surface complexes for concentrations corresponding to a surface loading far below a monolayer. Results of investigations of the curium interaction with the mineral surfaces of clay minerals, quartz, feldspars and calcite are presented.

Goal of this presentation is to demonstrate that TRLFS studies opens up the possibility to use Cm(III) as atomic sensor for the elucidation of geochemical reactions. The results therefore contribute to the required development towards process based geochemical modeling for long-term performance assessment of a nuclear waste repository.

Speciation of the functional groups at mineral surfaces in situ under water by sum frequency vibrational spectroscopy

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The properties of mineral/electrolyte interfaces are controlled by the surface functional species. In order to model surface reactivity and adsorption/desorption processes a large number of functional groups has been postulated. In most cases, however, a direct proof for the existence of these species in real aquatic environment is lacking because it is difficult to obtain chemical in situ information with interface selectivity. Thus we applied interface selective sum frequency (SF) vibrational spectroscopy in order to study the speciation of the (001) and (110) surface of sapphire ($\alpha\text{-Al}_2\text{O}_3$) under water between pH 3.7 and 12.0. This investigation is part of an ongoing fundamental study of the sorption mechanism of actinides at single crystal faces by various experimental and theoretical techniques. Sapphire is applied as a simple model for natural clay minerals and analogous iron phases.

In the OH stretch region of the infrared spectrum, we observe a surprisingly large number of 7 bands due to different aluminol species and to specifically bound water molecules. For two aluminol species of the (001) surface, we measure the tilt angle τ of their OH bond with respect to the surface normal ($\tau=10^\circ$ for species with resonance frequency ν_0 at 3690 cm^{-1} , $\tau=80^\circ$ for species with $\nu_0=3440\text{ cm}^{-1}$). The band positions and tilt angles agree well with recent molecular dynamics calculations. The former species is expected to act as a hydrogen bond donor, the latter species with its OH dipole almost in the surface plane can also act as a hydrogen bond acceptor. Its surface concentration increases substantially from pH 6 to pH 4.

In addition, SF spectroscopy allows us to determine the absolute dipole orientation of the water molecules adjacent to the mineral surface. At high pH, we observe the dipoles near the (001) surface to point into the direction of the crystal. This is consistent with a negative surface charge. Reducing the pH we expect a flipping of the dipoles near the point of zero charge. In fact, however, we observe that the dipoles flip twice between pH 7 and 4. This phenomenon cannot be explained by electrostatic interactions. It is due to hydrogen bonding. We interpret the data by the formation of two types of hydrogen bonds, one with the in-plane aluminol species (hydrogen bond acceptor) dominating at pH 4 (water dipoles point to crystal), and the other type formed with the hydrogen bond donors dominating at higher pH.

Time and length scales of crystal dissolution kinetics

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Corrosion and weathering are the results of crystal dissolution, and can be observed over a range of time and length scales. This range exists because net dissolution is not a single process, but a very large number of serial and/or parallel processes whose individual rates reflect energy distribution at the molecular and quantum mechanical level. In contrast, the useful prediction of dissolution rates in natural or industrial environments demands our ability to integrate rates appropriately over large spatial and temporal domains, and the uncertainty associated with this integration are large. This problem leads to several important questions. How are material fluxes at the global scale linked to relevant quantum mechanical processes at the water – mineral interface? At which level must a comprehensive theory describe these processes? What are the relevant tools that permit the study of crystal dissolution theoretically, experimentally, and in the field? How does our understanding at one scale link to results at other time and length scales? Lastly, how do we link our understanding of bond-breaking and bond-forming processes at the femtosecond and angstrom scale to the million year time and kilometer length scale of natural water – rock interactions?

Experimental work based on direct and indirect observations of water-mineral interactions using complementary analytical techniques such as interferometry, atomic force, electron microscopy and electrolyte chemistry, in combination with ab initio and stochastic computer calculations have begun to shed light on the question how crystalline matter dissolves. One surprising result is that observation and measurement of relevant processes at a fixed time and length scale are insufficient, regardless of the spatial resolution. Single-scale results, in and of themselves, are of but limited utility, and this constraint demonstrates that a comprehensive theoretical concept is required capable of linking observations made at the various time and length scales in a quantitative manner with each other.

We present a portfolio of observations and measurements at various length and time scales that represent key "parts of the puzzle" in our understanding of dissolution kinetics.

Conditioning film formation: bonding environment, crystallographic and chemical controls

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In the natural environment bacteria are found in the greatest abundance as sessile organisms attached to mineral surfaces. Prior to the attachment of bacteria it is generally believed that mineral surfaces are conditioned with macromolecules (proteins, polysaccharides and humic acids) and smaller molecules (fatty acids, lipids and organic acids). The development of the conditioning film and subsequent microbial colonisation are poorly understood at the molecular level and require further investigation. In this study model organic – inorganic systems have been used to gain insight in to i) the bonding environment of the organics at the surface and ii) mineralogic/crystallographic control on attachment.

It is difficult to study the *in-situ* adsorption of organic ligands directly due to low sorption densities and the presence of an aqueous phase, therefore a novel Multiple Internal Reflection-FTIR (MIR-FTIR) method has been developed. This has been used successfully to demonstrate that phthalic acid bonds to glassy olivine through a 7-member ring where oxygens from both carboxyl groups are involved in chelating with a single Mg surface site via adiffusion controlled process. Coupled with the *in situ* FTIR measurements X-ray surface scattering has been used to monitor the changes in surface morphology and chemistry during reaction. X-ray results show phthalic acid to be extremely efficient at preferentially removing Mg from the surface of the solid phase.

To examine mineral surface controls on adsorption density of organic ligands, Environmental SEM (ESEM) has been used image the attachment of Bovine Serum Albumen (BSA) on to olivine and pyroxene at pH 7.5. This has been achieved by taking a randomly orientated mass of each mineral, truncating it along a single reference surface exposing many crystallographic planes, determining orientation via electron back-scattered diffraction (EBSD) and observing the surface structures of the ligands. The results demonstrate both chemical and crystallographic control on adsorption. Pyroxene shows no adsorption while olivine has varying adsorbate densities depending the exposed crystallographic plane. Also, the ordering of the protein on the surface increases as the index of the plane becomes higher. Similar controls are also observed during microbial colonisation with bacteria preferentially adhering to a template laid out by the conditioning film, thus demonstrating underlying mineralogic and crystallographic control on biofilm formation.

High-resolution characterization of naturally weathered mineral surfaces by focused ion beam and transmission electron microscopy

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Understanding how mineral surfaces interact with fluids and organisms in soils, and their control on mechanisms and rates of chemical weathering, is necessary for the development of comprehensive geochemical models. However, determination of properties of mineral surfaces from soils is challenging, as they are invariably obscured by reaction products, as well as organic and inorganic debris. Using a focused ion beam (FIB) microscope, we have cut electron-transparent (~80-90 nm thick) cross-sectional slices from the outer surfaces of alkali feldspars for high-resolution imaging and chemical analysis by transmission electron microscopy (TEM). The feldspars were extracted without cleaning or any other treating from two soils of different ages: a 1.1 kyr soil from Glen Feshie (Scottish highlands) and a ~10 kyr soil from Shap (northwest England). Results of this work show that FIB and TEM in combination are exceptionally powerful tools for studying the structure and chemistry of mineral surfaces in cross section at spatial scales ranging from a few micrometers to sub-nanometer.

Surprisingly, we find two kinds of surfaces. The Shap feldspars are free of debris and display abundant etch pits. TEM images of FIB-produced cross-sections vividly demonstrate how the topography of grain surfaces and morphology of etch pits is controlled by the distribution of elastic strain within the feldspar. These images also show that crystal structure immediately beneath grain surfaces that have been in contact with the soil is completely unmodified. This result differs from findings from laboratory dissolution studies, which have shown that feldspars commonly develop an outermost amorphous and non-stoichiometric layer. By contrast, the Glen Feshie grains are covered with reaction products intermixed with algal, bacterial and fungal material. Most importantly, the feldspar surfaces are coated by crystalline and amorphous reaction products. The crystalline material comprises aluminosilicate clays with a ~1 nm basal layer spacing that are intimately associated with, and have probably formed from, amorphous silicate and aluminosilicate coatings. In a number of cases the clays lie directly beneath fungal hyphae, suggesting that crystallization of the clays, or recrystallization of the amorphous material, may have been organically-mediated. High-resolution images show that the interface of the feldspar with amorphous and crystalline reaction products is sharp on the atomic scale, suggesting that the models of 'preferential leaching' of silicate mineral surfaces derived from results of laboratory experiments may not accurately describe mechanisms of natural weathering in soils.

Water distribution profile in a weathered rhyolitic glass as measured by IR microspectroscopy

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It is widely known that volcanic glass hydrates during weathering. The hydrated glass has a higher index of refraction compared with unhydrated glass and therefore can be recognized at the rim of the glass under an optical microscope. Taniguchi (1980) measured the thicknesses of hydrated glass layer for 18 rhyolites from Kozushima, Japan, and estimated the growth rate of the hydration layer. The present study aims to investigate the mechanism and rate of water transport in the rhyolitic glass during weathering by means of IR microspectroscopy.

A doubly polished thin section of Ohsawa rhyolite from Kozushima was prepared. This rhyolite underwent weathering for 26,000 years (Yokoyama et al., 2004). IR spectral line profile analysis with a 10×60 μm aperture was conducted on a glass section from the glass surface to interior with 1 μm step for a length of 200 μm. In the glass section ~15 μm of altered layer was recognized under an optical microscope.

The concentrations of molecular H₂O and total water (molecular H₂O + OH species) were determined from the peak heights at 1630 cm⁻¹ and 3550 cm⁻¹, respectively. The concentrations of total water and H₂O showed increases toward the interior at depths 0–10 μm to reach maximum concentrations (total water ~0.75 wt%, H₂O ~0.5 wt%) and the concentrations were retained at depths 10–15 μm. The initial increases of the concentrations can be largely attributed to the artifact at the edge of the glass due to the technical limit of the aperture size. In deeper than 15 μm, the OH concentration was roughly constant (~0.15 wt%) while the H₂O concentration decreased with depth and became constant (~0.15 wt%) at >90 μm. Thus, the hydrated region extends beyond the layer observed by the optical microscope. The constant OH concentration in the hydrated region indicates that the hydration can be preceded by H₂O diffusion. Based on the concentration profile of molecular H₂O, the diffusion coefficient of H₂O was estimated to be ~10⁻¹⁰ μm² s⁻¹. This value is significantly larger than the H₂O diffusivity at 20°C (~10⁻¹³ μm² s⁻¹) extrapolated from the reported H₂O diffusivity data determined at >400°C, indicating very fast H₂O diffusion during glass weathering.

Impact factors on removal of perchloroethylene with nano-Ni/Fe methodology

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Chlorinated hydrocarbons are widely detected in groundwater but the conventional removal methodologies are not time and cost effective. Because of their toxicity and persistence, many chlorinated compounds have been listed as the most strictly controlled pollutants. Among the 129 most harmful pollutants listed by the USEPA in 1979, over 60 pollutants are organo-halocompounds and their ramifications. A survey of groundwater quality in a northern China city shows that TCE, followed by PCE, is at the first place in the list of compounds with high concentration and above the permitted level. 44.44% of the samples have TCE concentration above the standards issued by the USA Environment Protection Agency (EPA), and the highest concentration is 1000 μg/L, 200 times higher than the standard.

With the development of iron reducing technology in recent years, research on nano-iron and nano-bimetal has become a hot spot. Nanoscale metals can be directly injected into the contaminated soils, sediments and aquifers for in-situ remediation of chlorinated solvents without building a permeable reactive barrier. The paper presents the results of impact factors on PCE removal by nano-Ni/Fe method.

Appropriate amount of 1.0 mol/L FeCl₃·6H₂O (v/v=30% ethanol) is placed in conical flask, and in a closed system purged with pure nitrogen for two hours. Put 1.6 mol/L NaBH₄ solution into conical flask with 1.0 mol/L FeCl₃·6H₂O solution according to equal volume ratio on the magnetic agitator under 22±1°C. After finishing the adding of NaBH₄ solution, nano-iron particles appear in the solution in 5 min that is from Fe⁰ reduction. The reaction is described as: 4Fe³⁺+3BH₄⁻+9H₂O→4Fe⁰+3H₂BO₃+12H⁺+6H₂

The nano-iron was rinsed with de-oxygen water and ethanol three times respectively. NiCl₂ in ethanol was added to get the nano-Ni/Fe by reductive precipitation. The amount of Ni deposited on the nano-Fe can be got by analyzing the Ni²⁺ concentration in solution before and after reaction.

The data shows that the reaction rate of unexposed nano-Ni/Fe is 4 times higher than exposed one; Temperature is one of the important controlling factors. Reaction rate constant K_{SA} increases by 2–3 times with every 10°C increment of temperature. Within specific range, higher Ni/Fe ratio favors dechlorination process. When Ni/Fe is 8%, the dechlorination process reaches the highest rate. Dissolved oxygen in the solution does not favor the degradation of chlorinated hydrocarbons.

Precipitation of iron oxyhydroxide compounds in relation to stream and seawater chemistry in the Chinkuashih acid mine drainage area, Northern Taiwan

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Downstream variations in iron-oxyhydroxide mineralogy and water chemistry of Golden Falls acid mine drainage (AMD; pH = 2.7) and its downstream water (pH = 3.1) and seawater (pH = 8.0) were investigated by XRD, SEM, TEM, IR, ICP-OES, ICP-MS, and an on-site photometer in order to understand rock-water interaction processes in the Chinkuashih Cu-Au mining area, northern Taiwan. The As and Fe concentrations of AMD are significantly reduced by formation of As-bearing schwertmannite $[\text{Fe}_{16}\text{O}_{18}(\text{OH})_{10.12}(\text{SO}_4)_{2.80}(\text{AsO}_4)_{0.08}]$ and poorly crystalline goethite in addition to a dilution by the upstream water (pH = 6.0). Goethite is present at depths of all deposits greater than 2 cm in thickness and shows an increase in proportion relative to schwertmannite with depth. The As contents of AMD precipitates fall in the range of 1400–5000 ppm with no systematic variation with depth. Sequential dissolution analysis indicates that the S/Fe molar ratio of goethite is an order of magnitude smaller than that of schwertmannite but the As/Fe ratios of both minerals are similar. A high concentration of suspending particles occurs in the surface layer of shoreline seawater near the estuary. The particles consist mainly of non-crystalline iron oxyhydroxysulfate compounds with variable amounts of Fe (15.8–53.7 wt.%), Cu (0.1–4.1 wt.%), Al (0.2–14.3 wt.%), and As (up to 556 ppm), commonly encrusting very fine-grained quartz. Seawater samples collected at different distances from the estuary and at different depths contain virtually no Fe and As, but their Al and Cu concentrations (3.1–26.3 ppm and 2.7–9.9 ppm) are inversely proportional to those of the iron oxyhydroxysulfate compounds. The result suggests preferential uptakes of As and Fe by schwertmannite and non-crystalline particles. The transformation of schwertmannite to goethite involves partial dissolution and re-precipitation in which the aptitude for arsenate sorption remains virtually unchanged and goethite shows a great capacity for sulfate sorption. The Cu and Al concentrations of seawater appear to be directly affected by precipitation of the non-crystalline iron-oxyhydroxide particles with As and Fe contributions from the stream water and AMD being largely used up. The data collectively imply that the pH value of solution controls the formation of different types of iron-hydroxide phases, which in turn plays a major role in changing the Fe, As, Al, and Cu loading of waters in the Chinkuashih AMD region.

Processes of hardpan formation in extreme pH environments

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Two sites have been investigated in detail. A slagheap (pH 12) in Germany and a pyrite rich country rock pile (pH 0.5 to 2.5) in Spain.

The material at both sites is extremely heterogeneous on the macroscopic to microscopic scale regarding rock and mineral precursors, grain size, and sedimentation. The development of micro-environments and of focused drainage systems is the result of heterogeneity on all scales.

Despite the extreme differences concerning material, mineralogy, sedimentation, climate and chemistry, both sites developed hardpans on a silicagel basis some 40 years after deposition. Both heaps contain high percentages of highly reactive material, with which has to be regarded as a potential source of contamination. Due to the extreme reactivity an enormous amount of dissolved matter is made available per time unit. The brines migrate through the heaps and contribute to the high ion load in the rock drainage. However, not all of the pore waters contribute to rock drainage. Capillary transport, driven by climatic and sedimentological premises is able to focus portions of the solution at the air-water boundary resulting in formation of layer like zones of contrasting physical and chemical patterns regarding the precursor material (cemented layers or hardpans). Within these zones gels and secondary minerals precipitate, agglutinate fragments and reduce pore volume; thus permeability is minimized in defined narrow zones resulting in a protective cover which reduces water and air infiltration in, at least, parts of the heaped material.

Some of the mineral precipitates are highly soluble and will contribute to the first flush of the next rainfall. Gels, and in particular silicagels, form more stable coatings and agglutinated fragments. These gels appear to be extremely porous, acting as sponges for solutions. Furthermore, they have significant expanding behaviour; thus bottle necks between fragments might be locked reducing water infiltration in an effective way.

The result of such covers even in a very initial stage of agglutination (mm to cm thick) is a promotion of surface parallel transport of rainwater and, therefore, the reorganisation of internal parts of the heaps due to reduced accessibility. Geophysical measurements provide an insight into the internal structure of the heaps, and long-term monitoring allows interpret the effectivity of the retention capacity of such hardpans.

Minerals formed in weathering reactions zones on rocks in polluted atmosphere (examples from SE Poland)

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Extensive study was undertaken to determine mechanisms of weathering of several rocks types (e.g. carbonate rocks of various texture, sandstones differing in carbonate cement content) in polluted atmosphere in Cracow and other others localities in SE Poland. Visual weathering features are different (e.g. formation of dark gypsum crust with uneven surface tightly connected with the rock, exfoliating gypsum crust, granular disintegration of a rock, blistering, scaling, soiling, discolouration, development of honeycomb weathering).

Weathering reactions zones contain gypsum as a dominant newly formed component. It is related to high rate of influx of SO_4 and Ca with atmospheric precipitation (up to 4 g/m² per month). Gypsum can also be formed in reactions between rock and sulphur-containing gaseous components of atmospheric pollution. Almost 20 other minerals were determined in weathering reactions zones beside gypsum. Sulphates are very common (hexahydrite, epsomite, melanterite, langbeinite, mirabilite, syngenite, burkeite, celestite, barite, bassanite,). Carbonates are represented by calcite and dolomite. The number of documented nitrates and chlorides is relatively low (nitronatrite, nitrammite, halite, sylvite).

Distribution of secondary minerals can be related to the mineral and chemical composition of the rock (e.g. celestite in weathering crust on the Pińczów limestone), composition of atmospheric precipitation (mostly sulphates), humidity of atmosphere (hexahydrite or epsomite in alveoles on the Libiąż dolomite), humidity of rock surface (e.g. nitrates), regional and local variations in atmospheric pollution (e.g. gypsum or halite), solubility of secondary minerals, local variations in exposition of rock surface.

Weathering of the upper Jurassic limestone in polluted urban atmosphere: results of mineralogical and isotopic study

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The Upper Jurassic limestone was commonly used as building material in historical monuments in Cracow. The most characteristic feature of limestone weathered in highly polluted urban atmosphere is the presence of strongly contrasted black zones sheltered against direct rain-washing and white zones exposed to rain-washing. Black zones are covered by gypsum crust. Weathering reactions zones were studied using mineralogical methods (optical microscopy, SEM-EDS, XRD, IR spectrometry). Chemical analyses and stable isotope (C, S, O) determination of weathering zones and atmospheric precipitation were also performed.

Study of samples collected in Cracow (urban area) and in numerous natural outcrops in the Cracow-Częstochowa Upland (rural area) gives the possibility of comparison of weathering processes in relation to different concentration and composition of atmospheric pollution. Three types of weathering crusts on Jurassic limestone were distinguished: gypsum rich crusts, organic matter rich crusts and dark carbonate crusts with a thin black layer of gypsum. The first type occurs mostly in urban area, whilst the two others are characteristic for the rural area. Gypsum dominated crusts from urban and rural areas differ significantly in structure, morphology of gypsum crystals, concentration of various chemical elements. Differences are related to lower concentration of atmospheric pollution and slightly lower pH of atmospheric precipitation in rural area. Isotopic study suggests that gypsum in black crusts in urban area precipitates during evaporation of rain water and partly is formed by reaction between sulphate ions originating during oxidation of SO_2 adsorbed on humid wall surfaces and Ca ions. Newly formed calcite dispersed in gypsum crust exhibit the shift of $\delta^{13}\text{C}$ value toward lower values in comparison with carbonates in non-weathered limestone. It can indicate that CO_2 formed during fuels combustion participates in crystallization of secondary carbonates.

Calcite and anhydrite precipitation in the geothermal test field at Hijiori, Yamagata, Japan

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In the pipeline and production well of geothermal production field, silica and calcite scale often precipitate with fluid temperature or pressure change. These minerals precipitation is problem for stable fluid production especially in higher fluid chemical composition.

Then, Hot Dry Rock (HDR) system is one of method of geothermal production that cool water inject for heating in deep seated reservoir. Produced fluid is expected low chemical composition and precipitation problem is expected smaller. At Hijiori HDR test field, fluid circulation test was carried out from November 2000 to August 2002. In this system, river water injected to reservoir at 2,200m depth via HDR-1 well and after heated fluid return to ground via 2 production wells. HDR-2 well is 70 m and HDR-3 well is 130m distance from HDR-1 well. With circulation progress, scale precipitation was recognized in pipelines and in the production wells. Precipitation is related to the anhydrite dissolution curve and cooling in reservoir.

Properties of scaling as follows:

- (1) At deep part of production wells, anhydrite scale precipitated at the high temperature zones. Injected cool water dissolved the anhydrite in the reservoir rock and the anhydrite then precipitated at the higher temperature zones in and around the production wells because of the reverse solubility curve of anhydrite.
- (2) The pipeline of HDR-2 well, which is closer to the injection well and has a lower temperature, calcium carbonate scales such as calcite and aragonite precipitated at a rate of 13mm/month. In the pipeline, high concentrations of Ca reacted with CO₂. The high Ca concentration resulted from dissolved anhydrite in the reservoir. Anhydrite remained in solution when production temperatures were low after thermal breakthrough of cool injection fluids occurred.
- (3) At HDR-3 well, further from the injection well and higher in temperature, slight amounts of amorphous silica precipitated. The Ca concentration was too low for scaling and the concentration of SiO₂ was high enough to precipitate a thin layer of amorphous silica.
- (4) As circulation progressed and temperature decreased, the scale species changed from amorphous silica to calcium carbonate in well HDR-2.

A preliminary study on numerical modeling of seawater-sedimentary rock interaction for CO₂ sequestration

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A potential of CO₂ sequestration in deep sedimentary rocks of coastal areas near urban sites has been researched in Japan since FY 2005. In this study, a preliminary numerical modeling of seawater-sedimentary rock interaction was conducted to generate a hypothetical brine-altered rock system, inject the CO₂ into the system, and consequently evaluate the quantity of CO₂ fixed in the rocks of the system. The initial rocks were assumed to be mudstone and sandstone with representative chemical compositions and varied organic-matter contents. The modeling was carried out using the GWB software.

The mineral assemblages produced after the seawater-sedimentary rock interaction (calculated under the equilibrium condition) were carbonates (dolomite, calcite), micas (muscovite, phengite), smectites (nontronite, saponite), kaolinite, albite, clinoptilolite and pyrite. The seawater was altered to the Ca-Na-Cl to Na-Ca-Cl type brines with the reductions of K and Mg components and changes of SO₄ to HS and HCO₃ to CH₄ species.

Injection of CO₂ into this brine-altered rock system newly produced cristobalite, dowsonite, magnesite, siderite and alunite under the H₂O-dominated condition prior to the formation of CO₂-dominated condition, unless the injected CO₂ speciated to CH₄. At an initial water/rock ratio of 2 of the brine-altered rock system, the quantities of CO₂ fixed in rocks were about 100 g/kg for the organic-rich mudstone, 130 g/kg for the organic-poor mudstone, 70 g/kg for the organic-rich sandstone, and 90 g/kg for the organic-poor sandstone. At relatively high and low initial water/rock ratios of the brine-altered rock system, the quantities of CO₂ fixed in rocks decreased.

Thus, the sedimentary rock formation composed of organic-poor mudstone with water/rock ratio of about 2 tentatively seems to be most suit for the CO₂ sequestration, although a further study with consideration of mineral kinetics and fluid dynamics were needed.

Hydration mechanism of glassy rhyolite, Pleistocene Katsuma-Yama volcano, Okushiri Island, Hokkaido, Japan

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Katsuma-Yama volcano consists of three volcanic centers, Horonai-Gawa caldera, Katsuma-Yama tuff ring and west Katsuma-Yama maar. The glassy rhyolite herein described is the Katsumaya lava, which can be traced down the slope to the Horonai-Gawa caldera from the source Katsuma-Yama tuff ring and found to occur in-between the lake deposits of the Horonai-Gawa caldera. This lava comprises mainly of obsidian (0.3–0.8 wt % H₂O) over the thickness of 100 m but is hydrated in the upper and lower parts into perlite (1.5–2.8 wt % H₂O). The upper and lower flow breccias are also perlitic and prismatic cracks. The cracks normal to the prismatic cracks develop closely spaced throughout the lava. Phreatomagmatic eruption products in the Katsuma-Yama tuff ring also contain obsidian and perlite fragments identical in major and trace element compositions to the obsidian and perlite samples from the Katsuma-Yama lava except for H₂O content. The Sr isotopic ratios of these rocks from the Katsuma-Yama tuff ring are from 0.703018 to 0.703073, lower than those of seawater (0.708–0.709), providing negative evidence for their interaction with seawater. The δ D values of the Katsuma-Yama obsidian and perlite and the local meteoric water around the Katsuma-Yama volcano are -94–-77‰, -97–-76‰ and 58‰, respectively. The difference between δ D values of the Katsuma-Yama obsidian and perlite and the local meteoric water is about 40‰, close to the hydrogen isotopic fractionation values between OH in silicate glass and water vapor at high temperatures. As examined by a FT-IR micro-spectrometer, the glass in the Katsuma-Yama lava and pyroclasts contain both OH and H₂O, the latter of which does not shift from water to ice spectra at -110°C and is, therefore, interpreted to be structurally bound. We thus suggest that the Katsuma-Yama lava was hydrated with meteoric water at a high temperature while the lava was solidifying. Experimental hydration of rhyolite glass T-400–500°C and ambient vapor pressures occurs at a rate of 10⁻²–10⁻¹ μm s⁻¹. This hydration rate is likely fast enough for the solidifying Katsuma-Yama lava to be hydrated in direct contact with the meteoric water heated by the lava itself for months or years.

Characteristic features of radium-lead-strontium-bearing Tamagawa thermal water related to a deep-seated magmatic system in Akita Prefecture, Japan

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Tamagawa hot spring with precipitating Ra-Pb-bearing barite is a volcanic gas-bearing hydrothermal system derived from Quaternary andesitic to dacitic magma beneath Yakeyama Volcano. The gas has been mixing with circulating groundwater in a deeper part, and the mixed hydrothermal solution has been boiling at a depth of 400 m deep or more and has been separating into steam and residual hot water for these 5000 years (Matsubaya, 1996; Sumi & Takashima, 1972). The geology around Tamagawa hot spring consists of Miocene sedimentary strata, Pre-Yakeyama lake deposits (320 m in thickness), Tamagawa welded tuffs (Pliocene–Pleistocene: 200–300 m in thickness) and andesitic to dacitic volcanics of Yakeyama Volcano (200 m in thickness) (Ohba, 1991; Sudo, 1992). An active water/rock interacting zone in this system occurs below the horizon of the Tamagawa welded tuffs. Thermal water in Tamagawa hot spring is divided into three types: Cl-SO₄ type (Ohbuki hot spring: pH 1.2), SO₄ type (pH 1.8 to 2.9) and neutral type (pH 6.1). These hot springs occur from center to marginal parts in the order of Cl-SO₄ type, SO₄ type and neutral type. The SO₄ type thermal water, reacting andesitic volcanics of Yakeyama Volcano, was formed by mixing of fumarolic steam including CO₂ and H₂S with shallow groundwater and oxidation of H₂S at the surface. Concentrations of Na, K, Mg, Ca, Fe, Mn, Rb, Sr, Ba, Pb, total REE, Th and U in Ohbuki Cl-SO₄-type thermal water are 52, 50, 49, 177, 170, 4, 0.23, 0.42, 1.19, 2.41, 0.32, 0.009 and 0.005 ppm, respectively. Concentrations of these elements in the Ohbuki thermal water are about 10 times higher than those of the elements in the SO₄-type thermal water. The Chondrite-normalized REE pattern of the Ohbuki thermal water is flat, while chondrite-normalized REE patterns of the SO₄-type thermal water are light REE-enrich patterns similar to those of Yakeyama andesitic volcanics. Na/K and Rb/Sr ratios of SO₄-type thermal water are similar to those of andesitic volcanics with which the thermal water is reacting, while Na/K and Rb/Sr ratios of Cl-SO₄-type thermal water have similarity to those of dacitic volcanics of Yakeyama Volcano. These relations suggest that Cl-SO₄-type thermal water is formed by an interaction between groundwater containing volcanic gas and differentiated felsic rocks in a deep part. Lead in the Cl-SO₄-type thermal water could be extracted by interaction with deep-seated felsic rocks or magma and are transported upward to Ohbuki hot spring by Cl-SO₄-type thermal water.

Study of molecular structure of water in tiny clay minerals by the variable-angle polarized IR spectroscopy

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Molecular structure of water in clay minerals were studied by the variable-angle polarized IR spectroscopy. For quantitative analysis of water in clay, a small amount of clay (smectite) was dispersed into distilled water and then dried on a thin Si-plate to obtain an oriented sample. The Si-plate with clay was directly put in the variable angle cell which was developed originally, and then IR spectra were measured at a different angle of IR light to the Si-plate from -50 to 50°. The absorbance of stretching vibrational mode of hydroxyls (~3620 cm⁻¹) in clay depended on the angle of incident IR light. The obtained results were compared with the molecular structure simulated by the molecular dynamics simulations.

Kinetics of arsenopyrite oxidative-dissolution: a multiscale approach

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The process of arsenopyrite dissolution in acidic and oxygen-saturated solutions was investigated by coupling three different techniques: (1) solution chemistry by means of flow-through experiments, (2) micro Raman spectroscopy (μRS), and (3) in-situ Atomic Force Microscopy (AFM). The objective was to study the effect that pH, temperature and the presence of oxalic acid exerts on the arsenopyrite oxidative dissolution.

(1) Overall reaction rates were measured by partially dissolving a single fragment of arsenopyrite in a flow-through reactor, where the fast solution renewal ensured that interacting solutions were undersaturated with respect to both primary and secondary minerals (arsenopyrite, sulphates, arsenates, oxy-hydroxides). Total arsenic and iron were measured in the output solutions by ICP-MS, and the presence of significant amount of As(III) was detected by polarography. ICP-OES was used to measure total sulphur, which was only detected in the highest S concentrations. This showed that the output sulphur concentrations were by a factor of 2-3 lower than the As and Fe concentrations, suggesting an aqueous sulphur deficit. At steady state, dissolution rates in oxygen-saturated solutions (PO₂=2×10⁴ Pa) were measured at pH 1 and 2 (HCl) at 298, 323 and 348 K. Based on the steady-state dissolution rates, the apparent activation energy calculated was 37±10 and 47±11 KJ/mol at pH 2 and 1, respectively.

(2) Arsenopyrite surface before and after exposure to oxygen saturated solutions was investigated by μRS. The Raman analyses of the unreacted surfaces revealed the presence of only arsenopyrite and rare traces of pyrite, whereas the reacted arsenopyrite surface revealed the presence of a coating made up by native S, iron oxy-hydroxides and some phases containing As-O bonds. The latter likely contains As(V). In addition, the μRaman spectra of arsenopyrite surfaces after interaction with oxalate show some peak attributable to C-O bonds. The presence of S at arsenopyrite surfaces is partially responsible of the observed S deficit in solution, however S could escape from the reactor as a gas.

(3) The in-situ AFM experiments revealed little changes in the cleaved surfaces of arsenopyrite dissolving in acidic pH and oxygen saturated atmosphere. In addition, arsenopyrite surfaces seem to show the same behaviour in presence of a strong ligand such as oxalate (0.1 M). As mechanically polished cleaved surfaces yielded high rugosity that might impede identifications of possible nanometric surface changes, in-situ AFM experiments are currently running using arsenopyrite fragments whose cleaved surfaces were pretreated with concentrated HCl solution (10 % v).

AFM study of enargite-solution interface at basic pH

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The process of enargite (Cu₃AsS₄) dissolution in alkaline solution was investigated by different techniques: semi in-situ AFM, XPS, solution chemistry (flow-through experiments), SEM, and XRD. The main goal of the present study is to characterize the surface process occurring at the enargite surface upon dissolution at basic pH (8.5-12.2). The variation in surface topography can show how the dissolution of enargite and the expected precipitation of Cu oxide proceed. XPS analysis was used to identify surface speciation, and flow-through experiments were conducted to evaluate the release of Cu, As and S to the solution. SEM/EDS and XRD were employed to analyse the solid sample before and after the flow-through experiment.

Three semi in-situ AFM experiments were conducted at room temperature (22-25 °C) on freshly cleaved surfaces at different pH: 8.5, 10.2 (buffer borax solutions), and 12.2 (NaClO/NaOH solution). The AFM experiments results show clear evidence of topography changes at the sample surface, with appearance of a precipitate that covers the examined area. The highest reactivity of the sulphide was observed at pH 12.2.

XPS analysis of the unreacted (as received) surface revealed the presence of an oxidized nanometric layer. The detailed analysis of photoelectron peaks of As, Cu, and S on reacted surfaces shows differences in surface speciation depending on the pH. Cu(II)-O bond is determined at about 934 eV at pH 8.5 and 10.2, while Cu oxide/hydroxide at 934.9 eV is determined at pH 12.2. As-species were determined with a peak at 43.6-44.0 eV at pH 8.5 and 10.2 respectively, similar to As in untreated sample. Binding energies between 45.6 and 45.9 eV were associated with As (V)-O at pH 10.2 and 12.2. S-species were only found at pH 8.5 and 10.5. In both cases, sulphur occurs as monosulphide (162.1-162.4 eV), disulphide/polysulphide (163.5-163.8 eV), and sulphate (168.3-168.5 eV).

The flow-through experiment was conducted on the powdered sample with the solution at pH 12.2. After the experiment, the XRD pattern shows tenorite (CuO) peaks, and SEM/EDS analysis the presence of a Cu-rich coating on enargite fragments. ICP/OES and ICP/MS analyses of the output solutions show that the Cu concentration drops to below the detection limit after the first 5 minutes of reaction. As and S concentrations decrease with time, and after 5 h reach a constant value. The As/S molar ratio in solution is about 0.26, i.e. close to the stoichiometric ratio in enargite (0.25).

Dissolution of Fe-bearing silicate minerals under low P_{O2} conditions and implications for late Archean – early Paleoproterozoic weathering

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Biotite dissolution experiments were carried out in a glove box under O₂-deficient conditions (6 × 10⁻⁴ atm of P_{O2}; referred to as anoxic conditions) using a flow-through reactor at 25 °C and pH 6.9 for up to 65 days to better understand the dissolution kinetics and to give an insight into weathering in the late Archean to early Paleoproterozoic. Weathering and dissolution of biotite have been intensively studied for the past decades, while there have been a few studies under anoxic conditions concerning the effects of P_{O2}. We obtained the O₂-deficient conditions by bubbling Ar gas for solution in the glove box and measured the concentration of dissolved oxygen in solution during the experiments. For comparison, biotite dissolution was conducted under the present, ambient air (0.2 atm of P_{O2}; referred to as oxic conditions). The release rate of Si was faster by 4 times under anoxic conditions than under oxic conditions. The results indicate that biotite dissolves faster in anoxic weathering than in modern, oxic weathering. Fe was released at a similar rate to that of Si under anoxic conditions whereas the release rate of Fe was approximately one order of magnitude slower than that of Si under oxic conditions. Biotite contains Fe mainly as divalent state, and after released to solution, Fe(II) dissolved is oxidized to Fe(III) that is precipitated as Fe(III) oxides/hydroxides. Fe remaining in the reactor as Fe(III) precipitates after the experiments was extracted by dithionite-citrate treatment, which reveals that 61 % of whole dissolved Fe remains in the reactor and 39 % flows out under anoxic conditions whereas 99 % remains and 1 % flows out under oxic conditions. We conclude that the different redistribution of Fe between the two conditions is caused by the difference in oxidation rate of Fe(II) that is a function of P_{O2}. The increase of Fe retention fraction (Fe fraction in a paleosol against a parent rock) with time in late Archean to early Paleoproterozoic paleosols is well explained by the increase of atmospheric oxygen with time during the period.

In-situ observations of the dissolution of muscovite and smectite under alkaline conditions at 25-50°C by AFM with an air/fluid heater system

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The dissolution behaviors of muscovite and smectite under alkaline conditions at 25°C to 50°C were investigated using in-situ atomic force microscopy (AFM) with an air/fluid heater system, in order to understand the dissolution mechanism and to derive reliable dissolution rates of these minerals. The AFM air/fluid heater system used is composed of an air/fluid heater element (called Bio-Heater), Thermal Applications Controller (Vecco Metrology), and a MultiMode SPM unit (Digital Instruments), and it enables in-situ AFM study at elevated temperature up to 60°C (heater) or 57°C (sample) in a controlled environment.

The both minerals showed the same dissolution behavior in which the reactive surface was only the edge surfaces and any new etch pits were not formed on the basal surfaces within the experimental durations. The dissolution rates normalized to the edge surface area (ESA) of these minerals were also approximately the same. In addition, the effects of temperature on the ESA-normalized dissolution rates were very similar each other. These results suggest that the dissolution mechanisms (e.g., reactive surface, the rate-limiting step) of muscovite and smectite are identical each other. The dissolution rates normalized to the total surface area (TSA) of initial particle size (smectite) or initial etch pit size (muscovite) varied with the particle or etch pit size, respectively.

The anisotropic dissolution behavior was also observed along the edge surfaces of smectite, that is, the retreat of dissolution fronts along the {110} faces was much faster than that along {010} faces. This difference may be explained by that the smectite dissolution under alkaline conditions is controlled by OH⁻ attack, which are catalyzed by protonated Al-OH groups, on the bridging O atoms of both Al-O-Si sites, which locate only on the {110} surfaces, and Al₂O-Si sites on the {010} and {110} surfaces.

Alteration process of gabbroic building stone by CO₂ saturated water

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In order to predict the effect of acid precipitation impregnated with CO₂ gas on building stone, artificial chemical weathering of polished plates of the so-called Muroto Gabbro from Kochi, Shikoku Island, Japan, was conducted. An improved Soxhlet extraction apparatus was used with artificial CO₂ saturated water and distilled water for a different period of time up to 700 days. The gabbro was composed mainly of plagioclase (Ab₃₁An₆₉), clinopyroxene (En₄₆Fs₁₆Wo₃₈) and olivine (Fo₆₅Fa₃₅), and small amounts of orthopyroxene, hornblende and ilmenite. The leached sample solutions were collected, and analyzed for major and minor elements using ICP-AES and ICP-MS. Morphological and chemical changes of the each mineral surface and vertical plane to frontal part, which is in direct contact with the solutions, were studied by SEM, EPMA and microscopic techniques. Alteration products were collected from the surfaces of each mineral on the polished plates by hand picking and examined using XRD and TEM.

Molar ratios of each element in the leached solutions to those in the fresh gabbro varied depending on the experimental period. The ratios of the elements such as Mg, Mn, Ni, Co and Zn, which reflect the dissolution of olivine, were relatively high. Similarly, the ratios of Na, Ca and Sr, which reflect the dissolution from plagioclase, were relatively high. The SEM images of the artificial weathered plagioclase and olivine surfaces showed that many irregular fractures formed by dissolution have developed in the each mineral. Plagioclase and olivine are extremely altered, but clinopyroxene are rarely altered. (Na + Ca + K) / Total Al ratio for plagioclase and (Mg + Fe) / (Si + Al) ratio for olivine decreased with an increase in leaching time. No change in the chemistry of the clinopyroxene surface by CO₂ saturated water and distilled water was observed. It is evident that olivine changed into smectite and chlorite by exposure to CO₂ saturated water used in the experiment. Smectite appeared to be formed from plagioclase during the artificial chemical weathering. No altered product from clinopyroxene, however, was detected. Mapping data from an EPMA shows a decrease in Mg, Ca and Na near the frontal parts of olivine and plagioclase in the gabbro, respectively.

Key ward: CO₂ saturated water, gabbro, weathering, olivine, plagioclase, smectite

Artificial chemical weathering of olivine under earth surface conditions

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"Acid rain" is one of the global environmental problems. In order to predict the effect of acid precipitation on building stone, artificial chemical weathering of granitic and gabbroic building stones have been simulated chemically and mineralogically using distilled water and some acid solutions. As a follow-up study, olivine from San Carlos, Arizona, U.S.A., which is one of rock forming minerals, has been exposed to HNO₃, H₂SO₄ and HCl solutions at pH 4 at 55°C for different periods of time up to 700 days in an open system using an improved Soxhlet extraction apparatus. The chemical composition of olivine was (Mg_{1.771}, Fe_{0.204}, Al_{0.004}, Mn_{0.003})_{1.987}Si_{1.006}O₄. Morphological and chemical changes of the mineral surface were studied by SEM, EPMA and optical microscopic techniques. Alteration products were collected from the olivine grain by hand picking and examined using XRD. The leached sample solutions were analyzed for major elements such as Si, Al, Fe, Ca, Mg, Mn and Na, and minor elements such as Zn, Ni, Co and so on using ICP-AES and ICP-MS. Molar ratios of each element in the leached solutions to those in the fresh olivine varied depending on the experimental period. The ratios of the elements such as Mg, Si, Zn and Co were relatively high. On the other hand, the ratio of Fe that is one of the major elements is very low. Therefore the molar ratios of Fe / Si and Fe / Mg in the leached solutions were different from atomic proportions of the olivine. The SEM images of surface of the artificial weathered olivine showed that many irregular fractures formed by dissolution have developed on the mineral. Mg / Si ratio for the olivine surface decreased with an increase in leaching time, but Fe / Si ratio increased. In the artificial chemical weathering over 400 days using HNO₃, H₂SO₄ and HCl solutions, an orange colored secondary mineral appeared on olivine surfaces. It is evident that a frontal part of olivine, which is in direct contact with the solution, changed into Fe-rich secondary mineral such as goethite by exposure to the various acid solutions used in the experiment. Therefore, it is considered that any amount of dissolved Fe from olivine surface is not contained the leached solution, and the Fe precipitate on the olivine surface. Mapping data from an EPMA shows a decrease in some elements such as Si, Mg, Fe and Mn. Key words: olivine, artificial weathering, acid rain, pH4, HNO₃, H₂SO₄, HCl, Fe-rich mineral No change in the chemistry of the clinopyroxene surface by the three acidic solutions and distilled water was observed. Similarly, the ratios of Na, Ca, Sr and La, which reflect the dissolution from plagioclase, were relatively high. The plots of the ratio versus ionic radius are similar to the partition coefficient - ionic radius diagram for olivine and plagioclase systems (Matsui et al., 1977). It is seen, therefore, that olivine and plagioclase are easily weathered. SEM images were shown many irregular fractures formed by dissolution have developed in the olivine surface after 700 days. Smectite appeared to be formed from plagioclase during the artificial chemical weathering. However, altered products from clinopyroxene were not detected. Molar ratios of each element in the leached solutions to those in the fresh gabbro varied depending on the experimental period. The ratios of elements such as Mg, Mn, Fe, Ni, Zn and Co, which reflect the dissolution of olivine, were relatively high. Similarly, the ratios of Ca, Na, Sr, Ce, Sm, Nd and La, which reflect the dissolution of plagioclase, were relatively high. It seems, therefore, that olivine and plagioclase are easily weathered. It was also estimated from the molar ratios that the reactivity order of the acid solutions for olivine and plagioclase is H₂SO₄, HNO₃ and HCl.

Surface analytical approaches to artificial weathering of granite and its constituent minerals by AFM and XPS

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Dissolution experiments and surface analyses using AFM and XPS were carried out to clarify the weathering characteristics of granite and its constituent minerals (single crystals of annite, albite, microcline and quartz) under acidic conditions. In single crystal minerals, Fe-oxides, Al-oxides, Si-oxides, and both Si- and Al-oxides were formed. Under neutral to slightly acidic conditions, platelet-like Fe-oxides precipitated in annite, and particulate Al-oxides precipitated in albite and microcline. Between albite and microcline, there was the difference in dissolution. The absence of precipitate of Al-oxides in annite probably resulted from the inhibiting effect of some cations in aqueous solution. Si-oxides were formed by three types of mechanisms which depended on solution pH: (a) hydrolysis-repolymerization, (b) dissolution-precipitation, and (c) hydration. In quartz, only the (c)-type was confirmed. In the others except for quartz, the (a)-type proceeded at first. In annite and albite under a strongly acidic condition, the (a)-type was followed by the (b)-type with the product being almost spherical. In albite under an acidic condition, both Si- and Al-oxides precipitated by the mechanisms of (b)-type following (a)-type. These mechanisms were placed in order by the extent of dissolution: (c) < (a) < (b). In granite, Fe-oxides and Si-oxides were formed. Under neutral to slightly acidic conditions, solution pH increased because of the plagioclase dissolution. Thereby dissolved iron from biotite smoothly precipitates as Fe-oxides. Under low pH conditions, biotite dissolution was predominant. In granite weathering where some reactions exist, the dominant mineral depended on solution pH. Among the single crystals, annite and albite had higher reactivity than microcline and quartz. The difference in reactivity between the two assemblages resulted from the extent of Si leaching. In granite, biotite crystal grains showed high reactivity. In granite weathering under neutral to slightly acidic conditions, there are two relationships between biotite and plagioclase, which lead the reactivity of biotite to increase.

Measurement of feldspar dissolution rate and its implication to the underground CO₂ storage

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To mitigate the impact of the future atmospheric carbon dioxide increase, the underground CO₂ storage has been proposed. However, to ensure the stability of injected CO₂, the influences of long-term geochemical phenomena, such as CO₂-water-rock interactions, should be taken into account. If the CO₂ storage reservoir is a sandstone aquifer, feldspar dissolution in CO₂-dissolved water would be the most important geochemical process to consider because feldspar is the most abundant mineral in general sandstone. In this study, we measured the dissolution rate of feldspar under the condition analogous to those on the underground CO₂ storage. Since the feldspar dissolution rate is very slow, it is generally hard to obtain precise dissolution rate within a short time by the chemical analysis of the solution composition, especially under the temperature condition lower than 100°C. On the other hand, the surface observation of crystal sample on nanometer scale is expected to overcome these problems. Therefore, in this study, we applied the phase-shift interferometry (PSI), which enables us to detect the surface configuration changes on nano-scale based on optical interference between the reflected beam from the sample surface and the reference beam. Several cleaved anorthite single crystals were prepared and the batch type dissolution experiments were performed in aqueous solutions of supercritical CO₂ at 25, 50, and 80 °C with a constant CO₂ pressure of 10 MPa. We took out the sample after 6, 12, 24, 48, 72, 120, and 168 hours, and observed the configuration change on the crystal surface. The dissolution rates of anorthite were estimated from surface retreat based on vertical cross-section profiles. Our PSI data revealed that the feldspar dissolves faster in the initial stage of dissolution and that gradually decreases to the steady state dissolution rate. It is expected that the dissolution of aquifer rock minerals slightly reduces the volume of solid phase and thus results in an increase both in porosity and permeability. Such a structural change in an aquifer rocks would affect the subsequent evolution on the CO₂-water-rock system, because the enhanced transport process may promote the dispersion of chemical components far from the injection site. From this viewpoint, we tried to estimate the change in porosity of reservoir rocks during the initial stage of the underground CO₂ storage using our data set of feldspar dissolution rate.

Critical point measurements of binary and ternary fluid mixture by direct observation using the visible-type autoclave

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The critical point of CO₂+H₂O, X+H₂O (X: NaCl, MgCl₂, CaCl₂, Na₂CO₃, K₂CO₃), CO₂+NaCl+H₂O fluid mixture and seawater were measured by meniscus vanishing and appearance observation using the visible-type autoclave. And some critical points were calculated by EOS (Duan et al., 1995 and Shibue, 2003) and compared it with acquired data.

The critical point of pure H₂O and pure CO₂ showed the value which was almost similar to literature data. The critical point of the NaCl+H₂O fluid was shifted to high temperature and pressure region with the increase in the NaCl concentration, and, the critical point of the CO₂+H₂O fluid changed with the increase in the CO₂ concentration in low temperature and high pressure region. These results agree with previous works (Diamond, 2001). Therefore, it is considered that the measurement the critical points with that equipment/method is correct.

Critical point of the H₂O+NaCl+CO₂ fluid mixture which whole tendency was similar to the H₂O+CO₂ fluid mixture. However, increasing amount of critical temperature according to the increase of CO₂ is different by the NaCl concentration.

When the NaCl concentration is high, the critical temperature and pressure rapidly changed in comparison with the case with low NaCl concentration. The ion in the aqueous solution brings about the local change in the structure of the aqueous solution by drawing the water molecule in the circumference of the ion. This phenomenon decides the structure of the aqueous solution with the property, and it seems to give large effect for the decision of the critical point of aqueous solution.

Therefore, it is considered that the structure of solution where NaCl and CO₂ ion exist simultaneously is different from the structure of solution where the CO₂ ion or the NaCl ion is single and exists.

And, it is thought that differences are in the measurement value and the EOS value because ion's physical properties parameter in the vicinity of critical point has a problem for the EOS calculation.

Removal and immobilization of hazardous anions by blast furnace slag

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The disposal of granulated blast furnace slag from iron manufacturing is beset by leaching of fluorine into the surface environment. However, hydrotalcite-like materials (HT) altered from the slag could also serve as fluorine adsorbent. If these material phases would be expected in the disposal sites, the fluorine leached from the slag would be retained in the disposal site. In this context, formation of secondary HT and its fluorine adsorption behaviour were investigated to assess its feasibility for fluorine removal. HT synthesis from slag with different water to slag mass ratios, ageing times, and temperatures were conducted. The pHs of suspensions were monitored during the experiments. In addition, flow-through dissolution experiments of slag were also performed to estimate dissolution rate of HT-constituent elements from the slag. The synthesis experiments showed that pHs of all reactive solutions were above pH 12. From the results of syntheses, favorable conditions for HT formation from slag are therefore at relatively high temperature, smaller water to slag mass ratio, and mixing to facilitate more active reactions. It was also noted that fluorine concentrations during the synthesis were below regulatory limits even after long reaction. Fluorine adsorption experiments were also performed for the synthesized materials. It was found that fluorine concentrations were drastically reduced within an hour. These results also show that the synthesized HT from the slag would be a feasible and effective adsorbent for fluorine. The time scale to synthesize HT from solution by dissolving slag was estimated by dissolution rate of HT-constituent elements.

In situ neutron diffraction and synchrotron X-Rays tomography analyses of the influence of geometric confinement on the crystalline swelling of montmorillonites

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In the concept of deep geological repositories, compacted bentonites are planned worldwide as artificial clayey barriers between nuclear wastes and natural host rocks. Their porosity is the focus of numerous studies as it will be a key parameter controlling the potential migration of radionuclides. Determining the distribution of pores under confined conditions at various hydration states would represent a major advance for predicting transport properties. For fully hydrated and confined samples, rough calculations suggested that when the apparent density reaches a value of 1.6, external pores are no longer available and water molecules should only occupy interlayer spaces. At the opposite, SEM observations of MMA impregnated samples (state expected to be close to the fully hydrated state) revealed an unsuspected preservation of all pores types whatever their size which seems to result from a decrease of swelling properties. However, textural modifications linked to the resin impregnation protocol or the resin-clay interaction can always be suspected.

To study the influence of water relative pressure in compacted and confined conditions, in situ analyses were carried out by neutron scattering at ILL (Grenoble, France), to derive information on the microscopic swelling of clay layers and on the evolution of porosity < 150 nm while in situ synchrotron-based X-ray microtomography at SLS (Villigen, Swiss) was used to obtain 3D representations of the porous network of hydrated samples for pore sizes larger than 0.7 µm. For each experiment, the bentonite powder was compacted and confined into special cells and equilibrated at different water relative pressures along the water adsorption isotherm. The apparent densities, used for that study range between 1.4 and 2.0 and equilibrium relative water vapor pressures were 0, 0.23, 0.40, 0.65, 0.81 and 0.98. 3D image analysis of X-ray tomography was used to provide quantitative measurements of amount, size and connectivity of macropores. The thus detected changes in porous network can be thereafter used for 3D modelling of radionuclides diffusion.

Modeling of pore-water chemistry as a common base for understanding dissolution of montmorillonite and mass transport in compacted bentonite

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Dissolution of montmorillonite by aqueous alkaline solutions was investigated using compacted sand-bentonite mixture samples under activity of hydroxide ions, a_{OH^-} , of 0.04 to 0.57 (mol dm^{-3}) and temperatures of 50 to 170°C. The obtained dissolution rates were formulated as $R_A = 3.5(a_{\text{OH}^-})^{1.4}e^{-51000/RT}$, where R is the gas constant and T the absolute temperature. The dissolution rate was proportional to the 1.4th power of a_{OH^-} for compacted sand-bentonite mixtures, in which the a_{OH^-} was evaluated from external alkaline solutions of the compacted samples. On the other hand, the a_{OH^-} dependences of the dissolution rate for loose bentonite or montmorillonite samples have been reported to be the exponents ranging between 0.15 and 0.34. The difference in the a_{OH^-} dependence is probably caused by the difference between a_{OH^-} in the pore of the compacted samples and that in the external alkaline solutions. The Donnan effects and the local decrease in a_{OH^-} as a result of alkali – mineral reactions are presumed to be responsible for the difference between a_{OH^-} in the pore water and that in the external solution. To estimate the a_{OH^-} in the pore water, we have to know the distribution of OH^- in the pore space, which cannot be determined by direct measurements. Therefore we modeled the distribution of ions in the pores by integrating knowledge on the pore structure and the surface charge density etc, based on the electric double layer model. Because the pore structure and the surface charge of the minerals are determinatives of diffusivity of ions in and hydraulic conductivity of the compacted samples, we developed the model as a common scientific base for the dissolution of montmorillonite in, diffusion of ions in and hydraulic conductivity of the compacted samples. (284 words)

Development of a coupled mass-transport / chemical reaction code for simulating variation in hydraulic conductivity of bentonite buffer in radioactive waste disposal

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Highly alkaline environments induced by cement based materials in radioactive waste repositories are likely to alter montmorillonite, the main constituent of bentonite buffer materials. Over long time periods, the alteration may cause the physical and/or chemical properties of the buffer materials to deteriorate. For the purpose of simulating the deterioration, dissolution rates of montmorillonite in, diffusivity of hydroxide ions in and hydraulic conductivity of compacted sand-bentonite mixture specimens were experimentally determined under simulated groundwater conditions and formulated. We also performed an alteration experiment of hardened cement paste using artificial seawater to observe evolution of liquid phase composition with transition of dominating mineral phases. We developed a coupled mass-transport / chemical-reaction code, MC-BENT, for simulating the variation in the hydraulic conductivity of the bentonite buffer accompanied with the mineralogical changes in the cement-bentonite system by using the experimental results. The MC-BENT simulates long-term variations in hydraulic conductivity of bentonite buffer materials accompanied with space- and time-dependent changes in mineralogy, porosity, temperature and diffusivity. A widely-used and verified geochemical code, PHREEQC, is in charge of the chemical reaction calculations such as speciation of aqueous species, mineral-water equilibria, redox reactions and kinetic dissolution of mineral phases. The mass transport in the bentonite buffer materials is described by one- or two-dimensional diffusion and advection in the MC-BENT. The finite volume method was applied to allow variable mesh sizes. We also added the function calculating heat transfer to provide time- and space-dependent temperature. The temperature is an important factor to be evaluated because the dissolution rate of minerals and diffusion of alkali in bentonite buffer strongly depend on the temperature. The code sequentially calculates the groundwater flow, heat transfer, mass transport, mineral-water interactions, changes in porosity and effective montmorillonite dry density, changes in mass transport parameters including hydraulic conductivity and diffusivity. Calculations by using this code successfully reproduced observed results from lab-scale experiments on the bentonite alteration, the cement alteration and the mass transport of hydroxide ions. The changes in concentrations of major aqueous species in solutions and montmorillonite contents in the compacted sand-bentonite mixture specimens were reproduced by the calculation. These are indicative of partial verification of our simulation system that consists of data, model and code. Long-term hydraulic conductivity measurements for sand-bentonite mixtures using NaOH solutions are being performed for further verification of our simulation system.

O26-01

New approaches to studying individual small particles

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The study of individual aerosol particles has been of steadily increasing interest because of concerns about the environment, health, and climate change. The range of particle types in the atmosphere is wide, and many are minerals. Transmission electron microscopy (TEM) is uniquely able to provide information regarding composition, crystallographic structure, morphology, and associated phases, all on the same small particle. In order to understand the morphologies of complex particles such as soot and particle aggregates, we are making 3D measurements using electron tomography. With the goal of understanding cloud formation, we are using *in situ* microscopy with an environmental cell (ETEM) to study deliquescence/efflorescence phase changes in hygroscopic particles like salts.

The influence of aerosol particles on radiative forcing results in the largest uncertainty in the energy terms used to estimate and predict climate change. Light-absorbing particles such as soot (black carbon) play an important role, exerting a warming influence that may be second only to that of CO₂. The branching, fractal character of soot particles fundamentally influences their reactivity, atmospheric lifetimes, and interaction with radiation. Preliminary results of quantitative measurements from electron tomograms show that the imaged surface areas and volumes can differ from geometrically modeled values by one and two orders of magnitude, respectively. This result has important implications for the chemical aging of soot—the process of changing hydrophobic soot particles into a hydrophilic and more readily scavenged aerosol—which affects its atmospheric lifetime and its radiative forcing potency.

Many atmospheric particles interact with water vapor. The reaction determines whether the particles are crystalline or aqueous and whether they can act as cloud condensation nuclei. In the nano-size regime, physical state also depends on particle diameter, which implies that phase diagrams for bulk systems are shifted in ways yet to be determined for nano-size systems. Crystallization rates depend linearly on particle volume for bulk systems. Entering the nano-size regime, an open question is where and why this linear relationship falters. We are using ETEM for the study of nanoparticle reactions. This work provides significant insights into the formation, growth, and stability of particles in the atmosphere, all of which have implications for radiative, health, and visibility impacts of those particles.

O26-02

Compositions, structures, and surface properties of carbonaceous aerosol particles from the continental atmosphere

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We studied the chemical and physical properties of single atmospheric aerosol particles, in order to understand their formation histories and atmospheric effects. Aerosol samples were collected at a rural site in Hungary in all four seasons under variable meteorological conditions. We used analytical transmission electron microscopy (TEM) techniques for studying the compositional variations both among various groups of particles and inside single particles. The structural details of soot particles were studied using quantitative selected-area electron diffraction (SAED). We used atomic force microscopy (AFM) for studying the surface properties and the hygroscopic growth of individual particles under controlled relative humidities.

The majority of particles could be sorted into two broad categories, sulfate/organic and carbonaceous particles. Sulfates are mixed in the same particles with carbon-bearing species under both polluted and clean conditions. Carbonaceous particles have variable morphologies, and different morphologies are related to distinct compositions, presumably reflecting variations in the origins of their constituent organic compounds. On the basis of air mass back-trajectories and relative particle concentrations, we distinguished carbonaceous particle types that likely originated from combustion sources from those that could have formed from natural precursors. The latter particles likely contain water-soluble compounds, which can make them effective as cloud condensation nuclei.

The structure of atmospheric soot was studied using electron-diffraction-based pair distribution function analysis. First-neighbor atomic distances in soot were found to be as small as 0.134 nm, much shorter than in graphite or in amorphous carbon, suggesting the occurrence of a significant amount of small-sized aromatic clusters with a high molar ratio of hydrogen. Since the light absorption coefficient of soot depends on the sizes of aromatic moieties within the graphene-like sheets, this finding has implications for the optical properties of soot. The measurements also provide evidence for the presence of five-membered rings, which likely induce the curved nanostructure of soot.

The hygroscopic growth of both synthetic and atmospheric aerosol particles were studied in series of AFM images obtained under variable relative humidities (RH). Pure ammonium sulfate particles showed no significant changes in diameter or volume up to 78% RH. In contrast, mixed ammonium sulfate/malonic acid particles grew between 50 and 70 % RH. Friction images obtained from both synthetic and atmospheric particles showed contrast variations that were probably related to changes in the water coverage on the particles. Such surface heterogeneities might affect the atmospheric behavior of particles.

O26-03

Hygroscopicity of sulfate coated mineral-dust particles: Experiments using an environmental scanning electron microscope

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Mineral-dust particles are major constituents of atmospheric aerosols in the lower troposphere, playing important roles in cloud formation and thus affecting climate. Individual particle analyses have revealed that airborne mineral-dust particles can acquire coatings of hygroscopic material such as ammonium sulfate through processes including coagulation and reactions with gaseous species in the atmosphere. Such coatings may change the mineral surfaces to more hygroscopic ones and turn the particles into efficient cloud condensation nuclei (CCN).

In order to clarify how the coatings affect hygroscopicities of mineral-dust particles, we performed experiments using an environmental scanning electron microscope (ESEM). The ESEM enables *in situ* observation of deliquescence of small particles by using water vapor as the chamber gas (up to 4000 Pa) and controlling specimen temperature with a cooling Peltier stage. Commercially available kaolinite powder was used as representative mineral dust. A part of the kaolinite powder was mixed in (NH₄)₂SO₄ solutions and then dried to form sulfate coatings. The sulfate-coated kaolinite particles were loaded on the cooling stage through a sieve (< 25 µm across) and put into the ESEM chamber. Kaolinite particles without coatings were prepared in the same manner. We kept the chamber vapor pressure at 650Pa, gradually decreased specimen temperature from 20 °C to 0 °C, i.e., relative humidity (RH) from 28% to 106%, and observed changes of particle morphology indicative of deliquescence.

The kaolinite particles without coatings did not show any change until RH exceeded 100%. At temperature 0.8 °C (RH 100.4 %), water droplets formed on the particles and rapidly grew larger. On the other hand, water droplets began to form on the sulfate-coated particles at temperature as high as 3.7 °C (RH 82 %) and continued to grow entirely enclosing the kaolinite particles. The results indicate that coatings of ammonium sulfate significantly enhance hygroscopicity of kaolinite particles. Also, particles with thicker sulfate coatings formed water droplets at lower RH. Our experiments suggest that sulfate-coated mineral-dust particles can act as giant CCN, promoting coagulation of cloud droplets and thus precipitation.

O26-04

Environmental effects of micro- and ultramicro-channel structures of natural minerals

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Abstract: The micro-channel usually refers to structural channel of minerals with aperture in the range of 0.3 nm to 2.0 nm. Such microchannel include, i.e., Mn-O octahedron channel filled by K in cryptomelane, and also channel constructed by Si-O and Al-O tetragonal molecular sieve filled by Na and Ca in zeolite, and effectively have the function of molecular sieve. Here we point out that ultramicro-channels of natural minerals have apertures below 0.3 nm with the features of ionic sieves. The ultramicro-channels of mineral feldspar, accounting for half mass of the earth's crust, have been largely ignored because the aperture is too small. In this work, we present that feldspar displays a certain degree of ion exchange and owns a feature of channel structure under both high and low temperatures. At high temperature, Na⁺ can enter the channels of feldspars. The content of Na₂O in feldspar increases up to 15.9%. At middle temperature, Pb²⁺ can also enter the channels of feldspar as the result of ion exchange, leading thus to the formation of Pb-feldspar. At room temperature, about 97.94% Cd²⁺ can be removed and Cd-feldspar can be obtained. These phenomena indicate typical effects of ultra microchannels of feldspar, which may be suggested as a potential for treatment of heavy metal pollution and nucleus waste. The ultra microchannels of natural minerals have played special role in migration and exchange of geomaterials. The molecular sieves of microchannels of a few natural minerals have the property of purifying molecular gas pollution. And the ionic sieves of ultra microchannels of most natural minerals can purify ionic water contaminates.

Quantitative mineralogy applied to the prediction of acid mine drainage

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The quantitative mineralogy of 31 sedimentary, metamorphic, and intrusive and extrusive rocks was determined by Rietveld refinements of X-ray diffractometry data. An acid-consuming potential was assigned to each mineral or mineral group on the basis of previous measurements, and this value in combination with the quantitative mineralogy was used to compute the neutralizing capacity for comparison with that measured for each of the rocks. The computed values are generally lower than the measured ones, but both are of the same magnitude and a close relationship is evident. Thus, even semi-quantitative mineralogy of various rock types can provide to the field geologist or geochemist an indication of the behavior to be expected, and an alert to the unusual, during the generation and attenuation of acid mine drainage. Whereas olivine and serpentine typically are the source of the bulk of the neutralizing capacity of non-carbonated ultramafic rocks, in felsic intrusive and other rocks the presence of small amounts of carbonate minerals is commonly more important than the total silicate assemblage in providing neutralizing capacity. However, in most igneous rocks of intermediate and basic composition the presence of calcic plagioclase may have a dominating influence because of the abundance of the mineral and because its neutralization potential increases systematically as An content increases.

Geochemical and microbial controls of the decomposition and dispersion of depleted uranium in the environment

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Depleted uranium (DU) is now commonly utilised in armour-piercing munitions. Typically, DU used by the UK military for anti-tank penetrator rounds consists of DU alloyed with 0.75% titanium. The majority of DU entering the environment does so as large pieces of DU alloy, and any dusts which are produced from impacting targets are rapidly diluted to levels which are indistinguishable from the natural uranium background. After impact, the DU deposits on the ground and other surfaces and is generally in the form of partially oxidised fragments of various sizes. Penetrators which hit soft targets such as sand or soil can penetrate to depths of more than 50 cm and stay intact for long periods of time.

The environmental fate of DU fragments is not well known. Although DU deposited as oxide is expected to be immobile, predictions using data obtained from sites in Kosovo indicate that significant risks may occur even 15 to 30 years after the war. The possibilities of groundwater contamination from DU in terrestrial environments will vary depending on geochemical and microbiological conditions in the surrounding soils and rocks. Previous studies, where DU penetrators were allowed to weather in arid soils for approximately twenty years, showed that uranium movement occurred primarily through the dissolution and re-precipitation of uranium oxides. With increasing depth in the soil, the uranium oxides were found to be coated with amorphous silica or were found in aggregates with clays which limit the mobility of uranium. The uranium oxides found in these studies included schoepite, $(\text{UO}_2)_3\text{O}_4(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$ and metaschoepite, $(\text{UO}_2)_3\text{O}_4(\text{OH})_{12} \cdot 10\text{H}_2\text{O}$. In addition to geochemical studies, it is important to study soil microorganisms; these provide the potential for the metal to bind directly to the cell surface and hence alter the surrounding soil chemistry, leading to microbially-induced corrosion.

Currently we are involved in a multidisciplinary study of laboratory model systems and field samples to gain a predictive understanding of the processes involved in DU decomposition and dispersion. The effects of DU on bacterial and fungal communities are also being explored. The amounts of dissolved, colloidal and macroparticulate fractions as a function of decomposition time and biogeochemical conditions are being quantified, and state-of-the-art imaging and analytical techniques being used to characterise DU decomposition products. The dispersion of DU and its decomposition products are also being measured in column experiments and interpreted quantitatively using a mechanistic model. Our results from preliminary investigations will be presented.

Arsenic in soils, mine tailings, and former industrial sites

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Although arsenic occurs naturally in soils, human activities have greatly increased arsenic contamination in the environment, e.g. through releases associated with mining, waste disposal, indiscriminate use of certain pesticides, as well as the manufacture of As-bearing chemicals. Contaminated soils act as a source of arsenic, which can be further dispersed in the environment and may adversely affect the growth of plants and animals and, eventually, human health. Much progress has recently been made on the relation between arsenic crystal chemistry and its speciation and distribution at the Earth's surface. Aided by a rapidly expanding body of experimental data and by the information provided by modern analytical tools such as synchrotron radiation, a better picture of the control exerted by the crystal chemistry of arsenic on its biogeochemical properties is emerging. With this in mind, we will present some examples of studies of contaminated soils, former industrial sites, and mine tailings. The investigation of both natural high arsenic geochemical anomalies and old mining and industrial sites contaminated by arsenic provides good data to establish what the most stable As-bearing phases are. The examples presented show the importance of oxidation and dissolution reactions, microbial activity, and water regime. These studies show the importance of As adsorption on, or coprecipitation with, hydrous ferric oxides in delaying the long-term impact of As on the biosphere. In addition, arsenic mobility often depends on bacterial activity, even at extreme As concentrations, with major seasonal modifications of As speciation. Remediation technologies use geochemical affinities between arsenic and specific low-temperature phases and molecular scale data indicate the processes, which can be used to reduce the bioavailability of arsenic.

Ferrihydrite precipitates aged over 25 years: Structural evolution and reactivity with dissolved arsenic

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Amorphous hydrous iron oxides such as ferrihydrite are ubiquitous in the environment as mineral coatings and discrete phases and exhibit a high affinity for a range of potentially toxic elements, including arsenic. As such, knowledge of ferrihydrite structural evolution with time and its impact on trace element sorption is required in order to improve our understanding of the role ferrihydrite plays in regulating aqueous trace element concentrations. The identity and proportion of iron oxide phases evolved in an unique archive of ferrihydrite samples, aged for up to 25 years under different pH regimes, was characterized using conventional X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS), building on the work of Schwertmann et al. (2004). Ferrihydrite phases aged at pH >6 over 15-25 years recrystallized into goethite-dominated assemblages, with high pH (>12) conditions producing significantly larger diameter crystallites. Hematite was the dominant aged product at lower pH settings (pH <5). Ageing was accompanied by a marked loss in BET surface area.

As(V) and As(III) sorption experiments were conducted on three of the ferric oxide products that developed under contrasting pH conditions (pH 4.4, 7.1 and 12.8). Almost complete uptake (>99.3%) of As(V) was noted for all three mineral sorbents over 48 h, whereas 5 – 14% of the As(III) spike remained in solution for the iron phases aged at pH 7.1 and 12.8, possibly related to the lower surface area of these samples relative to the pH 4.4 aged product. Arsenic sorbed on the iron (oxyhydr)oxide phases retained its original oxidation state, although limited synchrotron beam catalyzed photooxidation of As(III) was observed in the hematite-rich sample. EXAFS analysis of the adsorbed arsenic is ongoing and results will be presented in the context of the effects of ferrihydrite ageing on arsenic retention in oxic weathering environments.

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Use of Fe(II)-Montmorillonite for the reduction of aqueous Cr(VI)

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Mobility and bioavailability of Chromium in soils and natural waters are linked to its redox conditions in the environments. The Cr(VI) is toxic to human-health and hence the reduction to non-toxic Cr(III) is the potential pathway for environmental remediation. Here, Fe(II)-montmorillonite (**Mont**), of which exchangeable cations are Fe(II), was prepared and its stability as well as its reactivity to reduce Cr(VI) were studied.

Fe(II)-Mont was prepared from homoionic Na-Mont, Kunipia-F (Kunimine Co. Ltd. Japan) by the following two-step process. In the first-step, Fe(III)-Mont was obtained by the conventional ion-exchange method with FeCl₃ solution. Subsequently, it was reduced to Fe(II)-Mont using ascorbic acid in aqueous medium. The Fe(II)-Mont was washed thoroughly with de-ionized water and vacuum dried. The total amount of Fe(II) extracted with 1M NH₄Cl solution was 110 meq/100g, which is close to the CEC of parent Mont (~120 meq/g). The stability of exchangeable Fe(II) in Fe(II)-Mont was studied in distilled water (solid /liquid ratio: 0.5 g / 200 ml) with or without Ar bubbling. The Fe²⁺/Fe_{total} ratio of the sample was determined by o-phenanthroline method for Fe extracted from the Fe(II)-Mont with 0.1 N H₂SO₄. It was found that Fe(II) gradually oxidizes. For example it took about 40 days to reach a Fe²⁺/Fe_{total} ratio of about 0.5 even without Ar bubbling. This finding suggests that Fe(II) ions in the interlayer of Mont are relatively stable.

The reactivity of Fe(II)-Mont to reduce Cr(VI) was studied by suspending Fe(II)-Mont in 0.5 mM of K₂Cr₂O₇ solution (solid /liquid ratio: 0.1g clay/100 ml). The Cr(VI) concentration was periodically monitored with spectrophotometer (λ_{max} 350 nm). It was found that more than 80 % of Cr(VI) was reduced within 10 min. No reduction of Cr(VI) was found for the cases of Na- and Fe(III)-Mont samples.

In conclusion, it can be considered that the exchangeable Fe(II) in Fe(II)-Mont is relatively stable even without Ar bubbling but could reduce Cr(VI) with high reaction rate in an aqueous solution. This suggests the potential application of Fe(II)-Mont for the environmental remediation of Cr(VI) contamination.

Minerals and disease: asbestos and apatite

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Environmental exposures to particulates via the air or water can result in either beneficial or hazardous health effects. Asbestos, a group of fibrous silicate minerals, are now regulated in many countries because high exposures in occupational environments may cause asbestosis or lung cancers. The biological mechanisms leading to these hazards are under investigation. The calcium phosphate group, apatite, are the minerals deposited in vertebrate skeletons. The continual precipitation, resorption and changes in composition and distribution of apatitic minerals throughout the skeleton over the lifetime of an individual is essential to health and well being. Understanding the metabolic events and the limits occupy both medical and materials scientists as well as mineralogists.

Surface structure, growth and Ca²⁺ incorporation on barite (001) and (210)M.C. Warren¹, K.J. Finch¹, A.I.R. Stark¹, P.L. Wincott¹ and D.J. Vaughan¹¹School of Earth, Atmospheric and Environmental Sciences and Williamson Research Centre for Molecular Environmental Science, The University of Manchester, Oxford Road, Manchester, M13 9PL
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Barite (BaSO₄) is a major component of inorganic scale that forms in well bores and oilfield pipework. Chemical scale inhibitors function by inhibition of nucleation and retardation of crystal growth. However, these processes are affected by the presence of cations such as Ca²⁺, for reasons that are poorly understood. AFM measurements have been combined with atomistic simulations in order to understand surface structures, growth processes and the effects of Ca²⁺ incorporation on dominant surfaces of barite.

Observations of barite crystals in air using atomic force microscopy (AFM) have shown that (001) and (210) surfaces have sets of parallel steps, thought to be caused by fracture propagation. Step heights are commensurate with the corresponding planar spacing. Acute angles between intersecting steps are characteristic of each surface, suggestive of crystallographic control. In situ AFM experiments have been used to study surface growth and dissolution processes in the presence of supersaturated solutions of BaSO₄. Growth occurred by the spreading of growth islands, which were sector-shaped on the (001) surface but needle-shaped on (210). In the presence of Ca²⁺, growth islands on (001) had a less uniform shape and spreading rates decreased. These effects were less pronounced on the (210) surface. In all experiments, increased ionic strength of solution resulted in increased rates of growth.

Atomistic simulations have been used to predict the structure and stability of candidate step edges and thus investigate whether the orientation of these steps may be crystallographically controlled. The most stable steps were found to be along the $\bar{1}210$ and $1\bar{2}0$ directions on the (001) surface, and along the $\bar{1}20$ and $\bar{2}41$ directions on the (210) surface. The intersections between these are consistent with the dominant angles observed with the AFM. Sector-shaped islands on (001) were simulated to investigate growth mechanisms and the effects of Ca²⁺. These calculations suggest that Ca²⁺ incorporation within growing (001) surface islands increases island stability, with preferential incorporation at the edges of the island. The addition of BaSO₄ and CaSO₄ clusters at island edges, simulating spreading, revealed differences in the strength of site preference and this is discussed in the context of the changes in island morphology observed with AFM.

Use of stable isotopes to distinguish mechanisms of calcite precipitation in response to different landfill operational environments

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This study proposes a model that associates carbonate mineral precipitation from landfill leachates to (i) biogeochemical processes responsible for waste degradation and (ii) mechanical factors that are an intrinsic part of landfill operation and leachate treatment. Stable isotope techniques can provide the waste management sector with spatial and chemical data that relate directly to site operation and engineering, allowing insight into the future development of waste management facilities.

Biogeochemical processes operating within landfill sites play a major role in the degradation of waste fractions (organic and inorganic) by generating large quantities of CO₂ and solubilising calcium and other metals. Because of this, carbonate minerals may precipitate from young and ageing landfill leachates as the waste continues to degrade. Mineral scaling in leachate drainage systems can be problematic as it causes blockages, increasing the risk of uncontrolled discharges to the environment. To identify key biogeochemical reactions associated with carbonate precipitation and to elucidate whether precipitation is influenced by mechanical or physical factors intrinsic to landfill operation, solids collected from seven UK landfills sites were subjected to carbon and oxygen stable isotope analysis. Samples analysed included: (1) suspended solids within young leachates from landfill cells, (2) crusty precipitates recovered from surfaces of concrete blocks, submersed in closed leachate tanks outside the landfill, and (3) solids encrusted inside drainage pipes that carried aged leachate from collection tanks to foul sewer. Mineralogical analysis indicated that calcite was typically dominant within solids, comprising 23-95 weight %. Substitution of calcium for magnesium and manganese (<8 mole %) was often evident, although FeCO₃ concentrations were more variable and iron was also associated with sulphides or hydroxides.

Calcite $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ -values group according to location of sample recovery. Suspended solids (1) and crusty precipitates (2) show increasingly heavy $\delta^{13}C$ values (-3.1 to +18.8‰) suggesting that bacterial methanogenesis gradually dominates carbon dioxide production with increasing waste degradation, and calcite incorporates progressively heavier carbon which has been kinetically fractionated ($\Delta^{13}C_{CO_2-CH_4} \approx 70\%$). A pH controlled kinetic fractionation also shifts these $\delta^{13}C_{PDB}$ values. Pipe solids (3) show negative $\delta^{13}C_{PDB}$ values (-5 to -9‰) which are probably explained through bacterial methane oxidation. Calcite $\delta^{18}O_{PDB}$ -values range from -5 to +12.5‰ and become progressively more positive with leachate age. Increasing kinetic fractionation ($\Delta^{18}O_{calcite-leachate}$) with decreasing temperature (to around 5°C, as leachates leave the landfill) in addition to greater interaction with atmospheric carbon dioxide (+9.8‰PDB) during aerobic leachate treatment, in isotopically open conditions, are also undoubtedly significant.

Investigation of the β - α TCP phase transformation in dependence of Mg-content

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Bone constitution material is used very widely for implantation surgery. Further improvement of the available materials is required with respect to degradation behavior. Tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (TCP) is an osteoconductive as well as bioresorbable phase. TCP can crystallize in three polymorphic modifications: β -TCP below 1180 °C, α -TCP between 1180 °C and 1430 °C, and α' -TCP above 1430 °C. Mainly β -TCP and α -TCP have reached acceptance in biomedical applications. In this investigation the determination of the influence of partial Mg^{2+} substitution of Ca^{2+} in the solid solution series of β -TCP $(\text{Ca}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ was determined at 1025 °C $\pm$ 10 °C in air. The temperatures for β - α -phase transformation were determined in dependence of the Mg²⁺ content.

Syntheses of β -TCP powders were carried out by solid-state reaction in a chamber furnace at 1025 °C $\pm$ 10 °C in air. Phase composition was examined by quantitative X-ray powder diffraction (XRPD) in combination with Rietveld refinements. All powders were proven to be single-phase β -TCP. Rietveld refinement was performed using the structural models (ICSD Database) of all possible occurring secondary phases: β - $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Hydroxyapatite), β - $\text{Ca}_3\text{P}_2\text{O}_8$ (Whitlockite), α - $\text{Ca}_3\text{P}_2\text{O}_8$ (CaMg)₃P₂O₈ (Stanfieldite).

Substitution of Ca^{2+} by Mg^{2+} in the β -TCP structure at 1025 °C $\pm$ 10 °C is correlated with a decrease of the lattice parameters. Refinement from lattice parameters led to the composition of the end member of the solid solution. At a temperature of 1025 °C $\pm$ 10 °C up to 14 mole% of Ca^{2+} can be replaced by Mg^{2+} in the β - $\text{Ca}_{1-x}\text{Mg}_x(\text{PO}_4)_2$. For the described synthesis conditions the Mg-rich end member of the solid solution has the formula $(\text{Ca}_{0.86}\text{Mg}_{0.14})_3(\text{PO}_4)_2$.

Transformation temperature of β to α -TCP can be increased from 1150 °C (Mg²⁺-free) to 1540 °C with a Mg²⁺-substitution on Ca^{2+} sites of 8 mole %. Samples with higher substitution than 10 mole % Mg²⁺ are not affected by the α - β transformation since the melting points were reached before transformation could take place. The formed melt fills up existing pores and thus lead to completely dense ceramic. Higher temperatures during sintering process lead to denser TCP ceramics and thus better mechanical properties. Sintering of Mg-containing TCP ceramics can be performed at much higher temperatures.

Low temperature formation of clay minerals from aqueous starting materials

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The formation of clay minerals in the natural environment takes place from ambient temperature to geothermal systems. Clay minerals may originate from the alteration of other minerals, precipitate directly from solutions (i.e. geothermal systems) or could both occur at varied rates and proportions. Most clay mineral synthesis methods that are intended to mimic natural processes are conducted at a higher temperature ($T > 250^\circ\text{C}$) and pressure. This effectively excludes aqueous starting materials. Starting materials in current methods involve either crystalline or amorphous phases that are similar compositionally to expected products. A few of the low temperature ($50^\circ\text{C} < T < 100^\circ\text{C}$) clay synthesis methods that use aqueous starting materials involve chemical components not available in most natural settings.

The low temperature formation of clay minerals from solutions via direct precipitation was investigated through ambient pressure and atmosphere experiments. Starting solutions' Mg:Si ratios considered range from 1:1 to 5:1 with varying Al concentrations. A temperature of 60°C and a pH of 9–10 were maintained during the synthesis experiments. The orders of addition are Al $\rightarrow$ Si $\rightarrow$ Mg (ASM) and Mg $\rightarrow$ Si $\rightarrow$ Al (MSA). All resulting suspensions are continuously stirred to prevent the formation of localized concentration gradients. Synthesized products were characterized mainly by powder XRD.

Results show that the difference in the order of addition resulted to two different materials despite having similar Mg:Si ratios and Al concentrations in both starting materials and synthesized products. ASM did not show any low-angle diffraction peaks common in phyllosilicate minerals although a developed peak at $\approx 1.54\text{\AA}$ (d_{060} reflection) indicates a trioctahedral nature. This is in contrast to MSA where both basal reflection (d_{001}) and d_{060} are relatively discernible (< 500 cps). The MSA's d_{001} peaks shift from $\approx 15\text{\AA}$ to $\approx 7.8\text{\AA}$ with an increase in Al concentration. An excess in Al concentration results to the formation of amorphous materials.

The low temperature formation of clay minerals by direct precipitation from solutions is mainly influenced by the order of addition and availability of individual components (i.e. Mg, Al, Si). Aluminum concentrations (i.e. in both MSA and ASM) appear to inhibit the formation of clay minerals. This is very much related to the relative mobility of Al with respect to Mg and Si. Its concentration and availability in the natural formation of clay minerals from solutions is controlled by its solubility and tendency to forms discrete Al-rich solid phases. The crystallinity of the synthesized materials depends on the reaction time available and ageing.

Kinetics of smectite dissolution for safety assessment of radioactive waste disposal

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Bentonite has been considered to be the most desirable candidate for buffer material in radioactive waste disposal. Extensive use of cement for encapsulation, backfilling, and grouting purposes has also been envisaged in the disposal. For this dual use, bentonite-cement fluid interaction should be a key research issue in performance assessment of radioactive waste disposal because the smectite (main component of bentonite) presumably lose some of their desirable properties by the interaction. In this context, stirred flow-through dissolution experiments, flow-through permeability dissolution experiment for compacted samples, in-situ and ex-situ AFM observation, and geochemical kinetic calculations were carried out to (1) determine reliable dissolution rates of smectite under alkaline conditions, (2) formulate the effect of pH and temperature on smectite dissolution rate, and (3) assess the impact of cement fluid on the long-term performance of bentonite. From the obtained rates in the dissolution experiments, it is unambiguously shown that the pH strongly affects the dissolution rate under alkaline condition, and the rates increase with an increase in the pH. The obtained dissolution speed was slower for the compacted samples than that for powder samples. AFM observations pointed out that the reduction in particle volume is mainly attributed to dissolution along edge surfaces despite the formation of a few etch pits on the basal surface. Based on the reactive surface areas defined by the edge surface area, the dissolution rate was fairly close to that obtained from the flow-through dissolution experiment at the same experimental condition. Therefore, the rates obtained from flow-through dissolution experiments were sufficiently reliable because of the above correspondence in the obtained dissolution rates. In order to formulate the effect of pH and temperature on the dissolution rate, model of two parallel reaction paths were proposed according to Cama et al. (2002). By fitting the whole data set, the rate equation was obtained, and the first and second reaction sites in the above reaction paths would be assigned to Si-O⁻ site and Al-O⁻ site, respectively. Although the results of kinetic calculations for bentonite stability were strongly depending on the term ΔG_r , it is now available to assess the impact of cement fluid on the performance of bentonite at different temperatures, pHs, and times.

Clay minerals from Lake Qarun sediments, Egypt and their climatic implications

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The clay minerals of the Holocene sedimentary cores from Lake Qarun, Egypt were investigated using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM). Results indicated that these clay minerals are smectite and kaolinite. Both XRD and SEM indicated the detrital origin of these clays based on the asymmetry and broadness of their characteristic diffraction peaks and deformations of their morphology. Therefore their relative abundance can be used as a proxy for paleoclimatic changes. Smectite abundance in general reflects the prevailing of dry conditions while kaolinite abundance reflects the prevailing of wet conditions. The general abundance of smectite over kaolinite in these sediments could indicate the prevailing of relatively dry conditions during the deposition of these sediments. However, the relative increase of kaolinite contents in some zones through the cores might reflect the prevailing of relatively wet periods. Four climatic zones ranging from dry to relatively wet can be identified during the last seven thousand years based on the relative abundance of kaolinite and smectite in the core sediments.

In vitro toxicity of the new fluoro-edenite amphibolic fibres from Biancavilla (Mt Etna, Sicily, Italy).

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Cases of environmental pollution by mineral fibres not classified as asbestos are becoming more frequent, in Italy and in foreign countries. The recent Italian case of Biancavilla is known to the international scientific community by the way it came about. This is a typical example of non-occupational exposure of an environmental nature caused by natural fluoro-edenite fibrous amphibole. Although these fibres do not belong to the asbestos group, epidemiological studies allow to consider them as the cause of the pleural mesothelioma observed in the local population. The finding of fluoro-edenite fibres in the parenchyma of inhabitants from Biancavilla died of a pleural mesothelioma and the recent results of toxicological studies, *in vitro* and *in vivo*, confirm that the exposure to these fibres may be the cause of the pleural mesothelioma. Fluoro-edenite, a new end-member of the amphibole group, occurs in asbestiform morphology into the autoclastes and incoherent products of metasomatised boninitic lavas belonging to the Etnan Volcanic Complex. These amphiboles are extremely difficult to investigate because their very small sizes (width <1 µm). Moreover, this material includes a complex mineralogical association mainly composed of microcrystals of alkali-feldspars, clino- and ortho-pyroxenes, fluoro-apatite, and Fe-Ti oxides. With the aim to obtain a almost pure material for biological investigations, a gravimetric sedimentation method was used which allowed obtaining a fibrous material with up to 95% of the amphibolic fibre content. In this research, these new well-characterized amphibolic fibres from Biancavilla were investigated in order to determine the degree of cell damage, in particular regarding some mechanisms involved in carcinogenesis. Our biological and toxicological tests were carried out on 50 µg/ml for 24 and 48 h fluoro-edenite-treated A549, MeT-5A, and J774 cells, human lung alveolar epithelial, mesothelial and mouse monocyte-macrophage cell lines, respectively. We performed TEM, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) proliferation assay, Time Lapse Microscopy and immunohistochemistry on A549. We examined the cell viability (MTT), the membrane integrity (lactic dehydrogenase, LDH release), the intracellular reactive oxygen species (ROS) production, and the amount of nitrite/nitrate (NO₂⁻, nitric oxide) in culture medium in MeT-5A and J774. Our results provide evidence of i) *in vitro* functional derangement (decreased cell viability and motility, increased LDH release, enhanced ROS production, induced generation of NO₂⁻), ii) morphological modification of nucleolar ultrastructure and iii) changed immuno-expression of VEGF, β catenin and F-actin. These modifications can be considered as parameters playing an important role in the development and/or progression of cancer.

P26-02

Nature and extent of the exposure to fibrous amphiboles in Biancavilla (Sicily, Italy)

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An epidemiological study on the mortality from malignant pleural mesothelioma was conducted in Italy between 1988 and 1992. The study evidenced a high and unusual cluster of malignant mesothelioma cases among the people living in Biancavilla, a 30.000 resident town located on the south-western side of the Etnan volcanic area in Sicily (Italy). Mesothelioma is considered a marker pointing out an occupational or environmental asbestos exposure. Environmental and mineralogical surveys in Biancavilla showed no asbestos exposure either from occupational activities or from the use of asbestos-containing manufactured products, but allowed finding some sites which resulted to be the sources of environmental diffusion of amphibole fibres with asbestiform habit. Moreover the presence of the amphibole fibre contents in building industry materials, such as plaster, mortar etc., was focused on the buildings over a period from the Fifties to the end of the Nineties. An abundant presence of asbestiform fibres was found in the samples, their concentrations ranged from a few thousands up to 40x10³ fibres/mg of plaster. In total the 71% of the plaster specimens resulted to be contaminated by asbestiform fibres. Such fibres were also detected in the lung parenchyma of an 86-years old woman, resident in Biancavilla, who died after the pleural mesothelioma diagnosis. *In vivo* toxicological investigations on rats were subsequently carried out and evidenced the high potential to induce mesothelioma by these asbestiform amphibole fibres. On the basis of these results it was suggested that the unusual cluster of mesotheliomas in Biancavilla might be caused by the exposure to the detected asbestiform amphiboles. Mineralogical and crystal-chemical studies carried out so far with specific methodologies on the asbestiform amphiboles from Biancavilla have evidenced that their compositions and crystal morphologies can be related to those of the prismatic fluoro-edenite. However, the fibres present a moderate compositional variability so that some of them appear to be similar to calcic amphiboles like tremolite, winchite and richterite. The aim of this study is to describe the diffusion of these fibrous amphiboles in the Biancavilla area and identify their source. These data will allow to define the past exposure of the Biancavilla population to the amphibole fibres and possibly to assess the possible hazard for future.

P26-03

Development of "in-situ" Measurement Device for Geochemical Diagnosis

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A brand new technique was developed for evaluation of the migration characteristics of the brick shaped rock sample with a remarkable reduction of measurement time. In the device, a Teflon plate having a micro channel (10-200 mm depth, 2 mm width) is placed just beneath the rock sample plate, and radionuclide solution is injected into the channel with a constant rate. A part of radionuclide can diffuse into the matrix and/or adsorb on the surface. This function results the inlet-outlet concentration difference and breakthrough curve is easily detected in a short observation period because the injection amount is extremely small and comparable to that escaping by diffusion into matrix. The advantage of this device was demonstrated by using radioactive tracer ³H, ¹³⁴Cs or ⁸⁵Sr. The time required for measurement was approximately over ten times shorter than that by the conventional method such as the through-diffusion method. The apparent diffusion coefficient and the sorption coefficient of granite were simultaneously obtained by the numerical analysis of the measured breakthrough curves and good accordance with the literature data were observed. This micro-channel device is modified and suitably designed for "in-situ" measurement by attaching on the borehole surface directly. Elastic material is chosen for the close contact on the curvature of borehole surface by the expansive force of rubber packer. The applicability of the modified device was confirmed with simulated boreholes of different rock types. In addition rare-earth element is tested as a non-radioactive tracer for wider application in the natural environment. The detection system is however large and not allowed to install in a small borehole. Instead, the outlet solution from the micro-channel is stored in a very thin tube as a position dependent concentration profile. This record of the breakthrough curve is extracted from the tube then the eluted solution is later examined by the laser fluorescence analysis for detection of extremely low solution concentration. The micro-channel device is optionally accompanied with the ground water sampling/measuring devices. Eh, pH, and electro-conductivity are measured using electrodes, and chemically active ions, Fe²⁺ and S²⁻ are measured by absorption/fluorescence system that is provided in the auxiliary devices. The ground water sample is held in the device for the post "in-situ" measurements of minerals and carbonate. All the set up of the modified device was manufactured and its applicability was confirmed by adopting the simulated borehole.

P26-04

Micro-Structural Modeling of Bentonite Barrier for Solid Waste Disposal by Means of X-Ray Computerized Tomography and Near-Infrared Spectroscopy

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Bentonite-soil mixtures have become use widely as compacted clay liner at waste disposal site in Japan. The permeability of the bentonite barrier is mainly a result of smectite constituting mostly of bentonite, that is, the sealing ability is attributable to the volume expansion of smectite due to the formation of smectite-water complex in the bentonite barrier. Therefore, the efficiency of the bentonite barrier is greatly influenced by mineralogical and geotechnical properties of the bentonite-soil mixtures. In addition, most of these properties may be varied in response to the change of hydro-geological conditions in waste disposal site, e.g., cation-exchange of smectite may proceed from Na to Ca with age. For the quality control and assurance of the bentonite barrier, full understanding for the relationships between the properties mentioned above and the permeability is indispensable. A micro-focus X-ray computerized tomography (CT) is expected to provide useful information on the microstructure of bentonite-soil mixtures. In addition the near-infrared (NIR) spectroscopy can be an effective non-destructive approach in evaluation of 'water' within the bentonite barrier. Preliminary X-ray CT observation of the bentonite-quartz mixtures prepared using Wyoming Na-smectite and quartz sand, shows that the quartz grain, the smectite-water complex and the vacant pore in the samples are clearly distinguishable. In this study, the 3-dimensional microstructure modeling of the bentonite-quartz mixtures variously conditioned is performed. In addition, the microstructures of the samples are compared with NIR spectroscopic data, and the relationship of microstructure and permeability of the bentonite barrier is referred.

Kinetics of smectite dissolution at highly alkaline condition: effect of dissolved silica and aluminum

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A high volume of cement for containment, structural support and grouting purposes is foreseen in subsurface repositories of TRU waste. Degradation of cement materials in the repositories can produce a high pH pore fluid ranging from pH 13.0 to 13.5. The high pH pore fluids can migrate and react chemically with the host rock and bentonites, which were employed to enhance the repository's integrity. These chemical reactions can affect the capacity of the rocks and bentonites in retarding the migration of radionuclides. Smectite, the main component of bentonites, can lose some of their desirable properties at the early stages of bentonite-cement fluid interaction. This study has been a key research issue in performance assessment of TRU waste disposal. Dissolution rate of minerals depend on several factors. Among them, measuring the effects of dissolution rate with deviation from equilibrium under alkaline condition has not been sufficiently investigated. In this study, the effect of dissolved silica and aluminum on the dissolution behavior of Na-montmorillonite was investigated. Flow-through dissolution experiments at alkaline condition (pH 13.3) with different dissolved silica concentration (0.05–0.5mM) and aluminum concentrations (0.1 to 1mM) at 70°C were performed. In experiments, Si concentration was analyzed with a UV-visible spectrophotometer following the molybdate blue method. The Al concentrations were measured by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS). Samples were taken from the reaction vessels for ex situ Atomic Force Microscopy (AFM). Separately, *ex situ* observations using AFM was also performed to obtain the dissolution rate. In flow-through experiments, high Si and Al concentrations are observed at the onset. The rise in Si and Al concentration steadily decreased until a steady state condition was achieved. Results of flow-through dissolution experiments and *ex situ* AFM observations suggest that the dissolved Si and Al concentrations in the solutions appear to be retarding the dissolution rate of smectite. The dissolution rate of smectite is a nonlinear function of the Gibbs free energy and fitted by a regression curve as proposed in Cama et al. (2000). This fit is also supported by results of dissolution experiments conducted with different silica concentrations in reacting solutions. The empirical Cama-equation obtained at neutral condition is also applicable to the estimation of smectite dissolution rate at high alkaline condition.

Complexation Reactions of Anions on Hydrotalcite Surface

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Hydrotalcite is one of the naturally occurring minerals with a formula of $[Mg_{1-x}Al_x(OH)_2][A^{n-}_{x/n} \cdot yH_2O]$. A^{n-} denotes an anion of which the valence is n . It comprises positively charged brucite-like octahedral layers and interlayers filled with anions and water molecules. The positive charge in the octahedral layers is formed by partial substitution of Al^{3+} for Mg^{2+} . Stacking of the layers occurs and the balancing interlayer anions can be exchanged.

Recently, hydrotalcite has received considerable attention in a variety of fields because of their considerable anion-exchange capacity. It has been used as a sorbent in the removal of various pollutants in aqueous solutions. The mechanism involved has not yet been elucidated specifically surface complexation reactions. This study focuses on anion sorption mechanism in hydrotalcite with a specific regard on surface complexation reactions.

Chloride, nitrate, carbonate, sulfate, phosphate and silicate ions are the sorbates considered in the experiments. Zeta potential and pH measurements were used to monitor the sorption reactions with these ions.

In distilled water, the change in zeta potential from +20 mV to +25 mV with decreasing pH was attributed to the dissociation of surface hydroxyls in the hydrotalcite. This zeta potential trend is similarly observed in chloride and nitrate-sorbed hydrotalcite in this study. It indicates that chloride and nitrate ions inspired simply sorption by anion-exchange reaction onto hydrotalcite because that reaction has little influence on zeta potential.

On the other hand, the zeta potential trends for carbonate, sulfate, phosphate and silicate-sorbed hydrotalcite are in contrast. These exhibited lower zeta potential values which would suggest that the point of zero charge (PZC) also shifted to lower pH compared to a pH_{pzc} of more than 11 for hydrotalcite in distilled water. These results suggest that the ions considered in this study formed inner-sphere surface complexes on hydrotalcite surface probably via ligand-substitution reaction. Such reactions are expected to change the physico-chemical properties of hydrotalcite (i.e. increased or decreased stability).

Hydrotalcite has two possible sorption sites indicating that sorption mechanism would vary for different anion species.

Adsorption and Polymerization of Amino acid on Mineral Surface

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This study is focused on the mechanisms of amino acid (i.e., glycine) oligomerization on mineral surfaces which serve as a catalyst during the wetting and drying cycles. The influence of combined mineral catalysts (e.g., clays, alumina, and quartz) and the conditions such as pH, salt concentration and relative humidity during drying experiments were also investigated. Experimental methods were largely based on the study by Bujdak and Rode (1997). A 0.01g mixture of catalysts was added to 1ml of 10mM glycine amino acid solution in glass vials. The suspensions were dried and heated in an oven at 95°C for 24 hours (the 1st step of a cycle) represents the drying period. The proceeding step involving addition of 1 ml distilled water (the 2nd step) represents the wetting period. The 1st and 2nd steps were repeated several times to simulate a drying and wetting cycle. Mixed catalysts consisting of two kinds of mineral oxide (e.g., α -alumina and silica), montmorillonite (e.g., acid clay, Ca-montmorillonite and Na-montmorillonite) in different proportions (i.e. 0:100, 25:75, 50:50, 75:25, 100:0) were also used. After the cycle, amino acid and peptide sorbed on mineral surface were extracted by 100mM $CaCl_2$ and then analyzed by a high performance liquid chromatograph (HPLC; Hitachi Lachrom Elite L-2455).

Results suggest that amino acid polymerization proceeded more favorably with existence of any montmorillonite (especially high yield in Ca-montmorillonite) compared to the metal oxides. On the other hand, the montmorillonite was often accompanied by the formation of cyclic anhydride. It is found that the use of mixed catalysts has an inhibitory effect on the anhydride formation. Usage of mixed catalysts does not disturb for the formation of linear peptide.

It is also found that the pH condition (i.e., isoelectric point) and high salt concentration affect the catalytic behavior of mineral surfaces. Under the high concentration of salt in solutions, amino acid polymerization did not proceed on the mineral surfaces. On the other hand, pH condition at the isoelectric point of each mineral surface facilitates the catalysis of minerals. Silica, for example, has experienced an increased catalytic effect at pH 2.5.

In addition, humidity is found to be important factor for the polymerization. In the case of clay minerals, amino acid polymerization proceeded under controlled relative humidity at 50°C. The changing humidity from high (90%) to low (5%) also facilitates polymerization process.

Decomposition of PAHs on mineral surfaces under relative humidity controlled conditions

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Polycyclic Aromatic Hydrocarbons (PAHs) are composed of two or more fused benzene rings, and are ubiquitous in the environment. Anthropogenic sources of PAHs are related to the incomplete combustion of almost any fossil fuel emitted in both gaseous and aerosol phases. The fate of PAH residing in the atmosphere has received enormous attention in recent years due to their mutagenic and carcinogenic risks on human health. In this context, the stability of pyrene as representative PAH on quartz, alumina, montmorillonite, kaolinite, humic acid and quartz coated with sorbed humic acid was investigated at controlled relative humidity with/without light irradiation in order to detect the presence of catalytic effect of mineral surface on PAH decomposition. The stability of pyrene was found to depend strongly on the physicochemical properties of the substrates in the dark. Quartz particles showed a strong catalytic effect for the decomposition of pyrene even though these were coated with sorbed humic acid. Pyrene sorbed on montmorillonite and humic acid remained stable during the experimental period (i.e. 3 days). Moisture in the experimental cell also affected on the stability of pyrene in particular minerals. Especially, pyrene sorbed on alumina particle was rapidly decomposed at higher relative humidity. However, there are almost no effect in the case of quartz, kaolinite and humic acid. Light irradiation decreased the stability of pyrene on quartz and montmorillonite but not on humic acid. However, it should be noted that the decomposition rate of pyrene on quartz in the dark was still faster than that on montmorillonite under light irradiation. As the preliminary results from this study, it is also clear that pyrene sorbed on montmorillonite and humic acid is more stable than on quartz and alumina. The relation of acid strength on the mineral surfaces and pyrene decomposition rate was examined to reveal decomposition mechanism of pyrene on the minerals. Depending on the physicochemical properties of aerosols, relative humidity and light irradiation, PAHs associated with minerals in the atmosphere would be decomposed and/or stably carried to leeward during their transportation.

Kinetics of transformation from schwertmannite to goethite

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Understanding of toxic trace metal distribution and cycling in the natural environment is important in predicting the long-term environmental effects of human activities. Schwertmannite has been known to adsorb significant amounts of arsenic from acid mine drainage (e.g. Bigham et al., 1994; Fukushima et al., 2003). The adsorption mechanism has been expounded by Fukushima et al. (2003, 2004) wherein arsenate would be taken up by ligand exchange with SO₄ sites on the schwertmannite surface. However, schwertmannite is a poorly crystalline iron oxyhydroxysulfate mineral that has a limited stability, and eventually transforms to goethite in solution for a few days to weeks at 25°C in natural (Bigham et al., 1994). This transformation is retarded after adsorption of arsenate on schwertmannite. In this study, adsorption stability of arsenate on schwertmannite was investigated. Long-term stability of schwertmannite after adsorption of arsenate was also investigated to predict the fate of arsenate fixed into schwertmannite in some polluted areas. Synthesized schwertmannite was used in the preparation of As adsorption samples at 25°C and pH4. The concentration of As range from 0.0mg to 85.1mg /g schwertmannite. Then, As adsorption samples were aged at 30 - 70°C and pH4. The aged samples were collected at 1, 2, 3, 9, 16, 27, 50, 100 and 200days later. ICP-MS was used to analyze As and Fe concentrations in solution samples. In the result, it was detected more Fe with increasing temperature, while it was not detected As in each case. The solid samples were analyzed by XRD to determine the mineralogical transformation. The solid samples were extracted by TAO solution. Residues remaining after extraction were identified as crystalline goethite. XRD analyses showed that some samples with less As adsorption were transformed to goethite after 200days. However, the samples with much As adsorption did not show any evidence for the transformation. The samples with much As adsorption after TAO extraction certainly remained residue, i.e. crystalline substance part of solid sample. These observations presumably indicate that the transformation rate of schwertmannite with As adsorption. From the above aging experiment, the obtained apparent activation energies are E_a=62.3kJ/mol and 38.5kJ/mol for schwertmannite with (85.1mg-As/g-sch) / without out As adsorption. From the obtained transformation rate, small portion of the schwertmannite with As adsorption would still be remained even after 100years later at 25°C even though the schwertmannite without As would easily transform to goethite after several years at the same condition.

P26-10

An EXAFS Study of Arsenate Sorption in Synthetic and Natural Schwertmannite

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Schwertmannite (Fe₁₆O₁₆(OH)_{12.4}(SO₄)_{2.3.5}nH₂O) is a poorly crystalline iron oxyhydroxysulfate, commonly formed in acid mine drainage (AMD) regions with high SO₄²⁻ concentrations. Because schwertmannite is an important sink for As under AMD conditions, an understanding of the sorption mechanism of As in schwertmannite is of great interest to resolving trace-metal behaviors and pollution problems in mining areas. A rapid decrease in As concentration in downstream water has been recently discovered to associate with precipitation of As-bearing (~0.33 wt% As) schwertmannite on riverbed rocks in the Chinkuashih AMD area, northern Taiwan, which triggered our interest in understanding the sorption mechanism of As in schwertmannite. This study examined synthetic and Chinkuashih As-bearing schwertmannite using the EXAFS beam line at National Synchrotron Radiation Center, Taiwan. The Fe and As K-edge EXAFS analyses of synthetic schwertmannite imply a structure consisting of chains of edge-sharing FeO₆ octahedra with a Fe-Fe distance of ~0.300 nm and having corner sharing between two other corners of each octahedron and two apical oxygens of the octahedra in a neighboring chain with a Fe-Fe distance of ~0.340 nm. Arsenic is coordinated by 4 oxygens to form AsO₄ tetrahedra (having an As-O distance of 0.168 nm with a coordination number of ~4.0) that connect with two apical oxygens of FeO₆ octahedra (bidentate mononuclear with an As-Fe distance of 0.324-0.328 nm and a coordination number of 1.79-2.01). A rapid decrease of the coordination number of the Fe-Fe shells implies the presence of a significant amount of disorder in the arrangement of FeO₆ octahedra and possible destruction of the schwertmannite structure at an As/Fe molar ratio greater than 0.4. On the other hand, the bonding between arsenic and other atoms does not seem to be affected by the chemical change, suggesting possible formation of a poorly- or non-crystalline arsenate compound, as also implied by XRD results. The Fe K-edge analyses of the Chinkuashih schwertmannite specimens show similar results regardless of an increase of goethite component at various depths indicated by FTIR and XRD analyses. The As K-edge measurements of the Chinkuashih specimens were not convincing due to inadequate intensities. In the future, desorption experiments may be needed to combine with EXAFS analysis in order to provide sufficient evidence to distinguish external surface sorption from structural incorporation of As in schwertmannite.

P26-11

A Novel Remediation Method Learnt to Natural Attenuation Processes in Acid Mine Drainage

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The oxidation of sulfide minerals in tailings of abandoned mines result to the generation of acidic mine drainage (AMD) that is rich in dissolved SO₄²⁻, Fe²⁺ and As. Currently, there are more than a hundred abandoned mines in Japan experiencing AMD. Neutralization is the main remediation procedure applied in AMD, however, it is beset by (1) an enormous expenditure due to its long term implementation, (2) a large amount of sludge is produced, and (3) possible leaching of hazardous elements from the sludge (i.e. arsenic). The sludge are not stable in the long run, thus, it is necessary to develop an alternative remediation technique. This study illustrates a novel remediation technique applied in an AMD affected area in Hokkaido, Japan (Horobetsu Mine).

The poorly-crystalline schwertmannite (Fe₁₆O₁₆(OH)_{9.6}(SO₄)_{3.2}·10H₂O) forms in AMD areas due to an iron-oxidizing bacteria. It has been known to uptake a large amount of dissolved As in AMD via ligand exchange. Thermodynamic modeling predicted the optimum condition for schwertmannite formation in drainage water of the Horubetsu Mine. Using laboratory batch experiments, schwertmannite was synthesized *in situ* and checked if arsenic was taken up by the schwertmannite. *In situ* formation of schwertmannite was implemented on a pilot scale flow-through experiment in Horobetsu Mine. Dissolved Fe and As in AMD was almost completely and continuously removed by the *in situ* formation of schwertmannite. Selective chemical extractions confirm that arsenic taken up was solely hosted by the schwertmannite.

The stability of schwertmannite-sorbed arsenic was also assessed by ageing experiments conducted at 50°C. XRD patterns indicate that a high arsenic loadings in schwertmannite leads to the formation of the more stable mineral scorodite (FeAsO₄·2H₂O). The *in situ* formation of the mineral host schwertmannite reduces the amount of sludge compared to the conventional neutralization process. Furthermore, schwertmannite transformation to scorodite ensures that arsenic is not leached out from the sludge.

P26-12

Absorbed characteristics of Arsenic in Holocene sediments: Comparison of drilling core samples from Niigata Plain, Japan and Bangladesh

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Arsenic contamination of Groundwater in the Ganges delta area and other regions in Asia has been reported as a serious health problem to millions of people (Welch and Stollenwerk, 2002). There are two important points concerning arsenic contamination in groundwater: what are arsenic sources? and how is arsenic released? Potential source of arsenic to groundwater is the oxidation of arsenic-bearing sulfides (Chakraborti, 1995) or reductive dissolution of ferric oxyhydroxides (Bhattacharya et al., 1997; Nickson et al., 1998). So, we investigated chemical forms of Arsenic in alluvial deposits of Niigata Plain and Bangladesh, applying SSE (Selective Sequential Extraction) analysis comparatively.

Sediment samples were collected from a borehole drilled at Yoroigata in Niigata Plain, Japan and two localities in Bangladesh. Samples were mineralogically examined in detail by a binocular microscope, polarizing microscope and XRD. Quantitative chemical analyses of the sediments were carried out by XRF.

SSE of the sediments was carried out for determining the association of arsenic with different phases. Procedures for extractions were basically those described by Kok et al. (2005), which were modified from Keon et al. (2001). The extractions for chemical forms are by following five steps. I) ion exchange form, II) phosphoric acid exchange form, III) highly amorphous Fe oxyhydroxides absorbed form(also adsorbed carbonate and Mn oxide), IV) amorphous Fe oxyhydroxides absorbed form, V) sulfide form. Arsenic concentrations in the solution were determined by HGAAS.

SSE results show that arsenic was leached mainly as forms of stepII and stepIV in Niigata sample, meanwhile arsenic was leached as forms of stepIII and stepIV in Bangladesh samples. In both samples less arsenic of form of stepI was leached. Form of stepV was characteristically leached in some Bangladesh samples. These results suggest differences between Niigata and Bangladesh in arsenic release mechanism into groundwater.

For Niigata samples, possible arsenic adsorbing matters were discussed, based on a correlation among SSE, XRD, and XRF data. From XRF data, positive correlation between form of stepII, Al content, and Loss of ignition was found. Positive correlation was also found between form of stepIV and Fe content of the sample. From XRD data, there was relatively slight correlation between form of stepII and quantity of kaolin mineral. These results suggest that soluble arsenic is mainly absorbed to Fe oxyhydroxides, kaolin, and organic matter for Niigata samples.

O27-01

A TEM/AEM survey of serpentine microstructures

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We report on a systematic transmission electron microscopy (TEM) study of the various microstructures encountered in natural and synthetic serpentine material. High-resolution TEM (HRTEM) imaging, selected area electron diffraction (SAED), energy-dispersive X-ray microanalysis (EDS-AEM) are combined to characterize better usual varieties and to work out new ones. They are markers of the local conditions of serpentinization. The known flat lizardite (*lzd*), the rolled chrysotile (*chr*) and the modulated antigorite (*atg*) display mostly order/disorder and/or twinning variants. The atomic structures of the quite common 15-sector and 30-sector polygonal serpentines (*PS*) are now better known. We will also present the intimate structure of some new natural members including the poorly-crystallized protoserpentine (*pserp*), conical chrysotile (*cchr*), polygonal lenses (*PL*), and the onion-like, polyhedral serpentine (*PHS*). TEM/EDS microanalysis of single grains confirms that crystal-chemical trends claimed from XRD-EMP data on bulk samples do not apply strictly for coeval microstructures at the particle scale. Instead, local solid/fluid ratio (*s/f*), departure from equilibrium and temperature play all a role in generating selected microstructures. In the MSH system, rapid precipitation of serpentine material from a gel results in *pserp* first. Rolled microstructures (*cchr*, *chr*, *PS*) are favoured by high supersaturation, low *s/f* ratio, and rather high *T* just below that of *atg* formation. On the other hand, *lzd* growth is favoured at low *T*, locally low *f/s* ratio, and at a closer approach from equilibrium. The *pserp* $\rightarrow$ *cchr* $\rightarrow$ *chr* $\rightarrow$ *PS* $\rightarrow$ *lzd* suite observed experimentally in the range 400°C - 200°C, P(H₂O) = 700 bar, illustrates a reaction path toward a better and better organization of the serpentine structure. The layer curvature is progressively eliminated while grain size increases. Thus all rolled microstructures look metastable and their longer persistence is observed at higher *T*. Addition of Al and/or Fe³⁺ to the MSH system shortens *PS* up to give *PL* by poisoning of (100) fiber terminations. Also, *lzd* appears sooner in that case, thus advocating a reduced intralayer misfit. The globular *PHS* contains also Al $\pm$ Fe, at least in minor amount. Its nucleation takes place on short *PS* on which they form first closing caps at both ends of the fiber. Short *PS* caps, *PL* and *PHS* most probably form at low *T*, during the retrograde episode of bastitization. As a cumular texture *lzd* is mostly encountered as the reaction product of olivine formed across a tight reaction boundary, down to the closing temperature of serpentinization.

O27-02

Crystal-chemistry of lamellar manganese oxides

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Birnessite is a lamellar manganese oxyhydroxide (phyllosilicate) whose layers are composed of MnO₆ octahedra. Their non-stoichiometry arises from the coexistence of heterovalent Mn cations (Mn³⁺/Mn⁴⁺) and/or vacant sites, and is compensated for by the presence of interlayer cations. Despite the low natural concentration of Mn, birnessite is ubiquitous in the Environment and plays a pivotal role in geochemical reactions and especially in the fate of pollutants such as organics or heavy metals. Its high reactivity arises from its high surface area, its high cationic exchange capacity, combined with adsorption and redox properties. In addition to the presence of random stacking faults, the random interstratification of different layer types and the occurrence of well-defined stacking faults are commonly reported in layered minerals, such as phyllosilicates. The high proportion of such defects strongly reduces the efficiency of structure refinement methods, and one effective way to determine the actual structure of defective systems is the calculation of XRD patterns using the mathematical formalism described in detail by Drits and Tchoubar (1990). The usefulness of this simulation technique will be illustrated with various synthetic and natural birnessite samples. In particular, this technique allowed showing that layer symmetry depends on the origin of the layer charge deficit. The symmetry of birnessite layers containing vacant octahedral sites is hexagonal, whereas an orthogonal layer symmetry is observed for varieties containing a high proportion (~1/3) of layer Mn³⁺ cations. This distortion arises from the unique azimuthal orientation of Mn³⁺ octahedra which are distorted by the Jahn-Teller effect. In addition, the structure of heavy metal sorbed synthetic birnessites was studied to improve our understanding of the interactions between phyllosilicates and environmentally important heavy metals (Me). The nature of Me cations sorbed from solution will be shown to control birnessite structure and more especially layer stacking, as well as location and coordination of Me, although octahedral layers systematically contain 0.833 Mn cations and 0.167 vacant octahedra, interlayer Mn³⁺ and Me compensating for the layer charge deficit. In some natural phyllosilicates, and especially in those resulting from biological activity, the abundance of random stacking faults leads to the occurrence of structures lacking three-dimensional ordering. Even in these turbostratic structures, XRD patterns exhibit noticeable modulations of the 20,11 and 31,02 bands (~2.45 and ~1.42 Å, respectively). These modulations can be used to provide relevant structural information, which includes not only unit-cell parameters but also atomic coordinates and occupancies of the different sites.

O27-03

Stacking structure in disordered talc: Interpretation of its X-ray diffraction pattern by using pattern simulation and high-resolution transmission electron microscopy

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Stacking structure in disordered talc, Mg₃Si₄O₁₀(OH)₂, has been investigated by using high-resolution transmission electron microscopy (HRTEM) and by comparison between experimental and simulated powder X-ray diffraction (XRD) patterns. The talc specimen investigated was massive aggregates of fine platy crystals from the Shirakashi mine, Nagasaki-prefecture, Japan. Although talc is regarded as one of the beam-sensitive phyllosilicates and near-atomic resolution TEM images were not reported before, we have successfully recorded such images to determine its stacking structure.

HRTEM observations revealed that the orientation of the 2:1 layer, which is described by the direction of the lateral shift of *a*/3 from the lower tetrahedral sheet to the upper tetrahedral sheet within the 2:1 layer (intralayer shift), is almost completely disordered. In contrast, lateral displacement between the adjacent tetrahedral sheets across the interlayer region (interlayer displacement) is relatively ordered. This result is completely different from our previous report for pyrophyllite, Al₂Si₄O₁₀(OH)₂, in which the direction of the intralayer shift is almost ordered whereas the interlayer displacement is heavily disordered. The interlayer displacement parallel to the intralayer shift in lower or upper 2:1 layers tends to be avoided.

A Gandolfi camera was used to record XRD patterns from a small fragment of the aggregates, to avoid preferred orientation and artifacts in stacking sequence by grinding. XRD patterns were simulated using the DIFFaX program and compared with experimental patterns. The experimental pattern from *hk* = 02, 11 and 1-1 reciprocal lattice rows is explained by a mixture of the stacking sequence with almost random directions of intralayer shift and a small amount of talc-1A dominant stacking sequence. The peak profiles for the reflections indexed with 20l, 13l or 1-3l are reproduced by a slightly different interlayer displacement from that reported in talc-1A, and by their variance. This work was partly supported by a Grant-in-Aid No. 17340160 [Section (B)] by the Japan Society for the Promotion of Science (JSPS).

O27-04

Fine structures of zeolites: TEM study

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Zeolites are generally very electron sensitive crystals, however through the technical developments in recording system, we can determine not only new structures of zeolites but also their surface terminations and fine structures by transmission electron microscopy (TEM). The knowledge of a surface fine structure or a defect structure can provide information of growth unit and growth mechanism. We have succeeded in solving new zeolite structures with SFE and BEC framework types, and recently in characterising a new structural modification of Ti-YNU-1 by pillaring from the "layer type" MWW structure. This explains well the reason why Ti-YNU-1 is high active in oxidation catalysis. In the conference, structural studies of zeolites of our group by TEM will be summarised and emphasised especially an importance of studying their local structures such as surface and defects.

Crystal growth of zeolites observed by atomic force microscopy

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Zeolites are hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T=tetrahedral atom, e.g. Si and Al). They contain well-ordered void spaces within their structures. Most zeolites are formed as metastable phase under hydrothermal conditions. Zeolite synthesis is readily affected by various experimental factors, e.g., starting composition, pH, temperature, mixing procedure, agitation, and synthesis time. Therefore, the crystallization mechanisms of zeolites have not been well understood, and the elucidation is still one of the major topics in zeolite science.

The crystallization mechanism of zeolites is becoming clearer; however, there are limitations of the performances as far as recent modern analytical methods are concerned. Atomic force microscopy (AFM) has contributed to the remarkable progress of surface science because the technique has made it possible to observe the surface of insulators with high resolution.

We have investigated changes in the atomic-scale height at a set of positions along with synthesis time using AFM, and it was revealed that faujasite and zeolite A can grow in the same aluminosilicate solution, but that their crystal growth behaviors are different. Corresponding aluminosilicate solutions for seeded growth are characterized by Raman spectroscopy. By combining the results of the surface characterization by AFM and the liquid characterization by Raman spectroscopy, key precursors of crystal growth for faujasite and zeolite A are proposed to be six- and four-membered ring (6R and 4R), respectively. Moreover, detailed observations of the changes in atomic-scale height show that most of the top surface structure of faujasite is terminated with double six-membered rings (D6Rs), and that at least one of the precursors for faujasite crystal growth is equal to or smaller than 6R.

Molecule-Mineral Interactions in Micro- and Nanoporous Silicates: A Vibrational Study Using IR and Raman Spectroscopy

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We have undertaken Raman and IR measurements on various micro- and nanoporous molecule-bearing silicates in order to investigate the nature of inner-surface molecule-crystal interactions.

Cordierite, $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot x(\text{H}_2\text{O}, \text{CO}_2)$, and beryl, $\text{Be}_2\text{Al}_2\text{Si}_6\text{O}_{18} \cdot x(\text{H}_2\text{O})$, can contain quasi-free CO_2 and H_2O molecules in small microcavities. H_2O molecules in both have their II-H vector parallel [001] and are dynamically disordered about it. They show little hydrogen bonding with their respective frameworks, as based on the energies of internal H_2O stretching vibrations. Low energy translations of the H_2O molecule are located roughly around 10 cm^{-1} and librational modes around 400 cm^{-1} .

Melanophlogite, $\text{SiO}_2 \cdot 2\text{M}^{12-6\text{M}^{14}}$, shows the presence of N_2 , CO_2 and CH_4 molecules, but no H_2O . The molecules partition between the $[5^{12}]$ and $[5^{12}6^2]$ cages and have only weak dispersion interactions with the SiO_2 framework. The stretching modes energies between indicate that the molecules are quasi free. Melanophlogite is hydrophobic and this may be related to the nature of the charge distribution of the SiO_2 framework.

Zeolites are, in contrast, strongly hydrophilic and the role of hydrogen bonding is important. In bikitaite, $\text{Li}_2[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O}$, H_2O molecules occur in infinite [010] channel ways and build a hydrogen-bonded H_2O chain. The temperature dependence of the line widths of the O-H stretching modes and the degree of hydrogen bonding between neighboring H_2O molecules show that the main cause behind line broadening is through modulation of the OH potential from low-energy thermal O...O vibrations in the H_2O chains. At elevated temperatures, the different O-H stretching modes become similar in energy and only a single symmetric H_2O stretching band is observed above 520 K. At these temperatures the H_2O molecules lose their hydrogen bonding and are only bonded to Li cations at the walls of the channels. The fibrous species natrolite, $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 16\text{H}_2\text{O}$, and scolecite, $\text{Ca}_8[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 24\text{H}_2\text{O}$ have eight-member tetrahedral rings that form channels about 2.5 X 4 Å in size that run parallel to [001]. Vibrational spectra show intense OH stretching and H_2O bending modes deriving from the hydrogen-bonded H_2O molecule(s) located between 3200 and 3700 cm^{-1} and around 1650 cm^{-1} , respectively. Raman spectra also show, in addition, first- and second-order scattering in the wavenumber range where O-H stretching vibrations occur. External H_2O translations occur between roughly 50 and 175 cm^{-1} and H_2O librational modes are located between 400 and 700 cm^{-1} . The dehydration behavior of H_2O in both natrolite and scolecite were investigated by Raman measurements made at elevated temperatures.

Complexes of methane hydrate and clay

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Previous work has shown that methane-hydrate complexes (with a d -value of ~ 22 Å) form between the 2:1 (silicate) layers of Na-exchanged montmorillonite. Preliminary results were presented on the stability of the intercalation of methane-hydrate complexes in two other smectite clays: (1) a Na-exchanged nontronite, which involves substitutions (Fe^{3+} for Al) in the octahedral sheet, and (2) a K-exchanged montmorillonite, where the exchange is in the interlayer. These smectites were selected because they are similar to smectites common on the ocean floor, where they represent clay derived from continental deposits (montmorillonite) and from alteration of ocean-floor basalt (nontronite).

In our continuing investigations, we are evaluating whether the 22-Å methane hydrate-clay phase is unique or if there are other methane-hydrate-clay phases in the smectite- H_2O - CH_4 system. In experiments at CH_4 pressures between 20 and 50 bars, the Na-exchanged montmorillonite (SWy-2, Clay Minerals Society Source Clay) shows discrete reflections with d -values of ~ 22 , ~ 20 , ~ 18.5 , ~ 17.5 , and ~ 16 Å. The ~ 22 and ~ 20 Å phases are smectites that are intercalated with a CH_4 hydrate structure in the interlayer. These phases are only stable at pressure-temperature (PT) conditions that are similar to where methane hydrate is stable. The phases with reflections at ~ 18.6 and ~ 17.5 Å are either associated with CH_4 pressure and show a similar dependency to varying PT conditions as the ~ 22 and ~ 20 Å phases, or they persist after pressure is released. This implies that there are two different smectite phases with similar d -values. The various CH_4 -bearing smectite phases have slightly different stability ranges. For example, the upper PT stability of the ~ 20 -Å methane-hydrate-clay phase nearly coincides with the high-temperature limit of the stability field of methane hydrate (methane hydrate = water + gas), whereas the upper PT stability of the ~ 22 -Å methane-hydrate-clay phase occurs at a ~ 1 °C lower temperature. The variation in d -values indicates that there are several possible structures of the methane-water complex in the interlayer of the montmorillonite.

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Interactions between Kaolinite Siloxane surfaces and Benzyl alcohol: Quantum chemical calculations

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Kaolinite is one of the simplest clay minerals and has significant implication for Earth's weathering processes. It also has diverse technological applications as industrial catalysis due to their larger surface areas. Exploring its interaction with organic matters including benzyl alcohol is one of the important problems in kaolinite, stimulating numerous experimental and theoretical studies. Whereas quantum chemical calculations have been used to reveal the nature of adsorption of organic matters on the kaolinite surfaces, those previous studies often utilized relatively small clusters and thus the effect of lattice topology on the adsorption behavior have not been carefully explored yet.

Here we report the results of quantum chemical calculations of interactions between benzyl alcohol and three different model clusters of kaolinite siloxane surfaces in order to give detailed insight into the adsorption processes of organic molecules on clay minerals. The first cluster is an ideal (flat) silicate tetrahedral surface that consists of 7 siloxane rings with identical Si-O-Si angles and Si-O bond lengths (model A). The second cluster is composed of 7 siloxane-ring cluster where each atomic position is from its crystallographic data (model B). Model C cluster has both tetrahedral and octahedral layers. The optimized geometries of benzyl alcohol adsorption on the model clusters show that benzene ring lies in (001) plane and inclines slightly toward alcohol functional group. The equilibrium distance between the basal oxygen and hydrogen of the alcohol functional group is about 2.5 Å. The results also demonstrate that the equilibrium configurations are dependent on the types of clusters and in general basal oxygen with the smallest Si-O-Si angle (130.1°) tends to have stronger interaction with alcohol group hydrogen. While the calculated binding energy between surfaces and benzyl alcohol ranges about 30 kJ/mol, implying strong hydrogen bonding between them, the binding energy between the benzyl alcohol and the clusters C is apparently larger than those between cluster B and A (the smallest). The current results with larger clusters given here manifest the importance of lattice topology on the adsorption behavior of organic molecules on the surfaces.

New remediating technology for contaminated soils and new barrier material for waste sites in urban areas with applications of mineral compounds, clays and zeolites.

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New remediating technique with protection of polluted soils and sediments with contaminations by heavy metal ions, arsenic, fluorine and others has been developed by application of some kinds of clays and natural zeolites. The utilized materials are of soils formed by weathering in the earth-surface, from acidic volcanics, granite rocks and others. The weathered soils are volcanic loam and weathered soils of granitic rocks etc., called "Masa Do" in Japanese. Mineral compositions of these weathered soils are clay minerals; low grade crystallinity halloysite, smectite, chlorite etc.; sandy materials; quartz, opal, feldspars, mafic minerals etc.; low crystallinity and amorphous matters; allophone, hydroxides of Si, Al, Fe and others. These sorts of weathered soils are named "Viscous Mud" in the working technology. Natural zeolites; mordenite, clinoptilolite. Other materials; dolomite, calcite and their calcined matters. The core of this treatment technique is the reaction of harmful elements in the contaminated soils to an insoluble state by water treatments. Outline of reactions is as follows: Early-stage-reaction: Adsorption, with insoluble state = cation-adsorption reaction by zeolites, coagulation reaction with amorphous matters etc. in addition with carbonate materials and ferric ion if needed. Intermediate-stage-reactions: Adsorption, fixation for clay materials. Long-term-reactions: Fixation as miner elements in newly formed crystals: $X(Y, (Si, Al)O_{3.4})_m(OH)_n \cdot xH_2O$ (with $X = K, Na, Ca, Mg, Y = Al, Fe, Mg, Ca$) and with minor elements of heavy metals in X, Y and As in Si). The reaction condition is on the surface of the earth. Before the treatments start at the actual working site, fundamental tests for the remediation done are as follows. For example: Contaminated soil: 100-200g, "Viscous Mud": 10-25g, two sorts of zeolites: 2-4g each, calcined carbonates: 1-2g. These testing materials are mixed perfectly while adding enough amounts of water. The effects are tested by water soluble testing treatment reaction by fundamental official testing methods after holding of one day, one week, a few weeks, several months etc.. This mineral mixture is named "Sealing Soil" and is developed for a new kind of clay barrier material. The technique received two different Japanese Patents recently, and has been applied at more than 20 cases.

Investigation of the stacking structure in sudoite by using high-resolution electron microscopy

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Sudoite is a di-trioctahedral Li-free chlorite with an ideal composition of $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_8$. Previous X-ray diffraction (XRD) studies reported that the stacking sequence in sudoite has a $11\bar{b}b$ arrangement and a regular two-layers structure was found in which the direction of the lateral shift of $a/3$ from the lower tetrahedral sheet to the upper tetrahedral sheet within the 2:1 layer (intralayer shift) is along $-X_1$ (X_1 represents the pseudohexagonal axes) and lateral shift between the adjacent 2:1 layers are displaced by $a/3$ alternatively along X_2 and X_3 axes. However, it is not well known whether this two-layers structure is common in sudoite and what kinds of stacking disorder exist. In the present work, high-resolution transmission electron microscopy (HRTEM) analyses were attempted to investigate the detailed stacking structure in sudoite, as well as XRD analyses. Specimens from two localities, lath-shaped crystals from Berosovska, Russia and fine platy crystals from Otter, Belgium were investigated.

XRD analyses with a Gandolfi camera showed that the patterns from both specimens are similar to that of $11\bar{b}b-4$ (or equivalently $11\bar{b}b-6$) polytype but the peaks that correspond to non-family reflections ($k \neq 3n$) are considerably broadened. The HRTEM observations revealed that the stacking sequence is characterized by the uniform direction of the intralayer shift. The lateral shift between the adjacent 2:1 layers is also almost in the same direction along either X_2 or X_3 axis. The two-layers periodic structure was seldom observed. The stacking disorder is primarily the mixing of the directions for the lateral shift between the 2:1 layers along X_2, X_3 and occasionally X_1 axes. The frequency of this kind of disorder is higher in the specimen from Berosovska than that from Otter. DIFFAX simulations of powder XRD patterns with this stacking model well explain the experimental patterns of both specimens.

Diagenetic evolution of clay minerals in Gulf Coast shales: New insights from X-ray diffraction profile modeling

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Despite the numerous investigations devoted to the diagenetic smectite-to-illite transformation, reaction mechanisms responsible for this process in shales remain poorly understood. In the present study, the multispecimen method recently developed by Drits and coworkers was used to determine the evolution of clay mineralogy as a function of depth in a single onshore well from central Gulf Coast. The lower Tertiary samples were collected over a 2150-5000 m depth interval.

Over the shallow part of the well (2150-4000 m), which corresponds to the usual "R=0" zone, three structures containing expandable layers (Exp) were found to coexist with discrete illite (Ill), kaolinite (Kaol) and chlorite (Chl). Over this depth interval, the evolution of the XRD profiles was related to the decreasing amount of a discrete smectite phase. The relative proportion of a randomly interstratified Ill-Exp mixed-layer structure was about constant over this depth interval, whereas its unusual (?) illite content (~60%Ill) increased only slightly with increasing depth. A Kaol-Exp mixed-layer structure, with a fixed composition, completed the clay paragenesis.

A significant recrystallization was found to occur below 4000 m depth. Discrete smectite was not present any more in deeper samples whereas illite, kaolinite, chlorite, and the Kaol/Exp mixed-layer structure were essentially unaffected. The randomly interstratified Ill-Exp mixed-layer structure was replaced by two mixed-layer structures: an ordered Ill-Exp one and a randomly interstratified Ill-Chl-Exp mixed-layer structure. The coherent scattering domain size of these two structures was significantly increased as compared to the shallow Ill-Exp mixed-layer structure. For the Ill-Exp mixed-layer structure, ordering was also found to develop with increasing depth, without significant modification of the mixed-layer structure composition.

The structural mechanisms of clay mineral diagenetic transformation will be discussed in details as a function of reaction progress.

Clay mineralogical characteristics of decollement zone at the Nankai Trough (ODP; Leg190-site1174)

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The Nankai Trough is located at 200km south from Shikoku Island, southwest Japan. It is elongated about 400km from west to east. The Nankai Trough is subduction zone between the Philippine sea plate and the Eurasian plate. Many earthquakes have been occurring along this Trough. Therefore the Nankai Trough is one of the major concentrations of strong seismic activity regions. The mud and sand deposits composed of marine and sub-marine sediments are found on the Oceanic crust as late Cenozoic Trench sediments. Numerous geophysical surveys and conventional coring transects have been completed in this region. Several legs of Deep Sea Drilling Program had performed the coring near the Nankai Trough. In this time, some drill core samples were collected from the bore hole of ODP Leg.190, Site 1174. This bore hole reaches to almost Oceanic crust about 1100m in depth. The primary purpose of this study is to synthesize the results of clay mineralogical analyzes for the core samples included of the trench-wedge deposits. The upper Shikoku Basin faces, and the lower Shikoku Basin faces with decollement. zoen In particularly clay mineralogical characteristics of specimens collected from decollement zone were compared with the other specimens to discuss about the formation mechanism of decollement zone. The following minerals were measured in this site: chlorite, smectite, illite, kaolinite, quartz and plagioclase. The weight % of clay minerals was analyzed by the peak-intensity weighting method, although clay mineral assemblages show some diversity through the depth. Smectite and illite are the most abundant clay minerals throughout the sampled section. Most abundant smectite was characteristically recognized in the specimens from decollement zone. Smectite is abundant in the Shikoku Basin faces and decreasing with depth. On the other hand, abundant of illite is increasing with depth. It is noted from these examination results that large amount of smectite characterized by clay mineralogy is formed in the decollement zone near the Nankai Trough. This future of smectite is close similar to that occurred along the slip surfaces of the landslides. It may be considered that both abundant of smectite and its mineralogical characteristics are one of the factors of the formation mechanism of decollement zone.

Investigation of Kazakhstan Bentonite

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This paper presents the results of investigations on bentonite from two Kazakhstan deposits of East Kazakhstan, namely Taganskoye and Southern Kazakhstan, namely Taukentskoye.

As it is known, the natural bentonites used as materials for drilling mud preparation on water basis in oil – gas and geology – prospecting industries.

Both studied samples are alkaline – earth bentonites, that coordinates to the dates X – Ray Diffraction and lithologic – and – mineralogical analyses. For receiving the qualitative clay suspension, being used at drilling works, the mineralogical clay composition and amount of thick-dispersed particles, i.e. colloid fraction play the main role. By its activity colloid fraction is basically obliged to a very small size of particles in ratio to their mass.

According dates of granulometric analysis the main clay mass make up 1.5 μm fractions (79.6 %) and < 15 μm fractions (8.4 %) for Tagansky bentonite and < 5 μm fractions (91.1 %) for Taukentsky bentonite that define their high dispersion, characteristic for bentonite, being the basic rock is montmorillonite. The amount of sandy particles in the investigated bentonite clay samples varies from 0.16 up to 4.3 % that corresponds to the requirements of a sandy fraction.

Clay plasticity is defined by a method based on finding the difference value of clay mass moisture corresponding to the bottom border of fluidity and pasting border. According to results received in the present work, clay researched samples are highly plastic, the number of plasticity is 50 – 62, that coordinates to the literary data.

The investigated bentonite clay samples have high values of the exchange cation contents (from 75.8 up to 96.8 meq/100 grams). Wyoming standard bentonite has cation exchange capacity of 76.65 meq/100 grams of clay.

For receiving technological properties according requirements of API 13A Specification (American Petroleum Institute) had been added polymers “Promafor”, France.

Polymers by which treatment to clay suspensions adsorbed on surfaces and disperse phase, increase its hydrophilic, increase a thickness of hydrate cover and consequently efficient volume of disperse particles that brings plastic viscosity suspension about the growing of. This perfects a stand ability mud, lubricating characteristics and promotes to stabilizations the walls of drilling hole.

Mineralogical study of Upper Cambrian glauconites from Texas, USA

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The study of the glauconite-rich Upper Cambrian Riley and Wilberns Formations, Texas, USA, can contribute to a better understanding of the formation conditions of glauconites during the Palaeozoic era. This work presents a mineralogical characterisation of these two Palaeozoic glauconite populations. Glauconite grains in thin sections of the host rock were analysed by polarized light microscopy and WDX. The in acetic acid (5 %) insoluble residue of the two rocks were separated into several tens of fractions upon grain size, magnetic susceptibility and density. Selected glauconite grains from these fractions were analysed by XPD, FTIR, ICP-OES and Mössbauer spectroscopy. The glauconite-hosted limestone concretion from the Lion Mountain Member (Riley Formation) is cemented by white sparry calcite. Glauconite (8 wt% of the whole rock for grains >32 μm) often forms dark green horizons within the rock and together with quartz exhibit geopetal fabric. Glauconite is very mature: 80% of the grains are of a density above 2.78 g/cm³. Glauconite grains are usually rounded, cracked (cracks are sometimes filled with “limonite”), some are bowl-shaped. In thin section they are inhomogeneous: green grains are in patches tinted brown. In XPD 001 is symmetric, $d_{001}=10.16 \text{ \AA}$, $d_{060}=1.517 \text{ \AA}$. Average formula (86 WDX analyses; Fe²⁺ estimated for 15% of Fe_{tot}): $\text{K}_{0.77}\text{Na}_{0.01}\text{Ca}_{0.02}(\text{Fe}^{3+}_{1.24}\text{Mg}_{0.40}\text{Fe}^{2+}_{0.22}\text{Al}_{0.18})[\text{Si}_{3.67}\text{Al}_{0.33}\text{O}_{10}(\text{OH})_2]$. Beside glauconite, the insoluble part contains rounded quartz with inclusions of sphere-shaped strongly magnetic, opaque grains; apatitic brachiopod shells (0.3 wt%) and elongated euhedral zircons. Grains are often cemented into aggregates by iron oxide(s). The limestone sample from the Morgan Creek Member (Wilberns Formation) has yellowish sparry calcite cement. Glauconite (1.8 wt% of the whole rock for grains >32 μm) is evenly distributed within the rock and mature: 65 wt% of glauconite is >2.78 g/cm³. Grains are mostly fragmented, have irregular shape. Elongated grains of biogenic origin also occur. In XPD the 001 is symmetric, $d_{001}=10.16 \text{ \AA}$, $d_{060}=1.521 \text{ \AA}$.

Beside glauconite, the sample contains euhedral dolomite (0.43 wt%) of some iron substitution, chlorite, biotite, muscovite, quartz and apatitic brachiopod shells. “Limonite” pseudomorphs after dolomite rhombohedra are frequent. The less evolved glauconite fractions are missing from both populations, thus glauconite grains are either allochthonous (separated by sedimentary sorting) or the glauconitisation process was complete on vast amounts of glauconitic grains.

The two populations are different in both crystal chemical and density distribution sense, thus the younger (Morgan Creek) cannot be regarded as re-deposition of the older (Lion Mountain).

Synthesis of Interstratified Clay Minerals from (K, Na)-Saponite Glass at Hydrothermal Conditions

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The hydrothermal synthesis of interstratified clay minerals is a subject of great interest for basic researches in natural environments (diagenesis, hydrothermal alteration and the design of clay barriers for high level radioactive waste) and material sciences (catalysis support and new functional nanomaterials). In the present study, a series of hydrothermal experiments were conducted to measure the effect of Na/K ratio on the rate and extent of the reaction of trioctahedral saponite glass to interstratified minerals. The results were compared with our previous results obtained from dioctahedral montmorillonite series. The reaction difference in trioctahedral and dioctahedral systems were mentioned.

Quenched glasses with stoichiometric dehydrated composition of saponite with different Na/K ratio ((K_{1-x}Na_x)_{0.66}Mg₆(Si_{7.34}Al_{0.66})O₂₂; x= 0, 0.5 and 1) were treated hydrothermally at 300, 350, 400, 450 and 500°C for durations of up to 60 days at 100 MPa. The products were characterized by XRD, TEM and simulation of one-dimensional X-ray diffraction functions.

In Na-rich system, a trioctahedral smectite (tri-Sm) was obtained as an initial crystalline phase from the starting glass. With increasing the run temperature and duration, tri-Sm changed to an assemblage of tri-Sm and a small amount of regularly interstratified trioctahedral smectite/mica (r.i.tri-Sm/Mica). In K-rich system, the reaction sequence was the same as that in the Na-rich system, but the amount of r.i.tri-Sm/Mica coexisted with tri-Sm was increased with the increase of K-content. The obtained time-temperature-phase change diagram showed clearly the effect of K-content to the reaction sequence in this system.

In the previous study of Na-rich dioctahedral system, montmorillonite obtained as an initial phase, montmorillonite decomposed to an assemblage of beidellite, saponite and silica mineral, and then to Na-rectorite completely with increasing the run temperature and duration. In K-rich dioctahedral system, the reaction rate from glass to rectorite through smectite and other phases was enhanced.

The present results were consistent with the previous researches. The species of alkaline or alkaline-earth cation in smectite have a profound effect on the nature and rate of reaction of smectite to interstratified minerals. The Mg/Al ratio in starting material may also indicate an effective enhancement on the rate and extent of reactions.

Crystal chemistry of ¹¹⁹Si-for-¹¹⁹Ge substituted phlogopites with interlayer K and Rb: similarities and differences for their evolutionsK. Ishida¹¹Department of Environmental Changes, Graduate School of Social and Cultural Studies, Kyushu University, 4-2-1 Ropponmatsu, Chuo-ku, Fukuoka 810-8560, Japan

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X-ray diffraction Rietveld structure refinement has been made for the tetrahedral Si-for-Ge substituted phlogopites with interlayer K and Rb ions. There is a complete solid-solution in each K- and Rb-phlogopite series on their tetrahedral Si for Ge substitutions throughout. Remarkable differences between Rb- and K-phlogopite series are: (1) the <O_{apical}-T-O_{basal}> tetrahedral angles in Rb-series decrease linearly with increasing Si-for-Ge substitutions, however, in K-series it tends to increase, showing that the tetrahedra in Rb-series are somewhat compressed in the plane of the layer, (2) the both octahedral flattening angles, $\angle_{\text{M1}}$ and $\angle_{\text{M2}}$, increase sharply at RbSi_{0.5}Ge_{2.5}- and RbGe₃-phlogopites, causing thinner octahedral sheet thickness for these phlogopites, (3) interlayer separations for Rb-series are much larger than those for K-series, and increases with increasing Ge substitutions, on the other hand those values for K-series tend to decrease gradually. These behaviors in synthetic phlogopite occurs mainly due to weakened repulsive forces between Rb-T(Si/Ge) for much larger A-T lengths than those for K-T(Si/Ge). Tetrahedral rotation angles in K-series increase linearly, however, in those in Rb-series increase with showing S letter, intersecting with K-series at the Si_{1.5}Ge_{1.5}-phlogopite compositions. Dimensional misfits for both series increase with nearly similar manner from Si₃- to Si_{1.5}Ge_{1.5}-phlogopites, but those values in Ge-rich compositions in Rb-phlogopites sharply increase.

Interstratified System of Illite-Tobelite for NH₄-bearing Mica Clay Minerals

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The distribution of interlayer cations and resultant interstratified structure for NH₄-bearing mica and mica-smectite is an interesting subject as Drits et al. (1997) first demonstrated remarkable interstratified system of I-T (illite-tobelite) and I-T-S (illite-tobelite-smectite) for sedimentary NH₄-bearing mica clay minerals in oil source rocks. In order to confirm the validity of this notable interstratification, hydrothermal NH₄-bearing mica clay minerals associated with pyrophyllite (Roseki) deposits in Japan have been studied in the present study. As compared to sedimentary specimens these hydrothermal specimens are rather well-crystallized (mostly nonexpandable) and more largely varied in NH₄ content; these properties may have the advantage of closer examination of interstratification for NH₄-bearing mica minerals. XRD basal reflections profiles have been calculated for random, ordered and segregated interstratified I-T models with varying I/T component ratio. As compared to homogeneous distribution of K and NH₄ in each mica layer, i.e. I-T solid solution series, these interstratified structures are individually most characteristic of the broadening of 005 reflection. Furthermore the peak position of 005 reflection is determinable of I/T component ratio since nearly linear variation of apparent $d(001)$ from 10.00 Å (illite) to 10.36 Å (tobelite) is evident and useful for such interstratified systems. In fact I-T interstratification can be discriminated by two reflections peak width ratio measured as FWHH(005)/FWHH(002) against the I/T ratio. The peak width ratio is varied gradually with the I/T ratio and shows a maximum at I/T=50/50 for both random and segregated interstratified models although the broadening is doubly magnified in the latter case. For the ordered interstratification, however, the broadening is less pronounced and shows bimodal maxima around I/T=75/25 and I/T=25/75. Another effect of particle size distribution is very critical in actual application. For the I-T-S interstratified specimens they can be treated as interstratified system of I-T since smectite layer is easy to be converted to mica layer of illite or tobelite through interlayer cations exchange and anhydration when the specimens are pretreated with KCl or NH₄Cl solutions and then X-rayed in atmosphere under controlled relative humidity 0%. Close XRD examinations of the hydrothermal NH₄-bearing mica clay minerals comprising Roseki deposits reveal that they are of intermediate nature between random and ordered I-T interstratification, which may be ascribed to different genetic condition and process from those of the random I-T(S) specimens often found in oil source rocks.

Derivation of an equation to quantify the layer proportion of randomly interstratified illite-smectite using the peak width of X-ray basal reflection

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Randomly interstratified illite-smectite (random I-S) is an important mineral phase in various low temperature geochemical processes. The layer proportion of random I-S has been traditionally identified using the peak position or intensity of its basal reflections. However, these methods are limited to providing semi-quantitative assessments if not given detail information on the coherent scattering crystallite thickness (CSCT) of random I-S, which is known to be related to the changes in basal peak position and intensity. As an alternative method, we show a convenient equation to evaluate the layer proportion of random I-S using the peak width of basal reflection. The NEWMOD[®] program was employed to simulate the basal reflections for two different random I-S samples: ethylene-glycolated (EG) and thermally dehydrated (TD). In these simulations, the proportion of interstratified illite layers (p_i) was set to range between $0 \leq p_i \leq 0.4$. The CSCT of random I-S was assumed to follow lognormal-type distributions with $3.5 \leq \bar{n} \leq 7$ ($\bar{n}$: the mean number of unit layers per crystallite). The (001) reflection of each sample was used in the equation derivation in order to minimize additional broadening effects. As a result, a quantitative equation was derived in the form of $p_i = (\beta_{EG} - 0.589\beta_{TD}) / (3.911 - 1.324\beta_{TD})$, where β_{EG} and β_{TD} represent integral peak widths (peak area/maximum intensity) of the 001 reflections for EG and TD samples, respectively. This equation provided more accurate and precise p_i values than the traditional methods, and details are discussed here.

Gasoline pollution modelling in laboratory

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The poster presents the preliminary results of a laboratory modelling for gasoline pollution during approximately one year. Aim of the modelling is to acquire more and exact information for the frequent hydrocarbon pollution in the nature, connecting to both oil industry and transport.

Gasoline was chosen as experiment material because it can very frequently be recognised in hydrocarbon polluted areas. Both characters and chemical composition of the original gasoline were determined by chromatograph at the beginning of the experiment. Given and measured quantity of gasoline was placed into glass tubes in which pure, homogeneous sand was placed in different heights (0.50 - 2.00 m), but pairs of the tubes were equal for the parallel measurements. Altogether eight tubes were filled. One tube of the pairs was capped by an 8 cm thick clay layer above the sand. The clay derived from the so called Kiscellian Clay Formation, which is widely spread in many areas in Hungary. The composition of the clay and the sand was determined by X-ray diffraction and DTA method. Grain size distribution and carbonate determination were also carried out.

In the starting period of the experiment the gasoline was sampled weekly. Based on the results of the measurements the sampling period was altered to monthly frequency. The air above the sand and clay filling was also sampled, as well as the sand and clay themselves. Samples were measured by gas chromatography and gas chromatography-mass spectrometry.

After about a year the measurements can be compared and evaluated. Based on the results of the measurements significant different can be recognized according to the different filling material, the different heights and the different sampling periods. Composition of the gasoline in the samples has shown well the volatile's leaving order. The enrichment of the heavier components depends on the height of the filling material in the tubes above the gasoline. Different composition of the samples acquired in the same time from the different material (from air and filling materials) can be caused by the different adsorbent characters of the sand and clay. Toluene, C8, xylene, C9, and C10 components have been adsorbed by the clay, while the sand adsorbed the components heavier than C14.

Natural zeolite deposits from Lower Tertiary volcanic formations in Southern Mountains region, central Java, Indonesia

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Natural zeolites are recently discovered within Lower Tertiary volcano-sedimentary rocks formations in the Southern Mountains region, central Java, Indonesia. Several small-scale mining operations have been working on these minerals in last several years, and current utilizations include for animal husbandry and fertilizer. We are now in progress of conducting geologic investigations on the geologic distribution of deposits, mineralogy and physical characterizations, genesis interpretation, resource estimation, utilizations, and exploration for new deposits. Zeolite is excavated from several thin, laterally extensive, dipping layers of sedimentary rocks of volcanic origin at the lowest part of the thickly accumulated Tertiary volcano-sedimentary rocks package. Zeolite-bearing strata are part of the Kebo-Butak volcanic formation whose age is Late Oligocene to Early Miocene. Zeolite is strata-bound, in which zeolite-rich layers are selectively located within thin (5-20 cm thickness) of green-altered fine sandstone layers of volcanic origin. Zeolite-bearing layers are intercalated with non-zeolite laminated mudstone, suggesting the primary rocks were deposited within under-sea fan with a lot of influx of volcanic materials. Evidence for a deep sea deposition, long history of thick burial before uplifting to present position, selective occurrences of zeolite only on 'clean' fine sand layers, and an extensive lateral distribution of green-alteration assemblage (more than 5 km lateral distance without observable change in color) suggest that the most influential geologic controls on formation of zeolite are original compositions of layered sedimentary rocks and district to regional-scale event(s) especially burial metamorphism. However, the syn-volcanic basaltic sill (24.25 Ma) in the proximity may have contributed on the alteration of volcanic glass into zeolite. Preliminary petrography, XRD, and SEM study demonstrate the presence of two groups of zeolite minerals (i.e., mordenite and clinoptilolite) in association with secondary clay mineral of montmorillonite as alteration products of volcanic glass. Primary minerals consist of feldspar, quartz, and volcanic ash, that suggest an acidic volcanism as the source of original volcano-sedimentary rocks. Physical characters of the zeolite-bearing rocks are: hardness 2.5-3.0 at Mohs scale, water absorption 12.92 - 17.54 %, and specific gravity 1.61 - 1.74 gr/cm³. Cation exchange capacity in normal condition is 78.27-139.88 (Meq/100g), while at activated stage is 82.06-143.50 (Meq/100g). Resource calculation estimated at least 4,150 metric tons of zeolite-bearing rocks are mineable using low-cost shallow open pit operations.

Synthesis and Characterization of Zeolite Using Slag Melted from Municipal Incineration Ash

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Melting ash generated from municipal incinerators has good potential for rendering the ash harmless and recyclable. Several approaches have been made for proper utilization of melting slag, either to reduce the cost of disposal or to minimize environmental impacts. One of the approaches is the conversion of the melting slag to zeolite, which has wide application in ion exchange as molecular sieves, catalysts, and adsorbents.

The slag was prepared by melting it by the top submerged lance (TSL) method in a municipal incineration plant in Mapo, Korea. Zeolite was synthesized using the melting slag by the alkaline activation processes. The synthesized zeolite was characterized by various techniques such as X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, cation exchange capacity measurement, heavy metal adsorptivity, and so on.

The cation exchange capacity of the zeolite product was determined to be in the 150-280 cmol/kg range. The results of the adsorption experiments suggest that the zeolite product can be applied for environmental technology.

Cation-exchange properties of natural zeolite-like sodium zirconosilicates: an experimental study in aqueous solutions at 80-90°C and 1 atm

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Zeolite-like silicates with heteropolyhedral frameworks consisting of Si tetrahedra and octahedra occupied by atoms of transition elements (Ti, Zr, Nb, Fe etc.) are typical minerals of agpaite alkaline complexes. Sodium zirconosilicates are especially important. Unlike titanite and niobosilicates, they form huge deposits and can play rock-forming role (eudialyte, elpidite, parakeldyshite and members of the lovozerite group). Microporous natural zirconosilicates are now considered not only as probable source of rare metals (Zr, Hf, Y, HREE) but also as potential carriers of technologically important ion-exchange, gas-sorption, catalytic, ion-conductive and other properties. Earlier we have studied cation-exchange properties of sodium zirconosilicate minerals in aqueous solutions under room conditions (Pekov *et al.*, 2005). Now the experiments at 80-90°C and 1 atm have been completed. Eudialyte (two chemical varieties), elpidite (both coarse-crystalline and fine-grained), lovozerite, litvinskite, petarasite, parakeldyshite, catapleite, gaidonnayite, hilairite, and sazykinaite (Y) from agpaite pegmatites of Khibiny-Lovozero complex (Kola, Russia), Mont Saint-Hilaire (Quebec, Canada) and Khan-Bogdo (Mongolia) were examined. Their grains (0.3-0.8 mm) were placed into 1M solutions of KCl, RbCl, CsCl, CaCl₂, SrCl₂, BaCl₂ and Pb(NO₃)₂ for 12 hours and after that examined using electron microprobe, on polish sections. Eudialytes and petarasite show no changes in their chemical composition while other minerals demonstrate ion-exchange properties, each with individual selectivity. The cations can be ranged into the following series by decrease of the ability for exchange with Na in the studied zirconosilicates: K > Rb > Ba > Pb > Cs > Sr > Ca. Almost all examined minerals absorb K but do not absorb Ca, an exception is parakeldyshite accumulating only Ca. Generally, number of exchangeable cations and an amount of absorbed cation inversely correlate with density of Zr-Si-framework of a mineral. Fine-grained aggregates show significantly stronger ion-exchange properties than large crystals of the same mineral (e.g. elpidite). Very heterogeneous distribution of exchanged cations is typical: they are mainly concentrated in boarder parts of a crystal and zones along micro-cracks. Cation-exchange properties of sodium zirconosilicates, especially lovozerite and hilairite group minerals and catapleite, strongly increase at 80-90°C in comparison with room conditions. From the data obtained, it can be considered that in nature the probability of cation-exchange alteration of sodium zirconosilicates, especially broad-porous minerals, under low-temperature hydrothermal conditions is high.

Synthesis of zeolitic material from waste sandstone filler using alkali fusion method

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Zeolitic material was synthesized from waste sandstone using the alkali fusion method. During quarrying, waste sandstone filler is discharged as industrial waste. Filler is mainly composed of crystalline phases, such as quartz, calcite, albite, muscovite, and clinocllore. We applied alkali fusion with NaOH on the filler to convert most of the crystalline phases into soluble phases to synthesize the zeolitic materials. We used two starting materials, one was original and the other leached filler, which was treated with 1 M HCl solution for removing Ca content. Each starting material was mixed with NaOH powder (the weight ratio of NaOH / sandstone = 1.6), and then heated at 600 °C for 1 h to make the fused material. This fused material was then added to distilled water for 1-day shaking, and heated at 80 °C, 120 °C, and 160 °C for 8 h in reaction bombs under autogenous pressure in order to synthesize the zeolitic materials.

Zeolite-X, hydroxysodalite, and tobermorite were synthesized. For the original filler, the mixture of zeolite-X and hydroxysodalite was synthesized at 80 °C, and only hydroxysodalite at 120 °C. Tobermorite was synthesized at 160 °C, together with hydroxysodalite. For the leached filler, only zeolite-X was synthesized at 80 °C, the mixture of zeolite-X and hydroxysodalite at 120 °C, and only hydroxysodalite at 160 °C. Tobermorite was not synthesized from leached filler at 160 °C, due to the lower Ca content of leached filler. The zeolitic material with the highest cation exchange capacity (CEC) was 230 cmol/kg, which had only zeolite-X synthesized from leached filler at 80 °C. Hydroxysodalite has a lower CEC than zeolite-X, and is easily synthesized due to the increase of heating temperature and Ca content. Therefore, the CEC of the product decreased with increasing heating temperature, and the product of the leached filler was higher CEC than that of the original filler.

Preparation and Characterization of Epoxy Resin/Vermiculite Nanocomposites

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Since PA6/ layered silicate nanocomposites was reported for the first time at the end of 1980s, polymer/layered silicate nanocomposites (PLS) have been attracted attentions of researchers from different countries because of their outstanding performances and wide range of applications. Large amount of PLS nanocomposites have been prepared by using montmorillonite and some other layered silicates such as kaolinite etc.. However few studies have been reported concerning the preparation and characterization of epoxy resin /vermiculite nanocomposites.

A vermiculite from Chengde, China was modified following the procedure reported by F.J. del Rey-Perez-Caballero *et al.*. Different amounts of hexadecyl trimethyl ammonium bromide (HDTMAB), equivalent to 1, 1.5, 2, 3, 5 and 10 times of the cation exchange capacity (CEC), were used for the organic intercalation of the modified and crude vermiculites for comparison. XRD analysis and CEC measurement show that the organic intercalation behavior of modified vermiculite is different from that of crude vermiculite. The modified vermiculite has lower CEC and hence weaker structure layer linkage. Very large interlayer spacing and even exfoliation can be obtained for the modified vermiculite when the amount of HDTMAB used is 10 times of the CEC of the crude vermiculite, which is of importance to the preparation of polymer/vermiculite nanocomposites.

Epoxy resin/vermiculite nanocomposite was prepared from epoxy, dimethyl benzylamine (curing agent) and modified vermiculite. The structure, microtopography, mechanical and electric property of the epoxy resin/vermiculite nanocomposite prepared were characterized. Results indicate that the mixing sequence of epoxy, dimethyl benzylamine and vermiculite, and the amount of curing agent and vermiculite used affect the dispersion and exfoliation of vermiculite in the resin matrix, hence the properties of epoxy resin/vermiculite nanocomposite. The tensile strength and elastic modulus of the prepared resin/vermiculite nanocomposite can be optimized when the amount of vermiculite added is equivalent to 3% in mass/ ratio of the resin. The volume resistivity of resin/vermiculite nanocomposite so prepared is relatively higher and its surface resistivity is relatively lower than that of pure epoxy resin.

Characterization and photocatalytic properties of synthetic allophane-coated titanium dioxide nanocomposites

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Photocatalytic nanocomposites built from an assembly of a titanium dioxide (TiO₂) anatase and an inorganic substance (e.g. apatite) have attracted considerable interest for the past decade. We focused our attention on a development of a highly efficient catalyst without a biomimetic material processing in order to explore a possibility as a photocatalyst, which can be applied for environmental purification. Incidentally, it is well known that allophane is a naturally occurring short-range ordered aluminumsilicate hydrate with chemical compositions of Si/Al = 0.5 - 1.0, consisting of spherical hollow particles with external diameters of 3.5 to 5 nm. The wall of particles is considered to consist of two sheets: an octahedral Al sheet and a tetrahedral Si sheet with accessible open pores of 0.35 nm in diameter. The allophane nanocapsules with controlled mesostructure have been synthesized from highly concentrated inorganic solutions by a hydrothermal process. Allophane has a high adsorptive activity because of its large surface area, and it is transparent to ultraviolet (UV) light. Photocatalytic TiO₂ coated with allophane (Allo-TiO₂) was prepared by a TiO₂ acidic suspension with an aluminumsilicate precursor solution. Hydroxyl groups of the TiO₂ surface were modified with allophane nanocapsules followed by a hydrothermal technique. The influence of the Si/Al ratio of initial solutions on the methylene blue (C₁₆H₁₈N₃S, λ_{max} = 660 nm) decomposition activity at ambient temperature and the humidity controlling ability at 25°C of Allo-TiO₂ compounds were investigated. The results showed that the as-prepared samples exhibited high photocatalytic activities to photobleach methylene blue in aqueous solutions under UV irradiation. Powder XRD patterns of the synthesized samples were indicative of a semi-crystalline aluminumsilicate structure and a TiO₂ anatase phase. According to a particle size distribution measurement, the mean particle sizes of the compounds were estimated to be 1 to 1.5 μm in diameter. The sample of Allo-TiO₂ nanocomposite (BET surface area = 200 m²/g) possessed the highest photocatalytic efficiency and its photodegradation ratio to methylene blue was 92.7 % when the irradiation for 30 min. The adsorptive nature of Allo-TiO₂ for methylene blue and the photocatalytic activity for bleaching were more effective than that of the commercialized TiO₂.

O28-01

Phase separation in Carbon-rich SiOC glasses; The evolution of Nano-Domains

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The nano-domain size evolution with increasing temperature of a carbon enriched SiOC ceramic was investigated. The high carbon content in the PHMS based polymer-derived ceramic was achieved by utilizing DVB as an intrinsic crosslinking agent. The incorporation of carbon- and silica-rich regions within the amorphous matrix implies the questions about domain size and thermal stability of those domains. The nanostructure of PHMS+60%DVB was studied in detail upon pyrolysis at 1000 °C and after additional heat treatment at 1450 °C. Bulk spectroscopic techniques such as solid-state NMR and Raman spectroscopy, in addition to spectroscopic and imaging methods with high lateral resolution, i.e., high-resolution TEM, energy-filtered TEM and electron energy-loss spectroscopy, were employed to gain detailed information on the size, composition and dispersion of nano-domains upon thermal treatment. Although a progressive structural rearrangement within the SiOC matrix was confirmed with increasing annealing temperature, the sample heat treated at 1450 °C remained predominantly amorphous. Emphasis is placed on the role of carbon with respect to the process of phase separation and the corresponding evolution of carbon- and silica-rich nano-domains, which in turn favor a unique viscoelastic response of such carbon-rich SiOC glasses.

O28-03

Spectroscopy of chromium in borate and borosilicate glasses: local structure, redox states and thermal expansion

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Transition elements, such as Cr, are important components in oxide glasses/melts. We present a comparative spectroscopic study of chromium in alkali borate and borosilicate glasses, using Cr K-edge EXAFS and XANES spectroscopies in conjunction with optical absorption (crystal field) spectroscopy. In addition, the modification of crystal field spectra of Cr^{3+} as a function of temperature, has been followed up to 800 K. In all investigated glasses, chromium occurs as octahedral Cr^{3+} coexisting with chromate groups in variable concentration. On the XANES spectra, the position, structure and intensity of the pre-edge structure varies systematically with the Cr oxidation state. This information may be calibrated with optical absorption data on the redox state of Cr in these glasses. In all investigated glasses, EXAFS data and crystal field spectra indicate that Cr^{3+} is preferentially located in a site related to a silicate environment. High temperature crystal field spectra have been obtained using a home-built photodiode array spectrometer, combined with a heating stage. In all glasses, the Cr^{3+} crystal field band (${}^4\text{A}_{2g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F})$ transition) exhibits a red shift with increasing temperature. This implies a modification in the relative position of the Fano antiresonances located on the ${}^4\text{A}_{2g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F})$ absorption band. Crystal field spectra appear to be strongly sensitive to temperature effects, even over small temperature intervals. Crystal field splitting energy as well as red shift amplitude are not the same for the different glasses investigated. The thermal dependence of the B Racah parameter has also been extracted for some glasses, which presents the highest contribution of Cr^{3+} . Using the dependence of crystal field splitting energy on cation-oxygen distances, local thermal expansion coefficients (TEC) can be extracted from these spectroscopic in-situ measurements. Local TEC values obtained in glasses are lower than the bulk TEC, and are similar to those observed for octahedral Cr^{3+} in crystals. These local TEC's vary by as much as 50% as a function of glass composition, the local and bulk TEC's varying in a similar way.

O28-02

The environment of transition elements in oxide glasses

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We will present a comparative review on the structural behavior of 3d and 4d transition elements in oxide glasses, including silicate, borate and borosilicate compositions. The compositional dependence of the glass coloration and the local environment of transition elements is followed using various spectroscopic techniques, including UV-visible and X-ray absorption spectroscopy. 3d transition elements, such as Ni and Zn, and 4d transition elements, such as Zr and Mo, present a good illustration of the diversity of local structures in multicomponent glasses. The coordination numbers of transition elements in glasses are often lower than those in crystalline compounds. Tetrahedral sites may correspond to a network-forming position for Ni and Zn, but may also indicate the presence of polyanions, structurally independent of the glassy network. However, in both cases, the charge compensation of the tetrahedral cation by coexisting alkali and alkaline-earth cations is important for rationalizing glass stability. 5-coordination is an original coordination state of Ni, which may explain the origin of the peculiar coloration of most Ni-bearing glasses. Higher coordination states may be encountered in some specific compositions, in relation with the presence of B. for instance, Ni-bearing, low-alkali borate and borosilicate glasses exhibit colors ranging from green to yellow, related to the presence of ${}^{55}\text{Ni}$ and distorted ${}^{60}\text{Ni}$, the latter indicating the presence of defective NiO clusters. The competition for charge compensation or the presence of two sublattices explains the variability of the observed colorations. The final example concerns Zr, which is generally encountered in regular octahedra, an unusual coordination seldom encountered in anhydrous minerals. Here too, a molecular scale approach helps understand the origin of the peculiar physicochemical properties provided by the presence of Zr in glasses, e.g. the resistance to alteration or the formation of glass ceramics. All these examples will show how transition elements illustrate the structure-property relationships in silicate glasses.

O28-04

Structural factors governing the sulphate incorporation IN Borosilicate glasses

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Abstract

Due to the relatively low solubility of sulphates in borosilicate glasses, the vitrification of sulphate-containing nuclear waste constitutes nowadays an important issue in the radioactive waste management industry. This work analyses structural factors determining the sulphate incorporation in a borosilicate matrix. In this framework, special attention is given to the role of the addition of V_2O_5 to the glass formulation. Glass samples were prepared at the laboratory scale (up to 50-100 g) by melting sulphate powders and oxide or glass frit under air in Pt/Au crucibles. X-Ray Fluorescence (XRF) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP/AES) chemical analysis, Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM) coupled with Energy Dispersion Spectra (EDS) and Raman spectroscopy were employed to characterise the fabricated samples. Raman spectra, in particular, measured from room temperature to 1500°C, revealed some structural modifications conditioning the sulphate incorporation in the glass. Spectra were recorded on six- and seven-oxide nuclear glasses, on quaternary glasses $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-V}_2\text{O}_5$ and on ternary systems $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$, $\text{B}_2\text{O}_3\text{-Na}_2\text{O-V}_2\text{O}_5$ and $\text{SiO}_2\text{-Na}_2\text{O-V}_2\text{O}_5$. The main mechanisms fostering the sulphate incorporation into the glass matrix seem to be the depolymerisation of the glassy network and the creation of suitable voids in the vitreous matrix. The two effects are obtained by the addition of a suitable percentage of network modifier. Besides alkali and alkali earth oxides, also V^{5+} seems to behave as a network modifier in the coordination state (IV). V^{5+} in the coordination state (V) can work as a network former, probably creating voids in the vitreous matrix suitable for the incorporation of sulphate molecules.

Synthesis of novel single crystalline materials for electrical, optical and medical applications using the advanced crystal growth technique

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Study of emission centers in different crystal lattices is an important topic and many researchers devote to this problem. In order to understand driving factors of the optical processes in the crystals, we need different concentrations of dopants. Interaction between the dopant ions and lattice phonons, asymmetric crystal field perturbations or the energy transfer processes are typical examples on which the research effort is focused. Furthermore, the distribution of the dopant ions in crystals is a very important factor to determine the spectral and temporal properties of the emission [1,2]. For this purpose, we need crystals with variety of dopant concentrations having similar (high) crystalline perfection.

In this presentation, we show the feasibility of the Micro-Pulling-Down (μ -PD) method to grow efficiently single crystals with variety of dopants and their concentrations and achieving high crystalline perfection. Review of the challenge to prepare novel single crystal optical materials using μ -PD method will be provided showing recent results achieved at both oxide and fluoride compounds. Micro-Pulling-Down method is a powerful tool to search for new materials. This method allows us to prepare single crystalline material relatively inexpensively and quickly. Grown crystals are of sufficient dimensions for all the necessary characterization by optical and luminescence methods, including absorption, photoluminescence, radioluminescence, emission decay, light yield measurements and others. Results obtained from laser materials and scintillator materials at Yb-doped and Tm-doped RE_2O_3 (RE=Y, Lu, Sc), Mn-doped and Ti-doped MgAl_2O_4 , Yb-doped YAlO_3 , (Lu,Y) AlO_3 , $\text{Lu}_3\text{Al}_5\text{O}_{12}$, Bi-doped $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $\text{Lu}_3\text{Ga}_5\text{O}_{12}$, Pr-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}$, Y_2SiO_5 , Lu_2SiO_5 and fluorides based on mixed binary fluorides $\text{AEF}_2\text{-REF}_3$ (Ce:AE:(Gd,Y) F_3 , AE=Ba, Sr, Ca) and more complex fluoride hosts like Pr and Ce-doped KY_3F_{10} , $\text{K(Y,Lu)}_3\text{F}_{10}$ will be presented.

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Conversion of the melting state of langasite from incongruent into congruent by an external electric field

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The external field is applied on the growth system deliberately in order to modify the growth mechanism. Imposing an external electric field on the crystallization process has two distinct consequences: (i) thermodynamic effect and (ii) growth-dynamic effect. The former pertains to the macroscopic picture and changes the equilibrium phase relationship, while the latter is on a microscopic scale and modifies the solute transport, growth kinetics, surface creation and defect generation related to crystal growth. In this paper, we specifically remark on the first effect.

The imposition of an external electric field on a growth system modifies the chemical potentials of associated phases in equilibrium which could convert the incongruent-melting state into congruent-melting state. Langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$), an incongruent-melting material in the ternary system of La_2O_3 - Ga_2O_3 - SiO_2 , became congruent-melting under an external electric field of 600 V/cm in experiment. This conversion was attributed to the inversion of the stability relationship in terms of the molar free energy between the liquid phase and the primary phase in equilibrium with liquid at the composition of langasite. Such a transformation is generally possible when the electrical permittivity of liquid is higher than that of solid in the compositional range of interest and both permittivities increase toward the end component of the primary phase. The possibility of applying this method to other incongruent-melting materials eventually would shed new light on a considerable number of incongruent-melting materials that have been disregarded because of their difficulty of growth although they have superior physical properties and functionalities.

However, the quantitative analysis yielded a considerably higher value for the required electric field than the value obtained experimentally. The electric field required for the transformation of the melting state of langasite from incongruent into congruent was semi-quantitatively and quantitatively evaluated. Both evaluation methods demonstrated that the required electric field was on the order of 10^4 - 10^5 V/cm. In addition, both oxide solid and melt are ionic and conductive at the melting temperature so that the electric field cannot penetrate into the bulk but merely acts on the skin of the material. Thus, a very weak electric field would be expected in the bulk melt that is too small for the conversion. We conclude that this large difference was attributed to the possibility that nucleation with the converted melting state occurred in the electric double layer, which could sustain a very large electric field.

Characterization of synthetic quartz crystals grown on cylindrical and V-notched seeds by the X-ray topography

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Synthetic quartz crystals for quartz resonators production are usually grown on seeds such as Y-bar or Z-plate along in Y-direction by the hydrothermal process. Y-cut plate of such synthetic crystals shows six distinct growth regions of +X, -X, two Z- and two S-regions. For quartz resonator fabrication, Z-growth regions are favored due to higher purity and lower amount of defects such as dislocations. It is known that the amount of growth regions in such synthetic quartz crystals depends on the growth conditions, but essentially of seed geometry. If a cylindrical seed is employed for the crystal growth, all growth regions, which grow perpendicularly to the seed axis, may be observed. This information will help us to realize the most optimized seed and growth condition. Furthermore, it is known that V-shaped notch seed appears as a good candidate for growing synthetic quartz crystals with low density of dislocations and large Z-region, even though the seed contains high amount of dislocations. In this context, specimens of synthetic quartz crystals grown on cylindrical seeds long in X, Y and Z directions and synthetic quartz grown on seed with multiple V-shaped notches on Z-face were investigated by the X-ray topography technique.

A total of six synthetic quartz crystals grown on cylindrical seeds with 18 mm in diameter and 20 mm long in X, Y and Z directions and four synthetic quartz grown on V-shaped notch seed with cutting angles of 25°, 45°, 60° and 90°, constant depth of 2.5 mm and long in Y direction were investigated by the X-ray topography technique. The cylindrical seeds were prepared by the ultrasonic machining from a synthetic quartz crystal with 150 dislocations/cm². The seeds with multiple V-shaped notch were prepared on Z-face employing diamond saw disc. Corresponding growth was conducted in an autoclave for commercial production. Specimens were cut perpendicularly to respective seed axis/direction using a diamond saw, and the thickness was adjusted to have 300 to 350 μm to get a better image contrast due to the intermediate kinematical and dynamical diffractions. To avoid residual tensions due to sawing and lapping processes, the specimens were etched in a HF solution for 30 minute at room temperature. X-ray topographic imaging was conducted by a high precision Lang camera with $\text{CuK}\alpha_1$ X-ray beam generated by a rotating anode with an ultrafine focus of 70 μm x 70 μm operated at 40 kV x 20 mA. The distance of X-ray source from the specimen is 110 cm. This configuration gives the geometrical resolution better than 10 μm . X-ray topographic images were collected with high resolution X-ray film (IX100: Fuji Film) and nuclear plate.

The cylindrical seeds have all the growth faces parallel to the X, Y and Z-axis and only a few growth regions have been observed. Nevertheless, new growth regions almost free of dislocation were realized in the sample grown on the seeds long in X and Y directions, in particular. Regarding to the synthetic quartz grown from V-shaped notch, even though the mechanism of origin and propagation of dislocations in synthetic quartz is quite complex, Z-region with a very low dislocation density can be obtained with the V-shaped notch method because the growth on Z-surface seeds with such special cutting resulted in annihilation of dislocations with the appearance of new and complex regions. Fluid inclusion and defect trail are created at each notch by a mechanism not yet understood and the depth and cutting angle of V-shaped notch influenced fluid inclusion in terms of length and size.

Therefore, authors maintain the view that the present new seeds can be designed to produce crystals almost free dislocation in near future.

Keywords: synthetic quartz, cylindrical seeds, V-shaped notch, x-ray topography, growth sectors, Lang camera.

Precise structural analysis and phase transition of inorganic materials through high-temperature neutron and synchrotron diffraction techniques

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Structural analysis of inorganic materials at high temperatures is of vital importance in various scientific fields such as mineralogy, physics, chemistry and materials science. In the invited talk we describe the neutron and synchrotron powder diffraction techniques that enable the precise structural analysis at high temperatures up to about 1600°C.

(1) **Neutron powder diffraction method:** Some merits of the neutron powder diffraction technique, overcoming the conventional X-ray powder diffraction method, are discussed [1]. The neutron powder diffractometry can determine exact structural parameters of light elements in materials comparing with the X-ray. Position and spatial distribution of oxygen and lithium ions in oxides have been investigated by the Rietveld method combined with the maximum-entropy method (MEM) and MEM-based pattern fitting (MPF) [2-5]. *In situ* neutron powder diffractometry at high temperatures is a powerful method to investigate the crystal structure and the nuclear-density distribution in inorganic materials. We designed and fabricated a new furnace for *in situ* neutron study at high temperature (RT-1600°C) [1]. Structural phase transition in the perovskite CaTiO_3 was confirmed to be $P6mm-I4/mcm-Pm-3m$ [6].

(2) **Synchrotron powder diffraction method:** Recent developments in high-temperature and high-resolution X-ray powder diffraction method in our research group are presented. The conventional X-ray diffraction peak has a broad and complicated profile. On the contrary, the synchrotron powder diffraction profile has much narrower and simple profile. It is demonstrated that the precision of the phase transition temperature is strongly dependent on the angular resolution of the diffractometer. We have investigated the electron-density distribution and the covalent bonding of cubic CaTiO_3 perovskite at 1401°C [7]. Recently we have devised and fabricated a compact furnace for high-resolution synchrotron powder diffractometry suitable for BL-4B₂ experimental station at the Photon Factory [8].

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Crystal chemistry of La- and Co-doped Sr-Hexaferites

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Sr-hexaferite $\text{SrFe}_{12}\text{O}_{19}$ is an important compound used for ceramic magnets. As a member of materials with magnetoplumbite crystal structure a wide chemical variation enables a "property fine tuning" for different applications.

In this study the doping with La and Co was investigated. The suggested solid solution should follow the formula $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$. The base for this substitution model is the 1:1 ratio of La:Co.

Samples of suitable mixtures were equilibrated at 1300°C in air in vertical tube furnaces and quenched. The temperature of 1300°C was chosen in order to avoid the valence change from Fe^{3+} to Fe^{2+} which takes place at 1395°C in air in the border system Fe-O. The equilibrated and subsequently quenched samples were prepared as polished sections and the paragenesis were characterized by optical microscopy and electron-microprobe-analyses. The results show clearly the stabilization of Fe^{2+} even at this low temperature due to the Co-doping. The "simple" solid solution model for a 1:1 doping ratio of La:Co does not apply. As a consequence employing the 1:1 model for the La and Co doping will lead to multiphase devices destroying the overall magnetic property.

Subsequently the solid solution series has to be described in the quinary system $\text{SrO-La}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CoO-FeO}$ and follows the formula $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Fe}_{x-y}\text{Co}_y\text{O}_{19}$ with $0 \leq x \leq 1$ and $0 \leq y \leq x$. The nonlinearity increases with a raising amount of Co.

Phase relations and crystal chemical aspects due to the substitution mechanism will be presented and discussed.

The structural analysis of disordered materials by the anomalous X-ray scattering coupled with reverse monte carlo simulation.

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Middle range ordering is known to be of great importance for discussing the structure of various substances in a variety of states. Recently the model calculation using reverse Monte Carlo (RMC) simulation, has received much attention for analyzing the middle-range ordering for disordered materials, in particular. In this context, we developed a new RMC method which estimates the realistic atomic model structure by fitting both the ordinary interference functions and the environmental interference function obtained from the anomalous X-ray scattering (AXS). The present paper demonstrate the usefulness of this new method by using selected examples of a chrysocolla sample from Cupiapo, nano-crystalline ZrO_2 and amorphous ZrO_2 .

Correlation between atomic thermal vibrations and cation-cation repulsions in vanadate garnets $\text{NaA}_2\text{M}_2\text{V}_3\text{O}_{12}$ (A = Ca, Pb; M = Mg, Mn, Co, Ni, Cu, Zn)

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Garnets can accommodate various chemical species, and commonly have di- or trivalent cations on dodecahedral site, trivalent cations on octahedral site and tetra- or trivalent cations on tetrahedral site, as in silicate garnets and rare earth garnets. The repulsion between cations with such a combination of valences contributes greatly to the structural stability of garnets.

Vanadate garnets, represented by palenzonaite (idealized formula $\text{NaCa}_2\text{Mn}_2\text{V}_3\text{O}_{12}$), are characterized by the mean formal valences of 1.67+ on dodecahedral site, 2+ on octahedral site and 5+ on tetrahedral site. Hence, the effect of the cation-cation repulsion on the structural stability of vanadate garnets is expected to differ from the cases of garnets with the common valence distributions such as silicate garnets and rare earth garnets. In the present study, we discuss the crystal chemistry of vanadate garnets with attention to correlation between the atomic thermal vibration and cation-cation repulsion. Single crystals of the vanadate garnets $\text{NaA}_2\text{M}_2\text{V}_3\text{O}_{12}$ (A = Ca, Pb; M = Mg, Mn, Co, Ni, Cu, Zn) were synthesized by a floating zone (FZ) method, and their crystal structures were refined using a single-crystal X-ray diffraction technique. The smallest RMS amplitudes of thermal vibrations of tetrahedral cations in $\text{NaCa}_2\text{M}_2\text{V}_3\text{O}_{12}$ garnets are in the direction of tetrahedral-dodecahedral cations, and this observation is consistent with thermal vibration behaviors of common garnets such as silicate garnets and rare earth garnets. In contrast, the RMS amplitudes of thermal vibrations of tetrahedral cations in $\text{NaPb}_2\text{M}_2\text{V}_3\text{O}_{12}$ garnets are the largest in this direction. In previously reported garnets, including the present vanadate garnets, we have found a linear correlation between the RMS amplitudes of thermal vibrations of tetrahedral cations in the direction of tetrahedral-dodecahedral cations and the repulsions between the tetrahedral and dodecahedral cations. From this correlation, the peculiar thermal vibration of tetrahedral cations in $\text{NaPb}_2\text{M}_2\text{V}_3\text{O}_{12}$ is concluded to be due to the weak repulsion between the tetrahedral and dodecahedral cations. Moreover, the unusually long dodecahedral-dodecahedral and octahedral-dodecahedral shared edges were observed in the present vanadate garnets. These unusually long shared edges brought about by the large size of the dodecahedral cations (Na^+ , Ca^{2+} , Pb^{2+}) are allowed because of the weak repulsions between the dodecahedral cations and between the dodecahedral and octahedral cations.

Measurement and description of water in synthetic Ettringite and Kuzelite

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Ettringite and Kuzelite are two minerals which are used in industry extensively due to their water bonding capacity. These minerals are mainly formed as hydration products of cementitious materials. The water bonding capacity is variable because excess water molecules can be bound in the interlayer of Kuzelite or in the channels of the ettringite structure. The water contents are measured by Karl-Fischer titration and thermoanalytical methods.

Ettringite can also be formed as secondary mineral when sulfate expansion occurs, the effect can be increased when a higher water containing mineral is formed because the volume is also increased. The water contents vary due to relative humidity, anion, and temperature.

New Members of Zeolite Family, (Cs,Rb)BSi₅O₁₂ Borosilicates: Preparation and Cs-Rb Substitution

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Alkali borosilicates are structurally similar to aluminosilicates studied extensively due to their wide occurrence in nature and technological significance. These glassforming materials demonstrate high cationic conductivity, low thermal expansion, chemical and thermal shock resistance, which enable them to be used for glass-ceramic production, immobilization of radioactive wastes and other applications. Recently a new SiO₂-rich borosilicate was found as a result of decomposition of cubic CsBSi₅O₆ boropollucite with CsBO₂ mass losses above 1000 °C (Bubnova et al., 2004). As it is shown here, this phase is a new CsBSi₅O₁₂ zeolite borosilicate. Therefore we present now the results of studies of the new member of zeolite family CsBSi₅O₁₂ and the solid solution series Rb_{1-x}Cs_xBSi₅O₁₂ (x=0–0.6) using powder X-ray diffraction (XRD) at room and elevated temperatures, annealing, DSC, and TG.

Polycrystalline CsBSi₅O₁₂ was prepared from the stoichiometric mixture by solid-state reaction above 1000 °C. The cell parameters of CsBSi₅O₁₂ are determined from XRD data in *Ama2* orthorhombic space group: *a*=16.242(4), *b*=13.360(4), *c*=4.874(1) Å. The compound is isostructural with CsAlSi₅O₁₂ zeolite compound (Araki, 1980). The CsBSi₅O₁₂ phase formation occurs through the intermediate boropollucite phase, which was observed in the XRD pattern after annealing at 800 °C for 3 hours. At further annealing at about 1000 °C the CsBSi₅O₁₂ crystallizes. The products of the reaction contain mainly CsBSi₅O₁₂ and the admixture of boropollucite or cristobalite depending on annealing time.

The solid solutions Rb_{1-x}Cs_xBSi₅O₁₂ (x_{Cs} = 1.0, 0.95, 0.8, 0.6) were obtained at 1000 °C during a long heat treatment of polycrystalline Rb_{1-x}Cs_xBSi₅O₆ boropollucites with appropriate Cs content by analogy to CsBSi₅O₆ (Bubnova et al., 2004). As we also found out for Cs,Rb-boropollucites the new phase formation is accompanied by a significant mass losses (10–15 wt. %) detected by DSC and TG. The following mechanism of phase transformations is assumed: (Cs,Rb)BSi₅O₆ → (Cs,Rb)BSi₅O₁₂ + (Cs,Rb)BO₂↑. Thus we observed the second possibility to get the zeolite phase using boropollucite decomposition at 1000 °C for 50–80 hours. In crystal structure of Rb_{1-x}Cs_xBSi₅O₁₂ solid solutions the changes of cell parameters are insignificant under the substitution of Cs by Rb atoms: *a* parameter decreases and *c* increases slightly, the *b* direction practically does not change. Over 1100 °C the new borosilicate decomposes and we observe SiO₂ tridymite reflections only in the XRD pattern.

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Trace element geochemistry of pegmatitic quartz and associated minerals in the Froland pegmatite field, Norway

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The Froland pegmatite field (5 km x 20 km) in southern Norway comprises different types of granitic pegmatites, some transitional to rare metal pegmatites. They formed during the Sveconorwegian orogeny, i.e. syn-orogenic (1.13–1.06 Ga), late-orogenic (~0.93 Ga, syn-Herefoss granite) and post-orogenic (<0.93 Ga). The largest volume of pegmatites formed during the syn-orogenic stage. They can be separated into a number of sub-groups including pegmatitic granites, simple granite pegmatites, simple and complexly zoned granite pegmatites and muscovite pegmatite dykes. The syn- and late-orogenic pegmatites represent relatively primitive melts in respect to granite differentiation and contain Fe-phlogopite and Mg-siderophyllite. The muscovite pegmatites related both to the final phase of the syn-orogenic stage and to the post-orogenic stage, have a more evolved chemistry reflected by zinnwaldite.

Lattice-bound trace elements in pegmatitic quartz were analysed by LA-ICP-MS. Quartz from syn-orogenic pegmatites has relative consistent chemistry with concentrations in the range 2–14 ppm Li, 0.7–2.2 ppm Ge, 21–65 ppm Al and 1–11 ppm Ti. Quartz of the late-orogenic pegmatites related to the Herefoss granite contains high Ti (15.1–30.8 ppm) and Al (18–105 ppm). Quartz from the muscovite pegmatites shows more variable trace element concentrations in the range 1.6–9.5 ppm Li, 2.0–2.5 ppm Ge, 17–164 ppm Al and 3.0–17.7 ppm Ti.

Ti, Ge and Al are applicable in monitoring the evolution of pegmatites, because Ti is compatible element in quartz whereas Ge is incompatible during magmatic differentiation. High Al in quartz may indicate oxidising conditions. The Ti, Ge and Al ratios in quartz from the syn-orogenic pegmatites show small variations within the Froland pegmatite field, i.e. within an area of 100 km². Sampling traverses across individual syn-orogenic pegmatite bodies reveal small variations in the trace element composition of quartz, but large variations for K-feldspar and plagioclase. However, syn-orogenic pegmatites which are located inside roof pendants or close to the contact of the Herefoss pluton, comprise non-predictable variations in the composition of primary quartz. High Ti in quartz indicates higher crystallisation temperatures for zoned pegmatites in the Herefoss granite compared to the syn-orogenic types. The large variation in quartz chemistry of muscovite pegmatites may reflect mixed types of quartz crystallisation (melt/fluid). Other interpretations and implications for the pegmatite genesis will also be discussed.

Al(H₂AsO₄)(H₂As₂O₇) – a novel strongly acidic structure type and the first structural characterization of a diprotonated diarsenate group

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The novel compound Al(H₂AsO₄)(H₂As₂O₇) was grown hydrothermally (493 K, 7 d) from a dry mixture of Ti₂CO₃, Al₂O₃ and H₃AsO₄ (volume-ratio ~1:1:4) and forms colourless acicular crystals. Single-crystal structure solution in *Pnma* led to the following unit-cell parameters (*Z* = 4, *R*(*F*) = 2.81 %): *a* = 4.869(1), *b* = 11.071(2), *c* = 15.807(3) Å, *V* = 852.1(3) Å³.

This novel structure type is the first compound to consist of both diprotonated AsO₄ and diprotonated As₂O₇ groups. Only few hydrogen-diarsenates are known; the title compound is the first where the rare H₂As₂O₇ group could be structurally characterized.

The structure is built of [010] chains of AlO₆ octahedra, connected via AsO₄ and As₂O₇ groups. The pyroarsenate groups link adjacent chains to *ab*-layers. Well defined weak to medium strong hydrogen bonds interconnect these layers. The structure is closely related to that of Cr₂H₂(As₂O₇)(As₄O₁₂) (*Pnmm*) (ICSD #100709). In Al(H₂AsO₄)(H₂As₂O₇) the pyroarsenate as well as the arsenate groups in adjacent layers point towards each other. An offset by *a*/2 due to the *a*-glide perpendicular to *c* allows for them to be connected by hydrogen bonds. In Cr₂H₂(As₂O₇)(As₄O₁₂) the *a*-glide is replaced by a mirror plane in the corresponding direction (perpendicular to *a*). This averts the formation of hydrogen bonds, but allows the two AsO₄ groups and As₂O₇ groups of adjacent layers to polymerize, forming As₂O₇ groups and As₄O₁₂ rings, respectively. Cr₂H₂(As₂O₇)(As₄O₁₂) also exhibits an H₂As₂O₇ group; however, the H atoms could not be located – they might be highly disordered as are the corresponding H atoms of the AsO₄ group in Al(H₂AsO₄)(H₂As₂O₇). The close relationship between the two structure types is also reflected in the very similar cell parameters of the Cr compound (*a* = 13.177, *b* = 11.249, *c* = 4.943 Å), *b*_{Cr} and *c*_{Cr}, corresponding to *b*_{Al} and *a*_{Al} respectively, are slightly larger, as can be expected from the larger ionic radius of Cr. The length of *a*_{Cr}, however, is considerably shorter than the corresponding *c*_{Al}, due to polymerization and loss of the interconnecting hydrogen bonds in that direction in the Cr compound. Heating and driving off the OH groups may result in the formation of an Al analogue of the Cr compound. TG investigations are underway as are further, spectroscopic studies (Raman, IR).

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Precipitation of amorphous silica from alcohol solution of Si-tetraethoxide

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It is well known that ammonia-catalyzed hydrolysis of Si-tetraethoxide (Si(C₂H₅O₄)) in ethanol at room temperature yields the precipitation of monodisperse spherical silica particles of virtually the same size (so-called Stöber colloids). As an analogue of formation process of silica precipitates on the Earth, opal in particular, the author has been focusing on this process. The author found that silica nanoparticles and thin film on flat substrate were simultaneously prepared by the Stöber method. The growth kinetics of these precipitates and the fine structure of the film surface were investigated by atomic force microscopy. The thin film formed on a hydrophilic substrate was flat and uniform, with RMS roughness of ≈ 1 nm. The growth of the film was observed to be slower than that of the particles which indicating that the growth of these silica precipitates was limited by the diffusion of reactive silica species. On the other hand, the thin film formed on a hydrophobic substrate was not flat, with RMS roughness of ≈ 10 nm, and was characterized by convex microstructures of two distinct sizes on its surface. The appearance of these microstructures and the delay observed in film formation on the hydrophobic surface indicate that these precipitates, including spherical Stöber colloids, formed as aggregations of primary particles appearing in the precursor solution, and then grew by the adhesion of primary particles continuously forming in the solution.

The author wish to point out the relationship between the presence of a substrate and the final products. Occurring under the same chemical reaction kinetics, the thin films deposited on the substrates are analogues of agate, and the particles forming in our solution are constituents of opal. Present results suggest that, in this analogy, a precipitation reaction taking place in a dynamic environment, for example, silica-supersaturated high-pressure hot water rushing upward in the earth's crust, will produce opal as a stack of spherical particles. On the other hand, the presence of an effective substrate, in other words, a static environment, will result instead in monolithic agate.

Structures and Properties of $\text{CaCu}(\text{AsO}_4)(\text{OH})$ and related mineralsS. Sakai¹, A. Yoshiasa¹, K. Sugiyama², R. Miyawaki³¹Department of Earth Science, Kumamoto University, Kumamoto, 860-8555 Japan²Grad School of Science, Department of Earth & Planetary Science, University Tokyo, Tokyo, 1130033 Japan³National Science Museum, Department of Geology, Tokyo, 1690073 Japan

The crystal structure of $\text{CaCu}(\text{AsO}_4)(\text{OH})$ (conichalcite) from Gosaisho mine, Fukushima, Japan and Higgins mine, Arizona, USA have been refined by the single-crystal X-ray diffraction method using the imaging plate detector. Specimens from various localities characterized in the National Science Museum, Japan. The Space group is orthorhombic $P2_12_12_1$. Lattice parameters are $a = 7.429(2)$, $b = 5.852(1)$, $c = 9.215(2)$ in Fukushima, $a = 7.3849(5)$, $b = 5.8379(4)$, $c = 9.1937(6)$ in Arizona. Hydrogen atom positions in the structure were determined by the difference-Fourier and bond-valence-sum methods. The structure consists of three kinds of coordination polyhedra of AsO_4 tetrahedron, $\text{CuO}_4(\text{OH})_2$ octahedron and $\text{CaO}_7(\text{OH})$ square antiprisms. These polyhedrons share corners and edges each other. These polyhedrons are largely distorted by Jahn-Teller distortion of $\text{CuO}_4(\text{OH})$ octahedrons and hydrogen bonding. In the comparison with isomorphous minerals such as $\text{CaNi}(\text{AsO}_4)(\text{OH})$, $\text{CaZn}(\text{AsO}_4)(\text{OH})$, $\text{PbCu}(\text{AsO}_4)(\text{OH})$ and $\text{PbZn}(\text{AsO}_4)(\text{OH})$, we found that they have systematic varieties on structural deformations. It is interesting to show that deformation type of $\text{PbCu}(\text{AsO}_4)(\text{OH})$ and $\text{PbZn}(\text{AsO}_4)(\text{OH})$ including Pb atoms differ considerably from that of $\text{CaCu}(\text{AsO}_4)(\text{OH})$, $\text{CaNi}(\text{AsO}_4)(\text{OH})$ and $\text{CaZn}(\text{AsO}_4)(\text{OH})$. These structures include linear $\text{CuO}_4(\text{OH})$ octahedral chains. The Jahn-Teller distortion in $\text{CaCu}(\text{AsO}_4)(\text{OH})$ is much like CuO_6 octahedral chains of spin-Peierls material CuGeO_3 . It may be observed spin-Peierls transition at lower temperature in $\text{CaCu}(\text{AsO}_4)(\text{OH})$. But $\text{PbCu}(\text{AsO}_4)(\text{OH})$ is different from $\text{CaCu}(\text{AsO}_4)(\text{OH})$ and CuGeO_3 in the direction of the elongated and shortened Jahn-Teller distorted Cu-O bonds. $\text{PbCu}(\text{AsO}_4)(\text{OH})$ should have a different spin-Peierls transition and magnetic properties with $\text{CaCu}(\text{AsO}_4)(\text{OH})$ and CuGeO_3 .

Local Structure Analysis of Rutile-type RuO_2 and TiO_2 by X-ray Spectroscopy

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The rutile-type structure is found in many dioxides. The rutile samples in this study, RuO_2 and TiO_2 , are important materials from the viewpoint of electronic and material science. Each cation is surrounded by six anions (nearest neighbor), forming octahedron. The octahedra form chains with share-edge along c-axis. The length of c-axis is equal to the interatomic distance between second-neighbor atoms. RuO_2 has been a negative thermal expansion (NTE) along c-axis in the high temperature region. In this study, we try to give an explanation of that behavior with the EXAFS and XPS technique.

We could evaluate the harmonic effective interatomic potential from the contribution to the thermal vibration which could be extracted from EXAFS Debye-Waller factors. As a general rule, the longer the distances between atoms, the smaller are the potential coefficient, α , which is equal to the force constant. In the case of RuO_2 , the potential coefficient between the third-nearest neighbor atoms (Ru-Ru) was 7.80 eV/Å², whereas the potential coefficient between third-nearest neighbor atoms (Ru-Ru) was 7.49 eV/Å². On the other hand, the α between nearest neighbor atoms (Ru-O) was 14.85 eV/Å². The α between second-nearest neighbor atoms was a half of that between nearest neighbor atoms. These results suggest that the spring between second-nearest neighbor atoms is weakest in RuO_2 .

In XPS measurement, it was discovered that the peak of O1s in RuO_2 was located at somewhat higher binding energy position than that in TiO_2 . This means that charge density around O atom in RuO_2 was higher than that in TiO_2 . It follows from this that the repulsive force in share-edge (O-O) in RuO_2 is larger than that in TiO_2 . The coefficient of expansion of the share-edge in RuO_2 (1.01%) was much larger than that in TiO_2 (0.27%) at 550K. It is reasonable to suppose that this large coefficient of expansion of the share-edge in RuO_2 is caused by the large repulsive force between O atoms. On account of the large coefficient of expansion of the share-edge and large α between nearest neighbor atoms, Ru atoms are attracted to share-edge with the rise of temperature. As a result, interatomic distance between second-nearest neighbor atoms, which have small α , decreases with a rise in temperature. It is concluded that this decrease in interatomic distance between second-nearest neighbor gives rise to the NTE in RuO_2 .

XAFS Study of the local structure changes in ATiO_3 , A_2TiO_4 and TiO_2 (A=Mg, Ca, Ba, Pb, Nb, Fe) compoundsTakafumi Hashimoto¹, Akira Yoshiasa¹, Maki Okube², Masatomo Yashima², Hiroki Okudera³ and Akihiko Nakatsuka⁴¹Faculty of Science, Kumamoto University, Kumamoto 860-8555, Japan²Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-850, Japan³Max-Planck-Institute FKF, Heisenbergstr.1, 70569 Stuttgart, Germany⁴Department of Advanced Material Science and Engineering, Yamaguchi University, Yamaguchi 775-861, Japan

The local structures of ABO_3 , A_2BO_4 and BO_2 compounds, which contain titanium, were investigated using X-ray absorption fine structure (XAFS) spectroscopy. The XAFS spectra for ATiO_3 perovskite, where A is Ca, Sr, Ba and Pb, and $\text{La}_{0.92}\text{Nb}_{0.08}\text{O}_3$ perovskite, MgTiO_3 ilmenite, Mg_2TiO_4 spinel and TiO_2 rutile were measured at various temperatures from 18K to 1100K. The X-ray absorption near edge structure (XANES) spectra in perovskite, ilmenite, spinel and rutile structures give different features. The obtained XANES spectra of Ti K-edge for each material changed obviously with the A site atoms, although CaTiO_3 , SrTiO_3 , BaTiO_3 and PbTiO_3 perovskite have the same structure with various kinds of phase transition. The temperature dependence of the main edge and pre-edge features of XANES spectra for these materials is negligible except BaTiO_3 , PbTiO_3 , MgTiO_3 and Mg_2TiO_4 . SrTiO_3 , BaTiO_3 and PbTiO_3 perovskite have ferroelectrics phase transitions in measured temperature range. No change in XANES spectra of SrTiO_3 perovskite were observed below and above the phase transition points. The pre-edge feature in BaTiO_3 and PbTiO_3 perovskite changed around phase transition points. Both BaTiO_3 and PbTiO_3 perovskite change from tetragonal to cubic undergoing this ferroelectrics transition with increasing temperature. The pre-edge peak size in PbTiO_3 becomes small with increasing temperature before transition point, on the other hand that of BaTiO_3 becomes large. These temperature dependences of the pre-edge feature indicate the changing in the site symmetry or the deformation of local structure around Ti atoms. The existence of PbTiO_3 and BaTiO_3 pre-edge at highest temperature suggests that the local distortion around Ti atoms remain existence after structural phase transition but change the degree of distortion. It is noteworthy the change in pre-edge feature and XANES spectra occur not only near transition point depending distortion on occupied site, but also the kind of A site atoms and atomic configuration.

Crystal Structure and Phase Transition of the Fast-Ion Conductor CuI

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Copper iodide CuI is known as an excellent ionic conductor. This compound exhibits a variety of structural changes and phase transitions. However, details of the phase transition and the crystal structure are not understood well. The present research aims to analyze the crystal structure and the disorder of Cu ion in the CuI, using the synchrotron radiation powder diffraction data and the Rietveld method. High-temperature synchrotron powder diffraction data were measured by using a Debye-Scherrer camera and an imaging plate at the beam line BL02B2 of SPing-8. X-rays of 0.05nm wavelength were obtained by a double-crystal monochromator. Crystal structure of CuI was refined by Rietveld analysis (RIETAN-2000). Synchrotron diffraction data measured at 750 K exhibited the pattern of the fluorite-type structure with the space group (Fm-3m). The complicated background of the synchrotron diffraction data was subtracted with a computer program (PowderX) before being analyzed. We analyzed the data using two structural models. One is an ideal fluorite-type model where Cu ion is put at 8c site. The other is a split-atom model where Cu ion exits at not only 8c site but also 32f site. In the Rietveld analyses, the split-atom model yielded a better fit to the observed intensity data, comparing with the ideal fluorite-type model. The result indicates that a part of the Cu ions is displaced from the regular 8c position in the $\langle 111 \rangle$ directions. The direction of this displacement is opposite to I ion. The split-atom model indicates that the Cu ion has a positional disorder. The high conductivity of Cu ions in the CuI is attributable to the disorder.

Growth of forsterite single crystal doped by Cr and their optical properties

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Since the forsterite doped with Cr³⁺ crystal was demonstrated as tunable near-IR solid-state lasers, Cr:forsterite crystal has been investigated by many researchers. Most of Cr:forsterite crystals in the earlier works were prepared in oxygen atmosphere with low initial concentration of Cr. Here we synthesized forsterite single crystal with higher Cr content grown in the N₂ atmosphere.

Large Cr:forsterite single crystal was grown using Czochralski-pulling method. The starting materials were high purity granular MgO and SiO₂ reagents of 1-3 mm size and 1.07 wt% of powder Cr₂O₃. We obtained a large crystal with size ca. 120 mm in length and ca. 50 mm in diameter.

The chemical compositions of as-grown crystal were analyzed by EPMA. The Cr concentration increases from the top to the bottom of the crystal, with 0.18 to 0.40 wt% (Cr₂O₃). The Cr, however, distributes almost homogeneously perpendicular to the growth direction.

The lattice constants were $a = 4.7580(4)$ $b = 10.1980(10)$ $c = 5.9840(9)$ Å with the space group Pbnm. The as-grown Cr:forsterite single crystal showed typical pleochroism. The colors change along a -, b - and c -axes from green, yellowish green to bluish green, respectively.

Absorption spectra were measured to see the detail of optical property of doped crystal. The spectra showed Cr³⁺ and Cr²⁺ absorption bands in the visible and near infrared region. Even though the existence of Cr²⁺ ion was clearly seen in the spectra, the weak Cr⁴⁺ absorption bands were also observed. The results of absorption spectra suggest that the Cr:forsterite crystal grown in the N₂ atmosphere contains three different valence Cr ions.

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EXAFS and diffraction study of AgI under high pressure and high temperature.

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Silver iodide (mineral name: iodicite) is a much studied materials because of the fast-ionic behavior of Ag ions in α -phase and disordered rock-salt type phase. The anharmonic effective pair potentials $V(u) = au^2/2 + bu^3/3! + cu^4/4!$ for I-Ag bond in various phases of AgI have been investigated by the pressure and temperature dependence of extended X-ray absorption fine structure (EXAFS) Debye-Waller factors. EXAFS spectra near the I K-edge and X-ray diffraction measurements were performed under pressure and temperature up to 6.0 GPa and 1100 K using a multi-anvil high-pressure device and synchrotron radiation from Spring-8, Hyogo. X-ray absorption near-edge structure (XANES) spectra are quite sensitive to the three-dimensional atomic configuration around X-ray absorbing atoms, they are useful for phase study under high temperature and high pressure. In the parameter fitting of EXAFS analysis, we have directly carried out the numerical integration of EXAFS function and evaluated the precise anharmonic effective pair potentials. The potential parameter a for wurtzite-type at 0.1 MPa is 2.37 eV/Å². The potential parameter a does not change appreciably through the α - β phase transitions at 0.1 MPa. The potential parameter a for rock-salt type is 1.66(5) eV/Å² at 1.0 GPa and which increases to 1.88(6) eV/Å² at 6.0 GPa. The anharmonic effective pair potential for each phase is influenced by pressure and becomes steeper with increasing pressure and the extent of anharmonicity decreases with pressure. The super ionic conducting α -AgI has a steeper interatomic potential than that in rock salt type AgI. The extent of anharmonicity is larger in α -AgI than in rock salt type AgI. The Debye-Waller factors of atoms in AgI were investigated by both the diffraction and EXAFS methods. The Debye-Waller factor determined by EXAFS is sensitive to short-range correlations of the atomic motion: the mean-square relative displacement (MSRD) of the backscattering atoms with respect to the absorbing atom can be determined by EXAFS. The mean square displacement (MSD) of each atom at crystallographically equivalent positions is determined by diffraction methods. The MSRD contains the contribution from the MSD of both absorbing and backscattering atoms and the displacement correlation function (DCF). It was revealed that the displacements of cation and anion in the phases of AgI correlate strongly with each other in thermal vibration.

O29-01

Geometallurgy of Australian iron ores and a comparison with their Brazilian counterparts.

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Australian and Brazilian hematitic iron ores account for about two thirds of world production of steel. Although the producers sell these ores in competition with each other, the geometallurgical characteristics of these ores complement each other. Geometallurgy is a new science which connects the geological and mineralogical characteristics of an ore with its processing behaviour; it is important because of its capability of predicting the metallurgical performance of lump and fine ores. The basis of iron ore geometallurgy is the classification of the ore. In Australia past classifications mostly relied on mineral association and hardness (see Pilbara Iron Ore Classification); in Brazil shapes of individual grains were also considered important. CSIRO Minerals developed a new classification scheme, which recognises the importance of ore textures, porosity and gangue mineralogy in iron ores. Although this classification is restricted to non-detrital ores, it covers the majority of iron ore produced in Australia and Brazil. The next step in the process is to carry out testing of the ore types. For lump ore, decrepitation index (DI), abrasion index (AI), tumble index (TI), reduction degradation index (RDI) and reducibility index (RI) are tested, while for fine ores, the geometallurgical characteristics will determine whether a blend can form good sinter which will meet steel mill specifications. There is also a correlation between ore types and the grade of an ore. Australian iron ores are overall richer in goethitic ore types than their Brazilian counterparts. Porous, goethitic Australian ores assist granulation and provide reactive material for the sinter matrix, whereas the relatively unreactive Brazilian fines give high iron content and dense, resistant nuclei. Australian lump ore, which is dominated by dense martitic ore and hard vitreous goethite, will generate a higher proportion of premium lump than the porous Brazilian ore. An example of a new Australian iron ore type, consisting of powdery nano-hematite, is used to illustrate how the presence of this significant (>20%) component can influence the performance of the ore. Because of the hematitic nature of Brazilian iron ores, it speculated that nano-hematite could be present in these ore as well, but this still needs to be confirmed, because nano-hematite has a major impact on balling and subsequent induration of pellets.

O29-02

Influence of arsenic on the recovery of gold from refractory gold ores evidenced from SIMS and XAFS studies

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Pyrite, one of the principal Au-bearing minerals in refractory gold ores, contains high concentrations of arsenic. Quantitative ion microprobe analyses indicate variable levels of Au in pyrite ranging from below the detection limit of 20 ppb to 5.212 ppm. Ion images of ^{197}Au indicate that gold is heterogeneously distributed within pyrite with sporadic enrichment along the outer grain boundaries corresponding to As-rich domains in pyrite. Micro-XAFS analyses of pyrite grains that exhibit different morphologies and various concentrations of gold and arsenic indicate that the dominant arsenic species is As^{4+} . Arsenic occurs at the corners of Fe octahedra as a substitution of the sulfur atoms. In addition to As^{4+} , highly variable concentrations of As^{5+} species are observed in semi-massive, inclusion-rich and framboidal pyrite grains. Extraction of gold from refractory ores requires roasting prior to cyanidation. During roasting, pyrite is initially transformed to pyrrhotite and then progressively to magnetite and hematite, liberating the structural and submicroscopic gold by creating highly porous iron oxide structures. Hematite is highly porous whereas maghemite is massive with no evidence of permeability needed for effective cyanidation. Maghemite can contain significant amounts of arsenic (i.e., up to 18.6 wt %), whereas hematite contains minor or negligible arsenic (i.e., <2.9 wt %). SIMS analyses indicate that maghemite is also enriched in gold containing up to 260 ppm Au. Arsenic species in maghemite and hematite include both As^{3+} and As^{5+} . Maghemite has much higher proportion of As^{3+} in comparison to hematite. Arsenic that occurs in -1 valence state in pyrite is volatilized as As_2O_3 and oxidized to As_2O_5 under the highly oxidizing atmosphere of the roaster. It appears that the oxidation of arsenic species to As^{5+} is incomplete in some particles. Based on SIMS imaging, it appears that maghemite originated from As-rich zones within the precursor pyrite. The presence of arsenic in pyrite appears to be detrimental to mineral transformations taking place during roasting and causes reduced gold recoveries. In addition, this finding has significant implications to the arsenic disposal practices as current arsenic fixing/precipitation processes assume arsenic as As^{5+} .

O29-03

Functional materials prepared by processing kaolin minerals

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Kaolin is widely used as coatings and fillers for paper, as a raw material for the manufacture of porcelain, glass fibers and honeycomb ceramics, and as a viscosifier in paints, etc. We have developed processes for producing functional materials from kaolin minerals. For example, an amorphous $\text{CaAl}_2\text{Si}_2\text{O}_8$ compound with a layered structure similar to hexaselecan can be obtained by mechanochemical reaction of kaolinite with calcite followed by heating at 800°C. This material shows very good simultaneous uptake ability and selectivity for heavy metal ions and oxyanions arising from the presence of three components with different chemical characters. Four different porous materials can be prepared from kaolin by heat treatment and selective leaching. Microporous silica can be obtained by thermally converting the kaolin to metakaolin at 600-900°C, followed by selective acid leaching. This silica has a specific surface area of 300-400 m²/g and 0.6 nm micropores, making it a good precursor for synthesizing both high silica zeolite (ZSM-5) and mesoporous silica. The ZSM-5 thus produced contains crystals which are very well developed in the ac-plane, giving them good catalytic properties associated with the straight cylindrical micropores running perpendicularly. The mesoporous silica product shows a very high specific surface area (about 1400 m²/g) but retains its original platy particle shape. Since this material is synthesized under mild hydrothermal conditions with NaOH solution and surfactants, its unique porous structure is somewhat different to the products synthesized from other silica sources. When kaolin is heated at about 1000°C, it converts to a segregated structure containing γ -alumina nano-grains dispersed in a matrix of amorphous silica but retaining the original platy shape. Mesoporous γ -alumina can be prepared from this material by selective alkali leaching. The product has a specific surface area of about 300 m²/g with 5-6 nm mesopores which give its porous structure very good thermal stability and humidity control properties.

O29-04

Quantitative X-Ray powder diffraction analysis of iron-ore sinters

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Iron ore sinters are important feedstock materials for the steel industry. As a result of increased quality requirements the chemistry and the phase composition of sinters are of importance. This investigation deals with the phase quantification of iron ore sinters and the factors that affect it, using XRD and the Rietveld method. Minerals present in the sinters are magnetite, hematite, magnesioferrite, periclase, di-calcium silicate, glass and silico ferrites of calcium and aluminium. The latter is abbreviated as SFCA, of which three varieties depending on the molar ratio of cations to oxygen have been described: SFCA ($\text{M}_{14}\text{O}_{20}$), SFCA-I ($\text{M}_{30}\text{O}_{38}$) and SFCA-II ($\text{M}_{26}\text{O}_{36}$) (M=Ca, Fe, Al and Si). Quantitative X-ray powder diffraction analysis is one method for determination of the relative quantities of phases present in sinters. Although no observations on textural features can be made, it is fast and can easily be adapted for process control.

Sinter samples used in this investigation were obtained from Mittal Steel SA. After addition of approximately 16.5 per cent Si powder (Aldrich 99% purity) for determination of the amorphous content and micronising in a McCrone micronising mill, the samples were prepared for XRD analysis using a back loading preparation method. A PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits using Ni filtered Cu K_α and Fe filtered Co K_α radiation was used. The phases detected are magnetite, hematite, beta- di-calcium silicate, SFCA, SFCA-II and minor quartz. SFCA-I was also included in the quantification as it is predicted to occur in high Fe sinters.

Due to micro-absorption effects the Si content is overestimated by more than 3 per cent in the runs employing Cu-radiation. Applying a micro-absorption correction the results are comparable to those of the runs with Co-radiation. Acceptable quantification with satisfactory errors were obtained for the sinters examined. The effect of micro-absorption is the largest source of error when using Cu K_α radiation. Results will be compared with SEM image analysis and in order to develop a reliable and proven method synthetic SFCA phases will be prepared and mixed in various ratios to verify results, using the XRD method.

Application of cathodoluminescence microscopy to fluor spar ores and concentrates: Fluorspar deposits, Okorusu, Namibia

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Cathodoluminescence microscopy (CLM) provides a valuable technique for the study of the mineralogy and textures of fluor spar ores, their carbonatite and marble host rocks, and their beneficiation products. Fluorite is readily recognized by its light to dark blue Cathodoluminescence (CL). The deleterious minerals, apatite, calcite, and quartz are easily recognized in the fluor spar ores, concentrates, and tailings by their characteristic CL, and their intergrowth with fluorite in the ores and locking in the beneficiation products can be very effectively studied by CLM. The character of the host rock carbonatites and marbles and the extent of replacement by fluorite can be readily assessed by CLM.

The fluor spar mines at Okorusu, north-central Namibia provide an especially useful example of the value of CLM microscopy in the study of those fluorite ores, beneficiation products, and host rocks. Most importantly, the recognition of the textures shown by the fluor spar ores provide an understanding of the type of host rock replaced by the fluor spar ore, and the rock type replaced controls the nature of the beneficiation problems encountered at the mill.

About 68% of the currently mined (and projected for mining) fluor spar ores at Okorusu have formed by the replacement of carbonatite. When this replacement occurs, part of the original apatite in the carbonatite persists essentially as an insoluble residue in the resulting fluor spar ores. The presence of apatite is the cause for about 2.5% P_2O_5 in the heads before beneficiation. The beneficiation of fluor spar ores that have formed by the replacement of carbonatite, however, decreases their P_2O_5 contents down to 0.3-0.5%. Phosphorous is a deleterious constituent in fluor spar concentrates when they are used as a flux in the steel-making industry.

In contrast, fluor spar ores that have resulted from the replacement of marble at Okorusu have negligible phosphorus contents. Those ores comprise about 32% of the fluor spar ores currently mined at Okorusu. The silica content of those ores averages 10-20% and can pose a problem with respect to diluting the grades of the concentrates produced from these ores. Effective beneficiation technique, however, reduces the silica contents to an average of 1-1.5% SiO_2 .

The calcite contents of some fluor spar concentrates such as those produced from the carbonatite-related fluor spar ores at Amba Dongar, India may also constitute a problem.

For the study of fluor spar ores, their host rocks, and beneficiation problems, CLM provides a uniquely useful instrument for the rapid determination of their mineralogy and textures.

The referenced rietveld analysis, a key tool to reduce energy consumption and CO₂ emissions in cement production

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In the traditional Rietveld method a high quality full diffraction profile is fitted according to a model with known crystal structures and a refinement strategy. Often this is the only method to analyze complex mixtures of several crystalline phases that show strong peak overlaps. The method yields precise, relatively correct results, but lacks absolute accuracy in complex cases.

PANalytical has linked the precise Rietveld quantitative data to other results obtained by established techniques like optical microscopy. This unique "referenced" Rietveld method allows an absolutely correct XRD quantification, accurate enough to push the limits of process control.

Examples of the analysis of Portland clinker and Portland cement will be shown. These more accurate determinations of all phases in cement allow the use of the maximum amount of possible additions and saves valuable clinker. One can also achieve a tighter control of the different sulfate phases in OPC, resulting in more constant hydraulic properties, which facilitates the use of the final product in building projects.

The high precision phase analysis is a key factor to save energy and also to reduce the CO₂ emission.

Gold in refractory ores: deportment and its impact on metallurgical processing

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From the perspective of metallurgical processing, gold ores are commonly classified into free-milling and refractory ores. Typically, free-milling ores are defined as those where over 80% of gold can be recovered by direct cyanidation, or a combination of gravity, flotation and cyanidation. Refractory ores are defined as those that give low gold recoveries or give acceptable gold recoveries only with the use of significantly more reagents or more complex pre-treatment processes.

Gold in refractory ores mainly occurs in two forms: gold minerals and gold locked in the crystal structure of sulfide minerals. Gold minerals include native gold, electrum, gold tellurides (such as calaverite $[AuTe_2]$ and sylvanite $[(Au, Ag)_2Te_4]$), austrobitite $[AuSb_2]$ and maldonite $[Au_2Bi]$. Native gold and electrum, once liberated, can be easily recovered by conventional techniques. If locked in other minerals as micron-size particulates, native gold and electrum can be lost to various process tailings. Calaverite, sylvanite, austrobitite and maldonite sometimes form surface coatings, which can result in refractoriness due to slow-dissolving kinetics, even though they are liberated. For example, austrobitite often forms austrobitite $[AuSbO_3]$ coating and maldonite often forms bismuth hydroxide $[(Bi(OH)_3]$ coating during cyanidation. These coatings are not amenable to cyanide solution, and thus will prevent further dissolution of residual gold minerals and cause gold losses.

Locking of gold in the crystal structure of sulfide minerals as isomorphic substitution is the major cause for refractoriness of many gold ores. Because it is extremely fine and can not be observed under optical microscope or by conventional scanning electron microscope, gold locked in sulfide minerals is called submicroscopic gold or invisible gold. Pyrite and arsenopyrite are the two most important submicroscopic gold hosts, with up to 11,000 ppm and 15,000 ppm Au, respectively. Morphologically, fine-grained pyrite and arsenopyrite often contain higher gold content than coarse-grained varieties. Other submicroscopic gold carriers include marcasite, loellingite, chalcocopyrite, realgar and iron oxide. In addition to ores containing refractory gold minerals and submicroscopic gold, gold ores containing carbonaceous matter are also refractory because the carbonaceous matter will adsorb gold from pregnant solution during cyanidation. Finally, some gold ores are refractory due to the presence of minerals in the ore that react with the reagents needed to leach gold (namely cyanide and oxygen), leaving the system starved of reagent and unable to leach gold. Examples are secondary copper sulfide minerals and oxidized base metal ores.

Deportment of gold in refractory ores and the abundance and type of other minerals in the ore have a direct impact on the selection of the optimum flowsheet for metallurgical processing of these ores. To recover gold from refractory ores in which the gold is locked as submicroscopic particles in a sulfide host, requires prior oxidative pretreatment of the sulfides to make the gold amenable to subsequent cyanidation. Pretreatment techniques that have been employed by the gold industry include pressure oxidation (autoclaving), roasting and bacterial oxidation. Pressure oxidation is often used to treat non-carbonaceous sulfide ores and concentrates; roasting is used to treat sulfide gold concentrates and carbonaceous ores (whose active carbon responds poorly to autoclaving); and bacterial oxidation is used to treat sulfide gold concentrates. Pre-oxidation technology selection depends on ores/concentrates mineralogical composition, metallurgical response and project economic considerations.

Quantitative ore texture characterization

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The characterisation of the mineralogy and textures of rock samples has traditionally been based upon the geologist's examination of hand specimens and the use of optical microscopy. Even between experienced geologists this descriptive based approach can result in widely varying data. The resultant observations are often qualitative and limited in number and thus the descriptions of any variation between samples is not statistically valid, nor reproducible.

Recently developed quantitative mineralogy tools (such as the JKMRC Mineral Liberation Analyser - MLA), enable the quantification and thus comparison of textural data obtained from drill core samples or polished blocks/thin sections. The mineralogy, grain size and mineral association of a large number of samples can be described and presented with known confidence limits.

The data acquired from the MLA enhances geologists' knowledge of subtle variations in rock types and mineralisation. This improved description of field samples assists in the production of accurate maps and planning of exploration programs. The MLA's quantitative data and mineral maps also assist with the accurate determination of the paragenesis of mineralisation and thus add to theories of ore genesis. The quantitative mineralogy and textural data can be incorporated into future Mineral Resource models and thus assist with mine design, scheduling and the identification of suitable mineral processing options.

Detailed chemical stratigraphy of PGE bearing horizons of the Bushveld complex, SA

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Drill cores from UG2 and Bushveld have been analyzed by the EDXRF-geoscaner along profiles in 250µm steps for major and trace elements. Elemental maps were obtained by EDXRF-microscopy in 100µm steps. Sub-samples were analyzed by XRF and the glass beads were analyzed by ICP-MS for REE and PGE. The samples were investigated by SEM for platinum group minerals (PGM). The chemical patterns obtained by EDXRF 1D and 2D scanning highlights areas with elevated Ni, Cu, PGE, K, Ti, P, Zr and other elements. The distribution of these elements are linked to specific mineral distributions and mineral ratios, e.g. higher K contents are linked to the presence of phlogopite and amphibole, Ni to olivine and pentlandite. Other elements like REE are related to the K-enriched areas which also contain REE-phosphates, spatially closely related to apatite and to Zr- and U-bearing phases. A large percentage of the PGM observed occur interstitial to the UG2 chromite and concentrate within zones containing higher levels of phlogopite. Pentlandite and chalcopyrite occur throughout the cores, but also show a denser population in a number of distinct zones.

The aim of the detailed investigation is to develop the EDXRF method as a fast tool to outline zones of interest regarding PGE, Ni and Cu mineralization by using these and other pathfinder elements.

Quantification of marble microstructure - a model for predicting the deterioration of marble

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Several modern buildings around the world are covered by marble cladding panels. Unfortunately on some of the buildings, the panels start to bow and loose strength after some years on the wall. This phenomenon is experienced occasionally for crystalline marble when used as exterior cladding and is assumed to be controlled by features of the rock, microclimate and construction specific factors. Most marbles investigated show deterioration due to thermal and moisture treatment. This cannot be explained without taking into account the rock microstructure. The microstructure, however, include a great number of parameters and the degradation is controlled by an interaction of these parameters. The aim of this paper was to quantify important microstructure parameters in marble used as cladding panels, find multivariate correlations with deterioration and use the correlated parameters in a regression model to predict the deterioration of marble. By means of deterioration data acquired by the partners of the European research project Testing and Assessment of Marble and Limestone (TEAM, 2000-2005), a model was developed. Deterioration of marble can for example be recognised as bowing, volume changes or loss of strength. Bowing data were available for the highest number of samples and were therefore used in the model. Thin sections from all samples were quantified by several microstructure parameters describing crystal growth, grain boundaries, grain shapes, grain size, cleavage, twinning, grain size distribution, grain shape factors and number of neighbours. By means of the microstructure parameters found to be correlated with bowing, a model describing the majority of the variance in the bowing dataset was generated. The variables that were used in the model are relatively easy to quantify when investigating new samples. The conclusions show that prediction of deterioration is possible to a high degree, by means of specific microstructure investigations.

O30-01

Mineral collections and mineralogical museums in Japan — A review

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Before the introduction of modern mineralogy into Japan, two significant collections of minerals and rocks were made by Sekitei Kinouchi (1724-1808), the author of “*Un-kon-shi*”, and Philipp Franz von Siebold (1796-1866), a German physician. Modern mineralogy was introduced by Karl Schenk, a German mining expert, immediately after the Meiji Restoration in 1868. Tsunashiro Wada, one of the first students of Schenk, built the first scientific mineral collection during his works at the Kaisei School, the University of Tokyo, Geological Survey of Japan (GSJ), and the National Ikuno Mine. Most of the Wada Collection is currently owned by Mitsubishi Materials Corp., with some exhibited at the Ikuno Mineral Museum.

Followings are other well known mineral collections in Japan; the Wakabayashi Collection at the University of Tokyo, the Ko Collection at Kyushu University, the Hideki Nambu Collection at Ibaraki Nature Museum, the Nagashima Collection at Nakatsugawa Mineral Museum, the Okamoto, Kinoshita, Matsuo Nambu, and Imayoshi Collections at the GSJ Geological Survey of Japan, and the Sakurai Collection. Among those, the Sakurai Collection, collected by Dr. Kin-ichi Sakurai, an amateur mineralogist, is the most famous. It contains extensive mineral species that are systematically classified. The collection was donated to and is currently managed by the National Science Museum, Tokyo (NSM) and Kanagawa Prefectural Museum of Natural History.

Museums of mineralogy and related sciences in Japan can be classified into three categories: governmental, university, and private. For the governmental museums, the GSJ Geological Museum, the NSM, the Fossa Magna Museum (Itoigawa, Niigata), and the Nakatsugawa Mineral Museum are good examples. The GSJ Geological Museum has large collections and exhibitions based on the researches on geology and mineral resources. The mineral collection in NSM contains many type specimens in Japan. These two museums are independent agencies under the national government of Japan.

Several university museums possess mineral collections. Mining Industry Museum of Akita University is a pioneer university museum of mineralogy in Japan. The University Museum, University of Tokyo also has a history of research and collection of minerals. In these ten years, several national universities such as those of Hokkaido, Tohoku, Nagoya, Kyoto, Osaka, and Kyushu have founded university museums, where specimens have been collected and stored in the course of researches and educations.

One of most active private museums in mineralogy is the Masutomi Geological Museum in Kyoto. It is considered as a center of amateur mineral collectors in Japan.

O30-02

Classic mineral localities of Russia: History and present day

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Thirty mineral localities of Russia can be considered as the classics: they are known more than half a century as source of numerous high-quality mineral specimens well-represented in famous long-lived museum collections. There are objects of Urals (19), South Siberia (9), and Kola Peninsula (2). Serious mineral collecting on Russian localities was started in 18th century in South Siberia (Adun-Cholon pegmatites; Sherlovaya Gora greisen deposit; Western Altai and Nerchinsk District polymetallic deposits; Slyudyanka and Akhtaragda skams) and Middle Urals (Berezovskoye gold deposit, Gumeshevskoye copper deposit, Murzinka and Sarapulka pegmatites). It was connected with rapid development of mining industry and gem business. Famous Russian minerals of this period: beryl-aquamarine, red tourmaline, malachite, crocoite, quartz-amethyst. 19th century, especially its second part, became “golden age” of Russian minerals in museums of all world. It is result of great development of mineralogy and wide popularity of mineralogical knowledge and mineral collecting in Russia. Most Russian mineral localities giving world-best specimens were discovered in this time: at Middle Urals (Nizhniy Tagil copper and platinum deposits; Emerald Mines; Shaitanka and Adui pegmatites; Saranovskoye chromite deposit; Tur’inskiye copper mines; Nev’yansk gold-platinum placers), South Urals (Ilmeny Mountains pegmatites; Akhmatovskaya and neighbouring skarn pits; placers of Miass and Sanarka rivers) and Siberia (Borshchovochnyi Kryazh pegmatites; Lena river gold placers). Classic Russian minerals of 19th century: native metals (gold, platinum, osmium, iridosmine nuggets, copper dendrites), chrysoberyl-alexandrite, blue and purple topaz, beryl (heliodor, aquamarine, emerald), colour tourmaline, perovskite, uvarovite, malachite, crocoite, phenakite, grossular, vesuvianite, zircon, ilmenite, aeschynite, samarskite, Khibiny and Lovozero peralkaline massifs (eudialyte, astrophyllite, lampophyllite, loparite and great number of rare minerals) at Kola, Dalnegorsk boron-polymetallic deposits (ilvaite, datolite, danburite, pyrrhotite, galena, sphalerite, fluorite, calcite, etc.) at Far East, Vishnevye Gory (zircon, pyrochlore, ilmenite, rare minerals) and Lipovka (elbaite) at Urals can be considered as Russian classics of 20th century. More than half of above-mentioned localities remain important source of nice specimens today. Big mines operate on Berezovskoye, Saranovskoye and Dalnegorsk deposits and in Khibiny and Lovozero massifs. Mineral collecting is still possible in dumps and open pits of some other Russian classic localities. Note that Russian localities found in last fifty years and now actively producing museum-quality mineral specimens (Kovdor alkaline massif and Keivy area at Kola; Subpolar Urals alpine-type quartz deposits; Norilsk Cu,Ni,Pt-deposits, Murun, Inagli and Konder alkaline massifs, Malkhan pegmatites, Mir and Udachnaya kimberlite pipes in Siberia, etc.) have a chance become the classics in future.

O30-03

Toward mineral database standards for World-Wide-Web utilization

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Museum mineral collections must serve society broadly in order to maintain their relevance. While galleries and exhibitions provide the most intimate connection for most Museum visitors, accessibility should include access to catalogues and databases via the World-Wide-Web. In this manner, the broadest community, including scientists, collectors, students and the general public, can utilize museum mineral collections more easily and appreciate their importance as a record of the natural world and material diversity. However, to suit a worldwide community, we must adopt standards on the format of the data which define and describe our specimens. Our goal here is to begin a dialogue towards generalized standards, which for the most part virtually exist but require more agreement.

The most critical information is species and locality. Species designations are administered by the IMA Commission on New Minerals and Mineral Names, but in practice, museums have found it necessary to include a variety of old or unofficial terms to deal with inadequately studied samples with general terms, e.g., tourmaline group, or odd samples, e.g., fake and obsidian. Variety can be a very useful field for gem species. Assemblages should be identified in some manner; cross referencing is of considerable value for specimens exhibiting multiple, well-developed species. Locality is highly problematic because of variability in political geography but generally is hierarchal by country, province, county (or equivalent), nearest city/town, place name such as a mine, geographic feature, etc., a detail field such as for mine level, etc., and ideally latitude and longitude or standardized map coordinates (e.g., NAD83)—for the latter standards of notation must be readily available in the search function or display. Transliteration of locality names can prove frustratingly variable and it is suggested that locality information be recorded in the written language(s) of the country-of-origin as well as in an English transliteration. Information such as type specimen category and references to published specimen data would also be valuable. Date fields are important for showing when the specimen was extracted and when it entered the collection. Images ARE worth a thousand words. They provide a valuable inventory tool and the closest facsimile to a museum visit for study or enjoyment. Implementing web-databases with images is extremely important for their and museum success.

A Web collection of collections would be valuable to science and society, but we need standards in order to achieve this important goal. Let us get busy.

O30-04

Fake gold but real history: The gold nugget replica collection of Museum Victoria

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Museum Victoria houses a collection of over 170 replicas of gold nuggets mainly made by the Victorian Department of Mines between the 1850s and 1910 from nuggets discovered on the Victorian goldfields. The collection represents a unique historical resource and may provide an insight into the formation of gold nuggets in Victoria.

Victoria has produced in excess of 2500 tonnes of gold (some 80 million ounces) since gold mining commenced in 1851. More than half of this production was from alluvial sources. The occurrence of large gold nuggets throughout the alluvium provided the greatest fascination on the goldfields and was a feature of some deposits. For example, over 75 nuggets, ranging in size from a few ounces up to 953 ounces, were collected from the Poseidon Lead at Tamagulla. Many large nuggets were discovered on or close to the surface while others occurred in buried palaeochannels.

The Victorian goldfields have produced more large nuggets than any other field. More than 1200 nuggets weighing over 620 grams (20 troy ounces) had been found by 1910, with at least 13 greater than 1000 ounces. The largest, *The Welcome Stranger*, weighed 2520 ounces. In comparison the largest California nugget weighed 787 troy ounces and the largest Russian nugget weighed 1157 ounces.

When significant nuggets were discovered during the 19th century, the Department of Mines recorded the information in a catalogue and assembled newspaper reports. The Department also made replicas of about 100 large nuggets, based on moulds or sketches and photographs. Casts or models were made using plaster of Paris, and were then painted. The collections of the former Department of Mines transferred to Museum Victoria in 1988 included these nugget replicas and associated information.

Since the late 1970s prospectors with metal detectors have caused a revival of nugget discoveries. The largest, *The Hand of Faith* weighing 845 ounces (the 11th largest Victoria nugget) was discovered in 1980. Nuggets greater than 50 ounces are discovered on a regular basis. Where possible, Museum Victoria continues to make replicas of newly discovered large nuggets. The Preparatory staff produce high quality replicas from plaster or silicon compounds and coat them using gold leaf.

This collection of gold nugget replicas is the only visual historical record of these icons of Victorian geology. Recently, Museum Victoria has image-captured all replicas and enhanced the dataset within keEmu database. Shortly this information will be available on a website.

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For several centuries the Slyudyanka region, lying at the southwestern termination of the Baikal Lake, has been of specific research interest – it is really the “Mecca” for mineralogists.

In the middle of the 18th century local people discovered the lazurite deposit in the Slyudyanka River valley. This stone was evaluated as the good one by explorer Laksman who studied Eastern Siberia in 1760s. When his mineral collections were delivered and evaluated at St.Petersburg, Katherine the Great ordered to launch development of the deposit and to decorate with lazurite one of halls in her premises located at Tsarsko-Selsky park.

Large crystals of scapolite (“stroganovite”), apatite (“moroxite”), diopside (“baikalite”), phlogopite and hyalophane from calcite veins of Slyudyanka were supplied in the 19th century to the mineralogical collections of Russia and some European countries as well. In 1837 Permikin discovered one more lazurite deposit in the Malaya Bystraya River valley. Its quality is comparable to the deposit of Afghany lapis-lazuli. Most minerals from Slyudyanka region were described by Koksharov in his monograph.

Early in the 20th century the Radium Expedition of the Russian Academy of Sciences, organized by Vernadsky was exploring the region. The main target objects were granitic pegmatites containing allanite, betafite, samarskite, fergusonite and other minerals with uranium and thorium admixtures.

Productive geological and mineralogical research was undertaken in the Slyudyanka region from 1920 through 1960s. This exploration resulted in discovering large deposits of phlogopite, the important material for electrical machinery. The results of investigations were published in the special volume (1939) and numerous scientific papers. Investigations conducted by Korzhinsky on metasomatic processes forming phlogopite and lazurite deposits contributed essentially. The composition and properties of many rock-forming and accessory minerals were studied at that time. Besides, new varieties of scapolite (glaucolite), diopside (lavrovite) potash feldspar (amazonite) were described.

The thorough exploration of the Malo-Bystrinsk deposit by Ivanov and Sapozhnikov showed wide distribution of afghanite. Some mineral findings were made, e.g. touunkite, and bystrite. In the other parts of the Slyudyanka region Reznitsky reported presence of many new minerals: florensovite, kalininite, natalyite, chromofyllite, vanadiodravite and magnesioicoulsonite.

Good natural outcropping of the region, presence of numerous phlogopite quarries and marble mines provide excellent study objects for students, geologists and excursionists. In time of XI IMA meeting (Novosibirsk, 1978) hundreds of specialists from many countries visited Slyudyanka and other mineralogical sites of the Baikal area. They highly appreciated and admired mineral diversity of the Slyudyanka phenomenon.

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At the time of its foundation, teaching at the Ecole Royale des Mines relied on the “cabinet de curiosité” of G.B. Sage. These samples, increased through confiscations during the Revolution, were mainly used by René Just Haüy, curator of the collections, to write his “Traité de Minéralogie”. If students were already trained in the field, resulting in the definition of a number of rock names, such as “lherzolite, eclogite, ophite, nagelluh”, which remained in the petrographical nomenclature, this early period was nevertheless mainly devoted to systematic mineralogy.

The situation changed drastically when the Ecole entered its present location (Hôtel de Vendôme) in 1815. The different branches of Earth's sciences reached a stage of maturity, and collections, under influence of major personalities: F. Le Play, A. Dufrénoy or L. Elie de Beaumont, were entirely re-organized, according to modern views. Petrography became thus of major importance, in line with new methods of investigation (polarizing microscope), industrial development and world-scale scientific expeditions.

Samples of high historical value entered then the collections, donated e.g. by Prince Louis Napoléon after his travel to Greenland or Egypt, J.P. Alibert (graphite and jade from Eastern Siberia), or F. De Lesseps (Suez and Panama canals). Major events of the time were the “Expositions Universelles”, repeatedly held in Paris between 1855 and 1914. Professors of the Ecole were involved in the organization of these displays which, for the first ones (1855, 1867), attached a great importance to the “ressources naturelles” (mines, building and decorative stones). The Ecole kept at this occasion reference marble samples used for official buildings (Palais Garnier, Sénat), gathered by A. Héricart de Thury or A. Delesse. At the end of the “Expositions”, a number of samples exhibited by foreign participants, were donated to the Ecole: silicified wood from Petrified Forest (Arizona, USA), Cryolites from Ivigtut (Greenland), Calamine (Laurium, Greece).... The first Exposition (1855) had been for Canada “the opportunity to show its vast mineral resources to the rest of the world”. After the show several containers of samples, took the way of the collections where they are still present.

This trend of rock collecting has continued during the end of the XIXth century up, to World War II, despite severe room problems, the core of authentic petrological collections was preserved side to side with mineralogy. Open to the public, experience shows that visitors are also interested by rocks. Reorganisation of the petrological collection in line with present-day science and environnement, while preserving the historical background, is currently the major project of the Musée.

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The Geological Museum of China (the GMC) is the largest museum on geosciences in China. It has not only a variety of minerals but also some high quality and priceless minerals. Nearly 6,000 fine minerals are shown on display in its mineral and gemstone galleries. It has become an important centre where mineralogical and geological sciences are popularized, understood and communicated.

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The Mineral Collection of the “Senckenbergische Naturforschende Gesellschaft” (SNG) (Frankfurt am Main / Germany) is actually older as the foundation of the society itself in 1817. Johann Christian Senckenberg (1707-1772) was extremely interested in minerals and rocks. His collection – together with the private mineral collection of Eduard Rüppell (1794-1884) – formed the basis of the Senckenberg Mineral Collection especially as cultural documentation of old and not anymore existing localities. Between 1847 and 1881 the mineral collection has been improved by the work of Friedrich Hesseberg (1810-1874) and Friedrich Scharff (1812-1881). The Pfeiffer-Belli heritage in 1904 and numerous dedications of Arthur von Gwinner (1856-1931) improved the collection before the First World War. In 1914 an “Institute of Mineralogy” was established by the SNG at the newly founded University of Frankfurt. The assistant of the newly founded institute Hans Schneiderhöhn (1887-1962) got in 1914 an amount of 2,000 marks for collecting samples of the Tsumeb-Otavi-Region (Namibia). Caused by the First World War he came back not until 1919 but with a special Tsumeb-collection of more than 100 excellent scientific samples. An obvious decline of the collection started in 1920 with the sale of numerous valuable platinum nuggets from the Pfeiffer-Belli Collection and the closing of the Section of Petrography and Mineralogy after the death of Wilhelm Schaaf (1855-1923). Considerable amounts of the collection have been handed over to the Institutes of the Frankfurt - University or have been sold. The collection kept without any person in charge up to 1962, when the geologist Siegfried Rietschel (* 1937) started a documentation about all existing mineral samples, but this documentation seems to be disappeared. For financing a new Mineralogy Gallery in the Senckenberg Museum between 2000 and 2004 parts of the collection have been sold; a procedure which came in for criticism because of bad documentation. Since 2005 the residual but still nice collection (including of new donations – e.g., the “Löw von Carlowitz – collection” with about 4,000 mineral samples) will be set up and newly documented.

Mineral collections and museums in Germany: Past, presence, futureH.-P. Scherl¹, G. Simon² and K. Schüermann³¹Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, 44780 Bochum, Germany²Bavarian State Collection of Mineralogy Munich, Theresienstr. 41, 80333 Munich, Germany³Mineralogical Museum of the Philipps-University Marburg, Firmeneplatz, 35032 Marburg, Germany

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In Germany, curating minerals has a long tradition, a fact that immediately becomes evident from the history of classical collections, their establishment and the people in charge. University collections like those of the Humboldt University of Berlin (founded 1781), Bonn (1818), Freiberg (1765), Jena (1779), and Marburg (1790), as well as museums like the State Museum of Mineralogy and Geology in Dresden (1587), the Hessian State Museum Darmstadt (1774), the Senckenberg Natural History Museum in Frankfurt (1817) and the Bavarian State Collection of Mineralogy (1803), are only a very small selection of well-known historical institutions. The people in charge were internationally known authorities, for instance A.v. Humboldt, A.G. Werner, P. v. Groth, F. Mohs, F.A. Walchner, H. Schneiderhöhn, H. Rosenbusch, V.M. Goldschmidt, A. Breithaupt and B. Cotta. At present, the general situation of mineralogical collections in Germany has become very problematic, financial funds and staff having been reduced. In addition, new duties have been imposed upon curators of mineralogical collections. Storing minerals is only one activity. Modern collections have to grow, all samples have to be documented in profound detail, and, finally, the collections have to represent an area of public information and scientific research. Apart from physical geography, geosciences are not taught in German schools. So one of the main tasks of curators at museums and at universities is to attract school classes and general public to the geosciences. With the support of their mineral collections they are able to illustrate the growing importance of applied mineralogy. The impact of mineralogy and crystallography, especially in the field of material sciences, must be brought to the attention of our whole society. Public information is one of the main tasks of mineralogical museums. Mineral exhibitions should introduce the lay public to mineralogy.

One of the main points discussed during various meetings of the working group "Mineralogical museums and collections" of the German Mineralogical Association (DMG) is how to manage the immense amount of data involved using innovative databases and www-technologies. Several curators of mineral collections already have parts or all of their mineral/rock collections computer-catalogued. Finally, to initiate possible international cooperation, we will present on our poster an overview of the most important mineral and rock collections in Germany, together with their major fields of research and interest.

Ko Collection of minerals and the Kyushu University Museum, JapanY. Nakamura¹ and S. Uehara²¹Kyushu University Museum, Kyushu University, Hakozaki 6-10-1, Fukuoka, 812-8581, Japan.

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The Ko Collection of minerals is one of the most important mineral collections in Japan as containing large crystal samples mainly from Japan. The mineral specimens, amounting to about 1,200 (159 species), are mainly crystal samples occurred from Japan, including from Korea and Taiwan in the period 1890's-1930's when metal mining of Japan was most active. It was collected by the late Sokichi Ko, who was a professor of economic geology at the Department of Mining, Kyushu University from 1911 to 1929. The arrangement of the mineral specimens was primarily made by the late Yohachiro Okamoto and is based on the classification of the Dana's System of Mineralogy, sixth edition (1892). Shirozu et al. (1971) published a comprehensive catalogue of the collection. Now, the collection is exhibited in an exhibition room of the Faculty of Sciences of Kyushu University, being in Hakozaki Campus located in Fukuoka city. Regrettably, because of a staff shortage, the collection is open to the public only twice a year, on 11th May and on the third Saturday of November.

Kyushu University has been collecting not only minerals but also valuable scientific specimens that were used for various research and educational activity. The followings are main specimens stored in various faculties of Kyushu University: 280,000 geological specimens, including 3,300 type specimens of fossils, at the Faculty of Science, 100,000 specimens of human bodies and parasites at the Faculty of Medical Science, 4,000,000 insect specimens, including 10,000 type specimens, at the Faculty of Bioresource and Bioenvironmental Sciences and Faculty of Social and Cultural Studies, and 66,000 plant specimens, including 300 type specimens, at the Faculty of Science and Faculty of Bioresource and Bioenvironmental Sciences.

The Kyushu University Museum was established in April 2000 for the purposes of unifying the scattered specimens and constructing databases of the specimens for supporting research and education both inside and outside the university. However, the Museum does not yet have its own buildings at the moment, various exhibit spaces outside the campus have been temporarily used for exhibitions. Scientific specimens and research activities in Kyushu University are also exhibited through the Internet at the website of our museum, <http://www.museum.kyushu-u.ac.jp>. The Ko Collection of minerals is also found at the site with beautiful pictures of minerals of high resolution.

The mineralogical collections of the Geological Museum, Geological Survey of JapanY. Banno¹, M. Bunno¹, M. Aoki¹, M. Haruna², Y. Okuyama-Kusumose¹, and C. Matsue¹¹Geological Survey of Japan, AIST, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan.

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The Geological Survey of Japan (GSJ), which was founded in 1882, owns approximately 400,000 geological specimens that have been collected for researches on mineral and energy resources and geological mapping. The Geological Museum was opened as an annex to the GSJ in 1980 when the GSJ moved to Tsukuba Science City, which is located about 60 km northeast of Tokyo. Geological samples investigated by the GSJ are stored and managed in the Geological Museum. The museum possesses approximately 75,000 mineral samples including ore minerals from Japanese representative metallic and nonmetallic mines. The GSJ mineral collection includes approximately 40,000 registered mineral specimens. They have been acquired either from domestic mineral occurrences (~80 %) or from abroad (~20 %), and about 40 % have been stored in digital data. The collection covers approximately 60 % of the mineral species described from all over Japan, including five type specimens: kamiokite, toyohaite, wadalite, magnesiosadanagaite and aspidolite. Several unique and valuable ex-private collections are included in the GSJ collection, such as the Okamoto Mineral Collection (~3,400 specimens collected by Dr. Y. Okamoto), the Kinoshita Mineral Collection (~1,700 specimens collected by Prof. K. Kinoshita), the Nambu Ore Collection (~1,500 specimens collected by Prof. M. Nambu), and the Inayoshi Mineral Collection (~7,000 specimens collected by Mr. T. Inayoshi). Most of the registered mineral specimens are stored in the repository according to chemical classification. Minerals in each chemical group are further arranged in alphabetical order. About 340 specimens of minerals, 70 % domestic and 30 % from abroad, are exhibited to public in the gallery of minerals, rocks, and fossils. One of the most remarkable specimens in this exhibit is the biggest native gold nugget in Japan (362.5 g) from the Shishiori mine. World-famous, giant stibnite crystals from the Ichinokawa mine are also noteworthy. The displayed specimen is an aggregate of columnar crystals with sword-like terminations. Single, columnar crystal of gypsum from Udo mine reaches 73 cm in length, the largest crystal of this species in Japan. World-class crystals of pyroxmangite from the Taguchi mine also attract attention.

Special exhibition, "Jadeite", and collection of jadeite-bearing rocks in NSMS. Matsubara¹, K. Yokoyama¹, R. Miyawaki¹, and Y. Tsutsumi¹¹Department of Geology and Paleontology, the National Science Museum, 3-23-1, Hyakunin-cho, Shinjuku, Tokyo 169-0073, Japan.

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Jadeite or "Jade" is one of most popular gem stones in Orient. The National Science Museum (NSM) had a special exhibition on jadeite from November 2004 to February 2005. The authors were in charge of preparation of the special exhibition in these years.

The name of "jade" is usually used not only for jadeite, but also for nephrite. These two different materials are distinguished from each other in Asia. Jadeite is much valuable than nephrite. The culture of Japanese jadeite artifacts has the longest history, ca 5,000 years in the world. The culture was suddenly disappeared in early 8th Century as a mystery in Japanese history. The rediscovery of jadeite from Itoigawa in 1938 was an impact for historians as well as for geologists. This special exhibition was the first comprehensive exhibition on jadeite from viewpoints of natural and social sciences.

Jadeite is an important mineral in geology as a geothermometer and/or geobarometer. Occurrence of jadeite is confined to serpentinite zone in the high-pressure metamorphic belt. So far jadeite-deposits have been developed in several localities in the world. Among them, great mass of jadeite as gem stones is from Myanmar.

Jadeite with gem quality occurs at Itoigawa area in Japan, but is rare now. Ancient jadeite-artifacts have been excavated in several hundreds remains, mostly in graveyard, in Japan. It is now accepted that the jadeites artifacts were brought parentally from Itoigawa area, because deposit in Myanmar was discovered in early 18th Century. Ten occurrences of jadeite-bearing rocks have been recognized in Japan, but most of them have poor quality as a gemstone.

For the preparation of the special exhibition, "Jadeite", jadeite-bearing rocks were collected from all the ten localities in Japanese Islands and many gemstones in jadeite-deposits in the world were purchased or donated. Jadeite specimens in NSM have increased in around two hundreds through the special exhibition. In addition to the enlargement of collection, it is worth to note that NSM and Fossa Magna Museum at Itoigawa City have discovered three new minerals in jadeite-bearing rocks from Itoigawa area: itoigawaite, renegeite, and matsubaraite. This is an example of special exhibition as driving force for the enhancement in collection building.

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Akita is one of the most geologically exciting areas in Japan. Neogene stratigraphy of northeast Japan has been established in Oga-Akita region as type localities. There are also a number of Quaternary volcano and evidence of crustal movement with active faults and folds in Akita. Akita is used to be the most prosperous mining areas in Japan, represented by oil fields in coastal of the Japan Sea and Kuroko-type deposit (strata-bound polymetallic sulfide-sulphate deposits) in the northeastern mountains area called Hokuroku. The formation of both natural resources is related to a middle Miocene tectonic event: opening of the Japan Sea. Since the foundation of Akita Mining School in 1910, a large number of valuable geology-related specimens and mining industry items have been collected for education and research. In 1961, a circular exhibition hall and a research building of Mineral Industry Museum were constructed with donations from alumni of Akita Mining School and Mining College of Akita University on a terrace on Tegata-yama hill, from which there is nice view of Oga Peninsula and Chokai active volcano.

About 4000 specimens of 16000 registered specimens of rocks, minerals, ores, fossils, tools used in mines, miniature models of mines and so on collected from all over the world are exhibited in our museum. The greatest attraction is a huge collection of metallic mineral and metal ore specimens from mine in Japan, especially in Akita, which are exhibited on the ground floor with many systematically distributed kinds of rock, mineral and ore. On the first floor, there are exhibits on the history of the earth and life, geology and resources in Akita and mining related items. Models of mine gallery and shaft imported from Germany in 1922 by Prof. Tsuboi, who studied in The Freiberg University of Mining and Technology, are also on display. Exhibits of energy resources and processing from natural resources to industrial products are displayed on the 2nd floor. Of particular interest concerning with economic geology in this floor are the specimens of recent hydrothermal precipitations on the ocean floor, which are displayed with a specimen of Kuroko ore for comparison.

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The Mitsubishi mineral collection consists of mainly "The Wada Collection", which is named after the collector, Dr. Tsumasirou Wada (1856-1920), and is one of the most representative mineral collections in Japan. Koyata Iwasaki of the Mitsubishi limited partnership was donated Wada's collection in his will. This collection was composed of 158 species, over 3000 samples, and some of them deserve to be named after national treasures. Most samples are being exhibited at the Central research Institute of Mitsubishi Materials Corp (Omiya, Saitama) and at the mineral museum built at the old mine Ikuno location (100km northwest of Kobe). For example, large and splendid stibnite, an antimony-sulfide minerals (Sb_2S_3) are very famous.

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1. Location and history Located at 499 Iryuda, Odawara, Kanagawa Prefecture, southeastward of Hakone Volcano. Separated from section of Natural History Section of Kanagawa Prefectural Museum, Yokohama, in March 1995. 2. Exhibitions Space: 2 floors with 4 halls. Total display area: 5,075m². Contents: The Earth- Solid Earth and its Formation; Life- Its diversity and history; Kanagawa - its land and life -; Human in Nature - Present and Future -; Encyclopedia by displayed objects. Altogether about 10,000 specimens are displayed. 3. Scientific collections Zoology: Sakai Collection (Crabs), Odawara Collection (Crabs), Shikama Collection (Shells), Nomura Collection (Shells), Nagai Collection (Insects), Abe Collection (Insects). Botany: Furuse Collection (Herbarium specimens), Ohba Collection (Herbarium specimens). Earth sciences: Sakurai Collection (Minerals), Nagami Collection (Minerals), Hagiwara Collection (Minerals), Case Collection (Fossils), Sakurai Collection (Fossils), Ozaki Collection (Fossils). About 500,000 scientific specimens are stored in total. 4. Research activities Researchers include specialists of zoology, botany and earth sciences, 21 in total. Bulletin of Kanagawa Prefectural Museum (Natural Science) published annually, averaging 100 pages with 10 articles. 5. Public service Public-opened library with ca. 15,000 copies. Daily, 15 minutes film services. Monthly, excursions and lectures of zoology, botany and earth sciences. Currently 56 members are in explanatory works on exhibited objects, including the services for handicapped persons. Museum shop is in public-opened area. Focused to the handling of natural history books and of scientific toys. 6. Mineral Collections

Sakurai Collection: A part of the largest private mineral collection in Japan formerly owned by Dr. Kin-ichi Sakurai, an excellent amateur mineralogist. After his death, his mineral collection was donated to The National Science Museum of Japan and Kanagawa Prefectural Museum of Natural History, respectively. The latter consists of about 15,000 objects in total, nearly all of them from Japan, including the holotype of okhotskite (No.KPM-NM0048571).

Nagami Collection: Donated by Mr. Itaru Nagami, amateur mineralogist and retired high school teacher of science. It consists of about 3,500 objects from Japan and foreign countries. From 1945 to 1950, he taught the third author chemistry and physics.

Hagiwara Collection: Collected by the late Mr. Yosuke Hagiwara, a mineral collector. About 900 gems and mineral specimens are included.

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Nakatsugawa Mineral Museum is a municipal museum of earth sciences, established in 1998, and is located in Naegi district, Nakatsugawa City, Gifu Prefecture, Japan. The district is known as a famous geological field of the Naegi-Agematsu Granite which is one of the Late Cretaceous-Paleogene granitic rocks intruded in central Japan.

The main objectives of the museum are following three. The first is the introduction to pegmatite fields extending over the district and various minerals therein, such as quartz (smoky quartz in particular), topaz, "naegite" (a variety of zircon), fergusonite, cassiterite, and beryl, from the scientific as well as industrial points of view. The second is provision of opportunities for youths to study natural history including general geology and mineralogy. Museum facilities are especially intended to be freely used by schoolchildren to encourage their interests in the surrounding nature. The museum is expected to be an effective educational institution. The last is management of the Nagashima Mineral Collection, which is the outcome of the collaboration of hunting and characterization of minerals done by the Nagashimas. Otokichi Nagashima (1890-1969), who was born in Naegi, contributed to modern mineralogy in Japan with his donations of mineral specimens to academic mineralogists. His son, Kozo Nagashima (1925-1985) was a pioneer of the chemistry of rare-earth minerals in Japan. The Nagashima Mineral Collection, consisting of more than 3,000 specimens, is installed in the museum and widely used for public exhibition. This collection covers many kinds of pegmatite minerals not only from the Naegi district but also from all over the world. In particular, the minerals often contain "rarer elements," which are either rarely found in the earth's crust or less available as major deposits.

Fossa Magna Museum in Itoigawa, Central Japan

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Fossa Magna Museum (FMM) is the Itoigawa municipal geologic museum opened in 1994. The Fossa Magna is a zone of late Cenozoic subsidence that has thick sediments and that cuts across central Japan. Its western rim, the Itoigawa-Shizuoka Tectonic Line, has also been a major active thrust in Japan. The Fossa Magna has long been noted as one of the most important tectonic features of Japan. It was discovered and named by E. Naumann who is German geologist and left great contribution to the modernization of the geology of Japan. Though a lot of natural history museums were in the Fossa Magna region, there was no museum where it had introduced the Fossa Magna and Dr. Naumann in detail until the opening of the FMM.

The FMM is built in the park with the area of 120,000 m² in the hillside of the height of 110 m above sea level. The Japan Alps and the Sea of Japan are seen from the FMM. The staff members in the FMM are one director, three curators and four clerks. Visitors during a year are about 50,000 people. The exhibition room area is 1,097 m² and the gross floor space is 2,452 m². The FMM is one-storied construction for the handicapped and senior person's use, and the exhibition of heavy specimen. The exhibition room has divided into seven as follows. 1st: the birth of the Earth, 2nd: the fascinating stones, 3rd and 4th: geology of Itoigawa, 5th: the Naumann gallery, 6th: the Fossa Magna Hall and 7th: multipurpose gallery.

In Japan, the museum where the mineral and rock specimens have been exhibited is unexpectedly few. However, there are a thousand of mineral and rock specimens in the FMM because Itoigawa is the first jadeite discovery field in Japan. The study of jadeite is one of the important research themes of the FMM. Four Sr-dominant new minerals such as itoigawaite, rengerite, matsubaraite and niigataite have been discovered by researching jadeite after the opening of the FMM. A unique feature of the FMM is frequent change in exhibition because the exhibition case in the FMM is a former opening. Another unique feature is to see the analysis machine such as EPMA, XRF and XRD, and thin section production room from the passage. The EPMA is not only used for mineralogical and petrological research also for archeological study to identify ancient beads.

Application of mineralogy and petrology to lifelong education in the Museum of Nature and Human Activities, Hyogo

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The Museum of Nature and Human Activities, Hyogo (called Hyogo ken-ritsu hito to shizen no hakubutsukan: HITOHAKU in Japanese) has opened since 1992. The purpose of this museum is to help Prefecture Hyogo residents and other people appreciate the beauty and dignity of the natural environment around us. Here visitors can enjoy unique exhibits and educational programs about nature and human life.

1. Outreach programs

The Museum has an outreach program called "HITOHAKU CARAVAN" which is operated by the executive committee formed by members of the museum and peoples of the community. The committee makes a suitable program for the community and put research, seminar and small exhibition into effect.

2. Programs at the exhibition area in the museum

Some event programs are put into effect at the permanent and temporary exhibition area. These events are not explanation but interpretation or facilitation on the exhibition. For example, many children make a sketch of the exhibits at "Artist Day". They observe the object in detail by the sketch and additional interpretations promote interesting to the exhibitions.

3. Two examples of petrological and mineralogical workshop in the programs

A. Kaleidoscope made by polarized sheet and cellophane tape

(1) Explanation on mechanism of the polarized sheet (2) Making the kaleidoscope by polarized sheet and cellophane tape (3) Observation of quartz, calcite and muscovite by the polarized sheet (4) Observation of thin sections using polarized light microscope

Participants understand the mechanism of the polarized light microscope and are interested in optical property of minerals by this workshop.

B. Making a fire using chert and teeth of saw

(1) Tool for fire making using teeth of saw (2) Research the convenient stones for fire making (3) Making a fire using chert (4) Lecture on the characteristics and origin of chert

Participants understand the characteristics of chert, and are interested in origin of Japanese Islands by this workshop.

Exhibition of rocks and minerals is not satisfactory in the HITOHAKU. Therefore, they are opened as temporary exhibitions with difference disciplines. The temporary exhibitions, seminar and above-mentioned programs are maintained by interdisciplinary studies with biology, archaeology, history and others.

Japan's oldest rocks and minerals stored at Nagoya University Museum

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Nagoya University Museum (NUM) holds an important collection of rocks and minerals. Among the most significant of its holdings are samples of the oldest rocks and minerals in Japan, recovered from the Jurassic Kamiaso Conglomerate in the Mino terrane of central Japan. A substantial specimen (1.0 x 0.8 x 0.5m) of the Kamiaso Conglomerate shows the occurrence of rounded cobbles and pebbles of gneiss, together with abundant angular to subrounded clasts of shale and sandstone. Paragneiss and orthogneiss cobbles and boulders from the Kamiaso Conglomerate are all well-rounded and range in size from 5 to 80 cm. They have been extensively studied by various dating methods.

K-Ar and Rb-Sr mica ages of gneiss specimens range from c. 1200 to 1700 Ma. Orthogneiss specimens having whole-rock isochron ages of 2060 Ma Rb-Sr and 2070 Ma Sm-Nd are the oldest rocks in the Japanese Islands. Granite was emplaced at an age of c. 2100, and subsequently underwent upper amphibolite facies metamorphism at c. 1700 Ma. Detailed CHIME (Chemical Th-U-Pb Isochron Method) dating of zircon and monazite from the oldest orthogneiss specimen has revealed the existence of unusually ancient recycled Archean zircons as old as c. 3400 Ma. The 3400 Ma core of zircon, rimmed by a c. 2000 Ma prismatic overgrowth is the oldest mineral in Japan. SHRIMP U-Pb geochronology on the orthogneiss has also shown the existence of a zoned prismatic zircon which has a c. 3300 Ma core rimmed by a c. 1900 Ma magmatic overgrowth.

CHIME dates for detrital monazites from Jurassic sandstones in the Mino terrane have shown the ubiquitous occurrence of c. 1700 Ma monazites. This suggests that widespread monazite-bearing metamorphic rocks were the provenance of the Jurassic clastic rocks. The oldest rock and mineral specimens housed at NUM possess an important key to Precambrian crustal evolution in East Asia as well as the Mesozoic tectono-sedimentary history of the Japanese Islands.

KEYWORDS: Oldest rock in Japan, Oldest mineral in Japan, Recycled Archean zircon, Precambrian geology, CHIME geochronology, Kamiaso Conglomerate, Mino terrane

Detailed records and sketching of minerals by collector, Nambu Mineral Collection of Ibaraki Nature Museum

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Ibaraki Nature Museum was opened in 1994 as a new type of the museum for the 21st century based on the concept "learning from the past, knowing the present and foreseeing the future", located in 50km north from Tokyo, and now over 400,000 people are visited this museum in every year.

1. Mineral Collections

About 7,800 mineral specimens are possessed in this museum, and especially Nambu Mineral Collections which are collected by Hideki Nambu, design engineer of dressing plant of mine, are contained. This collections consist 3,150 mineral specimens, mainly of hydrothermal minerals which were collected at Mitsubishi-organized 6 mine (Ikuno, Sado, Osarizawa, Arakawa, Takatori, Teine) and other minerals from Japan, such as teinite and other tellurium minerals from Teine mine, triangular chalcocopyrite from Arakawa mine, stibnite from Ichinokawa mine. Remarkable of this collection, collector sketched carefully and recorded in detail about each specimens, and these sketches and records are possessed carefully with mineral specimens (and added 2,604 specimens collected by Yoshiro Komuro, we called "Nambu & Komuro Mineral Collections"). And about 300 specimens of these are displayed as permanent exhibitions for visitors.

2. Exhibition and educational activity

In the permanent exhibition of Ibaraki Nature Museum, minerals are shown to visitors for having interests in various concepts, such as origin of deposits and minerals, fluorescence, presence of magnetism, radioactive minerals, uses as gems, and classification by chemical composition. In addition to them, the minerals from Ibaraki prefecture are locality-classified and shown to visitors.

And this museum performs education activity frequently, for example, field trips, kid workshops, workshops for families (called "Sunday Science") and nature seminars. Through these museum activity, we expect children come to think about nature as imminent existence by various opportunities.

Kitakyushu Museum of Natural History and Human History: Activities on mineralogy and petrology

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Kitakyushu Museum of Natural History and Human History (KMNH) is one of the largest museums in southwest Japan. KMNH was established in 2002 by integration of prior city museums of natural history, history and archeology. The exhibition is centering on coexistence of human and nature. About 6,000 exhibits show evolution of the earth, life and human. Free public lectures and activities are frequently held by staffs. KMNH also has an institute of natural history dealing with geology, paleontology, zoology and ecology. The research results have been published in journals as well as in the bulletin of KMNH.

KMNH stocks more than 12,500 mineralogical specimens and more than 5,500 petrological specimens. The representative mineralogical collections are the Tadaichi Matsumoto Collection and Kyushu Institute of Technology Collections. These collections are characterized by a lot of ore specimens from the eastern Asia, which have been mainly collected before/during the World War II. Although the specimens are typically small size, they are important to investigate ore deposits and mining in the eastern Asia.

The institute of KMNH carries out mineralogical and petrological researches using own equipments. The present main subjects are (1) jadeite from the Nishisonogi metamorphic rocks, Kyushu, Japan, (2) fluid-rock interaction in the Nishisonogi metamorphic rocks and (3) skarn deposits in Kitakyushu, Japan. A PANalytical MagiX Pro X-ray fluorescence spectrometer and a Perkin-Elmer 2400 II CHN element analyzer at KMNH are used to study these metasomatic products. These equipments are also employed for joint researches with the other institutes and for education of university students.

Introduction of Masutomi Geology Museum

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Masutomi Geology Museum was established by the late Dr. Kazunosuke Masutomi, a pharmacist on Oriental medicine, within his building for home-cum-office at the west side of Kyoto Palace Park in 1973. It is organized as a foundation with approximate 20,000 specimens, several thousands of books related to geology and laboratory equipments such as an X-ray diffractometer.

The collection consists of mineral, rock, ore and fossil specimens. The major part of collection is the private collection of Dr. Masutomi. The specimens and the books have been enhanced every year as the results of activities by the members of Museum Society.

The building of museum with floor space of 300 m² consists of three floors. The exhibition room is on the third floor. It is opened to the public on Saturdays, Sundays and national holidays. A group such as school lessons and training is acceptable on the weekdays on demand. Unusual rocks and minerals that represent each Prefecture in Japan are exhibited in glass cases. Microscopes are available for visitors in the exhibition room. Moreover, the guidance member is always ready and waiting for the questions by visitors. Identification service is made for the visitors by the staff.

The second floor is provided with laboratory and library. A powder X-ray diffractometer, as well as a diamond disk rock cutter, a grinder and a polarizing microscope, is usually utilized to assist the researches by amateur collectors. Books, loupes, rock hammers and mineral specimens are available at the museum shop on the first floor.

The museum is indeed small in scale, but is an active center for amateur and professional geologists. The Mineral Show is held under the auspices of the museum for propagation of the geological sciences, in the spring in Osaka and in the autumn in Kyoto. In addition, field trips and short lectures are regularly organized.

Introduction of the Kiseki Museum of World Stones

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The Kiseki Museum was established at the southern base of Mt. Fuji in 1971 as the first comprehensive museum in Japan to specialize in stones. Beginning was that the founder Ju-ichi Uemoto requested Dr. Kazunosuke Masutomi (1901–1993), one of the authority of mineralogy and also the founder of the Masutomi Geology Museum, to expertise a black and heavy spherical stone found in Hakusan, Gifu-prefecture (later the stone was certified as nodule of iron sulphide). The museum started with over 400 mineral specimens of Dr. Masutomi, and now, out of some 12,000 specimens in total, about 1,600 are permanently on exhibit. As stones are difficult to classify and have some image of insensitiveness, they are popular among limited people in Japan. Nomenclature may sound monotonous to many unfamiliar people. Our museum is introducing these unfamiliar stones with the viewpoint of “Kiseki”. Within the word “Kiseki” which consists a part of the museum name, there is Dr. Masutomi’s long-cherished aim of popularizing earth science. The word “Kiseki”, meaning the way of viewing stones based on the first impression of ordinary people, was created by Sekitei Kinouchi (1724–1808), who had published an enlightening book “Unkonshi” in the middle Edo period (about 200 years ago) that had caused public interest in stones as collectables. Although some “Kiseki” names may be unscientific to professionals, the concept of “Kiseki” is just like that of advertising copy, and its attractive idea really catches people’s hearts. Based on Dr. Masutomi’s spirit, the Kiseki Museum of World Stones takes a stance of placing importance on this sense-oriented concept of “Kiseki” as a means to arouse people’s interest in stones, and thus we plan unique exhibits.

Mineral collections of Natural History Museum of Tohoku University

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Natural History Museum of Tohoku University locates at Sendai, Japan, and exhibits geological and geographical collections that include minerals, rocks, ores, fossils and maps. It was founded in 1995. Before the establishment of museum, the mineral collections were mainly used for educations of mineralogy in Institute of Mineralogy, Petrology and Economic Geology, Faculty of Science. The mineral collections consist of the Takimoto, Shimadzu Corporation and Krantz collections, and the total numbers of mineral sample are over 8000. The Takimoto and Shimadzu Corporation collections consist of samples from Japan. Dr. S. Takimoto is one of authors of the second edition on “Wada’s Mineral of Japan”, published in 1916. These samples were mainly collected more than 60 years ago, and are typical and classic samples like the Wada collection. However, all samples are relatively small and up to 10 x 14 cm.

A systematic display of mineral specimens can be seen on the grand floor of exhibition hall. This museum is now managed by The Tohoku University Museum. Visitors and students with research interests in the stored collections can view them by prior arrangement with the collection manager. We construct digital catalogue of the collections, and a part of the database is available on our web site.

(http://webdb2.museum.tohoku.ac.jp/data_base/mineral/koubutu/index.htm)

Introduction of the Natural History Museum and Institute, Chiba

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The Natural History Museum and Institute, Chiba (called "Chiba ken-ritsu chuo hakubutsukan" in Japanese) is a facility of Chiba Prefecture, established in 1989. It is located about 20 km southwest from Narita Air Port and 20 km east from Tokyo Disney Land.

Research and Education Activities

Main purpose of the museum is to investigate the origin and the nature of the environment of the Boso Peninsula (Chiba Prefecture), and to contribute its conservation. The museum also offers a comprehensive program of lectures and field trips throughout the year. Seventy research curators work in the museum to execute this purpose. They conduct original research in diverse fields including zoology, botany, ecology, human history, and earth sciences. In earth science, twelve staffs investigating in the field of paleontology, petrology and mineralogy, sedimentology, geomorphology, and remote sensing technology. A unique feature of the museum is our Ecology Park, an outdoor living exhibit which recreates the various natural habitats, including rocks, found in the Boso Peninsula.

Collections

Because Tertiary to Quaternary continuous clastic sediments are widely exposed in this area, hard rocks show very limited distribution in the Boso Peninsula. The main petrology and mineralogy collections of the museum have been obtained from the Boso Peninsula, especially the Mineoka tectonic belt (Tertiary ophiolite) located southern part of the Peninsula, and specimens of noted tephra key beds obtained from the Tertiary to Quaternary sedimentary sequences. In addition, there are some donated private collections of minerals which include specimens from whole of Japan and many foreign countries, such as Mr. Toshiaki Suzuki Collection. About 8,700 rocks and 1,300 minerals in the museum are registered in computer database, and partly been opened to public on web site (<http://www.chiba-muse.or.jp>).

Publications

The museum publishes two annual scientific reports, Natural History Research (NHR) (in English with Japanese abstract), and Journal of the Natural History Museum and Institute, Chiba (in Japanese or English).

In addition to these periodical publications, some special issues are also occasionally published. It features heavy volume of a monograph, or collected articles under one cover. Earth Science Catalogue Series include the catalogues of the noted tephra key beds in the Peninsula (in Japanese), and the catalogue of the minerals of the Peninsula (in Japanese).

Geological exhibition of the Hokkaido University Museum and the database for the collection of rocks, minerals and ores

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Over the 130 years since the foundation of Hokkaido University in 1876, many scientists of the university have studied and collected materials. As a result of their efforts, today we are able to take pride in a collection of over 4,000,000 individual items, and about 11,000 type specimens. Based on the discussion on the best way to store and manage the collection and to make materials available for practice use, the Hokkaido University Museum is established in 1999 and has opened the exhibition rooms of 1st and part of 3rd floors in 2001 as 125th anniversary of the university utilizing the old Faculty of Science building constructed in 1930.

The present exhibition rooms are composed of "History of Hokkaido University and Academic Thematic Exhibition" in the 1st floor, "Sustainable Campus" in 2nd floor, and "Academic Exhibition of Specimens in the Hokkaido University" in 3rd floor.

Principal geological exhibition is mainly in the Academic Exhibition room of "The Island Are -The place where the northern land and the ocean meet-". About 1,000 specimens of rocks, minerals, ores and fossils are displayed in the rooms with new minerals discovered in Hokkaido and/or by the researchers of Hokkaido University. Otherwise, many rocks including ores and minerals are also displayed in the several corners of other exhibition rooms related with the exhibition theme in the museum.

Total storage of the geological specimens in the museum is roughly as follows; Rocks: 5,500, Minerals: 5,500, Ores: 6,000, Fossils: 19,000 as the sum total about 36,000. Many valuable and important specimens such as the type specimen are also contained in these. We have partly completed the construction of individual database for these storages. Conception of the museum database on the geological collections has realized to be "Minerals specimen database" since 2001, "Database for Geologic Specimen & Phenomena" since 2001 and "The Kamchatka Metallogenic Resource Database" since 2005 for the research field of Earth Science. They include digital informations of photo image, rock and mineral name, sampling location, collector, description and so on. Each database is now available for internet access in the Museum Website. The museum database contributes to the development of Earth Science study and the public benefit for culture and industry.

The Wakabayashi Mineral Collection

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The Wakabayashi Mineral Collection is one of the most valuable collections of The University Museum, The University of Tokyo stocked more than 23,000 mineral specimens. The Collection is famous for its scale, rarity and scientific value (and is) composed by 1932 specimens of 182 species, included element minerals of 10 species, silicates of 64, sulfides of 44, oxides of 21, and so on. It is known as one of the three best mineral collections in Japan as well as the Ko Soichi Collection (Kyusyu University) and the Wada Mineral Collection (Ikuno Mine).

Dr. Yaichiro Wakabayashi (1874-1943) was well known as a great mineral collector as well as a celebrated mining engineer. Soon after his graduation from the Imperial University of Tokyo (presently, the University of Tokyo), he entered the Mitsubishi Company, Ltd. and started his career as a mining engineer. Throughout of the year of his activities, he collected Japanese, Chinese and Korean minerals vigorously. On the occasion of his retirement, his entire collection was donated to Mineralogical Institute of the Imperial University of Tokyo, and after that, transferred to the University Museum.

Wakabayashilite ((As, Sb)₁₁S₁₈) was named after Dr. Wakabayashi and first discovered in a specimen from Nishinomaki Mine, Gumma Prefecture on 1970, mentioned in "Introduction to Japanese Minerals" published by the Geological Survey of Japan. Its crystal forms needle-like shape and produces with orpiment, so that it had been categorized as a sort of orpiment. On 1974, The Wakabayashi Collection was surveyed in the Univ. Museum by Sadanaga & Bunno. In this study, it is discovered that one of orpiment specimens from Nishinomaki Mine described by Dr. Wakabayashi is Wakabayashilite itself.

This collection includes other famous minerals, such as quartz with Japanese twin from Otome Mine (Yamanashi Pref.), bismuth from Ikuno Mine (Hyogo Pref.), Stibnite from Ichinokawa Mine (Ehime Pref.) and moonstone from Cheung-san, Korea.

O31-01

Giving names is not as easy as one thinks (J.W. von Goethe, 1807)

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The Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) was established in 1959 for the purpose of controlling and reviewing all proposed changes in nomenclature (new names, discreditations, changes in definitions) and of rationalising mineral nomenclature (international uniformity as far as may be practicable). The CNMMN has meanwhile taken a decision on more than 4000 minerals and mineral names, has brought order in many mineral groups (e.g., micas, amphiboles, pyroxenes, zeolites, labuntsovites, eudialytes, sulphosalts, epidotes, tourmalines), and has formulated general principles (definition of a mineral, nomenclature of solid solutions, polytypes and synthetic substances).

From the classical period until today, there have been two problems in mineralogical nomenclature: what are proper names for minerals, and how should they be composed. From the start there has been a dichotomy in rational and irrational nomenclatures (in Greek-Roman times, e.g., hematite and galena vs. nephrite and amethyst, nowadays, e.g., arcubisite and phyllotungstite vs. mandarinite and griceite).

Abraham Gottlob Werner was the first (at the end of the 18th century) to formulate clear guidelines for a rational naming of minerals, but he was also the first to disobey them by giving names after persons (prehnite, vivianite) and localities (vesuvianite, aragonite). From Werner until the formation of the CNMMN in 1959 there has been no control on mineralogical nomenclature, and the current CNMMN guidelines (most recent version: 1998) for naming minerals reflect the established historical diversity that grew during that period. A radical change of the nomenclature (as proposed, e.g., by Povarennykh in the 1960-70s) would thus not only be undesirable, it certainly would be impracticable. Mineralogy will thus have to live with inconsiderate names (e.g., bakhchisaraitsevite, pääkkönienite, uchachacuaite, vandendriesscheite, zhemchuzhnikovite) and with 'double names' so despised by many (e.g., henritermierite, thereseamaganite, thomascarkite, jacquesdetrichite).

But the CNMMN should/could do something about schemes which lead to such improbabilities as sodic-ferri-clinoferroholmquistite, and to easily corrected inconsistencies in prefixes (sodicgedrite vs. natrotantite; aluminotungstite vs. aluminoceladonite; arsenoclozite vs. arsenogoyazite vs. arseniosiderite), of two-word names (cobalt pentlandite, potassium alum, sodium boltwoodite), and of unnecessary hyphens (nickel-zippelite vs. nickelschlofite; hydroxyl-herderite vs. hydroxyllestadite). The use of prefixes in names (as desired by the CNMMN guidelines) for new minerals simply related to existing ones creates serious identification problems without chemical analyses, e.g., the division of apatite into hydroxylapatite, fluorapatite and chlorapatite. Such problems have been avoided by using suffixes in groups like zeolites, labuntsovites, arrojadites and epidotes.

O31-02

Alkali and hydrous sulfide minerals: classification and genetic aspect of crystal chemistry

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Sixteen sulfide minerals containing species-forming K, Na, Cs or/and H₂O molecules are known: nine anhydrous alkali sulfides (djferisherite, bartonite, chlorbartonite, galkhaite, rasvumite, pautovite, murunskite, chivilevite, caswellsilverite), four sodium-hydrous sulfides (erdite, coyoteite, gerstleyite, schöllhornite) and three sulfides containing only H₂O but no alkali metals in their idealized formulae (orickite, wilhelmramsayite, cronosite). In fact, the latter also contain significant admixtures (0.1 wt.%) of K or/and Na. Thus, alkali-free hydrous sulfides are unknown in nature for sure. Alkali and hydrous sulfide minerals are related also crystallochemically and genetically. The most important crystallochemical feature of alkali sulfides is arrangement of alkali atoms in structures. These minerals can be classified to three topological types using this sign: zero-dimensional (alkali atoms are isolated, e.g. djferisherite, bartonites, galkhaite), unidimensional (alkali atoms form chains in tunnels, e.g. rasvumite, pautovite, erdite), and two-dimensional (alkali atoms form layers, e.g. murunskite, chivilevite, caswellsilverite). The type determines properties: ability of leaching and exchange of alkali, conductivity character etc. All these sulfides are microporous minerals (Makovicky, 2005). Crystallochemical roles of larger K, Cs, Rb (and Tl) and smaller Na in sulfides are essentially different. Anhydrous sulfide minerals show strong affinity to larger alkali atoms while hydrous sulfides "prefer" Na. Recent discoveries of sulfides extremely enriched by Cs and Rb, especially pautovite, CsFe₂S₃, demonstrate earlier-unknown feature of geochemistry of these elements in peralkaline formation. Strong fractionation of K, (Cs+Rb) and Tl between simultaneously crystallized alkali sulfides of different topological types takes place. In the Palitra peralkaline pegmatite in Lovozero complex, Kola, Russia, chlorbartonite contains 9.5 wt.% K and 0.2% Tl; pautovite: 36.1% Cs, 1.3% Rb, 0.5% Tl and 0.2% K; murunskite: 24.7% Tl and 7.4% K. Layered sulfides can loose alkali atoms with their substitution by H₂O molecules. An example is the evolution chain: caswellsilverite, NaCrS₂ → (Na leaching, hydration) schöllhornite, Na_{0.3}CrS₂·H₂O → (cation exchange, hydration) cronosite, Ca_{0.3}CrS₂·2H₂O (Britvin *et al.*, 2001). It seems that hydrous sulfide minerals were formed mainly (only?) as a result of alteration of their alkali proto-phases. From this viewpoint, presence of alkali in all hydrous sulfides and occurrence of hydrous sulfides mainly in peralkaline assemblages become well-explainable. Galkhaite, (Cs,Tl)_{0.5}(Hg,Cu)₄(As,Sb)₄S₁₂, is only cesium mineral in some ore deposits, sporadically major constituent of mercury ores. Because of its unique "broad-porous" structure, galkhaite fixes mobile Cs and becomes principal geochemical indicator showing high activity of this element in the process of formation of mercury and gold deposits including very important Carlin-type objects.

O31-03

Crystal chemistry of the vicanite group

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A new mineral species from the Hundholmen granitic pegmatite, north Norway, can be added to the vicanite group, comprising okanoganite-(Y) and vicanite-(Ce). The chemical and structural data on the new mineral have significantly added to the understanding of the crystal-chemical properties of these rare minerals. There are three distinct layers parallel to (001) in the structures of these minerals (space group *R3m*):

- Layer A contains an octahedron with (Al,Fe³⁺,Ti) as the central atoms, sharing corners with six SiO₄ groups in the form of a pinwheel. B(1)O₄ tetrahedra form threefold rings, and each B(1)O₄ tetrahedron of the rings shares a corner with one SiO₄ tetrahedron, forming an (Si₃B₃O₁₀)¹⁵⁻ polyanion.

- Layer B contains a tetrahedron which may incorporate variable amounts of As⁵⁺, P, Si (As1 site). This tetrahedron occurs in two orientations with the same probability of occurrence. In vicanite-(Ce), a B(2)O₃ triangle is also present in this layer.

- Layer C contains two very close polyhedra, of As³⁺ in three-coordination (As2 site) and (Na,Ca) in ten-coordination, which are mutually exclusive. The As2 site is empty in okanoganite-(Y).

A three-dimensional network of five different polyhedra with coordinations from eight to ten (M1 to M5) contains Y, REE, Th and Ca and provides connections among the three layers.

Okanoganite-(Y) [described in 1980, crystal structure published in 2004], has the simplified formula: (Y,REE,Ca,Na,Th)₁₅(Fe³⁺,Ti)Na(P,Si)Si₆B₃(O,F,OH)₄₈.

Vicanite-(Ce) [described in 1995, crystal structure published in 2002], has the simplified formula: (Ca,REE,Th)₁₅Fe³⁺Na₃As₁₅(As⁵⁺,P)Si₆B₃(O,F)₄₇ (x = 0.58).

The simplified formula of the new mineral species from Hundholmen (IMA 2006-005) is: (Y,REE,Ca,Na)₁₅(Al,Fe³⁺)Ca_xAs_{15-x}(Si,As⁵⁺)Si₆B₃(O,F)₄₈ (x = 0.78).

Compared to the other two minerals, the Hundholmen mineral has Al > Fe³⁺ at the Fe/Al site in layer A, has Si > As at the As1 site in layer B, and Ca > 0.5 at the Na site in layer C.

With 13 possible cation sites, the vicanite group might potentially comprise a large number of species, especially if the M1 to M5 sites are considered separately. For instance, vicanite-(Ce) has Th predominating at the M5 site. The correct distribution of Y, REE and Ca between the five M sites is not easily made on the basis of site-scattering values. Therefore, it might be wise to treat M1 to M5 as an entity for nomenclatural purposes.

O31-04

The wyllieite group of minerals: crystal chemistry, nomenclature and stability

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The wyllieite group of minerals consists of Na-Mn-Fe-Al-bearing phosphates which exhibit a crystal structure topologically similar to the alluaudite structure. However, the ordering of cations in the wyllieite structure induces a splitting of the M(2) and X(1) sites of alluaudite into the M(2a) M(2b) and X(1a) X(1b) positions. Consequently, the C2/c space group of alluaudite transforms into P2₁/n in wyllieite, with no significant change of the unit-cell parameters, and with a structural formula which corresponds to X(2)X(1a)X(1b)M(1)M(2a)M(2b)(PO₄)₃.

In granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, wyllieite-type phosphates display chemical compositions ranging from Na₂(Mn,Fe²⁺)Fe²⁺Al(PO₄)₃ to Na(Mn,Fe²⁺)Fe³⁺Al(PO₄)₃, with Ca²⁺ or Mn²⁺ replacing Na⁺ on the X(2), X(1a) and X(1b) sites, Mg²⁺ replacing iron on the M(2a) site, and Mg²⁺ or Fe³⁺ replacing Al³⁺ on the M(2b) site, where □ represents a lattice vacancy. The name wyllieite corresponds to Na₂MnFe²⁺Al(PO₄)₃, whereas the name rosemaryite designates the more oxidized compositions, such as □NaMnFe³⁺Al(PO₄)₃. The prefix ferro- is then added if Fe²⁺ dominates in the M(1) site, thus leading to ferrowyllieite, Na₂Fe²⁺Al(PO₄)₃, and to ferrosemaryite, □NaFe³⁺Al(PO₄)₃. The name qingheite has been introduced for the Mg-rich equivalent of wyllieite, Na₂MnMgAl(PO₄)₃.

Single-crystal structure refinements of ferrosemaryite from the Rubindi pegmatite, Rwanda (*R*_f = 2.43 %, *a* = 11.838(1), *b* = 12.347(1), *c* = 6.2973(6) Å, β = 114.353(6)°, and of rosemaryite from the Buranga pegmatite, Rwanda (*R*_f = 4.01 %, *a* = 12.001(2), *b* = 12.396(1), *c* = 6.329(1) Å, β = 114.48(1)°), indicate that Al is predominant on the M(2a) site, not on the M(2b) site as observed in ferrowyllieite. The morphologies of the X(1a) and X(1b) crystallographic sites correspond to a distorted octahedron and to a distorted cube, respectively. The [7+1]-coordinated X(2) site of rosemaryite is a very distorted gable disphenoid, similar to the A(2) site of the alluaudite structure.

The infrared spectrum of rosemaryite shows absorption bands at 3450 and 1624 cm⁻¹, related to the vibrational modes of H₂O, and confirms the presence of molecular water in the channels of the wyllieite structure. A Mössbauer spectral investigation of rosemaryite and ferrosemaryite also permits a comparison with the Mössbauer spectra of more disordered alluaudite-type phosphates.

Finally, the structural features of rosemaryite and ferrosemaryite are compared to those of other natural and synthetic wyllieite-type phosphates, and the role played by Al to stabilize the wyllieite structure is discussed in detail.

Nano-scale phase intergrowths in crystals of a 'new' tungstate mineral from Pittong, Victoria, Australia.

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Strongly oxidised W–Mo–Bi deposits are ideal environments for the formation of a wide range of rare, unusual and potentially new species of tungstates and molybdates. For example, recent discoveries at localities in eastern Australia have yielded assemblages containing koechlinite, betpakdalite, russellite and the new species elsmoreite. In this paper we report on a synchrotron–TEM investigation of a secondary tungstate found at an abandoned W–Bi–Au mine at Pittong, about 35 km west of Ballarat, in Victoria. The mineral occurs as glistening yellow encrustations of platy crystals on etched wolframite (manganian ferberite) enclosed in reef quartz. SEM examination revealed that crystals are curved plates only about 1 µm thick forming open aggregates up to 0.2 mm across. Chemical analysis (EPMA and CHN) showed major W, Fe, Na and H₂O, giving an approximate formula NaFe³⁺[(WO₃(OH))₄·H₂O]. Powder X-ray diffraction (PXRD) obtained using synchrotron radiation gave a pattern which could not be matched and which showed a mixture of sharp and broad peaks. The positions and intensities of the sharp peaks are similar to those in the PXRD patterns for synthetic Bi–Fe niobate phases. Our recent structure determinations for these latter phases show that they can be described in terms of unit-cell-scale intergrowths of slabs of pyrochlore-type with hexagonal tungsten bronze (HTB)-type structures.

Single crystal diffraction patterns showed that the crystals have hexagonal symmetry, with *a* = 7.31 Å and with *c* approximately 19.5 Å. However the spacings of the diffraction spots along *c** are not commensurate, consistent with disorder in the stacking along the *c* axis. The nature of this disorder was studied using high resolution transmission electron microscopy (TEM) images. These show that individual crystallites consist of a core of pyrochlore/HTB intergrowth phase, surrounded by a thin (~30 Å) rim of pure HTB type. The ultra-thin rims of the HTB phase give the broad peaks in the PXRD patterns. Furthermore, the TEM images of the core show variations in the widths of the pyrochlore and HTB blocks, and it is this variation that gives the incommensurate character to the diffraction patterns. The special difficulties associated with preparing mineral-naming proposals for these types of disordered intergrowth minerals will be discussed.

Menezesite from Cajati, São Paulo, Brazil: The first heteropolyniobate mineral

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The new mineral menezesite, Ba₂MgZr₄(BaNb₁₂O₄₂)₁₂H₂O, cubic, has been found in the last years of the decade of 1970 by Luiz Alberto Dias Menezes Filho, but its study has begun only in May 2003. The mineral was named in honor of Menezes (born 1950), mining engineer, mineral collector and merchant. He studied the minerals from Cajati. The menezesite IMA number is 2005-023. It occurs in the contact zone between dolomite carbonatite and "jacupirangite" (= a pyroxenite) at the Jacupiranga mine, in Cajati county, São Paulo state, Brazil. This is also the type locality for quintinite-2H. The associated minerals are dolomite, calcite, magnetite, clinohumite, phlogopite, ancyllite, strontianite and tochilinite. Menezesite was formed as a vug mineral. The mineral forms aggregates of rhombododecahedra up to 1 mm. The color is reddish brown, the streak white and the luster vitreous. It is transparent. Menezesite is the first natural heteropolyniobate. The first synthetic heteropolyniobates were obtained in 2002. Heteropolyanions are negatively charged clusters of corner- and edge-sharing early transition-metal MO₆ octahedra and the heteroatom is usually located in the interior of the cluster. The geometry, composition, and charge of these clusters are varied through synthesis parameters, and cluster properties are highly tunable as a function of these characteristics. Heteropolyanions have been employed in a range of applications that include virus-binding inorganic drugs (including AIDs virus), homogeneous and heterogeneous catalysts, electro-optic and electrochromic materials, metal and protein binding, and as building blocks for nanostructuring of materials. The heteropolyanions of W, Mo, and V, which have found numerous applications, are formed simply by acidification of solutions of their oxoanions. Unlike other heteropolyanions, heteropolyniobates are basic rather than acidic, which means they can survive longer in the generally basic or neutral environments of radioactive wastes and blood, respectively. Once such compounds bind with a virus, it is no longer capable of entering a cell to damage it. Heteropolyanions may also bind with radionuclides (actinides), which remove them from the mixture by phase separation for easier and safer storage. The complete menezesite description is in preparation. Financial support by FAPESP.

Kintoreite–Corkite solid solution mineral from Japan

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Kintoreite is Pb–Fe–P-dominant member of the alunite–beudantite–crandallite group (Pring et al., 1995). This mineral is a member of segnitite (Pb–Fe–As-dominant) and plumbojarosite (Pb–Fe–S-dominant) series and is P-dominant. The chemical formula of the alunite–beudantite–crandallite group minerals is AB₃X₂(OH)₆, where A=Pb, K, Na, Ca, ...; B=Fe, Al, ...; X₂=(PO₄)₂, (AsO₄)₂, (SO₄)₂, (PO₄)(SO₄), (AsO₄)(SO₄). In the system of Pb–Fe series, corkite and beudantite are defined as P:S=1:1 and As:S=1:1 minerals, respectively. Kintoreite–corkite ss mineral was found with faustite from Kawazu mine, Shizuoka Prefecture, Japan (Matsuyama et al., 1996). This mineral occurs as brown crust and is accompanied with goethite and other Fe-oxides. EDS analysis was performed. The sample is zoned in the back-scattered-electron image. Since each zone is thin compared with electron beam diameter, chemical analysis was difficult. Cell parameters were obtained with XRD analysis and the mineral was identified as kintoreite–corkite ss mineral. The strongest lines of X-ray powder-diffraction pattern [*d* in angstrom (1)(hkl)] are: 5.92 (86)(101), 3.65 (39)(110), 3.06 (100) (113), 2.955 (26) (202), 2.811 (24)(006), 2.527 (27) (024), 2.251 (37) (107), 1.970 (27) (303), 1.820 (19) (220) and 1.487 (17)(0,1,11). The X-ray data were indexed on a hexagonal unit cell, giving *a*=7.2863 Å, *c*=16.865 Å. The chemical composition obtained with preliminary analysis was that of around the boundary of kintoreite and corkite. The typical composition is as follows: PbO 33.78, Al₂O₃ 3.33, Fe₂O₃ 32.5, P₂O₅ 16.46, SO₃ 6.35 and total 92.42.

Detailed data will be shown and we will discuss on the kintoreite–corkite ss.

Cs analogue of polyolithionite from rare-element granitic rocks in China

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Known examples of Cs-bearing micas to date include nanpingite (Cs₂O = 25.29 wt%, Yang et al. 1988), cesian biotite (Cs₂O = 5.97 wt%, Ginsburg et al. 1972) and rubidian cesian phlogopite (Cs₂O = 6.60 wt%, Hawthorne et al. 1999). Polyolithionite with extreme Cs enrichment has been found in the Yichun lepidolite-topaz granite (Jiangxi, E China) and in the Koktokay #3 pegmatite (Xinjiang, NW China).

Two types of occurrence of the cesian polyolithionite are described in the Yichun granite, one consists of inclusions of Cs-rich polyolithionite within rock-forming minerals, the other represents a replacement rim around the primary polyolithionite flakes. Electron-microprobe analyses shown dominant Cs₂O contents up to 25.8 wt%, or 0.9 apfu (based on 11O). Li₂O contents calculated according to Tindle-Webb's equation varies around 4.0 wt%. The estimated ^{IV}Al varies mostly in the range of 0.09 and 0.40 apfu, and the Cs/(K+Cs) ratio exceeds 0.50, even up to 0.96. These parameters plot the Cs-rich micas from the Yichun granites, in the diagram of ^{IV}Al versus Cs/(K+Cs), in the area of Cs-analogue of polyolithionite.

In the Koktokay #3 pegmatite, four types of occurrence of the Cs-dominant polyolithionite are characterized: (1) Cs-dominant polyolithionite as outer zone on compositionally conventional polyolithionite core; (2) Cs-dominant polyolithionite as fine-flaked overgrowth on muscovite veinlet; (3) Cs-dominant polyolithionite as veinlets in main polyolithionite; and (4) Cs-dominant polyolithionite veinlets in elbaite. Electron microprobe analyses revealed clearly extreme Cs enrichment in polyolithionite (also up to 26 wt% Cs₂O). F contents are determined in the range of 4–5.5 wt%. Calculated Li₂O contents oscillate about 4 wt%. The estimated ^{IV}Al varies in the range of 0.11 and 0.37, and Cs/(K+Cs) ratio ranges from 0.61 to 0.92. Therefore, Cs-rich micas are classified into Cs-dominant analogue of polyolithionite in the ^{IV}Al versus Cs/(K+Cs) diagram.

Micro-X-ray diffraction patterns of the polyolithionite with conventional composition (1.86 wt% Cs₂O) and high Cs contents (25.26 wt% Cs₂O) are characterized by several strong peaks [*d* in Å (1) (hkl): 2.983(48)(025), 2.593(38)(200), 1.506(100)(-3,32), 1.014(45)(446)], and are thus consistent, in the low-angle region, with the standard patterns for polyolithionite found in the JCPDS catalog.

Micro-Raman spectra show several characteristic peaks for mica, such as 1140–1150 and 708–711 cm⁻¹, thus revealing that Cs-dominant polyolithionite is structurally similar to that of the Cs-poor polyolithionite.

To summarize up, Cs-rich micas both from the Yichun granite and from the Koktokay pegmatite are in fact the Cs-dominant analogue of polyolithionite, which can be proposed as a new species in the mica group.

On the classification of amphiboles

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We present new criteria for amphibole classification which are based on the following major issues: (1) the role of (OH), Li and Fe³⁺ in the crystal chemistry of the amphiboles, and the need of separate schemes for amphiboles with (OH, F, Cl) < 1.0 apfu; (2) irreducible charge arrangements as the basis for recognizing distinct species; (3) use of the dominant-constituent principle (4) the use of prefixes to identify dominant homovalent substitutions; (5) the principal chemical variables used in classification procedures. We emphasize the need for complete major-element analysis of amphiboles, not only for classification purposes, but also to understand their crystal chemistry and their role in petrological and geochemical processes.

The current IMA-approved classification scheme is based on the *A*-, *B*- and *T*-groups of cations in the amphibole formula: AB₂C₅T₈O₂₂W₃. We argue that amphibole classification should be based on the *A*-, *B*- and *C*-groups of cations as (i) it is in these groups of cations that the maximum variation in chemical composition occurs; and (ii) as a result of (i), the scheme is more in accord with the IMA-sanctioned dominant-constituent principle that governs the recognition (and approval) of distinct mineral species.

We propose two new classifications involving the *A*-, *B*- and *C*-groups of cations, and based on the dominant-constituent principle. Both new schemes incorporate *B*-group Li-dominant amphiboles as a separate group. The first scheme gives six principal groups of (OH, F, Cl)-dominant amphiboles, defined on the basis of the dominant *B*-group cation (or group of cations): *magnesium-iron-manganese group* with ^B(Mg+Fe+Mn) dominant; *calcium group* with ^BCa dominant; *sodium-calcium group* with ^B(Na+Ca) dominant; *sodium group* with ^BNa dominant; *lithium group* with ^BLi dominant; *sodium-(magnesium-iron-manganese) group* with ^B(Mg*+Na) dominant and 0.75 > ^BNa / ^B(Mg*+Na) > 0.25. The second scheme sticks to the concept of charge arrangement, and gives four groups (those listed above discarding the *sodium-calcium* and the *sodium-(magnesium-iron-manganese) groups*. These two schemes serve to illustrate (1) the problems inherent in the classification of a group of minerals as complicated as the amphiboles, and (2) the sometimes disparate needs (and biases) of crystallographer, mineralogist, petrologist and geochemist. Scheme 1 conserves current formulae and names as much as possible, whereas scheme 2 minimizes the number of distinct species (formulae and names) as much as possible. The differences between the current classification and the two schemes presented here will be discussed, highlighting the problems associated with each scheme.

O31-10

Heterovalent substitutions in mineral nomenclature: the dominant-ion rule revisited

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According to the IMA-CNMMN nomenclature rules (Nickel & Mandarino, 1987), isostructural natural compounds are distinct mineral species if "at least one major structural site is occupied by a different chemical component". Substitution in this site commonly results in a solid-solution series, members of which are distinct mineral species if they differ by the dominant ion in this site, according to the "dominant-ion rule" – or "50% rule" in case of a binary system (Nickel, 1992). This rule is quite effective for any homovalent substitution but is actually fraught with difficulties in case of heterovalent substitutions. Indeed, heterovalent substitution in a given site is commonly charge-compensated by heterovalent substitution in another site. The problem arises in case of multiple occupancy in one such site, if several charge-balancing cations are dominant as a whole (e.g. 0.35 La³⁺ + 0.25 Ce³⁺ in the A2 site of an epidote-group mineral) but individually less abundant than the partly substituted cation (e.g. 0.4 Ca²⁺ in this A2 site). Strict application of the nomenclature rule to this example would recognize Ca as the site-dominant cation, whereas the first-order significant feature is the site-dominant (trivalent) valence state, which determines in turn the dominant valence state in the site at which the coupled, charge-balancing substitution takes place.

For this reason, the classical, dominant-ion nomenclature rule should be implemented as follows: "In a relevant site, the dominant ion of the dominant valence state is considered for nomenclature". Incidentally, this rule is strictly identical to the classical one in all the cases of homovalent exchange or of simple (two cations) heterovalent exchange. It will be shown on the examples of the epidote and arjadite-dickinsonite groups that this new wording carries a number of practical advantages, in particular the derivation of end-member formulae that are necessarily charge balanced.

O31-11

Does cation ordering justify approval of new mineral species? New data on labuntsovite-group minerals

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Labuntsovite-group minerals are of interest because of their great chemical and structural diversity and as possible materials for industrial applications in catalysis, ion exchange, adsorption, etc. Recently we were able to detect a new type of cation ordering in several labuntsovite-group minerals from Khibiny alkaline massif, Kola peninsula, Russia. One of these minerals has the composition Na_{2.32}K_{2.96}(H₂O)_{1.04}Ba_{1.74}(H₂O)_{1.68}K_{0.58}(Mn_{0.64}Mg_{0.2})[Ti₆((OH)_{0.6}O_{0.4})₆](Si₄O₁₂)₄·12.9H₂O and is an intermediate member of the lemmleinite-Ba and labuntsovite-Mn solid solution. In comparison with 'usual' labuntsovite-group minerals, it has a doubled unit cell, *I*2/*m*, *a* = 14.278(1), *b* = 13.778(1), *c* = 15.592(2) Å, β = 116.76(1)°, *V* = 2738.96 Å³. The structure has been solved by direct methods and refined to *R*₁ = 0.049 (*wR*₂ = 0.143) for 3349 reflections with $|F_{\text{hkl}}| \geq 4\sigma |F_{\text{hkl}}|$. This mineral is the first labuntsovite-group member which has an essential degree of *C*-*D* (= Ba-Mn) ordering in its crystal structure. This ordering can schematically be described as alternation in the structure of lemmleinite-Ba and labuntsovite-Mn unit cells. The unit-cell doubling is clearly expressed in appearance of additional reflections that make the *c* unit-cell parameter doubled. Discovery of the doubling was possible only due to the application of highly-sensitive CCD and Image Plate area detectors. This and other examples put some questions to the existing nomenclature of the labuntsovite group, which will be discussed in details. Also, reconstructed reciprocal space sections show some interesting diffuse scattering features. By analogy with vesuvianite, the appearance of the ordered species may indicate specific thermodynamic situations during formation of mineral deposits.

O31-12

Natural and synthetic fluoride carbonates: structural classification, properties and uses

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There are crystal-structure determinations of 27 fluoride carbonate phases. Of these 16 occur as minerals and 16 have been synthesized (five of the minerals have been synthesized). Of the mineral species, 10 contain essential amounts of rare earth elements (REE). Bastnäsite (Ce,La)(CO₃)F, together with monazite (Ce,La,Nd)PO₄ provides the major resource of REE of economic use. Other REE carbonate minerals are relatively rare. Most fluoride carbonates, particularly those containing REE's, occur in alkaline rock complexes. At present there is one very large deposit of REE fluoride carbonates that provides much of the world's requirements: Bayan Obo, Inner Mongolia, north-central China. There is a large range of REE applications: catalysis, metallurgy, solid oxide fuel cell electrodes, glass surfacing, optics, magnets.

Until 1990, very few synthetic fluoride carbonates were known: only precipitations of REE(CO₃)F and of several alkaline or Pb²⁺ phases were reported. Since then, new fluoride carbonates have been obtained by hydrothermal synthesis including 3d transition metal fluoride carbonates, which were previously unknown and have not been found in nature. Synthetic fluoride carbonates are of interest due to some of their unique optical, electrical and magnetic properties.

Both natural and synthetic phases are systematized using a unified description in terms of carbonate group arrangements. As (CO₃)²⁻ groups do not polymerize, due to simple bond-valence considerations, the crystal structures of carbonate phases tend to have a layered topology. The planar carbonate groups can be either parallel (flat-lying) or inclined (standing-on-edge) with respect to the overall structural layering. The addition of F⁻ can influence this topology. The development of a structural hierarchy of fluoride-carbonates requires consideration of ratios of these two anions. As the (CO₃)²⁻ / F⁻ decreases several structural features are noted: (1) The attitude (topology) of the carbonate group progressively transforms from flat-lying, to standing-on-edge, to open-flat-lying, then to lacunar-flat-lying. (2) The carbonate group adjacency with regard to sharing an edge with another polyhedron progresses from sharing all three edges, to sharing two edges to sharing one or no edge. (3) F coordination increases from an isolated cluster, to a chain, to a sheet to a framework.

The structural hierarchy can be utilized to framework areas of experimental interest for attaining a particular property of application.

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The formula $I_{2n}Y_{4+3n}[Ti_2(O)_{2-2n}Si_{4-4n}O_{14+10n}](O^n)_{2-2n}$ ($n = 0, 1, 2$) represents the polysomatic series of heterophyllosilicates, i.e. the layer titanosilicates which are based on *HOH* layers. Formally, these layers can be derived from a phyllosilicate *TOT* layer by periodic substitutions, in the *T* sheet, of tetrahedral silicate rows by rows of Ti-polyhedra, thus obtaining hetero (*H*) sheets whose composition is shown above in square brackets. Whereas the several members with $n = 0$ show quite different interlayer contents and form the meropsiotype bafertiste series, the members with $n = 1$ differ from astrophyllite only by isomorphous substitutions; only one member with $n = 2$ (nafertiste) was known till the recent finding (Lovozero massif, Kola Peninsula), of the new mineral species approved with code IMA 2005-031:

$(Na_{1.19}Sr_{0.62}Ca_{0.41}Mn_{0.33}K_{0.26})_{\Sigma 2.83}(Fe^{3+}_{7.98}Mg_{1.15}Mn_{0.40}Fe^{2+}_{0.38})_{\Sigma 10} \cdot (Ti_{1.87}Fe^{3+}_{0.13})_{\Sigma 2}(Si_{1.74}Al_{0.26})_{\Sigma 2}O_{54.10}H_{20.46}$, monoclinic, a 16.47, b 5.303, c 24.39 Å, β 93.5°. A nafertiste-like formula with I(interlayer cations) = $(Na_{1.19}Sr_{0.62}Ca_{0.41}Mn_{0.33}K_{0.26})$ and Y(octahedral cations of the *O* sheet) = $(Fe^{3+}_{7.98}Mg_{1.15}Mn_{0.40}Fe^{2+}_{0.38})$ has been proposed mainly on the basis of IR spectra.

Single crystals of the new species are submicrometric [001] lamellae, [010] elongated, and are not suitable for X-ray single-crystal diffraction. Starting from the crystal structure of nafertiste $([Na,K]_4[Fe^{2+},Fe^{3+}]_{10}[Ti_2O_5Si_2O_3](OH)_6 \cdot 2H_2O, a$ 5.353, b 16.176, c 21.95 Å, β 94.6°) and comparing the X-ray powder diffraction (XRPD) and Selected Area Electron Diffraction (SAED) patterns of the two minerals, the crystal structure of IMA 2005-031 has been modelled in space group $P2_1/n$. The structure model is validated by comparing calculated and experimental XRPD patterns and, even better, being the experimental pattern quite flat, by its satisfactory fitting to the chemical data. To balance the high content of Fe^{3+} in the *HOH* layer, with reference to the general formula, most of O' (bonded to Ti only) and O'' (belonging to the octahedral sheet only) are O^{2-} anions. Taking into account the structure model and possible replacements involving differently-charged cations, the following ideal formula can be attributed to IMA 2005-031 $(Na,Sr)(Fe^{3+},Mg)_{10}[Ti_2O_5Si_2O_3](OH)_6 \cdot 11H_2O$. In comparison with nafertiste, the new species, based on the same type of *HOH* layer with ideal composition $[Ti_2O_5Si_2O_3]$, shows 10 fully occupied octahedral sites and 11 H_2O molecules in the interlayer besides Na and Sr cations.

The structure modelling of IMA 2005-031 follows those of other heterophyllosilicates, e.g. nafertiste and bornemanite, and proves once more that classifying these titanosilicates, and in general modular structures, according to series is a powerful tool to crystal-chemically correlate minerals.

O31-14

Crystal chemistry of the new exhalative minerals (to 30th anniversary of Great fracture Tolbachik eruption, Kamchatka, Russia)S.K. Filatov¹ and L.P. Vorgasova²¹Department of Crystallography, St. Petersburg State University, University Emb., 7/9, St. Petersburg, 199034, Russia
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130 minerals (from about 230 exhalative minerals known in the world) were founded at fumaroles of the Tolbachik eruption 1975-1976, the largest fracture eruption in the modern history of Kuril-Kamchatka region. Among them 30 new mineral species were discovered (27 of them by our group) and studied. The O:Cl:S:F atomic ratio 8:4:1:1 in the minerals shows that conditions at the fumaroles are essentially oxidative. The maximum formation of ore at the Tolbachik basalt eruption was observed for copper (atomic ratio in exhalative minerals Cu:Pb:Zn = 20:2:1); of the 130 minerals, 47 ones contain Cu and 21 of them are new minerals. A clear tendency may be traced from initially high-temperature associations (anhydrous sulfates, chlorides, oxides, selenites, arsenates, vanadates, oxosalts (salts, containing "additional" oxygen atoms), native elements, etc.) to low-temperature ones (hydrous chlorides, sulfates, carbonates, etc.). X-ray powder diffraction and X-ray microprobe spectral analysis were used for diagnostic of the fine multiphase products.

Determination of the crystal structures of the new exhalative minerals made possible to interpret a structural role of the "additional" oxygen atoms. In particular, due to oxygen abundance, oxocentered OCu_4 tetrahedra exist in crystal structures of 18 (among 30) new exhalative minerals. In common, crystal chemistry of compounds with complexes of anion centered tetrahedral XA_4 has been generalized and developed on the basis of these new minerals and 500 another inorganic compounds (S. Krivovichev and S. Filatov, 2001).

Thermal decomposition of the new minerals was studied using high-temperature X-ray diffraction method. It occurred that many exhalative minerals with oxocentered tetrahedral are not stable on heating. So these minerals can decompose as a result of local temperature variations that are characteristic of active volcanoes during post-erupted period. There are no similar minerals among products of ancient fumaroles of Tolbachik valley. That is why these new minerals containing oxocentered tetrahedral were discovered after recent Tolbachik eruption which has been studied from the first day of the eruption up to now.

The existence of the oxocentered tetrahedral in the crystal structure of the initial exhalative minerals leads to a conclusion that these complexes are present in gases and play an important role in the transport of metals by volcanic gases. This conclusion was confirmed by results of gas chemical transport reactions method of exhalative processes modeling.

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O31-15

Contribution of the IR spectroscopy to the characterization of new mineral species

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Infrared spectroscopy (IRS) is comparable with X-ray based methods by its abilities in the identification of minerals. In some cases, such as analysis of local structures and minerals containing light atoms (H, B, Br, N, C) IRS has certain advantages. However the use of IRS for the identification of minerals is limited due to the absence of sufficiently full handbooks and by virtue of usual tradition. In order to fill this gap, a representative collection of IR spectra of well-characterized samples was formed. It includes about 3000 spectra of more than 2200 mineral species. In frames of this work, IRS database was created and more than 70 new minerals have been discovered. There are at least two different approaches to the IRS analysis of minerals. **Traditional approach** deals with discrete bands and absorption maxima. On the basis of this approach, fine structural or compositional specific features of a number of new minerals have been revealed. The typical examples of such kind are: shirokshinite (an analogue of tainiolite with Na instead of Li in octahedral position; the substitution of Li for heavier Na results in long-wave band-shifts); atencioite, nabalamphophyllite (additional band splitting demonstrates cation ordering accompanied by symmetry lowering in comparison with their analogues, greifensteinite and barytolamphophyllite); paratsepinitite-Na (additional band splitting demonstrates unit cell doubling in comparison with tsepinitite); clinobaryllite (band shifts and rearrangement of band intensities due to the change of framework topology in comparison with baryllite); vitimitite, rudenkoite (unique IR spectra demonstrate their unique structure types). In our **new approach** spectral curves of standard samples are considered as elements of a functional, or as elementary units of a multidimensional space. The IRS analysis is based on the expansion of a given spectrum over the full basis (i.e. full set of reference spectra) using the criteria of non-negativity, continuity and best approximation. On the basis of this approach, an IRS-based quantitative criterion (CCA) of the affinity between different minerals can be introduced. This criterion is based on empirical spectroscopic data. However in most cases it reflects real crystal-chemical relationships: minerals with similar structure type have the lowest CCA values. Within a given structure type, CCA characterizes compositional relationships.

O31-16

Deprotonation of Fe^{II-III} hydroxycarbonate green rust and fougérite mineral in gley soils; structure and thermodynamicsJ.-M. R. Génin¹, and R. Ruby¹Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564 CNRS-Université Henri Poincaré-Nancy 1, Equipe Microbiologie, Physique et Département Matériaux et Structures, ESSTIN, 405 rue de Vandœuvre, F-54600 Villers-lès-Nancy, France
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The fougérite mineral (IMA 2003-057) that is responsible for the bluish-green colour of gley soils that gets ochrous once exposed to the air has for chemical counterpart the Fe^{II-III} hydroxycarbonate $GR(CO_3^{2-})$ compound, which belongs to the layered double hydroxide family. It consists in the stacking of brucite-like layers $[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+}$ that alternate with interlayers $[CO_3 \cdot \sim 3 H_2O]^{2-}$ comprising carbonate anions and water molecules. It resembles strongly pyroaurite where the divalent cation is Mg^{II} . The preparation of $GR(CO_3^{2-})$ by co-precipitating Fe^{II} and Fe^{III} cations in carbonated medium shows that the domain of existence of $GR(CO_3^{2-})$ lies for $x = [Fe^{III}] / [Fe^{total}]$ within [0.25, 0.33] and the ordered upper limit is $[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+} \cdot [CO_3 \cdot \sim 3 H_2O]^{2-}$. Long range order within domains accommodates any intermediate value if considering periodicities of $2 \times a_0$ or $\sqrt{3} \times a_0$ where a_0 is the parameter of the hexagonal pavement. $GR(CO_3^{2-})$ gets oxidised into ferrihydrite that evolves to goethite by aerial oxidation, or into $[Fe^{III}_4Fe^{II}_2(OH)_4(OOH)_4]^{2+} \cdot [CO_3 \cdot \sim 3 H_2O]^{2-}$, the ferric green rust $GR(CO_3^{2-})^*$ by deprotonation of OH^- ions at the apices of the octahedrons surrounding the cations. A mass balance of iron ox(yhydrox)ides is drawn accordingly in the carbonated medium, which displays all the possible routes that can be followed by oxidation or reduction. Moreover, any intermediate value of ratio x between 0.33 and 1 was experimentally obtained by oxidising the classical $GR(CO_3^{2-})$ by using the exact amount of H_2O_2 solution leading to a partially deprotonated hydroxycarbonate, $Fe^{II(1-x)}Fe^{III}_{6x}(OH)_{4(4-3x)}(OOH)_{2(3x-1)}CO_3 \cdot GR^*(x)$, where $x \in [0.33, 1]$. Mössbauer spectroscopy allows us to monitor the deprotonation and spectra at 78 K display four quadrupole doublets, D_1 and D_2 attributed to Fe^{II} state and D_3 and D_4 attributed to Fe^{III} state. D_3 keeps its amplitude at 33% representing the Fe^{III} cations balanced by the charges of intercalated CO_3^{2-} whereas D_4 represents the Fe^{III} cations due to deprotonation with $(x-0.33)$ varying intensity. The structure of the deprotonated GR^* keeps essentially that of $GR(CO_3^{2-})$ as testified by X-ray diffraction pattern meaning that the long range order of anions is conserved within the interlayers. The electrode potential of the solution increases gradually when adding slowly H_2O_2 allowing to follow the standard chemical potential $\mu^0(x)$. Comparison of Mössbauer spectra of synthetic samples with those obtained from the field will be presented and the occurrences, which always present a ratio $x \in [0.33, 0.67]$ are now fully explained.

Numanoite, $\text{Ca}_4\text{CuB}_4\text{O}_{16}(\text{OH})_6(\text{CO}_3)_2$, a new mineral, the Cu-analogue of borcarite from the Fuka mine, Okayama Prefecture, Japan

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Numanoite, the Cu-analogue of borcarite, is found in an irregular patch in the crystalline limestone near gehlenite-spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. Numanoite (up to 1 mm long) is observed in a core of borcarite crystals (up to 5 mm long). The mineral is also found as a veinlet (up to 0.4 mm wide) in aggregates of borcarite crystals. The associated minerals are nifontovite, bultfonteinite, calcite and an unidentified magnesium silicate. In hand specimen, numanoite is blue-green to colorless with vitreous luster. The mineral has {100} and {110} perfect cleavages. Numanoite is monoclinic with space group $C2/m$, $a = 17.794(2)$, $b = 8.381(1)$, $c = 4.4494(7)$ Å, $\beta = 102.42(2)^\circ$, $V = 648.0(2)$ Å³ and $Z = 2$. The strongest lines in the powder XRD pattern [d Å (hkl)] are 7.57 (100) (110), 2.671 (84) (-421), 2.727 (68) (221), 1.887 (52) (041, 440), 2.272 (48) (-331), 2.899 (44) (600), 1.698 (34) (640). EPMA (WDS mode) and TGA gave B_2O_3 24.09, CaO 38.11, CuO 10.32, MgO 1.02, ZnO 0.51, CO_2 15.80, H_2O 9.75 and total 99.60 wt.%. The empirical formula calculated on the basis of $\text{O} = 18$ is $\text{Ca}_{3.898}(\text{Cu}_{0.744}\text{Mg}_{0.145}\text{Zn}_{0.036})_{\Sigma 4.075}\text{B}_{3.969}\text{O}_{5.615}(\text{OH})_{6.208}(\text{CO}_3)_{2.059}$, which gave the ideal formula $\text{Ca}_4\text{CuB}_4\text{O}_{16}(\text{OH})_6(\text{CO}_3)_2$. The $\text{Cu}/(\text{Cu}+\text{Mg})$ value shows the variation range from 0.721 to 0.956. The variation of Cu vs Mg (pfu) shows a strong negative correlation, and suggests the substitution of Mg with Cu. The IR spectrum shows absorption bands at 3540 and 3260 cm^{-1} for O-H stretching vibrations, 1410, 870 and 290 cm^{-1} for carbonate group, and 1410, 870 and 290 cm^{-1} for borate group. The DTA curve shows two endothermic peaks at 489 and 692°C. Optically, numanoite is biaxial negative with refractive indices $\alpha = 1.618(2)$, $\beta = 1.658(2)$, $\gamma = 1.672(2)$, and calculated $2V = 60^\circ$. The density is 2.96 (2) g cm^{-3} (maes.) and 2.96 g cm^{-3} (calc.). The Vickers microhardness is 376 (290-464) kg mm^{-2} (25 g load), and the Mohs' hardness is 4.5. The properties of numanoite are closely related to that of borcarite with similar type of XRD data, IR spectrum and thermal behavior. It is likely that numanoite from the Fuka mine formed as a primary mineral from Cu- and Mg-bearing late-hydrothermal solutions activity on crystalline limestone. Numanoite was named after the late Dr. Tadayuki Numano (1931-2001), Emeritus Professor of Okayama University.

A new mineral: PbHPO_4 , the phosphate analogue of schultenite

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The first natural occurrence of PbHPO_4 , the phosphate analogue of schultenite (PbHAsO_4), is reported from the famous Clara mine, central Black Forest, Germany. Both PbHPO_4 and PbHAsO_4 are well-known and widely studied synthetic ferroelectrics. The new unnamed mineral, found in August 2004, forms lanceolate-shaped (bladed on (010)) colourless transparent crystals up to a length of 0.2 mm. The blades often show subparallel or clustered intergrowths. Natural PbHPO_4 is closely associated with plumbogummite (containing minor As), mimetite (chemically pure), dufite and barite.

A single-crystal structure determination ($\text{Mo-K}\alpha$ X-radiation, CCD area detector, $R(F) = 2.7\%$) showed the new mineral to be monoclinic, space group $P2_1/c$ (no. 13), with $a = 4.694(1)$, $b = 6.661(1)$, $c = 5.790(1)$ Å, $\beta = 97.05(3)^\circ$, $V = 179.67(6)$ Å³, and $Z = 2$. According to the refinement, natural PbHPO_4 is slightly As-bearing and has the structural formula $\text{Pb}[(\text{P}_{0.93}\text{As}_{0.07})\text{O}_5\text{OH}]$; this was confirmed by subsequent SEM-EDS analyses, and is also reflected by the unit-cell parameters which are slightly larger than that of pure synthetic PbHPO_4 ($V = 178.56$ Å³).

The crystal structure is in good agreement with that reported for synthetic PbHPO_4 (cf. ICSD 29553). It is based on an interrupted three-dimensional framework of $(\text{PAs})\text{O}_3\text{OH}$ tetrahedra ($\langle \text{PAs} \rangle\text{O} = 1.549$ Å) connected to approximately [4+2]-coordinated Pb atoms ($\text{Pb-O} = 2.359(4)$ (2x), 2.492(4) (2x) and 2.860(5) (2x) Å). Hydrogen atoms could not be located, but there is a very short H bond ($\text{O}\cdots\text{O} = 2.47$ Å) between two $(\text{PAs})\text{O}_3\text{OH}$ tetrahedra related by a centre of symmetry. Slabs composed of $(\text{PAs})\text{O}_3\text{OH}$ and irregular PbO_6 polyhedra are stacked parallel to (010) and interconnected via the very strong H bonds.

A refinement in space group Pc (the symmetry of the paraelectric low-temperature phase) gave $R(F) = 3.0\%$ and indicated that the centrosymmetric space group is more probable, but that it is basically impossible to distinguish between the two space groups on the basis of X-ray diffraction data (the atomic arrangement in Pc is characterised by a strong $P2_1/c$ pseudosymmetry, and the paraelectric-ferroelectric phase transition is caused by a very small rearrangement of the hydrogen-bonding system). This also confirms literature reports. It is believed that the minor As-for-P substitution in the new mineral disorders the hydrogen-bonding system to some extent and indirectly stabilises the higher symmetry.

Sugakiite $\text{Cu}(\text{Fe,Ni})_8\text{S}_8$, a new mineral

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A new mineral, sugakiite, which was discovered from Horoman, Samani-cho, Samani-gun, Hokkaido, Japan, occurs as a minor mineral in hercynite of the Horoman peridotite massif. There is found a small amount of sulfide minerals such as unknown $(\text{Fe,Ni,Cu})_8\text{S}_8$ mineral(X), sugakiite, pentlandite, unknown $\text{Cu}_2(\text{Fe,Ni})_8\text{S}_8$ mineral(Z), heazlewoodite, bornite, troilite and talnakhite as anhedral grains 10~50 μm in size, and their aggregate 0.05~0.2mm in size, filled interstices of olivine aggregate in hercynite. Under the ore-microscope, sugakiite intimately assembles with X-unknown mineral, Z-unknown mineral, bornite, talnakhite and native copper. Especially, it often appears as a lamellar form along cleavage of X-unknown mineral. This suggests that sugakiite was produced by late-stage replacement for X-unknown mineral which was formed at last stage of hercynite crystallization. Sugakiite shows reddish yellow in color with metallic luster megascopically, and has following physical properties: micro-indentation hardness, $\text{VHN}_{0.05} = 130\sim 170$ kg/mm^2 ; cleavage, not observed; density (calc), 4.71 g/cm^3 using the formula $\text{CuFe}_6\text{Ni}_2\text{S}_8$ and $Z=4$. Under the ore-microscope, sugakiite is creamy white with reddish tint in color. Its prechoirism is not observed, but it has very weak anisotropy (dark gray to slightly light gray). The reflectance values are as follows: 33.2~39.1% (543nm), and 39.3~44.3% (648nm) in air. Chemical composition of sugakiite analysed by EPMA are as follows: Cu:0.91 (0.75~0.97), Fe:6.01 (5.99~6.06), Ni:2.07 (2.03~2.23), Co:0.01 (0.01~0.03) and S:7.99 (7.97~8.03) as based total atoms=17.00. However, there is possible that sugakiite may be form a limited solid-solution. Accordingly, the general formula of sugakiite is given as $\text{Cu}(\text{Fe,Ni})_8\text{S}_8$.

From the data of the precession photographs for a single crystal of this mineral and its X-ray powder diffractions by Gandolfi camera, the mineral is tetragonal with a space group $P4_2/mnm$. Its cell parameters are $a=10.566(5)$ and $c=9.749(8)$ Å, and $Z=4$.

Sugakiite with $\text{CuFe}_6\text{Ni}_2\text{S}_8$ was able to synthesize by using the evacuated silica glass-tube method at 850°C. The optical properties and X-ray powder data of this synthetic product good accord with those of sugakiite as above.

The new mineral was named for emeritus professor Asahiko Sugaki (born in 1923) of Tohoku University, who is economic geologist and sulfide mineralogist, and has principally worked on the phase equilibrium studies of the sulfide systems. This mineral named as sugakiite was proved to be a new mineral by the committee of the New Mineral and Mineral Name in IMA on October 31, 2005.

Two new minerals from Italy: ardenneite-(V) and allanite-(La)

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We describe herewith two new Italian minerals, both belonging to the family of sorosilicates. The new minerals and their names were approved by the IMA CNMNMN [ardenneite(V): proposal # 2005-037; allanite-(La): proposal # 2003-065].

Ardenneite-(V) is the V-dominant analogue of ardenneite, a sorosilicate with $[\text{Si}_2\text{O}_6]^{10-}$, $[\text{SiO}_4]^{4-}$ and $[\text{M}^{3+}\text{O}_4]^{3-}$ groups ($\text{M} = \text{As}^{5+}$, V^{5+}). Ardenneite-(V) was sampled in Sparone (TO), Val di Locana, Piedmont, Italy, where it occurs as yellow very thin elongated-tabular crystals up to 1 mm in length and a few μm in diameter and is associated with quartz, muscovite and piemontite. Electron microprobe analyses pointed to the following simplified chemical formula: $\text{Mn}^{2+}_4[\text{Al}_4(\text{Mg}, \text{Al}, \text{Fe}^{3+}, \text{Mn}^{3+})_2][\text{Si}_2(\text{V}, \text{Si})_2\text{O}_{22}(\text{OH})_6]$. Ardenneite-(V) is orthorhombic, $Pnmm$, a 8.760(3), b 5.838(2), c 18.56(2) Å. These parameters were refined from the X-ray powder diffraction pattern. A complete single-crystal X-ray diffraction study has been made difficult by the typical occurrence of ardenneite-(V) as very thin fibers, often intergrown in parallel aggregates. However, the chemical composition, Weissenberg [010] rotation photographs, and the identity of the XRPD pattern with that of ardenneite allowed us to unambiguously recognize the nature of the new mineral. Ardenneite (without any suffix) has to be considered now the As- dominant member. In the past, the name ardenneite was used to refer to mineral phases irrespective of the dominant M cation (either As^{5+} , or V^{5+} , or even Si^{4+} and P^{5+}).

Allanite-(La) is a member of the epidote group. It was sampled in the Buca della Vena mine, near Stazzema (LU), Apuan Alps, Tuscany, Italy, where it occurs as black prismatic elongated (up to 2-3 mm) crystals and is associated with barite and pyrite. Electron microprobe analyses pointed to the following simplified chemical formula: $\text{Ca}(\text{La}, \text{Ce}, \text{Ca})\text{Al}_2(\text{Fe}^{2+}, \text{Fe}^{3+})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$. Allanite-(La) is monoclinic, $P2_1/m$, with a 8.914(4), b 5.726(1), c 10.132(6) Å, β 114.87(4)°. Its crystal structure has been refined by single-crystal X-ray diffraction data up to $R = 0.033$. The role of allanite-(La) within the epidote group is briefly outlined. In literature, analyses of REE-bearing epidote-group mineral having La as the dominating REE are reported from a few localities (e.g., Waterford, CT, USA; Mitchell Twp., Québec, Canada; Serifos Islands, Cyclades, Greece). However the mineral allanite-(La) was never formally approved by the IMA CNMNMN.

New minerals from Italy: zinalstibite and a new member of the cancrinite-sodalite group

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Zinalstibite, a new mineral occurring within the cavities of marble of the Apuan Alps, Tuscany, Italy, has chemical formula $\text{Zn}_2\text{AlSb}(\text{OH})_{12}$, space group $P\bar{3}$, $a = 5.3270(8)$, $c = 9.792(2)$ Å. It is associated with submillimetric tufts of white crystals of mimetite and submillimetric stalactite aggregates of opal and an amorphous copper-silicate phase (possibly crisocolla). The crystals are colorless, transparent, with vitreous luster, white streak and {001} cleavage. They are trigonal prismatic, with forms {110}, {001}, elongated [001], generally less than $10 \times 10 \times 40 \div 50$ µm, with few larger crystals. The stronger reflections are [hkl], d(Å), I_{rel} : (002), 4.904, 100; (100), 4.620, 35; (101), 4.179, 57; (103, 110), 2.669, 31; (112, 11-2), 2.343, 88; (114, 11-4), 1.805, 57. Zinalstibite is structurally related to cualstibite, as evidenced by the structural determinations and refinements we present for both minerals. They are built up by layers of isolated $\text{Sb}(\text{OH})_6$ octahedra alternating along c with trioctahedral layers, which contain Zn and Al cations and Cu and Al cations in zinalstibite and cualstibite, respectively. In cualstibite the ordering of Al and Cu within these trioctahedral layers results in a supercell, with $a_{\text{cualstibite}} = 9.150(2)$ Å $\approx \sqrt{3} a_{\text{zinalstibite}}$. The superstructure of cualstibite could be refined by using synchrotron radiation data; on the other hand, no superstructure reflections could be observed in the synchrotron X-ray pattern of zinalstibite. The name of zinalstibite is related to its chemical composition and points to its relationships with cualstibite. Both the mineral and its name were approved by the IMA Commission for New Minerals and Mineral Names (IMA 1998-033).

A new mineral belonging to the cancrinite-sodalite group occurs at Sacrofano, Latium, Italy. It has ideal chemical formula $\text{Na}_3\text{K}_3\text{Ca}_2(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{SO}_4)_1.8\text{Cl}_{0.4}0.5\text{H}_2\text{O}$, $Z = 9$, space group $P\bar{3}$, $a = 12.904(2)$ Å, $c = 47.802(4)$ Å and corresponds to a 18-layer member of the family. Its framework is characterized by layers containing six-membered rings of tetrahedra, stacked in the c direction according to the sequence ACBACABACACABACB. Zhdanov symbol (8)211(2)112. It contains 8 cancrinite cages, 6 sodalite cages, 2 losod cages and 2 liottite cages, which host the extra-framework cations, sulphate groups, chlorine anions and water molecules. The reduction from the topological symmetry $P\bar{3}m1$ to the observed space group $P\bar{3}$ is due to the ordering of Si and Al cations within the tetrahedral sites.

Rare Earth Carbonates and an Unknown Ca-Y Carbonate Mineral in the Higashimatsuura basalts

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The Higashimatsuura basalts, distributed throughout the Higashimatsuura Saga Prefecture of Japan, consists of five lithological units based on the period of activity, and the most recent stage has yielded three new minerals; kimuraite, kozoite-(Nd), and kozoite-(La). The Higashimatsuura basalts are the only basalts reported to include these rare earth minerals, and the regional distribution and detailed mineralogy of these minerals have yet to be investigated. In the present study, samples collected from 15 sites in the 5th-stage basalt and 3 sites in the 2nd-stage basalt were analyzed with respect to chemical compositions and crystallography in order to clarify the regional distribution and mineralogy of rare earth minerals in these basalts. Calcite, aragonite, kimuraite, kozoite-(Nd), kozoite-(La), lanthanite-(Nd), lokkaite, tengerite and an unknown Ca-Y carbonate (no matches in the Powder Diffraction File) were identified as cavity minerals. The unknown Ca-Y carbonate occurs as druse or fissure mineralization in the basalt, is white in color with vitreous to silky luster, and forms spherical aggregates of small plate crystals with perfect cleavage. Lokkaite and tengerite are closely associated with the unknown Ca-Y mineral, the major elements of which are Ca and Y, with an average Ca:Y ratio of ca. 1:3. Periodicities of 0.61 nm and 0.93 nm are observed from the normal to cleavage plane by transmission electron microscopy, similar to the values for tengerite and kimuraite. A 3.2 nm periodicity parallel with the cleavage plane is also speculated from the x-ray and electron diffraction data, suggesting an alternating layer structure consisting of a half tengerite layer (0.75 nm) and a full kimuraite layer (2.4 nm). This structure is supported by the chemical composition (CaY_3). Lanthanite-(Nd) and kimuraite were also identified in the 2nd-stage unit of the Higashimatsuura basalt.

Aspidolite, the Na analogue of phlogopite, from Japan

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Aspidolite was first described by von Kobell as a Na- and Mg-dominant mica belonging to the biotite-phlogopite series in 1869. That was later interpreted as the Na-dominant analogue of phlogopite. The Na analogue of phlogopite was described as 'sodium phlogopite' without approval of the Commission on New Minerals and Mineral Names (CNMMN) in 1980. In 1998, the mica nomenclature was revised by the CNMMN, and the name aspidolite was restored as a formal species name to replace sodium phlogopite. Although aspidolite was defined as true mica with ideal formula $\text{NaMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, its mineral description including crystallographic data was not reported in literature. Therefore, the mineral aspidolite was not fully described as a species. The authors found aspidolite from a contact aureole in Kasuga-mura, Gifu Prefecture, central Japan and it has been approved as a mica species by the CNMMN. Aspidolite from Kasuga-mura is interleaved with and surrounded by phlogopite. It is associated with amphibole (pargasite-magnesiosadanagaite), titanite, calcite, scapolite, apatite, pyrrhotite and chalcophyrite. A representative chemical formula of the Kasuga-mura aspidolite is $(\text{Na}_{0.90}\text{K}_{0.10})_{\Sigma 1.00}(\text{Mg}_{2.27}\text{Al}_{0.41}\text{Fe}^{2+}_{0.23}\text{Ti}_{0.05})_{\Sigma 2.96}(\text{Al}_{1.44}\text{Si}_{2.56})_{\Sigma 4.00}\text{O}_{10}(\text{OH}_{1.97}\text{F}_{0.03})_{\Sigma 2.00}$. The Si contents are low (2.52-2.62 apfu) in comparison with its ideal formula, but still high enough (> 2.5 apfu) to claim the identity of the mineral as aspidolite rather than preiswerkite [$\text{NaMg}_2\text{AlAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$]. Aspidolite is optically biaxial negative with elongation positive and $Z \parallel$ cleavage. Two polytypes (1M and 1A) were identified for aspidolite in X-ray powder diffraction patterns. Aspidolite-1M is monoclinic, space group $C2/m$, with refined unit-cell parameters of $a = 5.291(8)$, $b = 9.16(2)$, $c = 10.12(2)$ Å, $\beta = 105.1(1)^\circ$, $Z = 2$. Aspidolite-1A is triclinic, space group $C1$, with $a = 5.289(6)$, $b = 9.16(1)$, $c = 9.892(9)$ Å, $\alpha = 94.45(9)^\circ$, $\beta = 97.74(9)^\circ$, $\gamma = 90.0(1)^\circ$, $Z = 2$.

Fluorophlogopite from Biancavilla (Mt Etna, Sicily, Italy): crystal chemistry of a new F-dominant analogue of phlogopite.

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Fluorophlogopite, a new F-dominant of the mica group (submitted to CNMMN of IMA; previous code 2006-011), was found at Monte Calvario, Biancavilla, lower southwestern flanks of Mt. Etna volcano (Catania, Sicily, Italy). The mineral occurs in outcrops of grey-red altered benmoreitic lavas, associated to fluoroderite (new mineral, IMA 2000-49), microgranular feldspars, clino- and orthopyroxenes, fluoro-apatite, hematite, pseudo-brookite, and originated by a metasomatic process on the original lava rocks, through very hot fluid enriched in F, Cl, and other incompatible elements. Fluorophlogopite occurs as very thin, flat lamellae, with a diameter of 200-400 µm. Bright and pale yellow in colour. Vitreous to resinous lustre. Transparent. Non-fluorescent. H Mohs: 2-3. Perfect cleavage {001}. Density (calc.) = 2.830 g/cm³ (with empirical formula and single-crystal data). Infra-red spectrum does not show a significant absorption band in the OH-stretching region (3800-3600 cm⁻¹). Optically biaxial (-), $\alpha = 1.5430(5)$, $\beta = 1.5682(5)$, $\gamma = 1.5688(5)$ (589 nm), $2V_{\text{meas.}} = 17(2)^\circ$. Acute Bisectrix (α) $\perp$ (001). Nonpleochroic. The empirical formula (based on 12 O+F+OH+Cl apfu) is: $(\text{K}_{0.72}\text{Na}_{0.082}\text{Li}_{0.041}\text{Ba}_{0.002}\text{Sr}_{0.850}(\text{Mg}_{2.87}\text{Fe}^{2+}_{0.072}\text{Li}_{0.042}\text{Mn}_{0.009}\text{Nb}_{0.000}(\text{Si}_{1.162}\text{Al}_{0.782}\text{Ti}_{0.055})_{\Sigma 2.999}\text{O}_{10.025}[\text{F}_{1.899}(\text{OH})_{0.074}\text{Cl}_{0.002}]_{\Sigma 1.975})$. As for Fe, no experimental evidences of its valence state are available to date. However crystal chemical arguments suggest it can be present both as Fe²⁺ and Fe³⁺.

Single-crystal X-ray studies, on a very thin (~15 µm) fluorophlogopite crystal, gave the following data: Monoclinic (1M polytype), Space Group: $C2/m$; $a = 5.3094(4)$ Å, $b = 9.1933(7)$ Å, $c = 10.1437(8)$ Å, $\beta = 100.062(20)^\circ$, $V = 487.51(6)$ Å³, $Z = 2$. Crystal structure: $R = 0.046$, $R_w = 0.049$ [$R = 0.034$, $R_w = 0.040$ when two different scale factors for family ($k = 3n$) and non-family ($k \neq 3n$) reflections, were used], $R_{\text{sym}} = 0.037$. Unit-cell parameters were calculated from the least-squares refinement of d values obtained from all reciprocal lattice reflections in the range $2 < \theta < 40^\circ$. A total of 18644 reflections, in the same θ range, were collected of which 728 with $I > 3\sigma(I)$ were used for the structure solution ($n/p = 11$). Intensities were then corrected for absorption, Lorentz and polarization effects, averaged and reduced to structure factors. The F-dominant analogue of annite, $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, from the Western Suburb of Suzhou City, near Shanghai, China, has been approved by the CNMMN (99-048) as fluorannite. The mineral at hand is the F-dominant analogue of phlogopite, $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$.

P31-09

A Mn-analogue of Allanite-(Ce) in Granite from JapanR. Miyawaki¹, K. Yokoyama¹, S. Matsubara¹, Y. Tsutsumi¹, and A. Goto²¹Department of Geology, the National Science Museum, 3-23-1, Hyakunin-cho, Shinjuku, Tokyo 169-0073, Japan.

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A Mn-analogue of allanite-(Ce), $\text{MnCe}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, occurs in granite at Shodoshima Island on Seto Inland sea, Kagawa Prefecture, Japan. It is monoclinic, $P2_1/m$, $a = 8.939(8) \text{ \AA}$, $b = 5.742(4) \text{ \AA}$, $c = 10.187(8) \text{ \AA}$, $\beta = 115.10(6)^\circ$, $V = 473.5(6) \text{ \AA}^3$, $Z = 2$. The four strongest lines in the powder XRD pattern [$d(\text{\AA})$, I/I_0 , hkl] are (2.92, 100, -302); (3.53, 54, -211); (2.71, 43, 013 120 300) and (2.62, 39, -311). Electron microprobe analysis gave: SiO_2 29.94, Al_2O_3 16.02, FeO 16.01, MnO 6.01, MgO 0.07, CaO 2.42, La_2O_3 3.09, Ce_2O_3 10.75, Pr_2O_3 1.83, Nd_2O_3 6.44, Sm_2O_3 1.35, Gd_2O_3 0.54, Y_2O_3 0.72, ThO_2 0.51, and lead to the empirical formula, $\text{Mn}_{0.51}\text{Ca}_{0.26}\text{Ce}_{0.39}\text{Nd}_{0.23}\text{La}_{0.11}\text{Pr}_{0.07}\text{Sm}_{0.05}\text{Y}_{0.04}\text{Gd}_{0.02}\text{Th}_{0.01}\text{Al}_{1.89}\text{Fe}_{1.34}\text{Mg}_{0.01}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}_{0.85}(\text{OH})$ on the basis of the 3 silicon and 1 hydrogen atoms per formula unit. The estimated content of H_2O is 1.50 and the total is 98.60. The variation in concentration of Mn in this mineral showed negative linear correlation with that of Ca. It suggests that isomorphous substitution of Mn for Ca. The crystal structure was refined to $wR_1 = 0.0337$ with single crystal XRD data. The refinement on occupancy parameters for the A and M sites converged with structural formula of $(\text{Mn}_{0.650}\text{Ca}_{0.350})(\text{Ce}_{0.914}\text{Fe}_{0.086})(\text{Al}_{0.873}\text{Fe}_{0.127})(\text{Al}_{0.988}\text{Fe}_{0.012})(\text{Fe}_{0.875}\text{Al}_{0.125})(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, and confirmed the replacement of Ca with Mn at the A site. Under the microscope it is biaxial negative and transparent with pleochroism from brown to yellow, but almost optical properties are too close to those of Mn-poor allanite-(Ce) to distinguish from each other. The Mn content in the present allanite-(Ce) varies grain by grain. This indicates that we can recognize Mn-analogue of allanite-(Ce) by only quantitative analysis. The Mn-rich and Mn-poor of allanite-(Ce) occur as short prismatic crystals less than 1 mm length in granite at the abandoned quarry. Crystals are black to dark brown in color. The calculated density of Mn-analogue of allanite-(Ce) is 4.11 g/cm^3 .

P31-10

Scandian garnet from Wiluy River, Sakha-Yakutia Republic, Russian Federation – a potential new mineral species in the garnet groupI. Galuskin¹, E. Galuskin¹, P. Dzierzanowski²¹Faculty of Earth Science, University of Silesia, Bedzinska 60 Str., Sosnowiec, 41-200, Poland

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The scandian garnets were discovered in unusual, aposkam, rodingite-like rocks on the shores of the Wiluy River, Sakha-Yakutia Republic, Russian Federation. Scandian garnet forms discrete zones in crystals with complex zonation. These zones appear only in garnet containing relict central cores of kimzeyite. Scandium is contained in varying amounts in all zones of garnet (kimzeyite-schorlomite-andradite series) that formed at an early stage in the development of the high-temperature skarns. Late garnet zones (grossular-andradite series) that represent later lower-temperature growth contain negligible amounts of scandium. Scandium, as a rule, concentrates in zones immediately succeeding high-zirconian and high-titanian zones. Maximum scandium contents range up to 11.20 wt% Sc_2O_3 . The crystal chemical formula has the form $(\text{Ca}_{2.98}\text{Y}_{0.01}\text{Mg}_{0.01})_{\Sigma 3.0} - (\text{Sc}_{0.82}\text{Ti}_{0.44}\text{Zr}_{0.21}\text{Fe}^{3+}_{0.15}\text{Mg}_{0.10}\text{Al}_{0.09}\text{Cr}_{0.08}\text{Fe}^{2+}_{0.06}\text{V}_{0.01})_{\Sigma 2.0}(\text{Si}_{2.48}\text{Al}_{0.21}\text{Fe}^{3+}_{0.31})_{\Sigma 3.0}\text{O}_{12}$. These are calcium garnets which belong in the $\text{Ca}_3(\text{Zr,Ti})_2(\text{Al,Fe})_2\text{SiO}_{12} - \text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12} - \text{Ca}_3(\text{Fe,Al,Cr,V})_2\text{Si}_3\text{O}_{12}$ system. According to the procedures and guidelines on mineral nomenclature, where more than 2 atom types occupy a structural site, the mineral species is established on the basis of the dominant atom in the site. Consequently, this scandian garnet is potentially a new mineral species with the following calculated end members:

scandian garnet $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12} - 41$, morimotoite $\text{Ca}_3\text{Ti}^{4+}(\text{Fe,Mg})\text{Si}_3\text{O}_{12} - 16$, schorlomite $\text{Ca}_3\text{Ti}^{4+}\text{Fe}^{3+}_2\text{SiO}_{12} - 14$, kimzeyite $\text{Ca}_3\text{Zr}_2\text{Al}_2\text{SiO}_{12} - 10.5$, andradite $\text{Ca}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12} - 9.5$, grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} - 4.5$, uvarovite $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12} - 4$, goldmanite $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12} - 0.5$. Various isomorphic schemes of scandium incorporation in the structure of such a complex garnet define its stability. It is notable that the described garnets are characterized by enhanced hafnium and yttrium contents. High-zirconian zones contain up to 0.8 wt% hafnium and zones enriched in scandium up to 0.41 wt% yttrium. Newly-formed zircon and baghdadite are occasional inclusions in the garnet. It is probable that detrital zircon and titanium minerals in the sedimentary protolith supplied the scandium now incorporated in garnet.

P31-11

A Bi-Te-S-O mineral and Al-rich phosphates in epithermal quartz veins from the Kawazu mine, Izu Peninsula, Central JapanT. Yamada¹, S. Matsubara², R. Miyawaki², A. Harada¹, Y. Kosgue¹¹Friends of Minerals, Tokyo, 4-13-18, Toyotamanaka, Nerima-ku, Tokyo 176-0013, Japan

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The occurrence of over one hundred kind of mineral species are known from the epithermal quartz veins of the Kawazu mine located at the southern part of the Izu Peninsula, Central Japan. The mine was worked for gold, silver, copper and manganese. About twenty ore veins exist in the volcanic and pyroclastic rocks within the mining area. The mine is famous for the occurrences of Te-bearing minerals, as well as bismuth chalcogenides and Al-rich phosphates. It is the type locality of kawazulite and kinichilite. During the mineralogical survey at the mining area for these eight years, we have recognized many kinds of mineral species as the first occurrence in Japan, such as sonoraite, waylandite, dzhallindite, cannonite, dugganite, metavariscite and aheylite. Moreover, we are studying an undetermined Bi-Te-S-O mineral. We report here the mode of occurrence and mineralogical properties of these minerals with special reference to metavariscite, aheylite and an undetermined Bi-Te-S-O mineral.

Metavariscite: brownish white stalactite form up to 4 mm long with variscite and tellurite in cavities of quartz associating with kesterite. Aheylite: aggregates of turquoise group minerals, faustite, turquoise and aheylite, are found as the earthy specimens in the fracture of quartz. Powder XRD patterns showed that they are very close to those of turquoise. Among 16 chemical analyses by means of an EDS, 2 analyses correspond to aheylite composition. The Bi-Te-S-O mineral: Pearly white clusters composed of foliated or hexagonal platy crystal up to 2 mm in cavities of aggregate of tetradymite in the quartz vein. The chemical composition and powder XRD pattern do not identical with any known minerals. The main lines in the powder XRD pattern are 13.7(100), 6.84(11), 3.82(3), 3.40(6), 3.30(3), 3.13(3), 2.95(3), 2.73(9), 2.28(6), 1.710(14), 1.549(2), 1.521(3), 1.368(3); (d/I). The ratio of Bi:(Te,S) varies from 2:3 to 3:4.

P31-12

Pyrochlore-group minerals: Brazilian occurrences

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A great problem with pyrochlore-group minerals is its IMA-approved nomenclature system because it does not follow the general IMA mineralogical nomenclature rules. In the A site, it does not differentiate the occupation of Ca and Na, as well as if there are one or more cation other than Na or Ca composing more than 20% total A-atoms, then the species is named by the most abundant A-atom, other than Na or Ca. In spite of this, the species fluomatromicrolite was approved with basis on the predominance of Na in the A-site. Regarding the B-site occupation, the division among the subgroups is not made with a tripartite symmetrical classification: the species with $\text{Nb} + \text{Ta} > 2\text{Ti}$ and $\text{Nb} > \text{Ta}$ are considered as a pyrochlore subgroup mineral; if $\text{Nb} + \text{Ta} > 2\text{Ti}$ and $\text{Ta} \geq \text{Nb}$, the mineral will belong to the microlite subgroup; and if $2\text{Ti} \geq \text{Nb} + \text{Ta}$, the mineral will belong to the betafite subgroup. Isostructural species with other predominant cations in the B-site are not included in the pyrochlore-group (for example, romeite, with dominant Sb). The anions are not taken into account in the classification but the fluor dominance was used for the approval of the species fluomatromicrolite. A new IMA subcommittee on nomenclature of the pyrochlore-group is now elaborating a new nomenclature system. Commonly the crystals of pyrochlore-group minerals are chemically heterogeneous. However, several species of this group were defined with basis on wet chemical analyses, which represent compositions of mixtures. Consequently, it is important to obtain EDS/WDS and microprobe data. These data are rare in the literature, including for Brazilian occurrences. Some pyrochlore-group minerals were described for the first time in Brazil (uranomicrolite, bariomicrolite, fluomatromicrolite, lewisite), and some are economically very important, as uranomicrolite from São João del Rei area, Minas Gerais, and bariopyrochlore from Araxá, Minas Gerais. Most of the Brazilian occurrences of pyrochlore-group minerals were not studied or were only partially characterized. Samples from the following occurrences are under study at present: Fluomatromicrolite from Quixabá, Frei Martinho, Paraíba; uranomicrolite from Brejaúba, Conceição do Mato Dentro, and São João del Rei area, Minas Gerais; lewisite from Tripui, Ouro Preto, Minas Gerais; uranopyrochlore from Cajati, São Paulo; Lavra do Jonas, Conselheiro Pena, Minas Gerais; Lavra do Morro Redondo, Coronel Murta, Minas Gerais; Aracuaí, Minas Gerais; Lavra do Ipê, Governador Valadares, Minas Gerais; Ponte da Raiz pegmatite, Santa Maria de Itabira, Minas Gerais; and Lavra do Urucum, Galiléia, Minas Gerais.

Occurrence of Spurrite-Tilleyite-Rustumite-Hillebrandite (Spurrite-Merwinite Facies) within the Limestone-Granite Contact in the Güneyce-Ikizdere Area, Eastern Black Sea (Pontides), Turkey.

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Rare high-temperature and low-pressure contact-metamorphic assemblages have been found in the Güneyce-Ikizdere area, Eastern Black Sea, Turkey (Pontides), well-known for mineable kuroko-type massive sulfide deposits (e.g., Çayeli, Murgul, Cerrattepe). Plutonic rocks of calc-alkaline affinity (Rize batholith) intrude Cretaceous volcanic and volcano-sedimentary formations. An unusual contact metamorphism resulted in the development of assemblages belonging to the spurrite-merwinite facies at the contact between a cupola of the Rize batholith and lower Cretaceous limestones. The following rare calc-silicate minerals, mostly forming monomineralic masses, have been identified: spurrite $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$, tilleyite $\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$, rustumite $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)\text{Cl}_2(\text{OH})_2$, cuspidine $\text{Ca}_4\text{Si}_2\text{O}_7(\text{F},\text{OH})_2$, hillebrandite $\text{Ca}_2\text{SiO}_3(\text{OH})_2$, killalaite $\text{Ca}_3\text{Si}_2\text{O}_7\cdot\text{H}_2\text{O}$, foshagite $\text{Ca}_4\text{Si}_3\text{O}_9(\text{OH})_2$, gehlenite $\text{Ca}_2\text{Al}(\text{AlSi}_2\text{O}_7)$, monticellite CaMgSiO_4 , dellaite $\text{Ca}_6\text{Si}_3\text{O}_{11}(\text{OH})_2$, bichchulite $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH})_2$, perovskite CaTiO_3 and hydroxyllellastadite $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4(\text{PO}_4)_2(\text{OH},\text{F},\text{Cl},\text{CO}_3)$. These minerals are associated in variable proportion with familiar skarn minerals, such as wollastonite, diopside, vesuvianite, garnet (andradite), Ca-rich amphibole, Ca-rich pyroxene, spinel, magnetite, quartz, calcite and graphite. The area contains the second known occurrence of rustumite and killalaite. Up to now, two new minerals, defernite $\text{Ca}_6(\text{CO}_3)_{2-x}(\text{SiO}_4)_x(\text{OH})_2(\text{Cl},\text{OH})_{1-2x}$ and trabzonite $\text{Ca}_4\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, have been discovered in the area. Most of these calc-silicates generally develop under high-temperature and low-pressure conditions. They are principally associated with intrusive bodies of mafic composition, but at this locality, the spurrite-merwinite facies seems to occur at a lower temperature, typical of the hornblende hornfels or of beginning of the pyroxene hornfels facies, perhaps owing to compositional factors. The maximum temperature at the intrusive contact may be estimated at about 600–700°C. A series of retrograde minerals (e.g., defernite, trabzonite, hillebrandite, killalaite, bichchulite, foshagite and dellaite) replace and form as alteration products of the primary skarn minerals in an environment characterized by influx of $\text{H}_2\text{O}-\text{CO}_2$.

Strontium-dominant new minerals found in jadeiteite and related rocks from Itoigawa, Central Japan.

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The Itoigawa district is the most famous locality for jadeiteite in Japan. During mineralogical research on jadeiteite from the Itoigawa district, we have found some Sr-dominant minerals such as three new minerals, itoigawaite $\text{SrAl}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$, rengerite $\text{Sr}_4\text{ZrTi}_4(\text{Si}_2\text{O}_7)_2\text{O}_8$ and matsubaraite $\text{Sr}_4\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_8$, and rare minerals such as stronsalite $\text{SrNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$, lamprophyllite $\text{Na}_2(\text{Sr},\text{Ba})_2\text{Ti}_3(\text{SiO}_4)_4(\text{OH},\text{F})_2$, slawsonite $\text{SrAl}_2\text{Si}_2\text{O}_8$, taunsonite SrTiO_3 , strontium-apatite $(\text{Sr},\text{Ca})_5(\text{PO}_4)_3(\text{OH},\text{F})$ and thomsonite- Sr $\text{Na}(\text{Sr},\text{Ca})_2\text{Al}_5\text{Si}_5\text{O}_{20}\cdot 6\text{H}_2\text{O}$.

In 1987 Kobayashi and coworkers found stronsalite in jadeiteite from Ohsa, Okayama, Japan. This is the first report of the Sr-dominant mineral from jadeiteite in the world. After our discovery, Sr-dominant minerals have been found from jadeiteites outside the Itoigawa district. For example, stronsalite: Ohya, Hyogo, itoigawaite and niigataite $\text{CaSrAl}_3(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$: Wakasa, Tottori, and Ba-bearing stronsalite: Myanamar.

In the Itoigawa district, other new Sr-dominant minerals such as ohmilite $\text{Sr}_3(\text{Ti},\text{Fe}^{3+})\text{Si}_4\text{O}_{12}(\text{O},\text{OH})\cdot 2\cdot 3\text{H}_2\text{O}$, strontio-orthojoaquinite $\text{Sr}_2\text{Ba}_4(\text{Na},\text{Fe})_2\text{Ti}_2\text{Si}_8\text{O}_{24}(\text{O},\text{OH})\cdot\text{H}_2\text{O}$ and niigataite were also found. These new minerals except niigataite are found in magnesioriebeckite-bearing albite, but niigataite was found in diaspore-bearing prehnite-rich rock. Strontium-apatite and stronsalite were also found in the magnesioriebeckite-bearing albite and corundum-rich rock, respectively. Although the host rocks of Sr-dominant minerals are tectonic blocks in the serpentinite mélange, no Sr-dominant minerals are found in other tectonic blocks such as schists, greenstone, metagabbro, chert and limestone. It seems that tectonic blocks in the serpentinite mélange can be divided due to the existence of the Sr-dominant minerals.

The jadeite crystals in jadeiteite with Sr-dominant minerals are euhedral to subhedral with interstitial natrolite. This indicates that jadeite has been crystallized in fluid during metamorphism. Although Sr is a member of alkali-earth elements like Ca, the chemical behavior of these elements for jadeite is quite different. The ionic radius of Sr is too large to occupy the six-fold coordinated M2 site in jadeite. Therefore, Sr content in residual fluid has increased after crystallization of jadeite. Sr-dominant minerals may be formed in such Sr-rich residual fluid during high-P/T metamorphism in the subduction zone.

Endemic Minerals as Products of Geocatalysis and Indicators of Highly Productive Ore-generating Processes

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Unique deposits are appreciably superior to ordinary deposits of the same raw materials in both the diversity of minerals and the degree of their endemicity. Of ~600 minerals identified in the world's largest deposits of phosphorous and rare metals associated with the alkaline massifs of the Khibina-Lovozero complex, about half are endemic to apgaitic nepheline syenites and more than 100 are unknown outside this complex. The greatest mineralogical diversity is found in hyperagpaitic silicate-salt rocks, strongly enriched in water-soluble carbonates, silicates, and phosphates of sodium – indicators of maximally alkaline mineral-forming conditions in magmatic processes. Detailed study of these rocks, occurring on the margins of these unique deposits, allowed the author to describe many tens of previously unknown minerals and formulate some new approaches to elucidating the formation of commercial metal superconcentrations in the lithosphere on the basis of typomorphism of minerals. In contrast to the traditional approaches based on comparative analysis of compositions and properties of common minerals, our research places emphasis on the typomorphism of minerals occurring only in associations of a certain type. Many of these minerals display unusual crystal structures that are inconsistent with the laws of classic crystal chemistry while showing no particular compositional differences from other minerals. Their endemicity is due to the involvement, in the rock- and ore-forming processes, of some additional components that are not part of the compositions of these minerals but are conducive to their formation, i.e., act as natural catalysts. This is clearly indicated by the fact that there are no synthetic analogues to most of the long-known endemic minerals, although phase diagrams with the corresponding compositional fields have been experimentally studied in detail. Are the processes of formation of superlarge deposits only extreme forms of ordinary ore-forming processes or are they a special class of processes? The second alternative appears to be better justified by field data. Formation of a giant deposit is accompanied by a substantial chemical transformation of the original material in crustal volumes exceeding $10^2\text{--}10^3\text{ km}^3$, which is in conflict with the commonly held view that lithospheric rocks have an unlimited buffer capacity. This suggests that not only the indicator minerals of superlarge deposits, but also these deposits themselves are products of geocatalysis or ore-forming processes with extensive natural catalytic reactions, which overcome the buffer capacity of the encompassing strata and create the conditions of self-development of large-scale ore-generating processes.

Arrojadites: new formula, new structure and constraints on crystal-chemistry

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Arrojadite, dickinsonite and sigismundite define a group of phosphates, the structure and crystal-chemistry of which were not yet understood in satisfactory way. We collected arrojadite samples from most of the known occurrences, and examined them combining electron microprobe and LA-ICP MS analysis, single-crystal structure refinement and Raman and FTIR spectroscopy. The resulting model for arrojadite crystal-chemistry is based on the following conclusions:

Arrojadites have the chemical formula $\text{A}_2\text{B}_2\text{Ca}_1\text{Na}_{2-x}\text{M}_{13}\text{Al}(\text{PO}_4)_{11}(\text{PO}_3\text{OH}_{1-x})\text{W}_3$, where A are either large divalent cations (Ba, Sr, Pb) plus vacancy, or monovalent (K, Na) cations, B are either small divalent cations (Fe, Mn, Mg) plus vacancy, or monovalent (Na) cations, and M are either small divalent cations (Fe, Mn, Mg) or minor Li. The number of hydroxyl groups in the arrojadite formula is generally 3 apfu, and can be lowered to 2 apfu in particular when the sum of non-(P, Al) cations is higher than 20 apfu. The existence and orientation of the OH bonds detected by structure refinement have been confirmed by Raman and FTIR analysis.

The correct space group of arrojadites is *Cc* (and not *C2/c*), and the lowering in symmetry implies recognition of strong cation ordering among the 21 cationic sites besides the 12 PO_4 groups. A strong preference is also shown for F incorporation at one of the W sites.

A new nomenclature has been proposed and approved by IMA-CNMMN, which is based on: (i) the nature of the dominant M cation (Fe^{2+} , arrojadite; Mn^{2+} , dickinsonite; Mg (if any), name to be proposed); (ii) the nature of the dominant cation of the dominant valence state at the A1 and B1 sites (cf. Chopin, this meeting, for more detail on this new concept): the mono- or divalent nature of the cation used implicitly specifies the dominant occupancy by Na or by vacancy, respectively, at the A2 and B2 sites; (iii) the dominant occupancy of the OH group coordinated by the P atom. The criteria (ii) and (iii) may give rise to the use of three distinct suffixes.

P31-17

Crystal Chemistry of Iron Atoms in Non-metamict Chevkinite-(Ce): Valence state and Site Occupation Proportions

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The minerals of the chevkinite group can be divided into the two subgroups chevkinite and perrierite including more than one dozen mineral species. About 80 analyses of samples in the chevkinite group have been reported to contain FeO (assuming ΣFe as FeO) ranging from 7.11 to 16.88 wt.%. However, only a few metamict as well as annealed samples have been investigated by Mössbauer spectroscopy. The idealized formula for chevkinite can be expressed as: $A_4B_2C_2D_2\text{Si}_4\text{O}_{22}$, where $A = (\text{REE}, \text{Ca}, \text{Sr}, \text{Th})$, $B = (\text{Fe}, \text{Ti}, \text{Mn}, \text{Mg})$, $(C+D) = (\text{Ti}, \text{Fe}, \text{Nb}, \text{Al})$. It is significant to determine the valence state and site occupation proportions for iron atoms among B , C and D octahedral sites since it may result in different mineral species in chevkinite group.

Natural non-metamict chevkinite-(Ce) from the aegirine-alkali granite, Mianning, Sichuan Province, China, was investigated by means of the Mössbauer spectroscopy. The Mössbauer parameters were compared with those from metamict and annealed samples of chevkinite-group minerals. For non-metamict chevkinite-(Ce) the ratio of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is 39.2 %. Significant increase of Fe^{3+} ions may occur during metamictization and annealing processes. In non-metamict and annealed samples Fe^{3+} and Fe^{2+} ions have octahedral coordination, in metamict sample the iron "ions" tend to lower coordination.

On the basis of electron microprobe analyses, the FeO content in the non-metamict chevkinite-(Ce) is 11.22 wt.%, corresponding to 1.96Fe in atoms per formula unit (apfu). According to the correlation between bond length and isomer shift (IS), the quadrupole doublets with IS = 1.10 and 0.94 (mm/s) can be assigned to Fe^{2+} in B and C octahedral sites, respectively. On the basis of relationship between octahedral distortion and quadrupole splitting (QS), the quadrupole splitting of Fe^{2+} with QS = 0.86 and 0.77 (mm/s) can be assigned to C and D octahedral sites, respectively. The formula for non-metamict chevkinite-(Ce) can be written as: $(\text{Ce}^{3+}_{1.76} \text{La}_{0.89} \text{Ca}_{0.46} \text{Nd}_{0.22} \text{Pr}_{0.18} \text{Sm}_{0.04} \text{Gd}_{0.04} \text{Th}_{0.03} \text{Ba}_{0.01} \text{O}_{0.37})_{\Sigma 4.00} (\text{Fe}^{2+}_{0.61} \text{Mn}^{2+}_{0.13} \text{Ti}_{0.12} \text{Mg}_{0.08} \text{O}_{0.06})_{\Sigma 1.00} (\text{Ti}_{0.99} \text{Fe}^{2+}_{0.58} \text{Fe}^{3+}_{0.30} \text{Nb}_{0.06} \text{Al}_{0.02} \text{O}_{0.05})_{\Sigma 2.00} (\text{Ti}_{1.32} \text{Fe}^{3+}_{0.46} \text{Nb}_{0.10} \text{Al}_{0.04} \text{O}_{0.08})_{\Sigma 2.00} \text{Si}_4 \text{O}_{20.24} (\text{OH})_{1.76}$. It indicates that the non-metamict chevkinite-(Ce) from Southwest China belongs to Fe^{2+} endmember of chevkinite group because Fe^{2+} is the predominant component in B site.

P31-18

The channel constituents of vishnevite

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Vishnevite is a relatively common member of the cancrinite-sodalite group, first found at Vishnev Gory, Urals, Russia (Beliankin, 1944) and later in several other occurrences (see Deer et al., 2004 for a compilation). Vishnevite is structurally characterized by a stacking ABAB... sequence, like cancrinite and davyne (e.g. Bonaccorsi and Merlino, 2005). These three end-members are differentiated by their anionic content: cancrinite is the carbonate-rich member, vishnevite is the sulphate-rich member, and davyne is the chlorine-rich member of the group. Their framework arrangement is such to give rise to open 12-ring channels running along [001], and by columns of base-sharing undecahedral cages. In the cancrinite-type minerals, the undecahedral cages contain chains of alternating Na cations and water molecules, while the large channels are filled by carbonate groups in ideal cancrinite and by sulphate groups in ideal vishnevite. There is a complete solid-solution between cancrinite and vishnevite, with intermediate terms named sulphatic cancrinite or carbonatic vishnevite (Hassan and Grundy, 1984). Recent work by Della Ventura et al. (2005) showed that several cancrinite-sodalite group minerals contain carbon as CO_2 in addition (or in alternative) to CO_3 in their structure. We relate here a single-crystal polarized-light FTIR spectroscopic study of several crystals of vishnevite from various geological occurrences, previously characterized by EMPA and X-ray diffraction. The samples were prepared as doubly-polished slabs. FTIR data were collected using a NicPlan microscope, equipped with an MCT detector and a gold-wire grid, ZnSe substrate, polarizer. In situ high-T spectra were collected using a Linkam FTIR600 heating stage, fitted with ZnSe windows and a BaF₂ sample-holder. All investigated samples from Latium (Italy) show a well-defined and strong band in their IR spectrum at 2351 cm⁻¹ which can be assigned to carbon dioxide groups. The specimen from the holotype locality Vishnev Gory (Urals, Russia) described and still accepted as a (SO_4 and CO_3)-bearing phase (Deer et al., 2004), does not contain CO_3 but CO_2 as main anionic constituent, whereas vishnevite from Scotland contains mostly CO_3 groups in the channels, and very minor CO_2 . Polarized-light spectra collected on the [001] section show that the linear CO_2 molecules are oriented in vishnevite perpendicular the crystallographic 6-fold axis, like in beryl or cordierite (Aines and Rossman, 1984) and in pitiglianoite (Della Ventura et al., 2005). In situ high-T spectra show that the release of CO_2 from the vishnevite structure occurs for $T > 500^\circ\text{C}$, at temperatures 50°C higher than those observed in the closely related pitiglianoite (Della Ventura et al., 2005). Preliminary synchrotron-radiation FTIR mapping for H and C shows that several crystals from Latium are inhomogeneous with respect to the CO_3/CO_2 content, suggesting that the structure of these minerals is extremely sensitive to the evolution of the chemical environment of formation. Therefore the anionic zoning of cancrinite-sodalite minerals can be regarded as a very promising tool for geological modelling.

P31-19

Study of isomorphous substitution in alunite-beudantite group minerals

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The alunite-beudantite group minerals have a general formula $AB_3(\text{XO}_4)_2(\text{OH})_6$, where A site is occupied by large cations such as Na^+ , K^+ and Pb^{2+} , and octahedral B site is occupied by Al^{3+} , Fe^{3+} , Cu^{2+} and Zn^{2+} . The anion XO_4^{3-} are SO_4^{2-} , PO_4^{3-} and AsO_4^{3-} . Extensive solid solutions are usually observed in this group of minerals. The specimens are often admixtures of quartz, kaolinite, halloysite and so on. The presence of these associated minerals disturbs XRD analysis of the alunite group minerals and prevents the determination of their chemical formula based on their chemical analyses. So, this is a problem of discussing the crystal chemistry of these minerals. It is therefore useful for characterization of the alunite group minerals to reveal a relationship between their chemical composition and lattice parameters. In this study, more than 60 specimens containing alunite group minerals collected from 20 localities were analyzed with a SEM-EDS. The lattice parameters were refined based on the XRD data measured by a Gandolfi camera and IP using fine samples picked up from the thin sections used for the EDS analyses. Mineral species examined in this study are: alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, natroalunite $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$, osarizawaite $\text{Pb}(\text{Al}_2\text{Cu})(\text{SO}_4)_2(\text{OH})_6$, jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, natrojarosite $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, plumbojarosite $\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, beaverite $\text{Pb}(\text{Fe}_2\text{Cu})(\text{SO}_4)_2(\text{OH})_6$, hinsdalite $\text{PbAl}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6$, corkite $\text{PbFe}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6$, hidalgoite $\text{PbAl}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})_6$ and beudantite $\text{PbFe}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})_6$. The concentration of Na^+ , Pb^{2+} and K^+ in the A site apparently related with the c axis length, reflecting the difference in the ionic radii: Na^+ (1.39Å), Pb^{2+} (1.49Å), K^+ (1.64Å). Solid solution between natroalunite and alunite and that between natrojarosite and jarosite followed the Vegard's law. Beaverite and jarosite showed no significant difference in their c axis lengths, despite the difference in the ionic radii of the A site cation. Moreover, the c axis lengths of osarizawaite are close to that of alunite. The substitution between Al^{3+} (0.535Å) and Fe^{3+} (0.645Å) in the B site induced a greater difference in the length of a rather than c . The a axis length for beaverite was intermediate between those of jarosite and alunite. Considering ionic radii of cations in the B site, the a axis length for beaverite should be longer than that of jarosite. This contradiction may be related with the presence of Jahn-Teller effect at the B cations in beaverite and osarizawaite, because they contain considerable amounts of Cu^{2+} in the B site. It was found that the c axis lengths were also influenced by substitutions of As or P with S in the X site.

O32-01

HPHT-treated colorless and colored gem diamonds

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Natural diamonds frequently contain point and/or extended lattice defects that selectively absorb visible light to produce coloration. Brown is one of the most common colors for natural diamonds, and is largely the result of plastic deformation. Annealing at high pressures and temperatures (HPHT) is being used today to markedly change the colors of gem diamonds by reorganizing their lattice defects. Heating conditions for this treatment lie within the graphite stability field ($\sim > 2000$ K and 5-6 GPa). Diamonds, either as rough unpolished crystals and fragments or faceted gemstones, are exposed to these annealing conditions for short periods of time ($\sim$ several minutes) in high-pressure presses. An important consideration in the procedure is the selection of appropriate diamonds for treatment, both in terms of their starting color and the absence of large fractures or mineral inclusions that could produce breakage during the process.

The major effects of HPHT annealing include: (1) removing deformation-related brown color to make the diamond more colorless or to enhance a pink or blue appearance; (2) producing isolated nitrogen which imparts a yellow-orange hue; and (3) introducing the H3 defect (ZPL at 503.2 nm) which imparts both yellow bodycolor and green luminescence. If certain HPHT-treated diamonds are irradiated and then annealed at lower temperatures, a pink or red color can be produced.

Identification of artificially treated diamonds is essential to maintain consumer confidence and the integrity of the jewelry industry. In some cases, visual evidence of HPHT treatment is present in the form of heat damage to surfaces (etched or pitted appearance), as well as graphite formation along fractures and/or around inclusions. However, such visual clues are rarely present, and the identification of HPHT-treated diamonds requires the use of visible, infrared, and/or luminescence spectroscopy to check for distinctive configurations of optically active defects. A reference database of information on known treated and untreated diamonds is also essential for this determination. Recognizing the subtle spectroscopic differences in lattice defects (type and concentration) between natural and treated diamonds is becoming increasingly important. Diamonds whose colors have been changed by the HPHT method are becoming readily available in the gem marketplace, making the identification of this treatment process one of the most significant challenges currently facing gem-testing laboratories.

O32-02

The first color center related to the brown graining in type Ia natural diamonds

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Brown, as almost any other color in diamond, may be due to several causes. Some are relatively minor. For example, it has already been stated that H-rich diamonds may be brown, due to H-related centers. The same color may be induced on occasions by a range of slightly defective substitutional nitrogen in type Ib diamonds. Although the relation to carbon dioxide is unclear, rare CO₂-containing diamonds are also brown.

By far the most common variety of brown color in diamond is that associated with « brown graining », that is thin lamellae of plastic deformation parallel to the (111) planes.

In type I a diamonds, the brown color is qualitatively correlated with a series of absorption in the near-infrared called the « amber centres ». They can be grouped in four varieties, all containing a major series called AC1, with a main absorption at around 4168 cm⁻¹.

For this band, the darker the brown, the stronger the absorption. This band also roughly correlates with the concentrations of A aggregates (di-nitrogen). This suggests that this particular absorption is related to a di-nitrogen center, possibly the W7 ESR center. Current research aims at establishing whether there is a direct correlation between brown color in the graining, the AC1 absorption, and the W7 center through the study of progressive HPHT annealing.

Similar brown graining is found in nominally nitrogen-free type IIa diamonds. However, in such gems the brown color is never very dark. Also, CVD synthetic diamonds may show a brown color only when they contain nitrogen. These two facts suggest that, besides the AC1 centre, there might be a more general relation between certain categories of brown color and nitrogen in diamond.

O32-03

X-ray Computer Microtomography – effective method of the investigation of the inclusion in diamond

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Inclusions in nature (15 samples) and artificial (8 samples) diamonds have been examined with the following methods: X-ray computer microtomography (XCMT), Raman spectroscopy, Secondary X-ray fluorescence spectroscopy (SXFS) and micro-beam analyses.

The theoretic x-ray density ($\alpha = \mu_{\text{sample}} / \mu_{\text{etalon}}$) was calculated and several groups of the inclusions in diamond were established with the XCMT (Geotom, Yakushina) according to their x-ray absorption: 8-12 – metals; 6-7,5 – sulphides; 4-5,5 – oxides; 1-4,0 – silicates and 0,5 – carbon. Transparent inclusions, such as garnet (pyrope), olivine (forsterite) and carbon-hydrogenic associations were established with the Raman spectroscopy. Graphite was not found and we can't determine opac inclusions, such as sulphides, chromites and ilmenites. Impurities of the Fe and Ni were established in diamonds with the SXFS method (XGT-2000W, GB, Ghitenko), but we can't determine light elements, such as sulphur, carbon and oxygen.

The following inclusions were determined in natural diamonds after their cracking and polishing with the micro-beam analyses (Camebax SX-50, France, Bryzgalov): chromite, olivine (fresh and after saponitisation), sulphides (millerite and Fe-Ni monosulphides), pyroxenes (diopside and orthopyroxene). Metals (Fe, Ni, Cr, Pt) and carbides were determined in the artificial diamonds.

The comparison of the results show, that the X-ray computer microtomography (XCMT) is a very effective method of the investigation of the inclusions in diamond and we can diagnose the natural and artificial diamonds without their cracking and polishing.

O32-04

Cenozoic fossil resins used in gemmology: towards a practical grouping

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Specimens of Eocene to Miocene fossil resins commonly used in gemmology under the generic name of *amber* were studied by several methods, to search for basic features which allow to identify their provenance. They include *rumanite* (Colti, Romania), *amber* (Bitterfeld, Germany), *krantzite* (Königsau, Germany), *Baltic amber* (Baltic Sea shores, Poland) and *Dominican amber* (Santo Domingo, Dominican Republic). The first four were generated by coniferous and deciduous trees, while the Dominican amber is the result of leguminous plants.

Optical microscopy in thin sections shows isotropy for Baltic and Dominican amber or slight anomalous anisotropy for rumanite, Bitterfeld amber and krantzite. Tiny mineral inclusions such as quartz or clay minerals, as well as vegetal tissue remnants or drops of vegetal liquid are common.

The XRD shows the diffraction lines at d values of 6,486₈₅, 6,020₁₀₀, 5,711₈₅ and 3,410₁₀ Å which can be assigned to the presence of a crystalline carboxylic acid (C₁₇H₃₂O₃). These lines were found for rumanite as well as for Bitterfeld amber and krantzite, while the Baltic and the Dominican ambers show only the characteristic lump of the amorphous substances.

Rumanite has similar FTIR spectrum compared with the Dominican, Baltic and Bitterfeld ambers, suggesting similar compositions: aliphatic (dominant) and aromatic (subordinate) compounds, alcohols, alkenes, esters and carboxylic acids (e.g. succinic acid). The Dominican, Baltic and Bitterfeld ambers reveal also almost identical FT-Raman features, while rumanite and krantzite present each a different spectrum.

The GC/MS shows a clear similarity among the composition of rumanite and Baltic amber as well as the presence of terpenoids and some steroids. The Dominican amber is characterized by the presence of fatty acids in high quantity, while krantzite has high amount of steroids.

By a combination of various methods, it is possible to distinguish three groups with different/common characteristics, as follows: A) rumanite, B) the Baltic, Dominican and Bitterfeld amber, and C) krantzite. Up to now, only few samples were analyzed in this complex way, thus the grouping cannot be supported by statistics yet. Nevertheless, our study revealed clearly that ambers can be grouped in terms of their provenance but only by a combination of various analytical methods.

The Mineralogy and Geology of Canadian gem deposits

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Gem deposits are rare because the geological conditions required are exceptional and thus are worthy of scientific study. There have been a number of important discoveries in Canada since the 1970's. The Ekati and Diavik diamond mines (both in the Northwest Territories) began production in 1998 and 2003, respectively, and the Jericho mine (in Nunavut) will open in 2006. These will soon be joined by the Snap Lake (in the Northwest Territories) and Victor (in Ontario) mines. By 2008 Canada will rank third in the world in terms of diamond production by value.

Vanadium-dominant emerald was discovered near the Lened stock in the Northwest Territories in the late 1970's. The crystals occur within quartz veins that extend from a thrust fault across a skarn assemblage and into an overlying limestone. The black shale footwall unit contains abundant (>3,000 ppm) vanadium, which might suggest a Colombian-type genesis, but there is no evidence that the beryllium is non-magmatic in origin.

Chromium-rich emerald was found associated with the Taylor 2 pegmatite in northwestern Ontario in 1989. The pegmatite intrudes a chlorite schist unit near the end of an ultramafic sill. Most of the emerald occurs in a "zone of mixing" consisting of relict potassium feldspar crystals in a matrix of albite, biotite, and tourmaline.

Emerald was discovered at Tsa Da Glisza in the Yukon Territory in 1998. The mineralization is associated with quartz-tourmaline veins and aplite dikes which intrude chromium-rich metavolcanic rocks. Beryl crystals up to 4 cm in length occur in 12 mineralized zones within a 1000 × 300 m area. The occurrence is underlain by a granitic pluton which is the most probable source of the beryllium. Baflin Island in Nunavut was the scene of an important sapphire discovery in 2002. The corundum occurs in calc-silicate lenses in marble and is associated with diopside, oligoclase, phlogopite, calcite, scapolite, altered nepheline, muscovite, albite, and graphite. This diverse mineral suite is thought to have formed during retrograde metamorphism accompanied by multi-stage fluid infiltration.

Dark blue aquamarine with up to 5.92 wt.% FeO was discovered in 2003 in the southern Yukon Territory. The beryl is found within quartz veins that fill sigmoidal tension gashes, which cut a syenite of Mississippian age. Accessory minerals in the veins include siderite, ankerite, allanite-Ce, and fluorite (dated at 171.4 ± 4.8 Ma). The evidence suggests a metamorphic origin for the mineralizing fluid and local derivation of vein constituents.

O32-06

Archaeological emerald provenance: A contribution from trace elements analysis by secondary ion mass spectrometry

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Emeralds are one of the most valuable beryl gems and one of the oldest used in jewellery. We have information of its use already in the Egyptian age. The finding of emeralds in archaeological sites around the towns of Rome and Pompeii testifies the diffusion of these gems also during the Roman Empire. The current interest for Cultural Heritage exploitation suggested investigating the provenance and working places of these gems. For archaeologists the identification of the source deposit and manufacturing sites means to collect information on the trade routes and fabrication processing of this kind of goods whereas for the material scientists it means to find a physical-chemical parameter that joints the single stone to its mine unambiguously. Many research groups are working on this field. Studies on emerald origin and provenance involved: 1) the Electron Micro-Probe Analysis (EMPA) joined to a statistical test of major-, minor-element distribution; 2) the characterization of the inclusion population; 3) the determination of the oxygen and hydrogen isotope ratios. Here we present a new approach to the investigation of the emerald provenance, which relies on the SIMS analysis of the trace elements. The wide set of samples selected for this study represents all the deposits mined in Roman times, to which we added some crystals coming from today's famous mines. From the EMPA results we can subdivide the gems into two sets: those related to granite intrusion and those associated with hydrothermal activity in tectonically-active areas in which fluids circulation is controlled by shear zone and faults. Ion microprobe (Cameca IMS 4f) studies were focused on elements such as Li, B, Na, K, Sc, Ti, V, Cr, Rb, Sr, Y, Zr, Nb, Cs, Ba, Th and U. Boron, Sr, Zr, Nb, Y, Ba, Th, U are generally at sub ppm level, whereas V, Sc, Cs, Cr show considerable variations in their concentration (in the range tens-thousands of ppm for a few of them). Significant variations exist also for alkaline elements such as Li, Na, K and Rb. Even if our study rely on a limited number of analyses (typically 3 for each crystal), the results so far obtained point out chemical compositions which are in some case peculiar in the gems investigated, allowing thus to foresee the possibility to answer the questions about provenance. Some elements seem in fact to be characteristic and, to some extent, discriminative of the various source deposits.

O32-07

Behavior of Beryllium diffusion in Corundum

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The heat treatment of corundum involving diffusion of beryllium is a popular technique to improve or change its color. Usually, this treatment has been conducted in high temperature just under its melting point (2400 K). However it should be important to derive the diffusion coefficient of beryllium in corundum also in relatively low temperature, not only to understand the behavior of beryllium diffusion in the wide temperature range, but for the gem testing.

Here, Molecular Dynamics (MD) simulation was carried out to derive the diffusion coefficient of beryllium in corundum. This technique also gives us a knowledge of the atomic behavior of beryllium diffusion. Furthermore, heating experiments were performed to ensure the efficiency of the simulation, where small cubes of synthetic white sapphire were heated with the powder of beryllium oxide in a furnace, and the behavior of beryllium diffusion in corundum was examined from the overall consideration.

In the present study, potential parameter sets of Be and Al for MD simulation were newly derived. The results calculated with these parameters reproduce well the structures and properties of corundum, bromellite and chrysoberyl. Moreover, the melting point of corundum can be reproduced. MD simulation of corundum containing a beryllium as an interstitial atom with new potential parameters shows that the diffusion of beryllium occurs between 1300 K and 2300 K, and that it diffuses more to the direction perpendicular to the c axis than in a parallel direction with that axis. The diffusion coefficient can be estimated to be around 10⁻⁶ cm²/s from these calculations.

On the other hand, white sapphire heated at 1700 K in 104 hours in the furnace turns to brownish orange in color. Chemical analysis of this sample with LA-ICP-MS reveals that beryllium diffuses into 2 mm in depth. From the profile of beryllium content, the diffusion coefficient of beryllium in corundum can be estimated to be 10⁻⁷ cm²/s. This value is smaller than that calculated with MD by only an order of magnitude, which indicates MD simulation in this system is considered to be efficient enough, and that beryllium could diffuse into corundum even in lower temperature than expected.

O32-08

Application of LA-ICP-MS (Laser ablation system with inductively coupled plasma mass spectrometry) to the gemological field

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In recent years gemological laboratories have been faced with diverse issues that are difficult to solve and have been the cause of confusion for many gemologists. Several techniques—including UV/visible, infrared, and Raman spectral analysis—have been employed to solve some of these gemological problems. However, each technique poses limitations and as a result the problems may not be solved. Two main of the problem areas are examined here:

1. Detection of new treatment techniques

Heat treatment processes aimed at color improvement or other alterations to a gemstone have developed from the simple or traditional "low temperature" methods to high temperature techniques involving diversified environments (oxidizing-reducing atmospheres through the controlled introduction of various gases) and/or the artificial diffusion of external additives. These developments have produced treated gemstones in which the treatment can be difficult to detect using only the conventional gemological techniques.

2. Geographic origin determination of a gemstone

For precious and rare objects it is certainly justified to enquire about their geographic origin. However, without reliable and detailed analytical data, indications of origin may sometimes be unreliable; at times they may also be regarded as anything from unprofessional, non-educated guesses to plain wishful thinking. Even the most experienced of issuing laboratories regard origin determinations as being opinions based solely on the experiences and/or data uniquely collected by that laboratory. To move away from expressions of opinion there is a need for origin determinations to be made on a more sophisticated scientific basis.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is becoming an important technique for direct solid sampling in chemical analysis. The authors introduce this technique to the gemological field to resolve the problems that would be difficult with only conventional gemological laboratory techniques. The advantages of LA-ICP-MS analysis include high resolution, rapid and direct characterization of gemstones whether loose or in jewelry, micro destructive analysis not separate for solution analysis, and precise analysis of elemental composition. We present an understandable summary of LA-ICP-MS principle, a comparing study with other analytical techniques SIMS and LIBS, and a applications such as the detection of beryllium diffusion in corundum, the identification of geographic origins for sapphire, ruby emerald and copper-bearing tourmaline from different country localities as examples used to explain the advantages of this technique. A laser logo was adopted for the micro-destructive laser ablation sampling process on the girdle of each testing sample, to avoid the damaging beauty of a gemstone.

Pigments in cultured freshwater pearls: identification using Raman scattering and UV-Vis spectroscopy

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Understanding the nature of the pigments in natural color cultured freshwater pearls can help separate them from their treated equivalents. Previous studies have established that Raman scattering is useful to detect the pigment in cultured freshwater pearls, but the exact nature of the coloring agent is still unknown. The originality of this work is that different excitation wavelengths are used for the same samples at relatively high resolution.

This study was carried out on 30 untreated and 10 treated colored Chinese freshwater pearls from the mollusk *Hyriopsis cumingi* covering their typical range of colors. All naturally colored pearls show the two major Raman resonance features of polyenic compounds assigned to C=C (at about 1500 cm⁻¹) and C-C stretching (at about 1130 cm⁻¹), regardless of their specific hue. These peaks are detected neither in white pearls nor in treated color pearls (or if they exist they are typically weak and possibly accompanied by 'suspicious' peaks). Thus they are believed characteristic of these pearls color. The exact position of C-C stretching demonstrates that these compounds are not members of the carotenoid family. With the change in excitation wavelength -four excitation wavelengths of an ionized argon laser were used at 647.1 nm, 514.53 nm, 487.98 nm and 457.94 nm-, changes in position, shape and relative intensities of the two more intense bands are noted from one sample to the next. Additionally, such changes occur for the same point of the same sample by simply changing the excitation wavelength. The exact position of the C=C stretching band of polyenic molecules depends strongly on the chain length (number of C=C bonds). Up to 7 pigments can be found in the same pearl. Their general chemical formula are R-(CH=CH)_n-R' with n= 7 to 13. All our samples are colored by a mixture of at least 4 pigments with n = 8 to 11, plus possibly others, more difficult to detect. Different colors are explained by different mixtures, not by a single pigment. Raman scattering results parallel at least qualitatively those in UV-Vis diffuse reflectance. These polyenic pigments seem to be characteristic of all pearls originating from the *Hyriopsis* genus. The origin of color of treated color freshwater pearls is different. The separation of untreated vs treated colored cultured freshwater pearls seems to be done simply using Raman scattering, for example through broad bands at about 1330 and 1600 cm⁻¹.

Two Types of the Blue Band-A Luminescence of Natural Diamond

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A broad luminescence band named Band-A is one of the most common bands observed in all type of diamond. Wave length of its peak is variable between 400 nm and 550 nm, and its width is also variable according to a number of reports (1). Defect structure responsible for the band has not been established.

In this study, we have measured cathodoluminescence (CL) spectra of natural diamond, HPHT synthetic diamond and CVD diamond, considering distribution of the luminescence from each specimen.

It was found that natural diamond exhibits two type of the Band-A in a blue region. One has a maximum at 415 nm and the other at 435 nm. The 415 nm Band-A is observed only from type Ia, and its distribution has a pattern of growth layers like an annual ring of tree. On the other hand, the 435 nm Band-A, which is observed from all types of diamonds, distributes in different ways. It appears along slip lines, near cracks or as network patterns. The distributions suggest that the 415 nm Band-A is attributed to some grown-in defects incorporated during growth, and the 435 nm Band-A is produced by lattice distortion formed in post growth process.

Reference

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Iridescent andradite garnets (*Rainbow Garnets*), newly-found from the Tenkawa area in the Yoshino district, Nara Prefecture, Japan

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Iridescent andradite garnets (*rainbow garnets*) were first found at the Adelaide mining district, Nevada and described by Ingerson and Barksdale (1943). They are extremely rare and have been reported from only a few localities in the world (e.g., the Sierra Madre Mountains, Sonora, Mexico). Recently, however, a large amount of iridescent andradite garnet were newly found in large quantities from near Kose mine, Tenkawa, Nara Prefecture, Japan. In the present study, this newly-found *rainbow garnet* is first explored by using optical microscopy, SEM-EDX and TEM. Iridescent andradites from Tenkawa occur in skarn and as brown translucent euhedral crystals with well-developed {110} faces. Polarizing microscopic observation reveals that they consist of {110} growth sectors with banding textures parallel to {110} faces. In addition to {110} growth lamellae, wavy lamellae (ca. 10-20 μm in thickness) were observed all over the specimen. In the (001) thin section, strong iridescence was observed only in the sectors in which {110} layers are oblique to the transmitted light, suggesting that interference of light with {110} layers originates the iridescence.

The wavy lamellae are different in chemical compositions; the thick lamellae (10 to 20 μm in width) brighter in BEI are And_{97.0}Gr_{2.5}Sps_{0.7} and the darker thin lamellae (1-2 μm) are And_{91.3}Gr_{8.0}Sps_{0.7}, respectively. They correlate with growth features of crystal surfaces, and are considered to be produced during the growth. This type of wavy lamellae was also observed in Adelaide andradites as described by Akizuki et al. (1984) and Hirai and Nakazawa (1986), but the periodicity of more than ten microns is too large in comparison with the wavelength of light and cannot be origin of iridescence.

TEM observation reveals the presence of periodic fine lamellar texture that is parallel to {110} and have quite regular interval (ca. 100 to 300 nm). A composition mapping using STEM showed difference in composition of Al/Fe between the both layers. The layer texture was found to be composed of alternating major (Fe-rich) and minor (Al-rich) lamellae with very sharp interfaces. The cause of iridescence can be concluded as multilayer interference of light produced by these fine lamellae.

The fine lamellae cross continuously across the wavy lamellae produced during the growth, so that this structure should be developed after the growth. As the compositional difference between the layers is distinctive and their interfaces are sharp, the fine lamellae are highly possibly developed by exsolution after the growth of garnet.

O33-01

Mineral Physics and Synchrotron Radiation

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Excellent feature of synchrotron radiation (SR), such as high brightness and energy tunability in wide energy range, has been widely recognized to be a powerful tool for the study of mineral physics. It becomes possible to open up the interior of the earth to the core when combined with state of art of the high temperature and high pressure technique, and also to search for the origin of the earth or the solar system through the precise analysis of meteorite or stardust.

Recent development of the laser-heated DAC can generate pressure and temperature to reach the core condition. MgSiO₃ perovskite structure was found to transform to Cmcm type structure just above the mantle-core boundary condition. It is noteworthy that the new structure is highly anisotropic, which well explain the seismic anomalies at this region. A challenge is in progress to combine Brillouin scattering technique with laser-heated DAC to obtain elastic properties of mineral at real earth's condition. Another technique to clarify the elastic property is to apply inelastic scattering method. Especially, inelastic scattering by nuclear resonant scattering is quite effective as Fe site is selectively measured. SR infrared spectroscopy using DAC is also an interesting technique for the investigation of phonon under pressure.

On the other hand, multi-anvil press system can generate pressure of 30 GPa with WC anvil and 60 GPa with sintered diamond anvil at temperature of 2000K. This can realize the lower mantle condition, and the phase boundary of upper and lower mantle was clearly determined. By utilizing the characteristic of relatively large sample volume, viscosity of melt can be precisely measured by falling metal technique. Density can be obtained by the X-ray absorption technique. By setting the oscillator at the outside of anvil, ultrasonic measurement technique can be applied to very high temperature. This technique is hereafter considered to be the most important to investigate the elastic properties of interior of the Earth, in addition to establish the pressure scale at high temperature.

A micro SR-CT was successfully applied to analyze meteorite and stardust. Chondrules were classified their external shape for the first time, and also internal structures of them were clearly observed. These observations gave important information to elucidate their origin. Furthermore, SR-CT was applied to cosmic dust, which is smaller than meteorites. In addition to CT, micro-diffraction and micro trace element analysis of the cosmic dust is under way.

O33-02

Mechanisms of arsenic mobilization in SE Asian aquifers: Shedding synchrotron light on a natural disaster

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The consumption of arsenic-rich groundwaters in West Bengal and Bangladesh is causing widespread deleterious health effects, with the situation in Bangladesh described as the largest poisoning of a human population in history. Elevated levels of arsenic have also been identified in aquifers located elsewhere in SE Asia, including northern Vietnam and southern Cambodia. The mechanisms underlying the development of such high-arsenic subsurface waters have been widely debated, however, the reductive dissolution of arsenic-bearing ferric (oxyhydr)oxides has become the prevailing theory. Nevertheless, the microbial component of this process has remained poorly characterized. We have used X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies, in tandem with geochemical and microbiological investigations, to help improve our knowledge of the biological drivers of arsenic mobilization in SE Asian aquifers.

West Bengal sediment, collected from an aquifer that hosts arsenic-rich groundwater, incubated under a range of biogeochemical regimes demonstrated that porewater release of arsenic occurred under reducing conditions only. In addition, sediment microcosms amended with acetate (as a proxy for organic matter used as an electronic donor for microbial respiration) showed marked arsenic release, apparently decoupled from Fe(III) reduction; no arsenic liberation was evident in identical experiments with autoclaved sediments. The solid phase association of arsenic in the sediment was probed using EXAFS spectroscopy, in conjunction with a selective extraction technique, which suggested that the bulk of the arsenic (<5 µg/g) was associated with iron (oxyhydr)oxides. Incubations using sediment from an arsenic affected aquifer in southern Cambodia revealed similar trends, providing support for the role of microorganisms in arsenic mobilization. Furthermore, significant solid phase reduction of arsenic, tracked by XANES spectroscopy, was observed in Cambodian sediments spiked with As(V) and acetate. The lack of arsenic reduction in analogous abiotic experiments suggests the presence of an arsenic-tolerant (and possibly arsenic metabolizing) bacterial community.

It has been suggested recently that the microbial reduction of ferric (oxyhydr)oxide to magnetite may cause species dependent mobilization of arsenic. Tetrahedral As(V) could be incorporated into tetrahedral sites in the magnetite structure, whereas trigonal As(III) would be excluded from the lattice framework. Lately, we have used X-ray absorption spectroscopy to test this hypothesis. These data will also be presented, and placed in the context of our earlier sediment incubation experiments to aid our understanding of the genesis of such high-arsenic groundwaters.

O33-03

Sensitive measurement of fluorescence XAFS using bent crystal analyzer and its application to radiogenic osmium in molybdenite

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Identification of the chemical-states of trace elements, i.e. speciation, is important for understanding the geo- and cosmo-chemical processes in natural samples. For the speciation of trace elements in rocks and minerals, fluorescence XAFS using energy-dispersive Ge detector has been often used. However, due to the upper count limit of the detector, high quality fluorescence XAFS for the trace elements cannot be obtained under intense scattering and/or fluorescence from other predominant elements in the samples. To deal with this problem, we developed a system for fluorescence XAFS using bent crystal analyzer to selectively extract fluorescence x-rays of a target element, combined with an intense synchrotron radiation source, such as an undulator, which was applied to the speciation of trace Os in rocks and minerals.

In this paper, speciation of Os in molybdenite, often used as a suitable mineral for Re-Os dating, has been studied as an example of the application. Radiometric dating using various radioactive decay systems has been widely applied to various terrestrial and extraterrestrial materials. Although the information is closely related to chemical stabilities of parent and daughter nuclides and the reliability of the radiometric dating, there have been few investigations on the speciation of the daughter nuclides. In this study, we chose 187Re-187Os system in molybdenite for the possible application of this idea, since initial abundance of Os in molybdenite is often negligible compared with radiogenic Os in old molybdenite minerals rich in Re. From XAFS spectra, we have investigated local structure of Re and Os in molybdenite from Onganja Mine in S. W. Africa (age: 530 million years). It was shown that bond length between Re and S and oxidation state of Re were identical to those of Mo in the mineral, which supports that Re can be enriched in the molybdenite. On the other hand, the local structure of radiogenic Os in the sample is different from that of Re or Mo in the sample, that is, Os-S bond length is shorter than Mo-S and Re-S bond lengths by more than 0.05 angstrom. In contrast, it was revealed that the structure is similar to that of Os in erlichmanite (OsS₂). These results show that the local structure of Os in the molybdenite is decided primarily by the chemical characteristics of Os and the effect of the lattice of original site, where it was stable site for Re before radioactive decay, is less important.

Reference

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O33-04

Mineral location and identification using a scanning transmission X-ray microscope

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Scanning Transmission X-ray Microscopes (STXMs) employ a focused x-ray beam to image an ultra-thin sample using monochromatic x-rays. The distribution of an element in the sample is mapped by comparing the transmission at two energies: one just below the K-edge of the element (where the element has a very low absorption cross-section) and the second just above the K-edge (where the element absorbs strongly). STXMs are generally employed to study organic compounds. However, STXMs can also locate and identify certain minerals that have strong, narrow absorption features, which occur as a result of transitions induced from the electron core to higher electron energy levels. For example, carbonates have a strong absorption, resulting from the C-O bond, near 290 eV, while graphite and diamond each have sharp exciton absorptions. These minerals can be located by comparing maps of the sample at the energy of the mineral-specific absorption and just off that energy. Positive identification of the mineral requires either a full X-Ray Absorption Near-Edge Structure (XANES) spectrum or Transmission Electron Microscope characterization at that location.

The ability of the STXM to locate and identify carbonate is particularly important. Kemper et al. (*Astronomy & Astrophysics*, 394, 679-690, 2002) reported the detection of Ca-carbonate in the dust ejecta from NGC 6302, while Lisse et al. (*Dust in Planetary Systems*, Lunar Planetary Institute, Abs.#4105, 2005) reported the detection of carbonate in the dust released from comet Temple-1 as a result of the Deep Impact excavation. Both of these results were unexpected, since carbonate is generally formed by aqueous processing. Its presence in NGC 6302 would suggest its formation as a condensate while its presence in Temple-1 might indicate that regions in that comet were warm enough at some time to allow liquid water. Neither identification is unambiguous, since each group detected a broad absorption feature that was "best fit" by the sum of several mineral absorptions. We have begun a STXM search, at the ~100 nm scale, for carbonate in primitive, anhydrous interplanetary dust particles, the best-preserved samples of the original condensate of our Solar System. We found carbonate in one particle (Flynn et al., *Dust in Planetary Systems*, Lunar Planetary Institute, Abs.#4011, 2005), suggesting carbonate may be a nebula condensate. We plan a STXM search for carbonate in the dust from comet Wild-2, collected by NASA's Stardust spacecraft, in the near future.

Development of High-Resolution X-Ray Micro-Tomography System with Fresnel Zone Plate Optics at SPring-8

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X-ray computerized tomography (CT), which was originally developed for medical diagnosis, is a non-destructive technique for three-dimensional observation using a strong penetrating power of x-rays. In this decade, CT method with high-spatial resolution (X-ray micro-tomography, μ CT) has been developed and has been applied to other fields such as biology, material sciences and earth sciences as well as for medical use. Using highly-collimated x-ray beam from synchrotron radiation light source and using high-spatial-resolution image detector, μ CT with simple projection geometry is now reached a spatial resolution of about 1 μ m. However, no more significant improvement in spatial resolution is expected with this system, due to the spatial resolution of the detector and due to the diffraction of x-rays.

On the other hand, x-ray microscopy using several kinds of x-ray imaging devices such as Fresnel zone plate (FZP), refractive lenses, and total reflection mirrors have been developed. In these days, spatial resolution of several tens of nm is achievable in the hard x-ray region. For example, the spatial resolution of 30 nm has been achieved with a FZP. Therefore, combining such an x-ray microscope optics with μ CT, very high spatial resolution three-dimensional imaging will be available.

We have been developed a high-resolution μ CT combining an x-ray imaging microscope system at the large synchrotron radiation facility, SPring-8. A FZP was used as an objective. A schematic diagram of the setup is shown in Fig. 1. The system consists of a light source, a Si(111) double crystal monochromator cooled with liquid nitrogen, high precision stages, FZP objective and a X-ray image detector. The FZP were fabricated by the electron-beam lithography technique. The material of the zone structure is tantalum with thickness about 1 μ m. The outermost zone of FZP is 100 nm. The x-ray energy was selected between 7 keV and 10 keV to obtain fine image contrasts for various samples. The spatial resolution of the system has been estimated using a resolution test pattern, and the finest line width of 150 nm has been resolved.

At the presentation the detail of the system and recent result are presented.

O33-06

In situ high temperature X-ray absorption investigation at the Al, Si and Ca K-edges in melts

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Structure of silicate and aluminosilicate melts is not well known at high temperature. X-ray absorption spectroscopy is a very specific and interesting way to probe the network structure and more specifically the Al and Si surrounding. Recent developments on X-ray absorption spectroscopy at light K-edges, made on the LUCIA beamline at the Swiss Light Source, enable to measure XANES spectra at high temperature on the Si, Al and Ca K-edges. We have studied SiO₂, Al₂O₃, Anorthite, diopside, and calcium aluminate (C3A and CA) at different K-edge and different temperature above to the liquidus temperature. The method and first results will be presented. Significant change on the XANES spectra at the Ca K-edge can be observed just after the melting point of CA and C3A, where important changes appear in the liquid state. At Al K-edge, we observed also important modifications in the mean resonances. These first measurements are a good illustration of loss of medium range order after melting characterized by the disappearance of structural features in XANES spectra.

O33-07

Second critical endpoint between aqueous fluids and a high-magnesian andesite by high-pressure and high-temperature X-ray radiography

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Aqueous fluids dissolve significant amounts of silicates under high-temperature and high-pressure conditions. Silicate components dissolved in aqueous fluids coexisting with mantle peridotite change their major element chemistry from andesitic at 1–2 GPa to peridotitic at 3 GPa and higher pressures (Ayers et al. 1997 EPSL; Stalder et al. 2001CMP; Mibe et al. 2002 GCA; Kawamoto et al. 2004 Am Min). In the present study, we show direct observations of unmixing between aqueous fluid and a high-magnesian andesitic melt by use of synchrotron X-ray radiography with multi-anvil type high-T and high-P apparatus at SPring-8. We observed aqueous fluid and a high-Mg andesitic melt coexisting in pressures lower than 3 GPa. And above 3 GPa, we observed only one fluid phase, suggesting that the HMA and aqueous fluids are completely mixing and under supercritical conditions. Therefore, the second critical end-point between this HMA and aqueous fluids should be at around 3 GPa.

By use of synchrotron X-ray radiography, Mibe et al. (2004, 2005 AGU Fall Meeting) reported a possible second critical endpoint between aqueous fluids and a peridotitic/ a MORB melt at 3.8/ 3 GPa, respectively. Based on these experiments, we suggest that slab-derived components should be under supercritical conditions on the surface conditions of downgoing slabs beneath the volcanic arcs (3 - 6 GPa). Whether the slab-derived component has chemical characteristics like a partial melt or an aqueous fluid depends on the temperature; slab derived-supercritical fluids in relatively warm regions can dissolve more silicate components than slab derived-supercritical fluids in relatively cold regions. In other words, the slab-derived components in warm conditions can be similar to partial melts of subducted slabs.

O33-08

CAESAR diffraction and the symmetry of CaSiO₃ perovskite with and without Al₂O₃

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We introduce a new diffraction technique for high-pressure high temperature studies of crystal structure. The technique, called Combined Angle-dispersive and Energy-dispersive diffraction for Structural Analysis and Refinement (CAESAR), takes full advantage of synchrotron radiation by scanning an energy-dispersive diffraction (EDD) detector as a function of two-theta. A two-theta step scan yields thousands of angle-dispersive diffraction (ADD) patterns, whose energy resolution is determined by the energy-channel width in the multichannel analyzer of the solid-state detector; the angular resolution is determined by instrument geometry. Sampling of this data in constant energy bands gives high quality angle dispersive diffraction patterns of sufficient range for Rietveld refinement. We have investigated the symmetry of CaSiO₃ perovskite (with and without Al₂O₃) up to 25 GPa and 2000 K in the multi-anvil apparatus SPEED-1500, at SPring-8, using the CAESAR technique. Superlattice reflections were clearly resolved throughout the P-T range of the experiments for the end-member CaSiO₃ perovskite, confirming that the crystal structure of this perovskite is noncubic. A combination of Rietveld refinements at selected wavelengths and analysis of the complete two-dimensional datasets show that the most likely space group is Cnmc. The perovskite with 3 wt% Al₂O₃, on the other hand, is cubic throughout the investigated P-T range. Implications to the transition zone and lower mantle are discussed.

Thermal expansion of mantle minerals at high-pressures

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The temperature gradient in the mantle is considered to be nearly adiabatic. The thermal expansion coefficient is the most important parameter to estimate the adiabatic temperature gradient in the Earth. It significantly varies with pressure and temperature. In this study, we determined thermal expansion coefficient of important mantle minerals, namely wadsleyite and perovskite, at high pressures and temperatures by means of in situ X-ray diffraction.

There have been a number of in situ X-ray diffraction studies for mantle minerals. However, they are not precise enough to determine thermal expansion coefficient as a function of pressure and temperature. By technical improvements, the pressure and cell parameters can be measured with precisions of 0.03 GPa and 0.0003 Å at P-T conditions up to 30 GPa and 2300 K, which enables us to determine thermal expansion coefficient with sufficient precision.

The volume measurement for Mg₂SiO₄ wadsleyite was conducted at pressures of 11 to 19 GPa and temperatures of 300 to 1700 K. The thermal expansion coefficient under the P-T conditions at the upper part of the transition zone (15 GPa & 1700 K) is found to be 2.8×10^{-5} /K, which is a little higher than that of ringwoodite (2.4×10^{-5} /K). We found that the thermal expansion coefficient of Mg₂SiO₄ wadsleyite decrease with increasing pressure with a relatively small ratio. Its Anderson-Grüneisen parameter is found to be 4.4(2). The adiabatic temperature gradient in the upper part of the transition zone will be 0.4 K/km.

The volumes of MgSiO₃ perovskite were measured at pressures of 17 to 30 GPa and temperatures of 300 to 2300 K. The thermal expansion coefficient under the P-T conditions at the top of the lower mantle (23 GPa & 1900 K) is found to be 3.5×10^{-5} /K, which is considerably higher than those of wadsleyite and ringwoodite. We found that the thermal expansion coefficient of MgSiO₃ perovskite largely decreases with increasing pressure. Its Anderson-Grüneisen parameter is found to be 10.6(2). The adiabatic temperature gradient at the depth of 660km is estimated to be 0.5 K/m, and decreases to 0.3 K/m at 1200 K depth.

Phase relations in the system MgO-FeO-SiO₂ up to 50 GPa and 2000°C

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High-pressure and high-temperature experimental techniques using sintered diamond anvils in Kawai-type multi-anvil apparatus were developed with synchrotron radiation at SPring-8, and it was enabled to generate up to 50 GPa and 2000°C. Using these newly developed techniques, MgO-FeO-SiO₂ system, which is one of the most important systems in the Earth's deep interior, was investigated to mid lower mantle conditions. High-pressure and high-temperature experiments were carried out in the range of 22-47 GPa at 1500 and 2000°C, using Kawai-type multi-anvil apparatus, "SPEED-Mk.II" installed at BL04B1 in SPring-8, and "Sakura-2500" installed at the Magma Factory, Tokyo Institute of Technology. In the experiments above 25 GPa, experimental pressure was determined by in-situ X-ray diffraction measurement using an equation of state of gold. We used a synthesized clinopyroxene, which has a composition of En₅₀, as a starting material. After high-pressure and high-temperature experiments, samples were quenched and recovered. Present phases in the run products were confirmed by MXRD and chemically analyzed using EPMA and ATEM. In every run product, starting material decomposed to three phases of (Mg,Fe)SiO₃-perovskite (Pv), (Mg,Fe)O-magnesiowüstite (Mw), and SiO₂-stishovite (St). Then it was able to determine the maximum iron solubility in Pv, and Mg-Fe partitioning between Pv and Mw as functions of pressure and temperature. The maximum iron solubility in Pv gradually expands with increasing pressure and temperature, and the most iron-rich Pv, which contains 32 mol% of FeSiO₃, was synthesized at 44 GPa and 2000°C. The iron content in Mw coexisting with Pv and St dramatically increases with pressure, and it exceeds 90 mol% above 40 GPa. According to these compositional changes, partition coefficient $K_D = (X_{Fe}^{Pv}/X_{Mg}^{Pv})/(X_{Fe}^{Mw}/X_{Mg}^{Mw})$ decreases from 0.21 to 0.03 at 1500°C, and 0.13 to 0.05 at 2000°C as a function of pressure. This significant change of K_D indicates that ferrous iron strongly concentrates into Mw as a function of depth in the Earth's lower mantle. The presence of iron-rich Mw would have some influences on geochemical and geophysical properties of the deep lower mantle.

Triple H experiments – MAX200x

HASYLAB HARWI-II High pressure experiments

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Twenty years ago geoscientists from all over the world launched in-situ X-ray diffraction experiments under extreme pressure and temperature conditions at synchrotron beamlines. One of

the first apparatus was installed at DESY-HASYLAB, MAX80, a single-stage multi-anvil system. MAX80 allows in-situ X-ray diffraction studies in conjunction with simultaneous measurements of elastic properties up to 12 GPa and 2000 K. This very successful experiment, unique in Europe, is operated by GFZ Potsdam and is used by more than twenty groups from several countries worldwide every year. The newly designed high-flux hard wiggler (HARWI-II) beamline is an ideal X-ray source for this kind of experiments.

One of the fundamental regions to study geodynamic processes seems to be the transition zone between upper and lower mantle. To make these conditions accessible and to achieve bigger specimen volumes the new MAX200x, a double-stage DIA-system, was installed at the HASYLAB HARWI-II beamline. The system is designed to reach pressures up to 25 GPa and temperatures of 2400 K by a resistance heater. MAX200x is driven by a hydraulic ram with a maximum load of 1750 tons. The press is mounted on a y-z-table to adjust the sample to the synchrotron beam. Furthermore, the press can be rotated to enhance statistics during the diffraction experiments. The whole system weights about 30 tons. Derived from the successful equipment of MAX80 and adapted to the new task MAX200x is equipped for XRD with a Ge-solid-state detector, for transient ultrasonic interferometry, as well as with a radiography system to measure the change of volume and shape of the sample under in situ conditions. A stepper motor driven slits system allows to optimize X-ray beam size and shape for the experiments. The whole system is remote controlled. The goniometer is mounted on a moveable table. Both, experiments with monochromatic and white X-rays are available. Besides the Ge-solid state detector new designed goniometers are used to enhance the precision of the experiments.

Some recent results on the non-quenchable high-P – low-P clinoenstatite transition and to the quartz-coesite transition will be given to discuss the different interferometric techniques, including the XRD-data and X-radiography results, necessary to detect the phase transitions under in situ conditions and to measure the sample deformation. Parallel to the installation of MAX200x some innovative experiments were carried out to improve the potentials of multi-anvil apparatus in terms of maximum pressure and limitation of stress inside the sample and the anvils.

Precise measurement of elastic wave velocities combined with X-ray and ultrasonic interferometry under high pressure and high temperature

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Ringwoodite (high pressure polymorph of olivine) and majorite (high pressure polymorph of pyroxene and garnet) are considered to be the abundant minerals at depths between 520km and 660km in the mantle transition region, and it is important to accurately determine the elastic wave velocities in order to discuss the mineralogy and composition of the mantle transition region. In this study, we have developed ultrasonic interferometry conjunction with in situ X-ray radiation techniques (X-ray diffraction and X-ray radiography) in a high-pressure apparatus, in order to obtain high-quality elastic wave velocity data under the conditions of the mantle transition region, and measured the elastic wave velocities of ringwoodite and majorite under high temperature and high pressure.

The specimen was hot-pressed at 19GPa and 1473K in a 3000-ton high pressure apparatus (ORANGE-3000; GRC at Ehime University). High-pressure ultrasonic experiments were performed using Kawai-type high-pressure apparatus SPEED-1500 at SPring-8. The unit cell constants of pressure marker (NaCl, Au) and sample (ringwoodite, majorite) were measured for estimation of pressure and sample density respectively. In addition, X-ray radiography was used for direct measurement of sample length under high pressure and high temperature. The ultrasonic signals were generated and received by a LiNbO₃ transducer (10°Y-cut), which can produce both longitudinal and shear waves at the same time.

The waveforms were very clear and the each echoes both P-wave and S-wave were identifiable at high temperature and high pressure. The elastic wave velocities on the ringwoodite sample were consistent with those of earlier studies at lower pressure/temperature conditions, whereas the velocities of majorite with the complex chemical composition were substantially lower than the earlier estimates based on the measurements for simpler compositions under lower P/T conditions. From these data we are able to derive elastic moduli and their pressure/temperature derivatives quite precisely, which can be used to tightly constrain the mineralogy and chemistry of the mantle transition region.

Sound velocity measurements on partial melting and melts at mantle pressures using combined ultrasonics and synchrotron X-radiation

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Combined synchrotron radiation and ultrasonic interferometric techniques have been successfully utilized in the last decade or so for simultaneous measurements of sound wave velocities, structure and unit cell parameters, stress and strain on mantle minerals up to the Earth's lower mantle conditions. The synchrotron X-radiography technique adapted in these studies also enables new opportunities for precise sound velocity measurements on materials undergone phase transition, melting, plastic deformation, and multi-phase aggregate (mantle rocks) at high pressure and temperature for which the sample length can not be easily retrieved from other methods. We have applied these techniques to mantle olivine containing a few percent of melts of basaltic composition to investigate the effect of partial melting on the physical properties of mantle minerals. We also conducted experiments on sound velocity measurement of bismuth across its solid-solid phase transitions at room temperature and up to temperatures about 200 degree above its melting temperature at 3 to 5 GPa. Pressure was measured in-situ using the equation of state of NaCl. We will report the results from these exploratory experiments to demonstrate the new applications of the current techniques to the study of partial melting/melts at high pressures and their applications for the study of the Earth's interior.

Detection of Platinum-Group-Element Nuggets in Terrestrial Rock Samples by X-ray Absorption and Fluorescence Imaging using Synchrotron Radiation

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Concentrations and isotopic ratios of platinum-group elements (PGEs) in the Earth's mantle are strongly controlled by chemical differentiation processes involving both silicate and metallic phases, and therefore are instrumental for understanding the differentiation and evolution of the Earth's interior. However, interpretation of the geochemical data of PGEs has been equivocal because the main host phases for PGEs in the mantle are not well constrained. PGEs in mantle rocks are thought to be concentrated in sulfide and metal minerals that consist mainly of PGEs, but such PGE-bearing phases are generally as tiny as 10 µm or less (so called micronuggets), preventing accurate mineralogical identification or even frequent discovery from mantle-derived samples. In this study, we attempt to develop a novel method for efficient detection of PGE-bearing micronuggets from rock samples by X-ray absorption and fluorescence imaging using the synchrotron radiation beam at BL20XU of SPring-8, Japan. X-ray absorption images of samples with 0.1-3 mm thickness were taken at energies slightly below and above the K-absorption edge of a target element, and distribution maps of the element were obtained from the difference between the high-energy and low-energy images. We successfully detected 5-µm-size Ru metal grains and 20-µm-size Os metal and iridosmine grains from 3-mm-thick synthetic samples. We also found a 50-µm-size Pt-bearing nugget from nominally homogeneous powder of sulfide concentrate, PTC-1a, reference material issued by CANMET-MMSL. X-ray fluorescence analyses were operated using an X-ray beam of 15 or 113 keV. The X-ray beam was focused to 2-200 µm using a sputtered-sliced Fresnel zone plate or a slit, and was applied to rock samples of 0.1-3 mm thickness. X-ray emitted from a sample was detected using a solid-state detector. Using a 15-keV beam focused to 10-20 µm, we successfully detected L lines from several grains of 1-µm Pt particle, even from behind a 100-µm-thick peridotite slice. Element map images were obtained by scanning the sample, which successfully reproduced the distribution of the 1-µm Pt particles behind the peridotite slice with 10-µm resolution. We expect that further optimization and combination of these methods will enable detection of µm-size PGE-bearing micronuggets from natural rock samples.

Detection of Sr in Dinosaur Eggshell by Wavelength Tunable LEBRA-PXR

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LEBRA at Nihon University has recently success to irradiate Parametric X-ray, PXR, produced by a "two-crystal system" (Hayakawa et al., 2004) using a LINAC operating at 80 MeV. One of characteristics of LEBRA-PXR is the wide tunability of X-ray wavelength, from 6 KeV, 2.07 angstrom, to 17 KeV, 0.729 angstrom. The tuned PXR is highly monochromatic itself. The recording of the X-ray images were carried out by IP, Fuji Film Co. Ltd., Polaroid film, Polaroid Co. Ltd, or X-ray CCD cameras, Hamamatsu Photonics Co. Ltd. Using this system, X-ray images of some silicified dinosaurs eggshell sections were taken at 16 KeV and 16.2 KeV, referred to 16.1 KeV for Sr K-absorption edge. The radiographs showed that particular portions were sensitive to the change of wavelength, indicating that these positions contained Sr. EDS analysis confirmed the presence of Sr in these portions. These dinosaur eggshell fragments kept the morphological features such as so-called mammillae on the inner surface and the tubular palisade texture on the sectioned plane with chimney-pore. The Sr-minerals were located at the small cracks parallel to the palisade. The minerals found in the dinosaur eggshell fragments were calcite and quartz substituted the palisades alternatively. The Sr-mineral as well as calcite and quartz found in the dinosaur eggshell were the secondary minerals. The origin and formation mechanism of these minerals are in consideration.

Three-dimensional structures of dust samples and their tracks captured in silica aerogel onboard EuReCa using SR micro-tomography

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In initial analyses of meteoroid samples collected by retrievable satellites and/or sample return planetary probes, it is crucial to obtain basic information by non-destructive methods, because farther detailed analyses usually involve destructive processes. We conducted X-ray computed micro-tomography (CT) measurements with high spatial resolution for three specimens in silica aerogel onboard the European Retrievable Carrier (EuReCa) spacecraft to obtain the three-dimensional (3-D) structures of impact tracks and to examine the 3-D distributions of fragments of impactors. EuReCa spacecraft was exposed in the Low Earth Orbit for 326 days in 1992-93. The X-ray CT measurements were performed at BL47XU in SPring-8, Japan. Using synchrotron radiation (SR) as an X-ray source, we obtained CT images with the spatial resolution of about 1 micrometer by high flux density monochromatic X-rays.

Impact tracks, radial cracks, condensed aerogel and fragments of impactors were observed in CT images. Subtraction images, where the aerogel specimens were imaged at X-ray energy level just above and below the K-absorption edge of Fe, showed no Fe-rich microparticles in the aerogel specimens, suggesting that their impactors might be artificial orbital debris, rather than micrometeoroids. The lengths of three impact tracks were about 200-400 micrometers. Two of them were branched into two at the ends. We also obtained spatial distributions of fragments of impactors and condensed aerogel particles along the impact tracks and the radial cracks.

Those results showed that SR based CT was functional to analysis of hypervelocity impact tracks formed in aerogel and obtaining spatial distribution of fragments of microparticles dispersed along impact tracks. Such a technique should be able to apply for other space exposed aerogel samples like the Stardust.

High-pressure XAFS Study of Germanate Melts

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Structures of liquid silicates, in particular their responses to compression, are of great interest for geophysics. However, the experimental study of structural change of liquid silicates is difficult because extreme pressures and temperatures are needed and the number of in-situ technique for observing liquid structure is restricted under such conditions. It is well known that germanates are structural analogs of silicates. Our previous high-pressure XAFS study has shown that a dense liquid phase with GeO_6 octahedron appears in $\text{Li}_2\text{Ge}_4\text{O}_9$ melts under pressure. However the transition mechanism and the effects of chemical composition have not been clearly understood. In this study, using a high-pressure and high-temperature XAFS technique, we have investigated effects of chemical composition on the pressure-induced coordination number change in liquid germanate by adding B_2O_3 or H_2O_2 to SrGeO_3 germanate melt.

High-pressure and high-temperature XAFS experiments were performed at a beamline BL14B1 of Spring-8. Pressure was generated by using a cubic-type multianvil press installed on the beamline. In situ XAFS measurements were conducted in transmission mode. XAFS spectra near Ge K edge with an energy range of 1000 eV above the edge were successfully measured up to 10 GPa at 1500 K. The extended X-ray absorption fine structure (EXAFS) interference function was extracted from measured XAFS spectra using standard procedure.

We obtained the variation of the first neighbor Ge-O distances in liquid SrGeO_3 up to 10 GPa and 1500 K. It is interested that pressure dependences of the Ge-O distances in liquid SrGeO_3 containing B_2O_3 and the liquid SrGeO_3 containing H_2O_2 show similar trend at high-pressure region. This indicates there would be less effect of coexisting ions on the local structural change around Ge.

Development of the density measurement of liquid sulfur at high pressure using the falling sphere method

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Density is one of the fundamental properties to understand the physical phenomena. The density of silicate melts provides important information to understand the processes of magma and volcanic eruptions. Also, the density of liquid iron alloy is an essential to understand the dynamics and evolution of the Earth's outer core. However, experimental density data are very scarce because of the technical limitation under high pressure and high temperature. Combining the large volume press and the falling sphere method using the synchrotron radiation, we have developed the newly density measurement method. Recently, the falling sphere method using an X-ray radiography technique has been successfully used to obtain the precise viscosity at high pressure. We have applied this technique to the density measurement using the Stokes' law. As the first attempt, we have tried to measure the density of liquid sulfur, because the melting temperature is relatively low at high pressure (800°C at 9 GPa). We used a multi-anvil large volume press (SPEED-1500) installed on the BL04B1 beamline at SPring-8. Pressure is generated by the Kawai-type system with tungsten carbide cubes having a 12 mm truncation edge length. The incident white X-ray beam irradiates the sample cell through the anvil gap, and real-time images of the sample can be observed using the X-ray radiography technique. The starting sample of pure sulfur powder was sealed with BN capsule surrounding a graphite furnace. The plural metal spheres (each diameter of 100-200 μm) with different each density (Ni, Mo, Ta, W, Au, Pt, Re) were embedded in the top of the sample. When the sulfur was melted, the spheres fell down into the liquid sulfur simultaneously, and each terminal velocity was observed to be constant. The densities of liquid sulfur were obtained from the Stokes' law up to 9 GPa. The errors of our values are estimated within 0.5 g/cm³. We have demonstrated that the falling sphere method using the X-ray radiography technique is useful for the density measurement at high pressure. It is considered that this technique is applicable to various liquid materials.

Application of high pressure X-ray microtomography: Measurement of interfacial energy of liquid Fe-alloy under pressure

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X-ray microtomography has been developed recently under high pressure condition using drickemmar anvil apparatus (Wang et al. 2005). In order to obtain a wider field of view (anvil gap) in tomography image, we have now used a Toroidal (Paris-Edinburgh) anvil apparatus for high pressure microtomography measurement.

High pressure tomography technique is applicable to measure directly the interfacial energy between two liquids using the sessile drop method. Surface/interfacial energy is one of the most important properties of molten Fe-alloy to control the interconnectivity of liquid Fe-alloy and, thus, the core formation process in the Earth and planets. In previous studies, interconnectivity of liquid Fe-alloy has been studied from dihedral angle measurement (e.g. Terasaki et al. 2005). There is no direct and no in-situ measurement of interfacial energy at high pressure condition. The aim of our study is to determine the effect of light elements on the interfacial energy of liquid Fe at high pressure.

Starting materials consisted of Na-disilicate and Fe-S pellet with 0, 22 and 50 at% of sulphur. X-ray radiographic images of entire sample part have been collected from all directions by rotating the rotational Drickemmar module on 13BMD beamline at APS. Used energies of monochromatic X-ray were 30 - 40 keV in which the best image contrast between Fe-S alloy and silicate can be obtained. Transmitted X-ray is imaged with a single crystal YAG scintillator and CCD camera. Resolution of tomographic image is 4 $\mu\text{m}/\text{pixel}$ in 2x2 pixel binning, which is enough to analyze the shape of the Fe-alloy droplet. Each radiographic sliced image was reconstructed to 3-D tomographic image. Temperature was increased to 1373-1873 K those were above melting temperatures of Fe-alloy samples and then we can clearly observe the shape change of the Fe-S droplet in Na-disilicate. Tomography images of Fe-FeS liquid with 3 different compositions were collected at 1GPa after quench the sample.

Quantitative-phase and crystal-structure simultaneous analysis of multi-mineral phase micro samples by synchrotron Gandolfi method

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The method for quantitative-phase and crystal-structure simultaneous analysis of micro amount mineral specimen has been developed by a newly constructed synchrotron Gandolfi camera system utilizing Rietveld refinement method to the diffraction data observed by the Gandolfi camera. The method is successfully applied for analysis of small amount extraterrestrial materials such as primitive meteorites or inter-planetary-dust particles, which are agglomerate of small single crystals.

The synchrotron Gandolfi camera system is constructed for the diffractometer of BL-3A experimental station of Photon Factory, KEK, Tsukuba, Japan, modifying the Gandolfi camera made by Tenno Co. Ltd., Italy. The monochromatized synchrotron radiation from bending magnet is exposed to the sample set on the Gandolfi camera and the diffraction pattern is recorded on an IP film. The obtained powder diffraction pattern is analyzed by multi-phase Rietveld refinement method. As the result of Rietveld refinements the crystallographic information for each mineral phase is obtained and from the refined scale factors, the weight ratio of mineral phases is calculated. We are planning to apply this method to characterization of mineral composition of extraterrestrial materials. We tried to analyze extraterrestrial samples, which are agglomerates of small crystals of silicate or iron-related minerals with diameters of about one hundred micro-meters, to evaluate the performance of this system and successfully obtained the crystallographic information of mineral phases and the weight percent ratio of them. The merit of this newly developed system is as follows. A) The use of synchrotron radiation realizes shorter measurement time and higher angular resolution diffraction experiments. B) This method is completely non-destructive analysis. C) An agglomerate of small single crystal is suitable for Gandolfi camera system.

The analysis method by this system will be demonstrated and the performance of this system including evaluation of errors will be shown in presentation.

Preliminary Test Experiments for Au Pressure Scales

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Since experimental pressures are difficult to measure directly, equations of states of standard materials, such as Au, Pt, MgO, NaCl, and Ar, are commonly used as pressure scales. However, Au has discrepancy between the two latest experimental results, Takemura 2001 and Dewaele et al. 2004, both used quasi-hydrostatic He pressure medium and ruby pressure scale. Dewaele et al. observed 3-4 GPa higher at 70 GPa. For testing two results, simultaneous measurements of ruby pressure and volume of Au, MgO, and NaCl were conducted up to 29 GPa using He pressure medium. Even if the most hydrostatic He pressure medium, non-hydrostatic effect can be seen in FWHM of diffraction peaks and scattering of peak positions. MgO and NaCl was not much affected non-hydrostatic conditions. Ruby pressure and volume relations are consistent with known pressure scales. Au becomes much less hydrostatic conditions waiting for next beam time at 14 GPa for 2 weeks. First series of experiments up to 14 GPa, diffraction peaks show hydrostatic conditions. Ruby pressure and volume relations are consistent with Takemura 2001. After getting less hydrostatic conditions, observed ruby pressure is 1-2 GPa higher at 14-29 GPa compared to Takemura 2001, and even higher than Dewaele et al. 2004.

The high pressure and high temperature phase relations and the elastic properties of the calcium ferrite and calcium titanite-type structures in MgAl_2O_4

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The phase relations in MgAl_2O_4 have been studied by in-situ X-ray diffraction experiments in the pressure range from 30 to 45 GPa and temperatures up to 2500 K using Kawai-type multi anvil apparatus availed the sintered diamond as second stage anvil. Three phases were found in this P-T range. The calcium ferrite phase is stable at relatively low temperature up to 44.3 GPa. The calcium titanite phase is stable at higher temperatures and was observed at 43 GPa and 2373 K. However, a new high-pressure phase was observed at pressures 38-42 GPa and at temperatures above 2100 K. The new phase can be recovered at ambient conditions, which is composed of single crystals of up to ~50 μm with the MgAl_2O_4 composition. This new phase is different from the unidentified high-pressure form of MgAl_2O_4 (ϵ -phase) reported earlier. The detailed structural analysis on this phase is currently under way. These results suggesting that the triple point among the calcium ferrite, calcium titanite, and the new phase is located at a P-T condition of 42 GPa and 2100 K.

The elastic parameters of the calcium ferrite and the calcium titanite phase were determined using Kawai-type multi anvil apparatus and the lever type diamond anvil cell with the pressure medium of helium, respectively. The obtained P-V-T data were fit with the third order Birch-Murnaghan equation of state. By the least squares fit, we derived the elastic parameters of the calcium ferrite as $V_0=240.1(3) \text{ \AA}^3$, $K_{T0}=211(5) \text{ GPa}$, $K'_{T0}=3.7(4)$, $(dK_{T0}/dT)_P=-0.039(6) \text{ GPa/K}$, and a volumetric thermal expansivity $\alpha_0=a_0+b_0T$ with values of $a_0=2.3(1)\times 10^{-5} \text{ K}^{-1}$, and $b_0=1.9(3)\times 10^{-8} \text{ K}^{-2}$. On the other hand, those of the calcium titanite phase were estimated as $V_0=239.9(2) \text{ \AA}^3$, $K_{T0}=204(5) \text{ GPa}$, $K'_{T0}=3.6(6)$ under room temperature. Based on the present results, the increase of the density on the phase transition between the calcium ferrite and the calcium titanite phase at 42 GPa and room temperature is only 0.8 %. However, the axial compressibility of the calcium titanite is more isotropic compared with that of the calcium ferrite.

Compact multianvil device for in situ angular-dispersive X-ray diffraction studies at high pressures and temperatures

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The 'Paris-Edinburgh' (PE) cell is currently used for a wide range of measurements such as neutron and X-ray diffraction, EXAFS, Compton scattering, inelastic neutron and X-ray scattering, and ultrasonic studies. This method provides excellent powder statistics, well defined and almost uniform temperature conditions, allows the study of liquids at high (P,T) and enables to recover macroscopic samples.

One of the limitations of the standard design of the PE cell so far is its accessible (P,T) domain, restricted to ~ 10 GPa and 2000 K. However, in situ X-ray diffraction studies at conditions beyond these limits are extremely attractive in various domains of research. To overcome these limitations, we have designed a new high pressure set-up for in situ angle-dispersive X-ray diffraction studies under high (P,T) using the V7 type Paris-Edinburgh press. The V7 has a capacity of 450 tonnes, i.e. almost twice as the standard press, but still a weight of less than 80 kg. The ~ 20% larger overall dimensions allow to accommodate a two-stage multi-anvil system similar to the Stony Brook "T-cup system" which operates routinely to 25 GPa and 2500 K. The advantage of such a combined V7-T-cup system is its extreme compactness compared to all other multi-anvil systems currently existing on other synchrotron sources. The reduced dimensions and weight allow to transport it easily between laboratories and to install it in almost any experimental hutch within ~2 hours. It offers also the considerable advantage of being able to work with several presses simultaneously, i.e. carry out experiments with one cell whereas other presses are being prepared for the following measurements. We present this new high-pressure set-up as well as first results obtained in both off-line and on-line experiments at the ID27 beamline of ESRF.

O34-01

Neutron diffraction applied to Mineralogy, an overview.

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Neutron scattering offers advantages in mineralogical research thanks to peculiar properties of the neutrons. When considering some of these properties, a large variety of favourable and sometimes unique applications can be envisaged.

- 1) - The low absorption cross section of neutrons for many materials, can make extreme sample environments (HT, HP vessels, Reaction Cells, etc.) easier to work with for neutron scattering than for other in situ experimental techniques, especially when gram-scale amounts of sample are available.
- 2) - Neutrons, unlike X-rays, are efficiently scattered by hydrogen ^1H and deuterium ^2H atoms. Many minerals have a structural hydrous component which is extremely important in regulating a large variety of behaviours and properties with implications spanning from the atomic to the continental scale.
- 3) - The neutron scattering cross section contrast between mineralogically common elements having equal or similar numbers of electrons, such as: Ti^{4+} , Ca^{2+} , K^+ , Cl^- or: Na^+ , Mg^{2+} , Al^{3+} , Si^{4+} or: Fe^{2+} and Mn^{2+} , allows the direct determination of site occupancies and distributions, independent of bond length analysis.
- 4) - The neutron scattering cross section does not change with scattering vector (i.e.: does not fall off as the inverse of the atomic radius) thus providing a large amount of information in a diffraction pattern yielding better and decoupled information on thermal motion and site occupancies.
- 5) - Inelastic Neutron Scattering (INS) can provide fundamental information for the prediction of mineral behaviour and phase transformations under pressures and temperatures of the Earth's interior allowing to model and interpret fundamental thermodynamic parameters.
- 6) - The high penetration of neutrons and the wide beam dimension can provide quantitative texture analyses with high grain statistics even on coarse-grained materials (rocks). Neutrons offer the sensitivity required for residual stress analysis of geological material where effects on rocks are orders of magnitude smaller than those on technological materials.
- 7) - Neutrons are very sensitive to magnetic moment making them an easy probe for magnetic structures, collective μ excitations, and crystal field energy levels of many magnetic elements.
- 8) - Direct imaging with neutrons, although still somewhat limited in resolution, offers the advantage of large volume sampling for in situ radiographic and tomographic studies of complex materials such as rocks and their constituents.

O34-02

Material science to be explored by advanced neutron beam technology

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Neutrons play four major roles in material science including mineralogy, (1) probing atomic/molecular structures and dynamics by diffraction/reflection/scattering, (2) imaging interior structures by neutron radiography, (3) detecting trace elements by neutron activation and prompt gamma-ray analysis, and (4) creating new materials by nuclear transmutation. In contrast to other probes such as x-ray and electron beams, neutron has a special capability of high sensitivity of light elements (particularly hydrogen) and high selectivity of isotopes and neighboring elements through nuclear scattering as well as high detectability of magnetism through magnetic scattering. Neutron's high transmissivity also offers a great advantage for experiment under extreme conditions such as high-pressure, high/low-temperature, or high-magnetic field. Several highlights explored by neutrons will be demonstrated in a variety of fields such as (1) crystal structures of gas-hydrates and dynamics of guest molecules, (2) phase transitions of ice, (3) trace elements in meteorites and so on. Also demonstrated is an example of very precise magnetic structures studied by a newly-developed polarized neutron instrument which is highly sensitive to magnetic property of specimens.

Other advanced neutron technology will be shown for both reactor- and accelerator-based sources, which will provide the state-of-the-art technology for promotion of materials science and mineralogy. In particular, the current status of the J-PARC (Japan Proton Accelerator Research Complex; <http://j-parc.jp/>) now under construction will be reported with an emphasis on its 1MW spallation neutron source (JSNS tentatively called) and associated new instrumentations available in 2008.

O34-03

Recent developments using the Paris-Edinburgh cell for neutron diffraction at high pressure and high temperature

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Neutron diffraction is a powerful tool of high pressure research and in many ways can be considered to be complementary to X-rays for crystallographic experiments. The special features of neutron diffraction include its sensitivity to hydrogen (deuterium) and other common light atoms, its contrast for atoms having similar atomic weights, and its sensitivity to magnetic order. However, despite these advantages, neutron diffraction has been much less used than X-ray scattering for high pressure studies because until recently, large sample volumes were required and the maximal attainable pressures were limited to ~ 2 GPa. These limitations were overcome in 1992 with the advent of the Paris-Edinburgh cell which allows structural studies by neutron diffraction at pressure up to 30 GPa.

In this talk, I will give an introduction to high pressure neutron diffraction techniques with a strong emphasis on recent developments, in particular the new design of a cell assembly with internal heating which enables neutron diffraction to be performed at simultaneous high temperatures and pressures (8 GPa, 2000 K). A novel non-invasive neutron radiographic method to measure the temperature of the sample in the high-P/T cell will be also briefly presented. I will illustrate the potential of these methods for fundamental Solid State Physics, Planetology and Earth Sciences by presenting some structural studies on a variety of materials under pressure. Finally, I will describe new techniques which permit the study of liquids and amorphous materials using neutron diffraction at these HP-HT conditions and I will illustrate this new method by recent data collected on D₂O water.

O34-04

Scientific achievements and technological advances of high P-T neutron diffraction at LANSCE, Los Alamos

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We have successfully conducted high P-T neutron diffraction experiments at LANSCE. To date, we have achieved pressures up to 30 GPa, and simultaneous high pressure and temperature of 10 GPa and 1800 K. With an average 3-6 hours of data collection, the diffraction data are of sufficiently high quality for the determination of structural and thermal parameters. We have studied the hydrous mineral Mg(OD)₂, perovskite (K,Na)MgF₃, clathrate hydrates (CH₄, CO₂, and H₂), metals (Mo, Al, Zr), and amorphous materials (carbon black, BMG). Our research aims at accurately determining crystal structure, local atomic environment, and phase stability in P-T-X space. High-pressure neutron diffraction is a multidisciplinary endeavor and we welcome researchers from all fields of science to come use and develop this advanced technique.

Several high pressure devices are available for neutron diffraction at high pressure. We have developed a 500-ton toroidal press, TAP-98, to conduct simultaneous high P-T (10 GPa, 1800 K) neutron diffraction experiments with HIPPO (High-Pressure and Preferred-Orientation diffractometer). Hydrostatic pressure cells made of Al-7075 allow users to perform experiments at high pressures (up to 200 MPa) and low temperatures (down to 20 K). We have also developed a large gem-crystal anvil cell -the ZAP cell- to conduct neutron diffraction experiments at high-P and low-T. The ZAP cell can be used for integrated experimental techniques of neutron diffraction, laser spectroscopy, and ultrasonic interferometry. Pressures up to 10 GPa are attainable. We are pursuing further developments of high P-T technology with a new 2000-ton press, TAPLUS-2000, and a cubic anvil package to reach a pressure of 20 GPa and temperature of 2000 K. The new design of a dedicated high pressure neutron beamline, LAPTRON, is also underway for simultaneous high P-T neutron diffraction, radiography, and tomography. We seek strong community support for this new development.

O34-05

High-P neutron diffraction studies of hydrous minerals: progress and prospectsM.D. Welch¹¹Department of Mineralogy, The Natural History Museum, London SW7 5BD, UK.

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Significant advances in experimental methodologies for high-pressure neutron diffraction have been made over the past 5 years, primarily improvements in sample containment, gasket design, pressure media and run automation. This presentation will focus on powder diffraction, although recent progress with studying single crystals will also be touched on. A variety of examples will be reviewed that illustrate the strengths, challenges and current limitations of neutron diffraction for studying minerals at high pressure. These examples will include chlorite, the DHMS-related phase leucophoenicite, perovskite-related hydroxides, β -Al(OD)₃ (bayerite), and also brucite at high-PT.

With good data it is now possible to find H(D) directly (rather than just refine assumed positions) in complex low-symmetry structures using Rietveld refinement coupled with difference-Fourier synthesis. This approach has been used successfully for chlorite and leucophoenicite, and it is clearly important for when high-pressure phase transitions occur in hydrogen-bonded polytypic systems and where split H(D) sites may arise (e.g. brucite).

Hints on refinement strategies for "difficult" samples will be described and suggestions on how to choose a tractable problem for a high-pressure neutron diffraction experiment will be given. The prospects for high-PT studies of hydrous minerals in the near future will be discussed, including single-crystal experiments.

O34-07

Powder neutron diffraction for topaz-OD under high pressureK. Komatsu¹, H. Kagi², W.G. Marshall³, T. Kuribayashi¹, J.B. Parise⁴ and Y. Kudoh¹¹Institute of Mineralogy, Petrology, and Economic Geology, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan

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A recent our IR and Raman study for F-rich natural topaz (F-topaz) and synthesized fully hydrated topaz (topaz-OH) revealed that the frequency of the OH stretching band [$\nu(\text{OH})$] of F-topaz increased with increasing pressure, whereas one of topaz-OH decreased (Komatsu et al., *Am Mineral*, 90, 266-270, 2005). In this study, our attention is focused on how the substitution of OH for F in topaz affects the behavior of hydrogen bonding under high pressure. Thus, the pressure response of the crystal structure for topaz-OH was investigated by powder neutron diffraction. Powder neutron diffraction patterns for topaz-OD [Al₂SiO₄(OD)₂] up to 7.4 GPa were measured on the PEARL/HiPr diffractometer at ISIS, Rutherford Appleton Laboratory, UK. A topaz-OD sample synthesized at 800°C and at 10 GPa using a Kawai-type high-pressure apparatus was loaded into a vanadium can in order to measure at ambient pressure. For high pressure measurement, the sample was in a soft-metal-encapsulated (SME) gasket consisting of a Ti-Zr alloy (Marshall and Francis, *J Appl Cryst*, 35, 122-125, 2002) with a 4:1 deuterated methanol and ethanol mixture, and it was loaded between opposed WC/Ni-binder anvils of a Paris-Edinburgh high-pressure cell. The H-bonding geometry at ambient pressure is characterized by a bifurcated H-bond relative to D1 and a trifurcated H-bond relative to D2. The D...O distances [$d(\text{D}\dots\text{O})$] increase or almost constant with increasing pressure when the O-D-O angles decrease, and the $d(\text{D}\dots\text{O})$ decrease with pressure when the O-D-O angles increase. In other words, a negative correlation between the $d(\text{D}\dots\text{O})$ and O-D-O angle is observed. An Al site in topaz-OD lies on a crystallographically general position, and hence, the Al octahedron has six distinct Al-O bonds. The $d(\text{Al-O1})$ and the $d(\text{Al-O2})$ decrease, the two $d(\text{Al-O3})$ and one of the two $d(\text{Al-O4})$ are almost constant, and another $d(\text{Al-O4})$ increase with increasing pressure. On the basis of the pressure response on H-bond geometry and $d(\text{Al-O})$, the reason why $\nu(\text{OH})$ in topaz-OH decrease with increasing pressure while $\nu(\text{OH})$ in F-topaz increase is discussed.

O34-06

Hydrogen bonding of goethite (α -FeOOD) at high pressureT. Nagai¹, H. Kagi², and J. B. Parise³¹Department of Natural History Sciences, Hokkaido University, N10W8 Kita-ku, Sapporo 060-0810, Japan

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Goethite crystallizes in space group Pbnm. Oxygen atoms occupy two crystallographically independent sites, O(1) and O(2), in a slightly distorted HCP arrangement. The O(1) is surrounded by three iron atoms to form an almost planar triangle. The O(2) is hydrogenated, and surrounded by three iron atoms and a hydrogen atom, which form a distorted tetrahedral coordination. A non-linear hydrogen bonding connects O(2)-H...O(1) in an adjacent octahedron. Prior to neutron scattering experiments, we performed synchrotron x-ray powder diffraction experiments at high pressure on goethite (α -FeOOD) (Nagai et al., 2003). The compression behaviour of goethite is anisotropic and the a-axis is almost two times more compressible than the b- and c-axes. Compression of goethite seems to be mainly controlled by shortening of the hydrogen bonded O...O distance. Since not only the O...O distance is important, but also the bond angle of O(2)-H...O(1) plays an additional role in hydrogen bonding, which becomes crucial during compression, it is interesting to determine the hydrogen position in goethite at high pressure and see what happens in hydrogen bonding with decreasing volume.

Since hydrogen has large amplitude of incoherent scattering for neutrons, deuterated goethite powder was synthesized as a target material. About 100 mg of the deuterated goethite was loaded into the Paris-Edinburgh opposed-anvil cell. Ti/Zr gaskets, which are almost invisible by neutrons, were used and deuterated methanol/ethanol 4:1 mixture was put into the sample chamber as pressure transmitting media in order to generate hydrostatic pressure up to 10 GPa (Marshall and Francis, 2002). TOF neutron diffraction patterns were obtained on the POLARIS beamline at ISIS. The generated pressure was estimated from the compression data of goethite in Nagai et al. (2003).

We obtained TOF neutron diffraction data of goethite at 0.1 MPa, 2.3, 5.2 and 7.2 GPa. A typical exposure time was from 3 to 5 hours. No significant peak broadening occurred at all pressure conditions. Rietveld refinement was carried out and we obtained structural parameters at each pressure. On the basis of those refined parameters, selected bond distances were calculated. It is interesting the O(2)-D...O(1) angle apart further from a linear geometry with shortening of the hydrogen bonded O...O distance at pressure. That seems to be due to repulsion between D atom and the 2nd neighbor Fe atom. Indeed, the distance becomes almost same as that between D atom and the 1st neighbor Fe atom at a pressure.

O34-08

High-P/T studies of mineral transformations by neutron scattering

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The development of high-P/T methods for the study of phase transitions in minerals by neutron diffraction will be discussed. These methods have been employed on a number of systems, using the ISIS neutron spallation source at Rutherford Appleton Laboratory, U.K. The ability of neutrons to measure intracrystalline cation distributions from site scattering is found to be particularly valuable, in particular in those phases which contain elements with huge scattering contrasts, such as the Fe-Ti oxides. Examples of cation order-disorder studied in situ at high P and T thus far include Mg-Al order-disorder in spinels, Fe-Ti order-disorder in titanohematites, and Mn-Mg order in tephroite-olivines. Results demonstrate that the enthalpies of order-disorder in these systems frequently show significant pressure dependences which modify the high-T disorder characteristics of order-disorder transformations.

Hydration of compacted bentonite : a neutron scattering and diffraction study.

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Clay minerals present industrial interest due to their exchange capacity and water retention properties. In the design of engineered barriers, swelling clays are used as compacted materials in order to inhibit the migration of contaminants from the waste to the surrounding environment. In the particular case of compacted materials, the prediction of clay sealing properties requires a proper understanding of the clay fabric as a function of both water content and compaction ratio. Thanks to neutron diffraction experiment on clay samples hydrated in confined conditions, it was recently demonstrated that crystalline swelling occurs in a similar way in free and constrained conditions for low relative humidity. For high water content, as macroscopic swelling can not take place, a swelling pressure appears. Its value depends on the compaction ratio and is about thousands of kPa for clays compacted at an apparent density of 1.7 g/cm³. This macroscopic phenomenon results from microscopic scale mechanisms, that is the penetration of water molecules in the interlamellar spaces to hydrate interlayer cations. Consequently, it may be assumed that a complete structural reorganization is associated with these major macroscopic changes, and all length scales are concerned from a few nanometers to micrometers. By combining neutron small-angle scattering and diffraction experiments it was possible to explore the association of swelling clay layers from the interlamellar spacing levels to the submicronic porosity in confined conditions. Whatever the density of compacted samples, the same trend was observed as a function of hydration: in the small-angle scattering range, the intensity falls off as a function of the scattering vector q following a power-law decay $I \propto q^{-n}$, with n ranging from around 3.5 for dry states to around 3 for hydrated ones. In the case of rocks, it is largely assumed that this kind of behavior is related to materials with fractal surface, or to porous materials with a power-law distribution of pore sizes. In the present case it was possible to simulate the scattering curves recorded for dry states on the basis of pores size distribution function calculated from nitrogen measurements. The evolution of the scattering curves as a function of hydration is deduced from the dry state by a filling of the smallest pores as water penetrates the materials. Changes in the mesoscopic porous network are then described as a function of compaction and hydration.

O34-10

Tectonic studies of the Alps by means of neutron texture goniometry

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The European Alps resulted from repeated subduction-related accretion of continental and oceanic units to the upper plate (Adria). Petrological and geochronological data prove that several units in different structural positions underwent high- or even ultrahigh-pressure conditions and were exhumed tectonically. Relative displacements between the nappes were mostly accommodated in shear zones. Kinematic interpretations of shearing and folding deformation within the orogen are therefore pivotal with respect to the restoration of palaeogeographical arrangement and individual history of tectonic units.

Mylonitization of rocks in deep-seated shear zones involves ductile deformation on the crystallographic scale, comprising crystal plastic deformation and dynamic recrystallization. These processes lead to reorientation of mineral grains and crystallographic preferred orientation (texture). Texture analyses, combined with microstructural and field-geological observations, strongly support kinematic reconstructions in that they provide information about shear direction, shear sense, deformation geometry and physical conditions.

Among the well-established techniques of texture investigations, neutron diffractometry has the advantage of a great beam diameter and high penetration capability of neutrons. This allows for investigation of large sample volumes and a good statistical quality even for textures of coarse-grained samples. At the goniometer SV7b at Forschungszentrum Jülich, the position-sensitive linear detector JULIOS and appropriate data processing facilitate the texture study of low-symmetry minerals and multiphase rocks. In the present study, we discuss textures of impure quartzites, combined with their shape-preferred orientations.

The boundary zone between two Penninic nappes, the eclogite-facies to ultrahigh-pressure Zermatt-Saas zone in the footwall and the blueschist-facies Combin zone in the hanging wall, is a major fault across which the pressure gap corresponds to a ca. 40 km thick missing rock portion. Textures of quartzitic mylonites from different levels of the nappe pile and developed during different stages of orogeny testify variable strain regimes, ranging from strongly rotational and prolate strain at the nappe boundary to oblate and almost non-rotational shear elsewhere. In some cases, the latter strain type is result of conjugate sets of ribbon-shaped domains with strongly rotational strain. The results of texture analysis are integrated in a stepwise kinematic restoration of the Western Alps. It shows that exhumation of the Zermatt-Saas zone due to crustal extension occurred only late and was of minor importance. Most of the exhumation took place during crustal shortening.

O34-11

Silicate melts and glasses: Alkali ion transport and structure

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Binary and ternary silica based melts are characterized by a highly non-linear dependence of viscosity on melt composition and a fast modifier ion motion. The viscosity of pure SiO₂ drops by orders of magnitude on addition of alkali oxides. It varies only slightly on further variation of the alkali oxide to SiO₂ ratio. Only addition of a second network former, e. g. Al₂O₃ to a binary melt leads to a significant increase of the viscosity at a given temperature.

The interplay of structure and transport properties is elucidated by means of quasielastic neutron scattering on binary and ternary silica based melts and glasses. We show that the fast alkali ion diffusion is based on the existence of percolation channels in the static structure. One signature is a prepeak in the elastic structure factor. The position of this prepeak is independent of the alkali concentration but depends on the alkali modifier. Moreover, the fast alkali self motion is decoupled of all other collective and self motions even at typical melt temperatures of 1600 K. Our experiments on alkali silicate melts compare well to recent molecular dynamics simulations by Horbach and Kob. The dynamics as observed by the simulations agrees qualitatively with the experimental data while the structure factors are even quantitatively reproduced.

The network of percolation channels is disrupted in ternary sodium aluminosilicate melts as evidenced by a decrease of the prepeak. It vanishes in samples containing equal amounts of Na₂O and Al₂O₃. Moreover, Na relaxation times increase on addition of Al₂O₃ to a binary sodium silicate melt. In contrast, the addition of SiO₂ to a binary melt has only minor influence on the microscopic dynamics and structure. Our results do not contradict other studies proposing the formation of triclusters as most likely scenario for incorporating Al₂O₃ into the structure.

By means of magnetic neutron scattering on Fe³⁺ which is the dominant Fe oxidation state in the investigated sodium iron silicate glasses we gain access to partial Fe-Fe structure factors. Partial elastic structure factors obtained by means of quasielastic neutron scattering are cross checked by means of neutron diffraction using polarization analysis. The partial Fe-Fe structure factors feature independently of the total iron concentration a first peak at the position of the prepeak in binary alkali silicate melts. Thus a hint is provided to an inhomogeneous distribution of Fe.

O34-12

Neutron diffraction coupled with isotopic substitution in the study of glasses and melts

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Neutron diffraction is a widely used structural tool for the investigation of structure in disordered materials. Case studies are reviewed to show some relevant results obtained on the cationic environment (Ti, Ca, Ni, Li) in glasses by neutron diffraction coupled with the method of isotopic substitution (NDIS). Neutron data have been obtained at the LLB neutron reactor (Saclay, France) and ISIS spallation source (Didcot, G.B.) on diffractometers dedicated to the study of amorphous materials, offering access to a wide Q range and high spatial resolution. A well-defined short and medium range environment around cations has been evidenced. The local site generally presents a lower coordination number compared to crystals of equivalent composition. For instance, the environment around Ti in K₂O-TiO₂-2SiO₂ glass corresponds to an unusual square-based pyramid. The distribution of cations at medium range can be directly extracted from the experimental data, revealing the presence of cation-rich regions in silicate glasses. The specific cation-cation distances often indicate a two-dimensional character in the cationic organization. However, such organization is not observed in metaluminous Li-aluminosilicate glass, in relation with the charge-compensating role of Li in this glass.

The structural evolution upon heating has drastic consequences on the structure-related properties of glass-forming liquids, such as transport properties (viscous flow, cationic diffusivity) and macroscopic thermodynamic properties (molar volume, thermal expansivity). NDIS of glasses at high temperature has been only recently extended up to the liquid state. The NDIS method has given an original description of the structural behaviour of cations in liquid oxides. Silicate and borate glasses and melts (up to 1350 K) were investigated and have shown different behaviour upon heating. The short range order is strongly affected in borates while more subtle, but significant, changes appears at medium range distances in silicates. The structural modifications can be used to account for the heat capacity change at T_g and understand the fragile/strong behavior of the melt viscosity. Alkali silicates are stronger melts than alkali borates, because temperature-induced structural changes are less important and reside mainly at medium-range distances. Structural reorganization is also intimately related to the dynamic processes of the viscous flow, which involves both the alkali migration and B-O or Si-O bond breaking and reforming. Important structural modifications occur in borate liquids, which show an increasing contribution of non-bridging oxygens in the first coordination shell of alkalis. These modifications contribute to the increase in ionic mobility.

Inelastic Neutron Study of THF+D₂ ClathratesK.T. Tait^{1,2}, F. R. Trouw², M.P. Hehlen², A. H. Shapiro², Y. Zhao² and R.T. Downs¹¹University of Arizona, Department of Geosciences, 1040 E. 4th Street, Tucson, Arizona 85721, USA

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Gas hydrates (clathrates) are elevated-pressure (P) and low-temperature (T) solid phases in which gas molecule guests are physically incorporated into hydrogen-bonded, cage-like ice host frameworks. Storage of hydrogen in molecular form within a clathrate framework has been one of the suggested methods for storing hydrogen fuel safely, but pure hydrogen clathrates form at high pressures (~2 kbar), which makes them impractical as a solution for hydrogen storage. Recent work has demonstrated that it is possible to obtain up to 4 wt% hydrogen ice clathrates when tetrahydrofuran (THF) is used to promote the formation of the clathrates structure and hydrogen takes up double occupancy of the small cage and then also starts to fill the larger cages as the THF concentration is reduced. The other interesting feature of this phenomenon is that the pressure of hydrogen required to stabilize the clathrates at 280K is reduced by a factor of 60 to 5 MPa. Although the kinetics of formation and subsequent release of hydrogen is far from acceptable if these mixed clathrates were to be used as a hydrogen storage medium, it is possible that similar materials and engineering improvements could result in suitable materials relevant to the future hydrogen economy.

Neutron inelastic scattering (INS) has frequently been used to probe the quantum rotor transitions and vibrational density of states of hydrogen adsorbed in a wide variety of substrates. Neutron INS measurements on hydrogen adsorbed in d-THF+D₂/D₂O ice clathrate were carried out on the Pharos spectrometer at LANSCE. In the absence of paramagnetic impurities the H₂ molecule converts slowly (tens of hours) from the J=1 to the J=0 quantum rotor state. At 10K, kT is approximately 1 meV and so neutron energy gain excitations above this energy arise from H₂ molecules still in the J=1 quantum rotor state.

Experiments at 8K yielded two excitations at neutron energy gains of approximately 14 and 4.7 meV as compared with the H₂ free rotor separation of 14.7 meV. These can only arise from two species of hydrogen adsorbed in the clathrate, under the influence of quite different crystal fields. There is also an excitation at a neutron energy loss of 9.3 meV, which must be a center of mass mode as it is not present in neutron energy gain. Further experiments and modeling are in progress to come to a detailed understanding of the adsorption sites of H₂ in THF/D₂O ice clathrate.

O35-01

Permian metamorphism in the Yeongnam and Gyeonggi massifs of the Korean Peninsula, revealed by the CHIME dating of monazite and zircon

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The Yeongnam and Gyeonggi massifs in the southern Korean peninsula are composed mainly of paragneisses and orthogneisses, and intruded by Jurassic granitoids. The gneisses have been regarded as Precambrian, but recent monazite dating revealed Permian age signatures in both the massifs (Cho et al. 1996; Kim et al., 1997). To reveal the extent of the Permian event, CHIME dating was carried out on gneisses from the Jirisan and Jangsugun areas in the Yeongnam massif and the Geojin, Chuncheon and Seosan areas in the Gyeonggi massif.

CHIME dating is a novel method for micron-scale dating of monazite and zircon on the basis of the EPMA analyses. Analyses were done on the JXA-733 EPMA equipped with 4 spectrometers under the conditions of 15 kV acc. voltage, 0.2 μ A probe current and defocused 3–5 μ m probe diameter. ThMa, UMB, PbMa and YLa lines were measured simultaneously with PET crystals and sealed Xe X-ray detectors. X-ray intensity was integrated over 400s period for the line peak position and over 200s period for two optimum background positions. To ensure possible changes of the sample surface had only a minimal effect on the results, we repeated measurement of peak and background positions five times for each analysis. CaKa, SKa, PKa, KKa, SiKa and NbL β lines are also measured. The standards were euxenite (Smellie et al., 1978) for Th and U, and synthesized glass (Suzuki & Adachi, 1998) for Pb. The spectral interferences of YLa, ThM ζ , NbL β , and NbL β on PbMa and ThMy on UMB were corrected, and the X-ray intensity data were converted into concentrations using analyses of natural monazite as the matrix composition.

Paragneisses and orthogneisses from the Jirisan and Geojin areas yield 1900–1600 Ma monazite ages. However, hornblende-biotite paragneiss from the Jangsugun area contains 1832–63 Ma relic monazite grains enclosed within 252–12 Ma allanite aggregates, suggesting metamorphism of post-1832 Ma sediments. Most monazite grains from paragneisses in the Chuncheon and Seosan areas are chronologically unzoned and yield c. 250 Ma ages, significantly younger than monazite (1900–1600 Ma with c. 250 Ma overgrowths) in associated orthogneisses. The detrital zircon and monazite in paragneisses give unequivocal ages as young as 440–90 Ma. These chronological data suggest that paragneisses in western parts of the Yeongnam and Gyeonggi massifs formed through a single stage of metamorphism at around 250 Ma from Paleozoic sediments. It remains to be seen how far this region of metamorphism extends in the Korean Peninsula.

O35-03

Monazite age-mapping and PTt evolution of Kodaikanal Metapelite Belt, Southern India

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The age-mapping of monazite derived from high resolution chemical mapping of Th, U, Pb, and Y combined with the chemical Th-U total Pb (CHIME) isochron age is a useful in-situ microchronological tool to explain the metamorphic and tectonic history of terrane. In this study we apply this method on aluminous pelitic migmatite suite from Kodaikanal Metapelite Belt (KMB) of the Madurai Block in southern India. This area was subjected to ultrahigh temperature crustal metamorphism. The rocks preserve textural evidence for illustrating initial-heating, dehydration melting to generate the peak metamorphic assemblage and later retrogression of the residual assemblages with remaining melt. The peak metamorphic assemblage is interpreted to be garnet+sillimanite+K-feldspar+spinel+Fe-Ti oxide+quartz+melt, stabilized at metamorphic pressure-temperature conditions around 7–8 kbar and 950–1000 °C. The interpretation of the reaction textures pointed out the possibility of a clockwise evolution path for the migmatites of the study area. The chemical mapping of monazite indicates a Th rich rim wild Pb rich core. The same grain has a Y rich outer rim while U is depleted in this thin-rim. On integrating the results to age map the core have a distinct older meso-Proterozoic age (ca. 1700 Ma) while the extensive overgrown rim have a neo-Proterozoic-Cambrian age. This clearly indicates that an ultrahigh temperature metamorphic event in the Kodaikanal Metapelite Belt, Madurai Block, an integral part of eastern Gondwana could takes place during the late neo-Proterozoic to Cambrian period while the sediments of Kodaikanal Metapelite Belt might have been derived from an older metamorphic province with a meso-Proterozoic age. This can be thus interpreted that the sedimentation must be younger than ca. 1700 Ma and the irregular nature of the core might suggest a nearer source of sedimentation. The point analysis of this sample also yields two isochrones of 1703 $\pm$ 251 Ma and 540 $\pm$ 47 Ma on a PbO vs. ThO₂ diagram, confirming the mapping results. Our approach reveals the widespread regional occurrence of ultrahigh temperature metamorphism in the Madurai Block during Gondwana assembly and points out the need for similar studies on adjacent continental fragments.

O35-02

Cretaceous monazite ages in migmatites of the Higo terrane, Japan: the importance of petrogenetic associations in accessory mineral geochronology

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The Higo metamorphic terrane of central Kyushu, western Japan is a 25km long body of metasedimentary and metabasic lithologies that increase in metamorphic grade from schist in the north to migmatitic granulite in the south, where granitoids are emplaced along the southern margin. The timing of granulite metamorphism has been intensely investigated and debated. Sm-Nd mineral isochrons for garnet-bearing metapelite yielded c.220–280Ma ages, suggesting high-grade equilibration older than the lower grade schist to the north, which has c.170–220Ma K-Ar muscovite ages. Ion and electron microprobe analyses on zircon have yielded detrital grains with rim ages of c.250Ma and c.110Ma. Electron microprobe ages from monazite and xenotime are consistently c. 110–130Ma. Two models have been proposed: 1) high-grade metamorphism and tectonism at c.120Ma, with older ages attributed to inheritance; and 2) high-grade metamorphism at c.250Ma, with resetting of isotopic systems by contact metamorphism during the intrusion of the c.105Ma Shiraishino granodiorite. Without petrogenetic evidence for the growth of datable minerals, it is difficult to evaluate the relative worth of these models.

Monazite commonly preserves textural and compositional features that have been increasingly associated with petrogenetic processes during metamorphic episodes. In situ examination of monazite grains in migmatitic metapelite from the Higo terrane demonstrates growth and dissolution features associated with metamorphic reactions. Monazite is particularly abundant in silica-undersaturated melanosome produced by partial melting of metapelite. Monazite inclusions in peritectic garnet porphyroblasts have highly variable Th contents (up to 20wt.% ThO₂) and preserve irregular and oscillatory zoning in Th, Y and Dy content. In contrast, monazite grains in the matrix are low in Th (<5 wt.% ThO₂). Both groups of monazite are interpreted to have grown from the breakdown of Th and LREE-bearing minerals, consistent with the presence of allanite relics in garnet cores and monazite-rich patches that may represent consumed phases. Both garnet inclusions and matrix grains have overgrowths and recrystallised patches with higher huttonite and lower YPO₄ and DyPO₄ components. These later growths are interpreted as having formed during dehydration melting involving the consumption of biotite, apatite, xenotime, and the production of garnet. Electron microprobe Th-U-Pb ages from all monazite grains yield c.110–130Ma ages. Earlier and later stages of monazite growth cannot be temporally resolved. The preservation of petrogenetic information, coupled with the low diffusion rate of Pb at temperatures <900°C in monazite, is strong evidence for Cretaceous timing of the high-grade metamorphism and deformation that produced the Higo gneisses.

O35-04

EMP Dating on Monazite from the Western Rayner complex, East Antarctica: Implications for the metamorphic evolution

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The Rayner Complex in East Antarctica has long been considered to be a Proterozoic mobile belt reworked after a part of the neighboring Archean Napier Complex (e.g. Sheraton et al., 1987). Recent geochronological studies have revealed that the Rayner Complex has been overprinted by Pan-African event at its western coastal area involving Mt. Vechemyaya (Asami et al., 1997) and Forefinger Point (Motoyoshi et al., 2005). In order to confirm these ages and extent of this overprint towards the inner area of the Rayner Complex, we newly analyzed trace element chemical compositions of monazite in metapelite assemblages from Condon Hills, Mt. Lira, Mt. Yuzhnaya and Sandercock Nunataks.

Petrographical evidence of the metapelite rocks are summarized as follows:

- 1) Garnet and biotite are dominant in the metapelite assemblages, along with cordierite and orthopyroxene occasionally.
- 2) Sillimanite occurs as inclusions in garnet. In other cases, sillimanite is associated with cordierite in the matrix. Kyanite has not been recognized yet.
- 3) Cordierite sometimes replaces garnet.
- 4) Symplectitic intergrowth of orthopyroxene and cordierite is observed around or along cracks in garnet from Mt. Lira.

Quantitative chemical analyses on monazite were performed by means of an electron microprobe (EMP) analyzer using JEOL JXA-8800 at the National Institute of Polar Research, Tokyo. The results of EMP dating are as follows:

- 1) From Condon Hills and Mt. Yuzhnaya, bimodal ages at 950–900 Ma and ~550 Ma were detected. Some of the monazite grains preserve older core and younger rim.
- 2) From Mt. Yuzhnaya, much older ages, e.g. ~1900 Ma, ~1400 Ma and 1100 Ma were detected on a few grains. Even in this case, the same monazite is armored by 500 Ma rim.
- 3) From Mt. Lira, only ~950 Ma monazite were observed. No younger ages have been detected so far.
- 4) From Sandercock Nunataks, only c. 1000 Ma were obtained. The results are consistent with the previous SHRIMP dating on zircon (Shiraishi et al., 1997).

On the basis of the monazite dating, it is inferred that the metapelite rocks from Condon Hills and Mt. Yuzhnaya have been subjected to two metamorphic events, namely at 950–900 Ma and at ~550 Ma. The second event should be attributed to the Pan-African event which is regionally recognized in the neighboring Lützow-Holm Complex (Shiraishi et al., 1994, 1997). Although we have not reached any definite conclusion, the Pan-African overprint could be extended eastwards within the Rayner Complex.

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The Bohemian Massif (BM) is one of the largest and most geologically complex outcrops of the central European Variscides, bounded by the Saxothuringian and Moldanubian tectonic zones. The Sudetes Mountains, located along the NE margin of the BM, consist of a collage of amalgamated Neoproterozoic to Early Carboniferous terranes. The easternmost part of the West Sudetes Mountains comprises the Orlica-Snieżnik dome (OSD). The structural and metamorphic evolution of the OSD is controversial. The dome includes the Śnieżnik and Gieraltow orthogneiss lithologies, with minor amounts of granulite and eclogite occurring in several localities. The origin and age of the various rock complexes forming OSD have been variously interpreted during the past decades. Protolith ages determined for the Śnieżnik and Gieraltow gneisses by dating zircons concentrate around 500 Ma. High-T metamorphism is recorded by metamorphic rims on igneous zircons as Viséan in age. To resolve disagreements between plate tectonic interpretations, further geochronological analysis is required to determine the precise age of the parental crust, magmatic activity and metamorphism.

In this study we present in situ chemical dating of monazites from granulite in the Gieraltow gneiss. A total of 161 analyses on 6 monazite grains were obtained by Electron Probe Microanalyzer (EPMA) and Proton Microprobe (PIXE). For reliable age calculation, grains were selected with relatively low yttrium content (up to 1.12 wt% Y₂O₃). The analyzed monazites contain 2.38-7.41 wt% ThO₂, 0.18-0.16 wt% UO₂ and 0.038-0.117 wt% PbO. Some monazite grains are enriched in strontium. Apparent (single analysis) ages were calculated using the Chemical Th-U-total Pb Isochron Method, yielding an isochron age of ca. 341 Ma, with a range of apparent ages of 278-411 Ma for EPMA and for PIXE 314-368 Ma.

The monazite isochron age corresponds to the Variscan Orogeny, and is significantly younger than recently published ca. 375 Ma age for UHP metamorphism in the OSD. There is significant overlap of age estimates from various isotope systems that represent different segments of the P-T-deformation path, thus preventing a clear temporal resolution of distinct stages in the evolution of the Orlica-Snieżnik dome. This overlap can be ascribed to rapid cooling from peak temperature conditions. The combined age constraints indicate that peak temperature conditions associated with metamorphic monazite growth must have been reached shortly before 340 Ma.

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Q35-06

Radiation damage or chemical composition? Raman spectroscopy of zircon
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Abstract

Raman spectrum of zircon shows a distinctive pattern according to the amount of radiation damage stored (e.g., Zhang et al., 2000). Nasdala et al. (2001) demonstrated a linear relationship between a full width at half-maximum (FWHM) of $\square_3(\text{SiO}_4)$ band and alpha fluence calculated based on uranium and thorium contents and its age. Their finding could lead to a new micro-spectroscopic method to obtain zircon ages. This study examines the effect of chemical composition on the Raman spectra by analysing synthetic zircons which are doped with elements using Li-Mo flux. The Raman spectra were measured by the FT-Raman SPECTROM 2000R at the Wakasa Wan Energy Research Center. Chemical compositions were measured by the Eximer LA-ICP-MS Agilent 7500S at Kanazawa University. Zircons doped with each element of Group 3 of periodic tables (including lanthanide and actinide series) show high concentration of the element, on the other hand, elements of other groups are less incorporated. The FWHM at $\square_3(\text{SiO}_4)$ band of zircons doped with Group 3 elements shows a linear relationship against their concentration, showing clear evidence that FWHM is a function of chemical composition as well as radiation damage. The concentration of Group 3 elements should be extreme to affect the Raman spectra (e.g., more than ~5,000ppm), although such a high concentration is rarely observed for natural zircons.

Q35-07

An update of "More SHRIMP for the Geological Feast"; new developments and future trends

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Since development in the early 1980s, the Sensitive High Resolution Ion MicroProbe or SHRIMP has revolutionised many aspects of geochronology, isotope geochemistry and petrology, and is now considered a "conventional" analytical technique. SHRIMP has had its biggest impact in the field of geochronology, specifically U-Th-Pb dating of zircons. Routine U-Th-Pb analyses are made on monazite, titanite, rutile, baddeleyite and authigenic xenotime; many in situ in polished thin sections. Recognition that internal complexities from multiple growth episodes are common and can be resolved using cathodoluminescence or backscattered electron imaging techniques, has made the SHRIMP in situ option a powerful tool (usual spot dimensions ~20 μm diameter by ~1 μm depth). Recent advances in hardware configuration have been a multi-collector system and the flexibility to analyse samples in both positive and negative ion modes. The dynamic range of ion beams measured can be very large, necessitating a configuration comprising five CDEMS (Continuous Dynode Electron Multipliers) and three Faraday cups. This enables oxygen isotope ratios of igneous zircons to be determined in multi-collector mode and so one can trace the degree of crustal recycling within zircons. The multi-collector and caesium primary ion beam configuration developments mean that sulphur isotope ratios are measured with sub-permil precision.

Software developments have enhanced flexibility in operation and now after-hours analytical sessions are run in fully automatic mode, with the capability of remote monitoring and intervention. This protocol for very rapid automated analysis has had significant impact on our analyses of large numbers of detrital zircons for provenance and other studies. Such studies are linked with Lu-Hf isotope analyses. Given the internal complexity, it is essential that both U-Pb and Hf isotope data be obtained on the same growth zone within a single zircon. Combination of the initial SHRIMP U-Pb measurement followed by LA-ICP-MS Hf isotope measurement on the same spot is the optimum procedure. If required, oxygen isotopes also can be measured before the destructive LA-ICP-MS analysis, altogether yielding a wealth of important information on a well-dated zircon grain. SHRIMP development was motivated by recognition that geological materials are complex and heterogeneous on all scales. This requires in situ analysis of areas within grains at a scale that allows resolution of internal complexity. It is also a virtually non-destructive technique. These factors are as important today as they have ever been, with improved applications and instrumental advances pushing the SHRIMP into new and exciting areas.

Q35-08

Reworking of Hadean continental crust into Acasta gneisses in northwestern Canada: Evidence from in-situ zircon U-Pb and Lu-Hf isotope analyses

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Knowledge of continental growth history is central to understanding the evolution of the Earth. The oldest known rocks are 3.9–4.0 Ga rocks in the Acasta Gneiss Complex of northwestern Canada; no crustal rocks have been found from the first five hundred million years of Earth's history. On the other hand, evidence for the existence of continental crust older than 4.0 Ga has so far been obtained only from zircons in the Yilgarn Craton of Western Australia. A major issue in the study of continental growth is whether the extreme rarity of evidence for the existence of continental crust older than 4.0 Ga is resulting from following plate-tectonic recycling (crust-mantle recycling), or it reflects the amount of crust that formed. The issue can be approached by radiogenic isotope systems, such as Lu-Hf and Sm-Nd, of early Archean rocks, because they reflect the degree and timing of geochemical differentiation of the silicate Earth. However, the differentiation of the early silicate Earth has so far been cloudy in view of the potential for disturbances to these isotopic systems by later metamorphisms. In order to avoid the isotopic disturbances, isotopic data from robust minerals, such as zircon, were highly desired.

In this study, we carried out in-situ U-Pb dating and Lu-Hf isotopic analyses on zircons from early Archean Acasta gneisses in order to constrain the early continental evolution. The U-Pb dating reveals 5 main granitoid formation events at 3.9–4.0 Ga, 3.74 Ga, 3.65 Ga, 3.58 Ga and 3.55 Ga during the early Archean in the complex. The Hf isotopic compositions of the early Archean granitoids are nearly chondritic to markedly unradiogenic, demonstrating that some of them formed by remelting of significantly old crust (crustal reworking). The calculated chondritic Hf model ages indicate that the reworking crusts are older than 4.0 Ga. Importantly, we found out a very old zircon xenocryst with a U-Pb age of 4.2 Ga in the 3.9 Ga Acasta granitoid. Trace element compositions of the xenocryst suggest that it crystallized from a granitoid magma. This finding is consistent with the Hf model ages, providing the direct evidence for the existence of 4.2 Ga granitoid continental crust outside the Yilgarn Craton. These results imply that granitoid continental crust was more widespread than previously thought in the late Hadean, that it played an important role as a geochemically-enriched reservoir, and that it was reworked into early Archean continental crust.

Tectonothermal events in high-grade metamorphic complexes in Vietnam: Evidence from SHRIMP U-Pb zircon dating

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High-grade metamorphic complexes in Vietnam are well exposed in the Kontum massif and in the Red River Fault zone (RRFZ) area, and traditionally thought to be Precambrian in ages. Zircons separated from these complexes have been dated to establish their protolith ages and the timing of high-grade tectonothermal events using SHRIMP U-Th-Pb technique. Six zircon samples from four complexes of RRFZ area were dated. SHRIMP U-Pb zircon analyses of three orthogneiss samples from the Ca Vinh complex yield three age groups of 2.84-2.91 Ga, 2.36 Ga and 1.96 Ga, corresponding to three periods of zircon generation. An early thermal history of the Ca Vinh complex has been constrained, including a primary magma-crystallization stage starting at ~2.9 Ga, followed by two Paleoproterozoic (~2.36 and ~1.96 Ga) high-grade tectonothermal events. One orthogneiss sample from the Xom Giau complex (south of the Day Nui Con Voi shear zone, North Vietnam), that has given K-Ar muscovite date of 770 Ma, yields SHRIMP U-Pb zircon ages of 2.26 Ga indicating the protolith age for the complex. Orthogneiss sample of the Po Sen complex within the RRFZ give SHRIMP U-Pb ages of 750 Ma for major zircon population and age of 1810 Ma for inherited core, while a migmatite sample from the Red River complex within the Day Nui Con Voi shear zone gives a wide range of ages for its zircon population, including 29-42 Ma of Indo-Asia collision and 850 Ma of Jingning orogenesis. The central part of the Kontum massif is mainly composed of orthopyroxene granulites and associated rocks, which were previously interpreted to be Archean ages. Recent SHRIMP U-Pb zircon dating has shown that high-grade granulite facies metamorphism occurred during Indosinian times of ca. 245-255 Ma, recorded in zircon from both charnockite and granulite samples. Other zircons from orthogneiss samples that were previously thought to be Paleoproterozoic in age in the Kontum massif yield SHRIMP U-Pb ages of ca. 440 Ma for major zircon population, indicating magma-crystallization age for the study complex. Some of inherited zircon cores from the orthogneiss complex record ages of 830 Ma and 2.54 Ga, suggesting old crustal relics and Neoproterozoic tectonothermal events.

Recent development of LA-MC-ICPMS and a multi-ion counting system for micrometer scale U-Pb chronology of complex zircon grains.

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A first aim was to determine the precision and accuracy really attained through U-Pb dating using laser ablation (213 nm UV laser) and MC-ICPMS (NEPTUNE) equipped with a multi-ion counting system. This recent development allows the high-sensitivity measurement of isotopes of interest (²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) simultaneously with the collection of ²³⁸U ions with Faraday cup. The good precision and accuracy of this configuration and the soft ablation at high spatial resolution (20 µm), were checked on four reference zircons already dated using other methods (ID-TIMS and SHRIMP). These zircons were specially selected so as to cover a wide range of ages (290-2400 Ma) and compositions.

Once this method had been proven rapid and efficient for in situ U-Pb dating on reference simple concordant zircons, we then sought to demonstrate its potential for dating complex zircons, namely elongate zircons from a granodiorite of the Ivory Coast showing spherical and botryoidal patches on BSE images. Electron microprobe (EPMA) analyses showed Zr and Si depletion, and Ca and Fe enrichment related to the amorphous domains. EPMA dating of these domains yielded abnormally young ages related to Pb diffusion. Most of the analyses indicate large amounts of U (~1000 ppm or even more). The high U content and the associated metamictization make these zircons poor candidates for age determination. Nevertheless, most of the available methods for zircon dating were tested in order to better understand how the calculated ages are disturbed for such complex zircons. Conventional U-Pb analyses showed discordancy, but the high intercept of the discordia gave a reliable age of zircon crystallization. After preliminary outgassing of the grains, the Pb evaporation method gave numerous high-precision step ages on each of the analysed grains due to the high U content. Although SHRIMP was the most suitable method for selecting unaltered domains, only some rare spot analyses gave subconcordant ages from which a weighted average ²⁰⁷Pb/²⁰⁶Pb age was calculated. Finally, U-Pb dating using LA-MC-ICPMS applied to unaltered domains was in complete agreement with the other methods.

The studied U-enriched zircons showed clearly that the botryoidal domains, variably amorphous, enriched in Ca, Fe, and depleted in Zr and Si, cannot give significant ages. In contrast, the U-enriched domains from the same zircons can lead to reliable ages if the grains are preliminary outgassed or cleaned with HNO₃. An easier option is to apply an in situ method such as SHRIMP or LA-MC-ICPMS.

Ion microprobe U-Pb (zircon) geochronology of the Hidaka Metamorphic Belt, Hokkaido, Japan: New results and implications for granite generation at convergent margins

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Debate continues as to whether silicic magmatism in arcs involves the fusion of pre-existing crust in the granulite facies or the differentiation of juvenile mantle-derived magmas in a 'deep hot zone'. The implications of these contrasting scenarios for crustal growth processes are fundamentally different. The Hidaka Metamorphic Belt in Hokkaido (northern Japan) offers an unparalleled opportunity to test these competing models. Uplifted by a Tertiary collision between the Japan and Kurile arcs, the Hidaka Belt exposes a remarkably complete island arc section that encompasses upper mantle to shallow crustal depths. Mafic rocks, mostly olivine gabbro, comprise up to 30% of the section. Their generation is thought to reflect spreading-ridge subduction prior to arc-arc collision, the thermal pulse from which triggered metamorphism. The lower part of the Hidaka sequence exposes voluminous S- and I-type tonalite intrusives juxtaposed with their potential sources, partially melted metasedimentary and metabasic granulites, respectively. Large felsic plutons emplaced at higher crustal levels are the putative differentiated equivalents of these deep-seated intrusives. However, the temporal links between mafic magmatism, granulite formation and silicic magma genesis in this important area are not well constrained overall. To address this, we here report new ion microprobe U-Pb (zircon) data aimed at determining the crystallisation ages of key gabbro and tonalite/granite samples, and the age of partial melting in the granulites. Preliminary results suggest that peak granulite facies metamorphism and granite emplacement was significantly younger than previously thought. The new geochronological data will be combined with in situ Hf isotope data determined on the same zircon crystals, which reveal the ancestry of the source rocks to the tonalites/granites. The implications of these results for the mechanisms of silicic magma generation and the tectono-magmatic evolution of the Hidaka Metamorphic Belt will be discussed.

From 2000 to over 16 giga years by laser probe ⁴⁰Ar/³⁹Ar dating: A review

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The first application of laser probe dating technique using ⁴⁰Ar/³⁹Ar method was carried out in 1973 on a lunar breccia by Megruc. In the first decade, applications were mostly focused on obtaining ages utilizing the fine beam of a pulsed laser with a high-spatial resolution. However, the sample sizes, in particular for ³⁶Ar were often in the order of magnitude smaller than the detection limit of most mass spectrometers at the time. Researchers have struggled with a lack of sensitivity of mass spectrometers until giving up the idea of using a high-spatial resolution, and use of defocused beam from a continuous laser on a conventional mass spectrometer was introduced in 1981. After the development of vacuum techniques and instrumentations, the number of geological applications rapidly increased in the 1990s. For the pulsed laser applications, the spatial resolution of a single spot became as small as 5 microns.

Recent studies indicate that the ages which can be measured by laser probe technique range from 2000 to 16 giga years in various geological settings. Considering the half life of ⁴⁰K (1.25 giga year), the age range is extraordinarily wide in particular on the results of younger side. The advantage of low blank laser heating and purification system allows to measure such young ages using sample sizes of bulk analyses. With the high spatial resolution of lasers, detailed sampling in a single mineral grain revealed mechanisms of degassing and its thermal histories as well as step heating of single minerals. In cases of the highest ages older than the age of the earth or even the universe, they are simply reflecting various excess argon environments during formation and/or cooling of lithological units. Localized nature of excess argon may provide constraints on origins of the source rocks and/or the cooling processes.

Comparing with bulk analytical results, techniques by both pulsed and continuous lasers are reviewed, and the direction of the future development will be discussed.

Excess argon wave trap zone in Barrovian type metamorphic belt, Eastern TibetT. Itaya¹, H. Hyodo¹, T. Tsujimori², S. Wallis³, M. Aoya⁴ and T. Kawakami⁵¹ Research Institute of Natural Sciences, Okayama University of Science, Okayama 700-0005, Japan

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Potassium bearing minerals such as biotite and muscovite are widely used as a tool in K-Ar geochronology. One of the assumptions in K-Ar dating is that above a certain temperature all the accumulated Ar gas will be released from the host mineral and dispersed into the surrounding rock. During cooling, radiogenic argon will again build up in the host mineral. The fate of the released gas is rarely considered except for an example of excess argon wave that is recognized near boundaries between mafic intrusions and their hosts or along major tectonic boundaries. During the systematic Ar-Ar dating of biotites in a Barrovian type metamorphic belt in eastern Tibet, we recognized a zone containing trapped remains of an excess argon wave. Here we report the results of Ar-Ar analyses of biotite and muscovite from this region of Barrovian type metamorphism, and demonstrate the existence of a regional excess argon wave in the crust.

Laser step heating Ar-Ar analysis of single crystals of biotite yielded moderately consistent ages of 37 - 52Ma in the sillimanite zone with metamorphic temperatures higher than 600°C and discordant ages from 28 to 200Ma in the zones with peak metamorphic temperatures lower than 600°C. The higher kyanite zone, in particular, yields extremely old ages more than three times the metamorphic age deduced from a CHIME monazite age (65Ma) and a SHRIMP apatite age (67Ma) in same sillimanite zone. We suggest biotite grains with apparent ages of 130 to 200Ma have trapped excess argon derived from degassing of K-rich phase in the sillimanite zone when the stable muscovite in peak metamorphism decomposed to form K-feldspar during the adiabatic retrogression. There is a clear zone in the higher-grade part of the kyanite zone with extreme amounts of excess argon. We refer to this as a trapped 'excess argon wave'. The presence of such excess argon waves in the crust has major implications for the interpretation of Ar based radiometric studies. Biotite grains with ages 50 to 100Ma in the lower grade zone trapped moderate excess argon inherited from the host lithologies during the exhumation and cooling of the host rocks. Coexisting biotite and muscovite in the excess argon wave zone give 200Ma and 64Ma, respectively, suggesting that the argon wave trapping of biotite took place when the rocks cooled down into the closure temperature of biotite just after that of muscovite.

P35-01

Comparison of EPMA Correction Procedures in CHIME DatingT. Kato¹¹Center for Chronological Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan

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A CHIME age is obtained from the function of a set of chemical compositions of U, Th and Pb. Therefore, accuracy of quantitative electron probe microanalysis (EPMA) is an important factor of accuracy in CHIME dating. Correction procedures including models and parameters control accuracy of quantitative analysis in addition to a chosen set of standard materials and conditions of sample. In many cases, correction procedures in EPMA have been optimized for particular categories of sample, such as low or high overvoltage range and atomic number range. Therefore, many correction procedures need to be considered and a suitable procedure should be chosen by the analyst to achieve accurate CHIME dating. Three ZAF models (conventional exponential, surface-center Gaussian and full-PAP double parabolas models) and two alpha-factor tables for the Bence-Albee method were compared in EPMA-CHIME dating of monazite. Those models represent standard computer programs provided with commercial EPMA equipments. In comparison of ZAF models, two sets of mass attenuation coefficients (m.a.c.s) were also compared. Comparisons were performed using two sets of standard materials: the high-concentration set (pure oxides for Th and U, and crocoite for Pb), and the low-concentration set (silicate glasses, about 5 wt. % of U and Th, and about 10 wt. % of Pb). Chosen X-ray lines were: Pb Ma, Th Ma and U Ma lines, and the energy of incident electron and the X-ray take-off angle are 15keV and 40 degrees, respectively. The surface-center Gaussian model is the most sensitive to m.a.c.s and the full-PAP model is the most insensitive. The high-concentration set of standard materials gives about 2 times wider CHIME age variation with correction procedures than the low-concentration set of standard materials. Furthermore, the latest alpha-factor table by the author provides similar CHIME ages to the full-PAP model. From the comparison in this study, it is concluded that (1) the full-PAP and the alpha-factor table by the author are more suitable correction procedures in CHIME dating than other procedures, and (2) the low-concentration set of standard materials can reduce uncertainty from a chosen correction procedure.

P35-02

Micro-chronology of Kohistan lower crustal tonalite, northern Pakistan: implication to the timing of India-Eurasia collisionT. Nakajima¹, I.S. Williams², H. Hyodo³, K. Miyazaki¹ and A.B.Kausar⁴¹Institute of Geology and Geoinformation, Geological Survey of Japan, AIST Central-7, Higashi, Tsukuba 305-8567, Japan.

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Micro-chronology with pin-point age determination can be a strong tool for the study of tectonic history if geologically well-defined and specified targets are chosen.

The Kohistan block in northern Pakistan exhibits a well-exposed crustal cross section of an ancient island arc which was sandwiched by Indian and Eurasian continents during the Tethys closure. The Kohistan block is tilted to the north due to uplift by subduction of the Indian continent from the south. Within the lower crustal banded amphibolite unit of the Kohistan block, tonalite sheets of various sizes are intruded. They are layer-parallel to the structure of the host amphibolite, indicating syn-tectonic intrusion. This tonalite (Dasu tonalite) is extremely poor in K, Rb, Zr and Y, and have low ⁸⁷Sr/⁸⁶Sr initial ratios. These features suggest the Dasu tonalite formed from juvenile granitic magma generated from mantle-derived lower crustal components without interaction with Indian craton.

With the two micro-chronological approach, SHRIMP U-Pb age of zircon and laser-ablation ⁴⁰Ar-³⁹Ar age of biotite of the Dasu tonalite were determined to figure out the tectonic history of the Kohistan arc. The SHRIMP zircon U-Pb age of 98Ma and the biotite ⁴⁰Ar-³⁹Ar age of 70Ma were given. The 28 m.y. discrepancy between the two microchronometers is interpreted to be the deep crustal residence time of the Dasu tonalite. The tonalite magma was generated and crystallized at 98Ma and had stayed in the lower crustal depth before cooling to 300°C at 70Ma, probably when the Kohistan block was tilted by jack-up of the Indian plate at the initial stage of collision. Considering that the Paleotethys had already closed and the Kohistan was located at the leading edge of the Eurasian continental front at that time, these micro-chronological data might show that the Indian collision had already started before 70Ma.

P35-03

Ion microprobe U-Pb dating of zircons in jadeitites and jadeite-bearing rocks from JapanY. Tsutsumi¹, K. Yokoyama¹, R. Miyawaki¹, S. Matsubara¹ and H. Hidaka²¹Department of Geology, the National Science Museum, 3-23-1, Hyakunin-cho, Shinjuku, Tokyo 169-0073, Japan.

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Jadeitite is usually associated with serpentinite occurring in the high P/T metamorphic belt. Gem quality jadeitite was found only at several localities in the world. Although gem quality jadeitite was found only at the Itoigawa-Ome district in Japan, there are more than 10 localities of jadeitite and jadeite-bearing rock in Japan. Most of the jadeite-bearing rocks exist as blocks in serpentinite mélange. There are a few age data for the rocks. The jadeite-bearing rocks often contain zircon grain. In this study, we analyzed zircons from five samples: three jadeitites from Kotaki (Itoigawa-Omi area), Osa and Tone (Nagasaki area), and two jadeite-bearing rocks from Kochi and Yorii. U-Pb ages of zircons were obtained using SHRIMP II. Zircon in the jadeitite from Kotaki area is euhedral to subhedral chasmy crystals with a few mm in diameter. Zircons from Osa area are a few mm euhedral and uncracked clear crystal. These coarse-grained zircons show no clear compositional zoning. It is considered that they were crystallized with jadeite. Zircons from Kochi, Yorii and Tone areas are fine euhedral crystals with oscillatory zoning, similar to zircons from igneous rocks. Zircon ages in Kotaki, Osa and Kochi samples are around 500 Ma. On the other hand, zircons in Yorii and Tone samples range in age from 120 to 160 Ma. The samples from the Kotaki and Osa areas belong to the Renge metamorphic belt with K-Ar ages of 300-350 Ma. The Kochi area belongs to the Kurosegawa tectonic belt where ages of the associated high-pressure metamorphic rocks are 200-250 Ma. The sample from Tone area belongs to the Nagasaki metamorphic belt with K-Ar age of 60-80 Ma. No age datum was reported from the jadeite-bearing block from Yorii area. At least, in four localities, there is clear difference between zircon age and K-Ar age of the associated metamorphic rock. Three zircon ages with oscillatory zoning are explained as crystallization ages of parental igneous rock. Hence, they are older than the metamorphic ages. Zircons with 500 Ma in jadeitites are chemically homogeneous. They are still remained to be mysterious as well as origin of jadeitites.

U-Pb zircon dating of Neoproterozoic anorthosites from Wadi Dib, North Eastern Desert, Egypt

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The present paper reports U-Pb zircon ages for anorthosites, that occur at the top of a mafic-ultramafic intrusive complex at Wadi Dib, northern Eastern Desert, Egypt. These anorthosites consist of plagioclase megacrysts (An₄₅₋₁₇), augite (En₃₂₋₅₀ Wo₂₇₋₄₃ Fs₂₃₋₂₄), enstatite (En₅₁₋₅₆ Wo₃₋₅ Fs₄₀₋₄₇) and minor amounts of ferrosilite (En₄₂₋₄₆ Wo₂₋₇ Fs₄₇₋₅₅) and amphiboles (magnesian-hornblende to actinolite). They contain large zircons, that occur in the interstices between plagioclase megacrysts. Some of these zircons carry unusual inclusions of K-feldspar, albite, quartz, apatite or hornblende. This indicates that zircon grew late in the rock, probably from a strongly enriched residual melt fraction.

After separation with heavy liquids and careful handpicking, small weight fractions of these zircons were dated by conventional ID-TIMS technique. All analyzed zircon fractions yielded high radiogenic lead contents and provided concordant to near concordant ages. Measured ²⁰⁶Pb/²⁰⁴Pb ratios are variable and range from ca. 550 to 3700. The partly high common Pb is probably due to the inclusions. A concordia age of 592 ± 3 Ma, calculated with five of the six analyzed fractions (fraction 4 excluded), is interpreted as the crystallization age of the zircons. In agreement with field relationships, this age shows that the anorthosites and the associated mafic-ultramafic rocks of Wadi Dib are broadly coeval with the "Younger Granites" of the Eastern Desert. They intruded during a late, post-collisional stage of the Pan-African orogeny, in a regime of post-orogenic extension.

Late Cretaceous igneous activity predating Ladakh batholith in northern India: K-Ar ages of Hunder granite - diorite complex in the Shyok Suture Zone.

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The Shyok Suture Zone is situated between Ladakh and Karakoram batholiths in northwestern Trans- Himalaya and consists of mafic – ultramafic rocks, sedimentary rocks and metamorphic rocks. The sedimentary rocks are considered to have been deposited on the continental shelf, which probably had matured continental hinterland, because they comprise terrigenous clastic rocks, including quartzose sandstones and conglomerate with granitic clasts, and yield shallow marine molluscs and land plants. We discovered the Hunder granite – diorite complex that intruded into the sedimentary rock sequence in the Hunder river section and carried out their petrographic and K-Ar analyses to compare with the calc-alkaline Ladakh batholith that formed as a paleovolcanic arc at a convergent margin of the Tethyan oceanic plate and Eurasian continental plate. Hunder area is composed mainly of the complex magmatic sequence of granite, diorite, leucogranite and dykes of andesite and leucogranite. They have thermally metamorphosed the sedimentary rock sequence to form the contact aureole. The granite and diorite occur not as an independent mass but as a complex magmatic sequence depicting mechanical mixing of granite and diorite magmas. We collected the granite and diorite from the Hunder river section and also coarse-grained granite and granodiorite from the central part of Ladakh batholith at Khardung La pass for K-Ar dating of biotite. The granite and granodiorite samples of the Ladakh batholith has given the age of 50-51Ma. Granite, diorite and the mixed rocks in the Hunder area have yielded an age of 64 to 66 Ma. The later is significantly older than the former, indicating that the late Cretaceous igneous activity of Shyok-Hunder section took place before the formation of main Ladakh batholith. On the other hand, the porphyritic granodiorite collected from the southern part of the Hunder section occurring as a large mass has given an age of 62 Ma for biotite. Thus subduction related igneous activity in Ladakh-Shyok area took place at least for 16 million years from 50 Ma to 66 Ma before the collision event between Indian and Asian continents.

K-Ar phengite age - temperature relations in the Ishigaki high-pressure schist belt of the southern Ryukyu Arc, Japan

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The Pre-Tertiary rocks of Ishigaki Islands within the southern Ryukyu Arc situated more than 1000 km southwest of the Honsyu Island, Japan. These rocks can be broadly divided into two formations namely Tomuru and Fusaki formations. Based on their petrological and geochronological studies the high P/T metamorphic rocks of Tomuru formation has been correlated to the Suo high P/T schist belt in southwest Japan. The Tomuru Formation composed mainly of basic and pelitic schists intercalated with siliceous and psammitic schists. These rocks have been completely recrystallized during metamorphism and the metamorphic sequence can be subdivided into three zones, namely zone-A, -B and -C based on the mineral assemblages in the widespread basic schists. The low-grade zone-A is characterized by the pumpellyite-glaucophane assemblage with minor occurrence of lawsonite and aragonite. The medium-grade zone-B is marked by the disappearance of pumpellyite, lawsonite and aragonite and the presence of epidote-glaucophane assemblage. The high-grade zone-C is characterized by the appearance of barroisite in basic schists and of garnet in pelitic schists. The metamorphic grade increases from the lower to the upper stratigraphic levels, representing an inverted metamorphic gradient. The present study mainly concentrated on the K-Ar phengite age-temperature relations in the pelitic schists from the Tomuru formation. The pelitic schists were collected from all three zones for the K-Ar dating of phengites and the XRD analyses of carbonaceous materials. The K-Ar phengite dating result gives 188-205 Ma for zone-A, 196-206 Ma for zone-B and 208-220 Ma for zone-C. The apparent d₀₀₂ spacing of carbonaceous materials is 3,590-3,437 Å in zone-A, 3,415-3,390 Å in zone-B and 3,387-3,364 Å in zone-C. The age-apparent d₀₀₂ relation shows that the K-Ar phengite ages become older with increasing in the metamorphic temperature. This positive relation of age and metamorphic temperature in the Ishigaki area contrasts with the negative relation of the Nishiki area in the Suo belt. Both areas also have the contrasting thermal structure that the former area has an inverted metamorphic gradient whereas the latter one has a thermal structure with the higher-grade zone totally in lower part of apparent stratigraphic succession. It is interpreted that the ductile deformation in the metamorphic sequences of Ishigaki area has suffered significantly longer time compared to the Nishiki area. Thus the two contrasting age-temperature-structure relations in a metamorphic belt could be due to the difference in the exhumation processes of metamorphic sequences.

K-Ar ages of white micas in metapelites from the Lesser Himalaya, central Nepal: Implications for the timing of metamorphism

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The Lesser Himalaya in central Nepal is composed of Late Paleozoic-Early Tertiary Tansen Group underlain by Late Precambrian-Early Paleozoic Nawakot Complex. The Tansen Group consists of very low-grade (diagenetic) to non-metamorphic sediments. The Nawakot Complex consists of low- to medium-grade Barrovian-type metasediments with an inverted metamorphic zonation where metamorphic grade increases from structurally lower to higher positions towards the Main Central Thrust (MCT). Petrological studies show that the Nawakot Complex experienced two metamorphic events: the anchizonal regional metamorphism of the Pre-Himalayan stage (M₀) and the subsequent garnet-grade dynamothermal inverted metamorphism of the Neohimalayan stage (M₂) associated with the MCT activity. The Nawakot Complex shows two foliations, S₁ and S₂ that are synchronous with M₀ and M₂, respectively.

We carried out K-Ar dating of various-sized fractions (0.5-1, 1-2, 2-4 and 4-6 µm) of white micas separated from low-grade metapelites by the decantation method and on white mica concentrations from higher-grade rocks. The Tansen Group gives extremely old ages ranging from 850 Ma for 0.5-1 fraction to 1,045 Ma for 2-4 fraction. The ages could result from old detrital materials because of less-recrystallization. The Nawakot Complex yields the ages ranging from 458 to 9.5 Ma. Relatively less-sheared and lower-grade (anchizone) samples containing only recrystallized white micas defining S₁ give the ages of 280 - 458 Ma, representing the timing of M₀. The youngest age (9.5 Ma) was obtained from the upper part of the MCT zone which experienced intense ductile shearing resulting S₂ and recrystallization (M₂) at the temperature of 500-650°C during the MCT activity. Intermediate ages are observed in the epizone to the lower part of the garnet zone where the rocks have two types of white micas defining S₁ and S₂. Petrological evidence and EMP mica chemistry show that recrystallized white micas defining S₁ and S₂ have different compositions, and M₀/M₂ mica ratio decreases towards the north close to the MCT. The northward younging of white mica separate ages may have been resulted from mixing ratio of two types of micas in the separates.

Rb-Sr Isochron and K-Ar ages of igneous rocks from the Samnua Depression Zone in Northern Vietnam

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The Samnua Depression Zone (SNDZ) runs NW-SE over 400 km from Northern Vietnam to Southwestern China. It represents the Northern edge of Indochina block and is contiguous to the Southern China block by the Songma fault. The zone is mainly composed of Paleozoic and Mesozoic volcano-sedimentary successions that are intruded by the Mesozoic intrusives and extrusives and by Cenozoic extrusives. The igneous rocks, considered as of Mesozoic age, are widely distributed in the northwestern part of the SNDZ and comprise mafic-ultramafic, granitic and volcanic rocks. They constitute the Nuichua mafic-ultramafic (NCMUM), Songma granitoid (SMG), Piabioe granitoid (PBG), Banmuong subvolcanic granite (BMSVG), Banchieng granitoid (BCG), Dongtrau felsic volcanics (DFV), and Muonghinh felsic volcanics (MFV). The Cenozoic basaltic rocks (CBR) are mainly restricted to the southeastern part of the SNDZ.

Representative igneous rocks of the SNDZ were geochronologically analyzed by the Rb-Sr whole rock and K-Ar biotite methods. The Rb-Sr whole rock isochron ages give 222 Ma for the NCMUM, 213 Ma for the SMG, 203 Ma for the PBG, 138 Ma for the BMSVG, 27 Ma for the BCG, 218 Ma for the DFV, 186 Ma for the MFV and 5.8 Ma for the CBR. The K-Ar biotite ages give 252 Ma for the SMG, 237 Ma for the PBG and 24 Ma for the BCG. The groundmass fraction of the CBR yields an age of 1.9 Ma. The age data show that the Rb-Sr whole rock isochron ages are relatively younger than the K-Ar biotite ages for the same rocks, except for the Rb-Sr whole rock isochron age of the Cenozoic basaltic rocks is older than the K-Ar age. The resulting apparent ages together with the field evidences reveal that the major igneous activity of the SNDZ took place during Triassic time and is most probably related to the continental volcanic arc magmatism, while minor intraplate igneous activity occurred in the Neogene. This suggests that the tectonic environment of the SNDZ changed from a convergent plate margin to a matured continental margin (within continental plate regime) in the time span between the Triassic and Neogene.

Dating of uranium ore by cathodoluminescence: experimental basis by He ion implantation in relation to the radiation effects detected by ESR

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It is well known that halos of 30-40 micrometers in width are often observed by cathodoluminescence (CL) in quartz adjacent to the minerals bearing radionuclides. Similarly, bright CL rims are observed in quartz of uranium ore surrounded by the matrix containing high concentration of uranium. The bright CL rims were simulated by the experiment of He ion implantation into quartz, which confirmed that the rims and the halos have been created by natural alpha particles. The spectra of CL of those rims including sample dependence and change with He ion doses will be presented in the aspect that CL intensity may be used to determine the ages of the minerals and of the uranium accumulation.

The samples were also measured with ESR (electron spin resonance) in order to make quantitative analysis on the lattice defects created by radiation. The characteristics of the E_1' center (an unpaired electron at an oxygen vacancy) in He implanted quartz was found to be different from that in natural and in electron irradiated quartz. Major part of the E_1' center in natural quartz seems to be created by external beta and gamma rays, indicating that the CL halos are not directly correlated with the oxygen vacancies in quartz.

O36-01

Mineral clusters as ready-made catalysts in the emergence of life and oxygenic photosynthesis

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Chemosynthetic life first emerged autogenically at the apex of a hydrothermal alkaline submarine mound where physical and chemical gradients were at their steepest. This mound was where hydrothermal H_2 and NH_3 converged to react with atmospheric CO_2 dissolved in the acidulous Hadean Ocean to produce acetate and other organic molecules between 40° and 90°C. The 'ready-made' catalyst for the reactions was greigite ($NiFe_3S_8$), which, with other spontaneously precipitated minerals, constituted the semipermeable compartment walls within the mound. Greigite thus had a chemical as well as a physical function: comprising elements of variable valences, greigite served both to help catalyze reductions to carboxylic and amino acids, and to protect these organic products from dissolution, hydrolysis and dispersion. Peptides sequestering inorganic catalytic clusters such as the cubane-comprising greigite, emerged as proto-enzymes, e.g., CODH, which employs an $[Fe_4NiS_4]$ cluster where CO_2 is reduced to CO. Peptides also eventually took over membrane function from the iron-nickel sulfides.

Emerging first as acetogenic bacteria, life expanded into the surrounding ocean-floor sediments and crust, to be conveyed by ocean floor spreading toward an island chain where a portion of its host sediments was thrust up into the photic zone. Once there some of the more evolved bacteria happened to invade littoral manganese-rich precipitates at sulfurous springs. Shielded from UV radiation by a thin film of manganese oxide, these bacteria evolved light-harvesting antennae and photochemical reaction centres (RCs) to exploit low energy solar photons, oxidize the H_2S to sulfur, and so gain electrons and protons for biosynthesis. As the H_2S supply waned an alternative reaction complex (RC II) evolved from the ancestral complex (RC I) that could oxidize organic detritus ($CH_2O_{detritus}$) from dead cells at a higher redox potential. This photosynthetic bacterium switched between RC I and RC II, depending upon prevailing redox conditions. At the same time, the UV shield, comprising photo-oxidized rancieite ($CaMn^{IV}_4O_{10} \cdot 3H_2O$) now oxidized a small proportion of the ambient water to O_2 . Cooption of this 'ready-made' $CaMn_4O_{10}$ cluster by RC II produced a photosystem (PS II) that gained 4 electrons and 4 protons from two water molecules ($2H_2O$ in place of $CH_2O_{detritus}$). At the same time, a simple mutation disabled the redox switch and allowed RC I (as PS I) to accept electrons directly from PS II instead of H_2S . So the two newly co-existing photosystems became connected by shared electron carriers, allowing generation of electrochemical potential high enough to oxidize H_2O for biosynthesis.

O36-02

A universal phylogenetic tree having roots

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Almost all experiments and theories on the origins of life have long been based on an a-priori assumption that pre-biotic molecules had appeared and evolved somewhere in ancient and genial sea water. Recent Earth science is, however, revealing dynamic history of the early Earth that would have offered chemically more reasonable places and situations for pre-biotic molecular evolution than those in sea water. Microbial genome phylogeny, on the other hand, doubts recently Darwinian mechanism of evolution at the deeper level than Eukaryotes and proposes a phylogenetic tree terminated by "the ring of life" as a result of genome fusion and horizontal gene transfer. A new scenario of pre-biotic molecular evolution connected reasonably with evolutions of the Earth and life, is, therefore, required for guiding studies related to the origins of life.

Here we propose a phylogenetic tree having roots. The concept represented in the tree is that geological events of the early Earth were the environmental pressures for the evolution of organic molecules as those in life's evolution.

As more than 85% of known meteorites are of ordinary chondrite composed of mafic silicates, metal sulfides, Fe-Ni alloys and a small amount of carbon, the Late Heavy Bombardment of extraterrestrial objects to sea water would engender a reducing atmosphere and produce a wide variety of organic molecules as well as ammonia.

In them, hydrophilic and clay-affinitive molecules could have only survived strong UV radiation and oxidation decomposition, because they could escape into sea water and be adsorbed on clay particles that finally deposited on the sea ground. Polymerization of organic molecules would be a way of their survival in sediment that experienced dehydration condition at high-pressures and high-temperatures by thick stacking. Polymers would survive hydrolysis by forming cells when hydrothermal water would soak the sediment. Cell fusion would be a mechanism for making a better cell that would leave sediment and adapt to life in sea water. Genome fusion might be a relic of such cell fusion.

O36-03

Impact vaporization of extraterrestrial objects: importance of liquid water and implication to the early Earth

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Late Heavy Bombardment of extraterrestrial objects impacted dominantly onto the oceans during the late Hadean age. Such impact would have been vaporized large amounts of the meteorites. Impact vaporization is very important process to consider about environment of the early earth. Experimental evidence of impact vaporization of extraterrestrial objects has been lacking, because velocity of impact generated in laboratory is much lower and the effect of water on vaporization had little been recognized. In this study, we report the formation of the ultrafine particles in shock-recovering experiments targeting iron, olivine and water. The ultrafine particles of transition metal oxides and olivine exhibit morphology characteristics of "smoke particles" of vapor growth. Their compositions also indicate that these particles were formed by elements from different sources. We speculate that super critical water, formed during shock experiments, expands the solubility of solid materials and enhances the vaporization of the starting materials. This evidence suggests impact vaporization at low velocity and low water content implying that extraterrestrial objects that impacted to early oceans must have been vaporized extensively thereby formed large amounts of ultrafine particles. Because these particles have been supposed about 100 times larger than formed in this study, such ultrafine particles launched to the stratosphere would have stayed long and formed post-impact clouds that obstructed sunlight and UV radiation for much longer than previously believed.

O36-04

Pressure dependence of peptide formation in solid-state: Implications for the chemical evolution under the deep crust

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Almost all previous experiments and theories on the origin of life have been based on an assumption that chemical evolution proceeded in the ancient oceanic environment. However, peptide formation is the dehydration reaction and the reaction is unfavorable in the presence of liquid water at all temperatures. Alternative possibility that chemical evolution would have been performed in the deep crust was proposed. Therefore, we attempted the solid-state polymerization of amino acids at high-pressure and high-temperature conditions to synthesize the peptide. Experiments in this study indirectly examine the possibility of chemical evolution in crustal conditions.

Experiments were conducted in a test-tube-type autoclave using gold-tube reactors. Solid glycine was weighed and placed into the gold-tubes and run at elevated pressures (5 ~ 100 MPa) and held at 150 °C for 1 to 8 days. Glycine peptides were identified and quantified by high performance liquid chromatography (HPLC) and liquid chromatography mass spectrometry (LC-MS).

Products were colored, grading from white (at 100 MPa) to a deep brown (at 5 MPa). A HPLC chromatogram of the products indicated at least five oligomers: di-, tri-, tetra-, penta-, and hexaglycine were formed. We also identified hepta-, octa-, and nonaglycine with LC-MS. These highly polymerized peptides were preferentially formed, at 25 ~ 100 MPa. On the other hand, polymerization of glycine proceeded to only pentamer at 5 ~ 15 MPa. The yields of each oligomer were increased with the duration of the experiment. This suggests that there is pressure dependence of peptide formation in solid-state. Pressure is effective to obtain longer peptide from amino acid. In addition, formation of polycyclic aromatic hydrocarbon (PAH) was also confirmed as secondary products.

These results from this study support the theory that chemical evolution could happen in deep Earth environments, such as inside of upper crust. If conditions allowed, not only amino acids but also peptides could form in the crusts of other planetary bodies.

Transition metal sulfides, organosynthesis, and the emergence of life

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The majority of Origin's of Life Scenarios link the emergence of life to the natural synthesis of molecular building blocks that would have served the bridge between abiotic chemistry and the first biochemistry. The probability of the synthesis of any specific molecule or molecular group on the early Earth must be a function of the chemo-synthetic qualities of the environment. The recirculation of reduced CO₂ bearing fluids through deep-sea hydrothermal systems has been invoked as a particularly favorable scenario for providing certain critical prebiotic reactions. Chemical potential alone, however, is insufficient for useful organosynthesis; rather heterocatalysis (e.g. on mineral surfaces) is required to direct the chemical potential to generate useful organic products. Transition metal sulfides have been shown to have excellent catalytic properties for the promotion of the synthesis of fatty acids, metabolic intermediates (for example, di- and tri-carboxylic acids), and alpha-keto acids. In the presence of ammonia, the synthesis of a number of amino acids, promoted by the catalytic hydrogenation promoted by transition metal sulfides. In addition to catalysis, the direct participation of transition metal sulfides in organosynthetic reactions may be similarly important. For example, it has been shown that carbonyl sulfide, COS (formed through the reaction of CO and H₂S, and catalyzed by transition metal sulfides), promotes the facile oligomerization of amino-acids to form small peptides. It is possible this reaction can also occur during acidic dissolution of some transition metal sulfides. The coupled reduction of NiS to Ni₃S₂ with oxidation of alkanes to alkane thiols has also been demonstrated; this latter reaction is critical to establishing robust organosynthetic pathways that are functionally similar to that of central extent anabolic metabolism. Hydrothermal vent environments are not ideal environments, however, for the prebiotic synthesis of other useful molecules, e.g., sugars and nucleobases. Thus, linking various natural environments capable of different types of prebiotic chemistry appears to be essential to beginning to explain the spontaneous emergence of life on Earth.

Genesis of biogenic iron-oxide nodules (takashikozo) in reducing sediments

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ABSTRACT

Fe-oxyhydroxides nodules, known as takashikozo in Japan, occur as cylindrical nodules ranging from a few mm up to 3 cm in diameter with cm to several tens of cm long in unconsolidated clayey to silty Quaternary lacustrine sediments. It is however unknown that the formation process of takashikozo and its preservation in reducing subsurface environments. Results of a detailed geological and geochemical investigation show that Fe-oxyhydroxides nodules takashikozo is formed by a redox reaction and that it can persist in a reducing sedimentary environment for at least 0.3Ma. During takashikozo formation some elements such as S, P, Mn and U are also sporadically accumulated in the nodules. Microbial analysis with 16S rDNA shows that a consortium of iron-reducing and iron-oxidizing bacteria contributes to the formation of the zonal structure of takashikozo as well as the preferential accumulation of some major and trace elements. These lines of evidence suggest that microbial consortium obviously can generate both redox reactions and substantial elemental accumulation under anaerobic conditions. The observations outlined here have profound implications for the role of microbial consortium for secondary elemental migrations associated with biomineralization invariably identified in the geological environment.

Roles of metal ions in chemical evolution in submarine hydrothermal systems

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The present biological system requires a number of trace metals, such as iron, zinc and molybdenum. Trace essential trace metals are generally more abundant in seawater than non-essential metals. In 1970s, submarine hydrothermal systems are discovered, where concentration of metal ions in high-temperature fluid is much higher than surrounding sea water. The hydrothermal systems are now considered as possible sites for the generation of life on the Earth. A number of laboratory experiments have been conducted simulating the conditions of submarine hydrothermal systems. We here report our experimental results on possible roles of trace essential metal ions in chemical evolution in submarine hydrothermal systems. Amino acids were, for example, formed when simulated hydrothermal fluid with metal ions and ammonium ion in an autoclave was heated while pressurized with a mixture of methane and nitrogen. We will also show some results of our recent experiments where a flow reactor system with a gold image furnace is used.

Origin of graphite in 3.8 Ga Isua Supracrustal Belt: three different origin?

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Occurrence of graphite has been known in the 3.8 Ga Isua Supracrustal Belt (ISB), West Greenland. Origin of the Isua graphite may constrain as to when the first life flourished on the early Earth. Novel graphite schists were found through the course of this study in the western part of ISB. In situ carbon isotope analyses were performed on graphitic schist samples using the Nd-YAG laser microprobe. Micro-scale heterogeneity of carbon isotope compositions were found: -22.4 to -18.9 per mil in sample 1 and -22.3 to -17.5 per mil for sample 2. These heterogeneity was created by hydrocarbon loss from graphite during diagenesis and/or metamorphism at 3.8 to 3.7 Ga. This further suggests that organic matter, depleted in C13, were existing rocks were metamorphosed. Graphite found in this study were, therefore, most likely remnants of micro organism living in the 3.8 Ga ocean, adding more evidence for the early life (Rosing, 1993).

Geological occurrence and geochemical nature of novel graphite (type A) are completely different from previously recognized metazomatic graphite (type B: van Zuilen et al., 2002) and veined graphite (type C) in ISB. Origin of veined graphite has not been certain, but most likely formed either by (A) methane oxidation, or (B) solidification of migrated oils. Oils or methane were most likely formed from older marine sediments containing type A graphite. Formation of type C graphite may have been common process even in the pre-biotic world.

Bio-activity in the 3.46 Ga hydrothermal system; ferruginous marble bar chert, Pilbara, Western Australia

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It has been debated among researchers on the genesis of Archean Marble Bar chert (banded iron formation). It has been said that the Marble Bar chert was precipitated from the hydrothermal solution near ocean ridge like environment, based on the complex geological evidences of banded sedimentary chert and hydrothermal veins. The red and black band in the Marble Bar chert contains abundant Fe minerals; hematite, magnetite and siderite, as well as organic carbon. In this study, we discuss on the bio-activity in the Marble Bar chert to understand the oxidation of aqueous ferrous iron. We have examined the mineral assemblages, textures and chemical compositions of the fresh cores of the Marble Bar chert by ABDP.

The ABDP#1 core of the Marble Bar chert is composed of two kinds of chert: rhythmically banded sedimentary chert composed of the band rich in Fe oxide and carbonate, and Fe free band, and hydrothermal carbonaceous quartz vein (or dyke). Euhedral grains of syngenetic pyrite are observed to be coexisted with hematite and magnetite in the sedimentary chert, suggesting that the hematite and magnetite are primary 3.46 Ga minerals, but not productions of later weathering.

In the red and black sedimentary chert, numerous hematite and/or magnetite grains are accumulated as spherical to euhedral grains of about 100 nm to 1 micron in quartz crystal. The quartz shows botryoidal texture. This botryoidal texture resembles that of modern bacteria mat of benthic coccoid cyanobacteria. SEM images show bacteria like cells connecting with and enveloping hematite grains in the botryoidal quartz. The intensity image of cathodoluminescence from the botryoidal quartz is associated with bacteria like texture. The carbon 1s X-ray photoelectron spectra (ESCA) acquired from banded cherts contain peak at about 285 eV, suggesting C-C and C-H bonding. Furthermore, the Raman spectrum from the black band obtains the peaks at about 1300cm⁻¹ and 1600cm⁻¹, derived from organic carbon. The Raman spectrum image reveals the heterogeneous distribution of organic carbon. The C isotopic ratios both of sedimentary chert and hydrothermal veins are -20 to -35 permil, suggesting the inhabitation of Fe bacteria, cyano-bacteria and methanogen.

The occurrences of mineral and organic carbon suggest that the original texture has remained unchanged. The occurrences suggest that bacterial remain exists in the banded cherts, and that the precipitation of iron oxides was related with biological activity.

P36-01

Hydrothermal formation of organic globules in the presence of porous rocks

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Organic globules were found in the Tagish Lake meteorite (carbonaceous chondrite fallen in 2000) and their similarity to bio-membranes was suggested based on their infrared (IR) spectra (Nakamura et al., 2002). On the other hand, film-like products were reported to be formed during the hydrothermal heating of an OH-bearing amino acid (threonine:Thr) solution (Nakashima and Shiota, 2001). In order to simulate formation processes of the organic globules, hydrothermal heating experiments of Thr solutions have been conducted in the presence of porous rocks.

By heating 40ml of Thr solution with a piece of porous rock (about 1 cm in diameter) in the hydrothermal vessel at 160 °C for 4 days, globules of 2 to 20 µm in size were observed under Scanning Electron Microscope (SEM) on the rock surface. Elemental analysis of the globules with Energy Dispersive X-ray Spectrometry (EDX) showed that they consist mainly of carbon.

For elucidating mechanisms of globule formation, thin section samples of porous rocks with different chemical and mineral compositions are used in the hydrothermal experiments. The products in the thin sections are analyzed for their characterization by IR microspectroscopy and Near-Field IR spectroscopy (a new nano-scale characterization method).

The changes of dissolved components in solutions have been analyzed by Liquid Chromatography (LC), UV spectroscopy and ATR-IR spectroscopy. Thr transformation processes appeared to include multiple complex reactions and their kinetic analyses were tried.

These results suggest that the organic globules found in Tagish Lake meteorite could be formed during aqueous alteration of carbonaceous chondrites by hydrothermal interactions of amino acids and minerals.

P36-02

Instability of adenosine in the presence of hydroxyapatite under hydrothermal conditions

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Among various roles of minerals in chemical evolution, phosphate minerals might have served as a phosphate source for the formation processes of RNA. In order to evaluate this possibility, hydrothermal interaction experiments have been conducted using hydroxyapatite (HAP) as a phosphate mineral and adenosine as a nucleoside.

In our experiments, 4 different types of starting mixtures were heated in an electric oven at 140°C for 1–8 days, 10 ml of 10 mM adenosine, 10 ml of 10 mM adenosine with 0.1 g HAP powder, and 10 ml of 10 mM adenosine with 1 g HAP powder. The 4th type is 10 mM adenosine solution containing dissolved phosphate and calcium. Obtained solutions were analyzed by UV-Visible spectroscopy, ATR-IR spectroscopy and HPLC. The concentrations of Ortho-phosphate and calcium in the obtained solutions were measured by colorimetric methods. Precipitates were analyzed by SEM-EDX, XRD and FT-IR spectroscopy with the KBr pellet method.

As a result, adenosine was completely lost by this hydrothermal heating. Adenine (base) was first formed and then decomposed, while hypoxanthine was produced. No phosphorylated nucleoside (AMP, ADP, ATP) was detected. The decomposition rate of adenosine increased in the following order: with 1 g HAP powder > with 0.1 g HAP powder > with dissolved phosphate and calcium > adenosine only. The precipitates obtained from heating of adenosine with dissolved phosphate and calcium were needle-like crystals. They were found to be phosphate minerals containing carbon based on the XRD and SEM-EDX analyses. These results indicate that the phosphate mineral accelerated the thermal decomposition rate of adenosine at 140°C. This temperature condition is considered to be unfavorable for the chemical evolution to RNA, because of instability of the nucleoside and no phosphorylation.

P36-03

Thermal stability of nucleotide and formation of ATP: importance of temperature and phosphate concentrations

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It has been uncertain how to synthesize nucleotide on the early Earth environment. Among previous studies, results from Ponnampuruma et al. (1965) are considered as the standard model to produce the first RNA. Ponnampuruma et al. (1965) reported that nucleotide is produced by heating nucleoside mixed with phosphoric acid at 160°C for 2 hours under vacume conditions. On the other hand, heating experiment of the nucleotide at 150°C resulted in decomposition in a few minutes (Kawamura, 1998). These results are contrasting each other and creating ambiguity.

In this study, series of experiments were performed by heating nucleotide and nucleoside under the various conditions. It is found that nucleotide easily decompose in all conditions if the temperature exceeds 160°C. This result supports the Kawamura's result and is not consist with Ponnampuruma's experiment. On the other hand, the nucleotides, e.g., ATP, were easily formed under the low temperature conditions like 25°C or 80°C, when the free oxygen gas was evacuated. In addition, Nucleoside are not phosphorized in concentrated phosphoric acids.

This further suggests that RNA World could have developed in the ancient cold to warm reduced oceanic environments rather than hot submarine hydrothermal environments.

Metamorphic and metasomatic effects on carbon isotope and REE compositions in 3.8 Ga metasedimentary rocks in Isua Supracrustal Belt

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The 3.8Ga rocks are distributed in Isua Supracrustal Belt (ISB), West Greenland. From detail field investigation, new graphite schist was found inside of Banded Iron Formations (BIFs) in western part of ISB. Graphite schist contains up to 4.12 wt % C_{graphitic}. CI Chondrite normalized REE patterns shows the sedimentary origin of graphitic schist, thus black shale.

Carbon isotope compositions of graphite were determined on 200 samples. Their compositions vary -20.7 per mil to -13.2 per mil. Notable feature of these carbon isotope compositions are systematic change in compositions correlated to geological occurrence. Lightest carbon isotope composition was found in the most western area in where the highest graphite contents were found. On the other hand, heaviest carbon isotope composition was found in the most eastern area.

Such characteristics were also found in REE patterns. Chondrite-normalized REE patterns are similar to Archean sedimentary rocks in the western area. Chondrite-normalized REE patterns of the eastern rocks are depleted in Sm, Nd and very different from the Archean sedimentary rocks.

These carbon isotope and REE characteristics are explained by more intense metasomatism in the eastern area even in the same formation. Metamorphism and/or metasomatism may make carbon isotope compositions of graphite heavier, but no mechanism is known to make them lighter. Therefore, the lightest isotope compositions found in this study is most likely closed to the initial carbon isotope composition of graphite. Microbial process is the only considerable process to form graphite which isotope composition is lighter than -20 per mil.

Geochemical study of 3.0 Ga Steep Rock Group in Canada: microbial diversity corresponding to the redox change in 3.0 Ga Steep Rock ocean.

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Steep Rock Group of northwest Ontario is situated in the Wabigoon Subprovince of the Superior Province, Canada. The Steep Rock Group includes an assemblage of ca. 3.0 Ga extrusive and intrusive igneous rocks and sedimentary rocks, comprises five formations: Wagita formation (clastics), Mosher Carbonate, Jolliffe Ore Zone, Dismal Ashrock, and Witch Bay Formation (metavolcanic). Mosher Carbonate contains diverse stromatolites morphologies, indicating that the biological productivity was high in the 3.0 Ga Steep Rock ocean. Jolliffe Ore Zone contains Banded Iron Formations (BIFs), and the mechanisms of their deposition might have connected to redox conditions of contemporary Steep Rock ocean.

In addition to geological survey, detailed petrographic, X-ray diffraction, electron microprobe and X-ray scanning microprobe studies were performed to identify constituent minerals and elemental distributions in thin section scale. Concentration of organic matter and their carbon isotope compositions were also determined using the elemental analyzer.

Through the course of investigation, new lithofacies, black chert and black shales were found to be situated in the middle layer of Mosher Carbonate and Jolliffe Ore Zone. Mineralogy, including siderite, Mn-oxides and V-oxides occur through the examined stratigraphy. Because of redox sensitivity of Mn and V, occurrence of Mn- and V oxides in the specific horizon of examined strata indicate the presence of redox boundary (chemocline) in the 3.0 Ga Steep Rock ocean. This chemocline is most likely corresponded to CCD.

The black shales contain high concentrations of organic matter and shows slightly low carbon isotopic ratio (TOC: 0.14-0.87wt%, $\delta^{13}\text{C}_{\text{PDB}} = -32.5 \sim -28.2 \text{‰}$) compare to carbonates, including some stromatolites (TOC: 0.03-0.13wt%, $\delta^{13}\text{C}_{\text{PDB}} = -26.1 \sim -23.5 \text{‰}$). These changes are roughly corresponded to change in nature of carbon sources for biological activities and the high biological productivity at around the chemocline in the Steep Rock ocean. While there was dissolved oxygen above chemocline, deep ocean was anoxic, like the modern Black Sea. These data further suggest that the diverse of microbial life forms based on oxygen cycle have established well before ca. 3.0 Ga.

Mineralogical examination of Archean Biosphere Drilling Project samples of Marble Bar Chert, Australia

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Search for "the origin of life" is an significant theme for mankind. It is still in dispute whether "microbe fossils of ~3500 million years ago" from Archean cratons (Pilbara, Australia; Barberton, South Africa, etc) are genuine fossil or not. We examined the Marble Bar Chert drilling core samples from ABDP (Archean Biosphere Drilling Project; international joint project of 2003). We described their textures and mineralogy and searched for some traces of life. Mineralogical viewpoint is important as fundamental data. Among drilling cores of 260m in depth were examined by polarization-microscope, XRD, TEM, SEM. The samples can be classified into following six; (1a) Chlorite-rich altered basalt (1b) Clay-mineral rich altered basalt (2) Banded black chert (3) Banded white chert (4a) Banded iron chert (iron oxide minerals) (4b) Banded iron chert (goethite). These rocks suffered hydrothermal alteration. Carbonaceous matter contained in banded black cherts is about 0.1-0.5µm in diameter and round or film shaped. All the carbonaceous matter are not always amorphous but some crystalline graphite grains were contained. It means that the samples have not been completely affected by metamorphism. Some unique textures suggesting a possibility of microfossils of organisms are listed as follows; (1) "The bunch of grapes" shaped textures (oval-shaped, ~4mm in diameter) that are composed of quartz and hematite are found in a part of banded white chert. (2) Filament-like structure (length ~50µm) and double concentric circle structures (composed of quartz and siderite) are found in some parts of banded black chert. These shapes and sizes are similar to modern cyanobacteria colony, bacterial fossils from Gunflint chert, Canada and microfossils of the early Archean Apex chert, Australia. There is a possibility that these unique textures and structures were microbe traces. Based on these data etc, a model for formation process of Marble Bar Chert incorporated with bacterial activities is proposed. The model is as follows: (1) Basalt and chert (or its precursors: silica, iron-hydroxide, etc) were formed by igneous and hydrothermal activity at deep sea floor. (2) Bacterial activities supplied the carbonaceous matter into sediments at reductive environment. But some of them oxidized iron minerals locally. (3) Rock textures and mineral compositions effected by hydrothermal alteration.

O37-01

Nanoparticles in the Earth Sciences: Making the Link Between Size Dependent Properties and Reactivity

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Naturally occurring nanoparticles are high-surface-area mineral phases that can be formed through inorganic and biologically-mediated precipitation reactions. Although these materials are metastable with respect to their bulk counterparts, numerous natural nanoparticles are sufficiently stable in low temperature aqueous environments to represent a durable sink of nutrients and contaminants. By now, it is well established that small particle size can have profound consequences for the structural and chemical properties of materials. Considerable progress has been made in determining how small particle size affects the static structure and phase stability of nanoparticles relative to bulk minerals. More recently, we have shown that studies of nanoparticle structure at high pressures reveals new aspects of bonding in nanocrystals. By analyzing the pressure dependence of the structure of ZnS nanoparticles, we observed that the compressibility of this material increases substantially with decreasing particle size. The data indicate that smaller particles are more compliant because there are additional structural responses to stress that are not available to bulk ZnS.

In common with bulk environmental minerals, nanoparticles can undergo chemical transformations and catalyze redox processes at their surface. Experimental studies of nanoparticle reactions have uncovered reaction rates, pathways or products that cannot presently be predicted from experience of similar reactions involving the bulk materials. For example, nanoparticles of iron sulfide and can be transformed by oxidation or reduction reactions into new nanoparticles of an unexpected mineral phase, with little apparent growth. Furthermore, ferric iron oxide nanoparticles can catalyze the oxidation of adsorbed Mn(II) more than ten times faster than the bulk oxide, but the mechanism that accomplishes this is unknown.

In order to develop theoretical descriptions of the reactivity of nanoparticles, it is essential to link the characterization of particle size, structure and electronic properties with experimental observations of reactivity. An approach that is anticipated to be of great value is the use of x-ray absorption and emission spectroscopies to provide the energy position and structure of the conduction and valence bands, respectively, of semiconductor materials. Combining these measurements reveals size effects on nanoparticle electronic structure in a way that can be quantitatively linked to the thermodynamics of charge transfer processes at nanoparticle interfaces. Preliminary data show that the surface and interior electronic structure of iron oxyhydroxide nanoparticles exhibit a considerable evolution with increasing particle size.

O37-02

Reactivity of Iron Oxide Nanoparticles

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Iron oxides and oxyhydroxides commonly occur as nanoparticles in the 3-10 nm size range and strongly impact the biogeochemical cycle of iron and other species at and near the Earth's surface. We use surface-area normalized rates of reduction and oxidation of iron oxide nanoparticles with a range of organic chemicals in batch experiments. Results enable comparisons of reactivity as a function of particle size, shape, and composition. We have characterized the reactivity of several different ferrihydrites, goethites, and magnetites of controlled particle size and with varying composition. Interestingly, low amounts of aluminum doping result in increased reactivity in the ferrihydrite system whereas aluminum doping in the magnetite system results in substantially depressed reactivity. The impact of small changes in synthetic and storage procedures will also be specifically addressed.

O37-03

Nature and genesis of ferrihydrite

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Ferrihydrite (Fh, nominally FeOOH or $\text{Fe}(\text{OH})_3$) is common in surface oxic aquatic environments and is believed to be an important transportation vector for nutrients and trace metals. Only the more crystalline 6-line variety (6L-Fh) is an accepted mineral and there appears to be a continuum of crystallinity from six to two lines in the powder X-ray diffraction (pXRD) pattern. Fh may be the only accepted mineral that is intrinsically nanoparticulate, with observed particle diameters always in the range ~1-5 nm. Its structure and chemistry are ill-defined and recent high-resolution transmission electron microscopy and convergent beam electron diffraction measurements have shown it not to be a single-phase material as generally believed. My group and collaborators have studied many natural and synthetic end-members and co-precipitates of Fh and Fh-bacterium systems using: pXRD, Mössbauer spectroscopy (MBS), mineral magnetometry, TEM, light and major element analyses, and thermal analysis; combined with simulations of pXRD patterns of disordered nanoparticles, ab initio electronic structure calculations of hyperfine parameters, and kinetic theory simulations of precipitation. We find that Fh always forms by rapid homogeneous precipitation and co-precipitation. As it precipitates in a burst of nucleation and surface controlled growth, it readily incorporates various elements such as P, Si, C, and As, and organic molecules, depending on their aqueous concentrations. The resulting solid $^{56}\text{Fe}^{3+}$ oxyhydroxide clusters can represent several different incipient structures having similar surface free energies, can be stabilized to different degrees by co-precipitates and surface poisoning, and all have significant degrees of atomic positional disorder, as quantified by both pXRD and MBS. Contrary to the present predominant view, in the presence of bacteria Fh is never formed by a template or cell wall precipitation barrier reduction mechanism. Fh has a strong affinity for phosphate and there is evidence for Fe:P 1:1 compound formation from both water column field studies and laboratory syntheses. Under sediment early diagenesis conditions the precipitate formed is always predominantly nanogoethite rather than Fh as generally believed. The solid state physics phenomenon of speromagnetism was first described in Fh but can be shown to be an artifact of an incorrect interpretation of the Mössbauer spectra that does not admit the effect of coordinating anion positional disorder on the hyperfine field. The magnetism of Fh has recently been shown to be consistent with high-defect collinear antiferromagnetism and the intrinsic magnetization can approach that of magnetite.

O37-04

Migration of trace elements via nanoscale processes

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A huge volume of material at the Earth's surface exists as nanoscale, particularly in the ambient low-temperature environment, the so called "critical zone". Importantly those nanoscale particulates are often involved in the migration of trace and/or toxic elements. A detailed investigation of the nanoscale phases in natural samples provides critically important insight to the understanding of the mechanisms of migration of the trace elements. In this presentation, we highlight recent research and collaborative work focusing on a detail observation for the natural samples: (i) Fate of Pb in the Archean zircon, and (ii) the migration of Pu and fission products as facilitated by colloids in groundwater. The state-of-the-art analytical methods, utilizing electron microscopy, have been employed for the nanoscale characterization.

(i) A direct, near atomic-scale characterization of Pb is demonstrated in zircon (>3.3 Ga). Two forms of Pb have been identified: Pb concentrated at ~3 atom% as a nanoscale patch in zircon structure, and Pb concentrated within the amorphous domain created by fission fragment damage. The first result suggests that the Pb atoms directly substitute for Zr^{4+} in the zircon structure, and the latter observation demonstrates that Pb diffusion can occur through amorphous regions created by radiation damage.

(ii) In order to investigate the phase of colloid responsible for Pu-sorption and the form of adsorption at far-fields, a systematic analysis of the solution chemistry and redox state of actinide-bearing colloids were investigated in the groundwater from the highly contaminated site of the radiochemical plant of the Mayak Production Association, in the Urals, Russia. Plutonium activities reach 0.16 Bq/l even at distances of 3.0 km from the source. At distance >2.4 km, 70-90% of the Pu is bound to nanoscale colloids, 1-15 nm, confirming the significant role of colloids for Pu-transport. Elemental maps obtained by nano-SIMS revealed that Pu(IV) species, hydroxides or carbonates and adsorbs onto an amorphous hydrous ferric oxide with a uranyl carbonate species, likely due to the high point zero charge of its surface. Similar behavior of Pu and U species in adsorption phenomena is the key mechanism for Pu-migration under the oxidizing condition of Mayak groundwaters. Such a mechanism may be important in actinide migration at other sites, where oxidizing conditions prevail, such as at the proposed geologic repository for high-level nuclear waste at Yucca Mountain.

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Sunagawa et al. recently reported the occurrence of unusual topological amphibole whiskers and frost column of quartz associated with hedenbergite crystals in druses of skarn at Kakino mine, Gifu prefecture, Japan [1]. These whiskers are bundles of single crystalline amphiboles, showing straight, twisted, curled, helical, coil, ribbon or rope forms. A vapor-liquid-solid (VLS) mechanism has been proposed as a possible growth mechanism for both amphibole whiskers and frost column of quartz, based on scanning laser microscopic observations and selected micro area X-ray diffraction and fluorescence analyses [1]. Here we report the positive results concerning the VLS growth of the topological amphibole whiskers.

High-resolution transmission electron microscopy and nanometer order point to point energy dispersion X-ray (EDX) and electron diffraction analyses were made on these topological amphibole whiskers. It was found that (1) the whiskers are covered by amorphous thin layer in which amphibole crystallites of nanometer order as well as pyrrhotite and quartz are formed, (2) in addition to the elongation in [001] direction of whisker, the elongation in [102] and [111] are present, (3) chemical composition of the whiskers are various from point to point, and (4) some amphibole straight whisker slightly curl in nano-order. The EDX analysis also revealed that the amorphous layer covering the amphibole is quite S-rich composition. These observational results support the argument that the topological amphibole whiskers were formed by the VLS mechanism through reaction between earlier formed hedenbergite crystals and later introduced vapor phase resources containing H₂O, S, SiO₂ etc.

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Biominaleralization and biodissolution as examples of interaction between microbes and minerals occur at first as nano scale processes. Furthermore, in relation to such bio-mineral reaction, nano-scale structural changes in related minerals are often associated. Biogenic ore formation is an important process but the details are not always clarified for many ores. We demonstrate several examples of biogenic ore signatures and show characteristic nano structures and textures for Gunma Iron ore, Kuroko ores, sedimentary manganese ores and manganese nodules.

Gunma mine is characterized as Biologically induced iron ore (Akai et al., 1999); goethite has nano crystalline in size. Sedimentary manganese ores occur in green tuff region in Japan. Modern and recent manganese precipitation at Yunotaki (Mita et al., 1994) was also examined. In the former samples todorokite trillings are often found. Colloform or stromatolitic textures are also characteristic. In recent Yunotaki ore specimens, nano-formation of precursor for trilling structure was found on the host busenite-like structures. That is, trillings in todorokite may nucleate originally at different sites with three equivalent directions based on host planar busenite or similar layer structures, which are often formed by biological process. Manganese nodules from the Pacific Ocean also showed stromatolitic rhythmic band textures in 0.1mm scales with growth direction. Fractal-like repeated ball-shapes were characteristic. Spherical forms on the surface and inner structure of the nodule could be interpreted as bacterial mineralization traces. TEM observation showed stacking disorder in nano scales in constituent busenite-like structures.

Kuroko ore characteristically occur in Japan. The genesis has variously been discussed (Kajiwara, 1983). Kuroko ores could be classified into three types (Enohji, 1987). We carried out detailed texture observation by microscopic methods. Type I has fine grained textures. We found stromatolitic textures in type I specimens. Furthermore, sphalerite in type I has thin lamellar twin structures. On the other hand, sphalerite in type II and III having nano scale GP zone has been found. The correspondence of these nano structures, ore types and biosignature in type I is characteristic in ore formation processes. GP zone has enrichment of Cu in nano region. This may be due to Cu-containing solid solution in sphalerite which correspond to the growth under Cu rich environment in later stage of the Kuroko formation. Sphalerite in type I with less Cu contents corresponds to the earlier formation stages with stronger biological activities.

Thus, characteristic nano structures and micro textures could become clues for biogenic ore formation processes.

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Efficiency of magnetic alignment of solid particles is believed to occur only on materials which possess spontaneous magnetic moments. This property is generally lost at high temperatures above Curie point. Nonmagnetic particles have the potential to cause magnetic alignment due to their anisotropy of diamagnetic susceptibility ($\Delta\chi$)_{DIA}. This efficiency should be preserved up to its melting point, because ($\Delta\chi$)_{DIA} originates from a diamagnetic anisotropy of individual bonding orbital composing the crystal. ($\Delta\chi$)_{DIA} of a mineral is hence preserved with its crystal structure. Here we report significant rotational oscillation at temperatures above 1000 °C for the first time on diamagnetic single crystals, in a weak field below B = 4000 G produced by a horseshoe magnet. ($\Delta\chi$)_{DIA} of a material is obtained from the period of oscillation. Measurements were performed on grain aggregates as well. The magnetically stable axes of grains were aligned in one direction in the process of producing the aggregate; ($\Delta\chi$)_{DIA} can be obtained even if a large single crystal cannot be obtained for a material. In the present study, measurements were performed on SiC, forsterite, corundum and graphite for the purpose of investigating the possibility of magnetic alignment of presolar grains due to a circumstellar field; this field intensity is theoretically deduced to have the level of B = 100–300 G. The above materials are major components of presolar grains which are formed in the envelopes of AGB (Asymptotic Giant Branch) Stars. Recently, polarimetry deriving from grain alignment was detected in the envelopes. The distribution of scattered light shows clear evidence of axisymmetry. The efficiency of magnetic alignment of presolar grains provides a basis to observe stellar field. Up to now, magnetic field has not been detected based on observational results for most of the stars except for the Sun. It is noted that alignment due to spontaneous moments do not occur in high temperature environment such as the circumstellar envelope (T > 1000 °C). It is generally accepted that magnetically stable axes of small diamagnetic crystals dispersed in gas align almost parallel to magnetic field B, when field-induced energy (1/2)M $\Delta\chi$ B² is one order of magnitude larger compared to Brownian motion energy (1/2)k_BT. Partial alignment in the field of B = 200 G is hence expected for micron-sized crystals of the measured materials at T = 1000 °C, according to the ($\Delta\chi$)_{DIA} – T data obtained in the above experiment.

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Various fine minerals are contained in carbonaceous chondrite matrix. Carbon minerals in carbonaceous chondrites are well known as nano-diamond, graphite and various organic matters such as "Carbonaceous Globules (Nakamura et al., 2001)". It is important to clarify the details of carbon minerals in these meteorites, which suggest the early process of solar system formation. Some Antarctic meteorites have some unique characteristics such as thermal metamorphism in CM chondrite (Akai, 1988; Nakamura, 2005) in contrast to non Antarctic chondrites. We examined fine structures and textures of these carbon minerals by HRTEM. Specimens examined in this study are nine Antarctic carbonaceous chondrites, Allende(CV3) and Murchison (CM2). The nine Antarctic meteorites are as follows: Asuka-882094(CO3), Yamato-694(C4), Y-86751(CV3), Y-790992(CO3), Y-81020(CO3), Y-74662(CM2), Y-793321(CM2), Y-86720(CM2), Belgica-7904("CI")

These samples were chemically treated by HF, HNO₃, aqua regia and H₂O₂ in order to derive high concentration of carbon minerals. The TEM observations were carried out using a JEM-2010 (JEOL, operated at 200kV).

Nano-diamonds are included in common in CM2 type chondrites such as Murchison and Y-74662. Most of particles are 3nm in diameter or less. A lot of nano-diamond grains have the shape of a more or less rugged sphere. The contrast of the lattice image of nano-diamond is very low. Graphite is clearly observed in some of CV3, CO3 type chondrites such as Allende and A-882094, and also from CM2 type chondrites after H₂O₂ processing in specimen preparation. However, the amount of observed graphite is less compared to C3 types.

Low-crystalline carbon minerals are commonly found for many carbonaceous chondrites and are the main component of CM2 type chondrites. Carbonaceous Globules are commonly observed in CM2 type chondrites. However, Carbonaceous Globules are not contained in C3 type (Allende, Asuka-882094) and C4 type chondrites.

Furthermore, the characteristic nano carbon minerals were newly observed; "carbon onion" which have 1 to 4 layers, 0.8-3nm in diameter and "carbon nano-capsule" that may be graphite coating structure around spinel grains.

These data were classified and arranged for each meteorite and meteorite types. However, no clear correspondence between thermal metamorphic degrees and crystallinity of carbon minerals, but the characteristics of carbon minerals are well corresponding to petrological types. These facts suggest the formation of carbon minerals is prior to the thermal metamorphism.

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Significant advances can still be made in developing even the most common characterization methods simply by improving our theoretical understanding of the measurement itself – because most of the difficulty often does not reside in obtaining good data but rather in being able to analyze the data. In my group, we have made advances in the areas of powder X-ray diffraction (pXRD), ^{57}Fe Mössbauer spectroscopy (MBS), and mineral magnetometry; that allow unprecedented information extraction from complex environmental samples. In MBS, we are the originators of the popular RecoilTM software that implements our methods for treating several correlated distributions of hyperfine parameters. More recently we have performed ab initio electronic structure calculations that link Mössbauer hyperfine parameters to specific local structures and local degrees of chemical and positional disorder. This allows accurate quantitative degrees of disorder to be measured, for example, in ferrihydrite co-precipitates, that are then imposed in structural models used to simulate pXRD patterns. In pXRD, we have recently established the fundamental theoretical relation between a phase-specific contribution to a diffraction pattern and the corresponding weight fraction of that phase, that is valid for any type of phase (crystalline, amorphous, nanoparticulate, quasicrystalline) and that directly leads to calibrationless and standardless absolute quantification with multi-phase samples. We also routinely simulate the pXRD patterns for arbitrary size and shape nanoparticles having arbitrary compositions, structures, and degrees of disorder. In mineral magnetometry, we have developed the theoretical expressions for field and temperature magnetization curves from samples containing arbitrary distributions of superparamagnetic particles, blocked ferrimagnetic particles, distributions of paramagnetic cations, and a diamagnetic matrix. These expressions allow the maximum amount of mineral magnetic information to be extracted from the data and have allowed us to extract intrinsic magnetizations of many different nanoparticle Fe oxyhydroxide systems, and precise mean particle masses and mean supermoment magnitudes. Some of our recently published contributions to environmental mineralogy, using the above and other methods, include: (1) a demonstration that the dominant diagenetic Fe oxyhydroxide phase in lake and marine sediments is nanogoethite, rather than the expected ferrihydrite; (2) quantitative discrimination of the hydrogen loss and vacancy mechanisms of oxidation in Fe-bearing layer silicates; and (3) a demonstration that ferrihydrite precipitated in the presence of bacteria does not, as generally believed, form by a cell wall template mechanism.

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At present rapidly developing nanosciences and nanotechnologies have achieved striking results in obtaining nanocrystalline materials of unusual composition and properties: fullerenes, fullerites, nanopipes etc. However, long before the origin of nanotechnologies of artificial materials physio-chemical processes in nanometer range of scales were widely spread in natural laboratories during mineral formation, mineral associations, rocks and deposits. The constant confinement of mineral deposits to zones of faults, thrusts, subduction, various pipes of explosion etc. is due to particular thermodynamic, physical, chemical, catalyst, kinetic and other abnormal properties being formed during dispersion of minerals of nanoparticles. Their abrasion also leads to mechano-chemical synthesis of new compounds. High sorptional and reaction activity of nanoparticles of coaly, argillaceous terrigenous material are responsible for localization of gold deposits and other elements in certain types of rocks. After crystallization of minerals from various heterogeneous solutions, fluids and colloids, in the massive matrix (pyrite, tetrahedrite, quartz etc.) as a result of disintegration of solid solutions, metastable compounds, radioactive elements, diffusion processes etc, nanoparticles and nanoensembles of minerals nonexisting in macroforms are localized in defects of structure. Undoubtedly, all the minerals have passed nanostate stage, but over million years of evolution, tendency to minimization of free energy has led to aggregation of nanoparticles and formation of large ensembles. The processes of natural nanotechnologies were of key importance during formation of concentration of elements, commercial content of which make up 0,0000n-0,00n% (Au,Pt,Pd,Os,Re,Se,Te etc.). Formation of similar deposits was due to the laws of nanochemisyy and nanomineralogy – nanogeosciences of the XXIc.

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The phases of tetranite¹⁾, enstatite²⁾, and spinel³⁾ which are some commonly observed minerals in interplanetary dust and for carbonaceous chondrites can be produced by the reaction between particles and film. The diffusion process during compound formation has been elucidated on the basis of the morphological changes of the film and the particles. Since the sulfur film can not be produced, the similar experiment was not done for the formation of sulfides in spite of a lot of ionic conductors. In a precious paper, we succeeded to produce sulfur ultrafine particles by the gas evaporation method⁴⁾. In this paper sulfide formation due to solid-solid reaction between copper ultrafine particle and sulfur particle has been presented. Copper sulfide crystal with the characteristic flower shape, which was similar to the Shinobu stone, were produced by the solid-solid reaction by the preferential diffusion of copper atoms to the sulfide particle. Both the copper and sulfur ultrafine particles were produced by the gas evaporation method without to exposure in air before the reaction. Nonstoichiometric Cu_xS and $\text{Cu}_{1.94}\text{S}$ phases were produced around Cu particle and sulfur particles at room temperature, respectively. G.P contrast which suggests the excess of copper was seen at the grown crystal of Cu_xS . Direct observation on the phase transition with temperature has been done in electron microscope. The morphological alterations hardly observed by heating at 500°C. But the phase transition can be clearly observed. These phases began to alter to the Cu_2S phases above 450°C. Hexagonal and cubic phases were produced at 200°C. By further heating up to 500°C, the cubic Cu_2S phase was obtained. When the specimen was cooled down to the room temperature, the polymorphic transformation have been observed between the room temperature and 300°C for the Cu_2S structure.

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Meta-stable sulfide minerals crystallized under low-temperature condition in organic carbon-rich sedimentary rocks were discovered from drilled core samples in the Mt. Roe Basalt. The Mt. Roe Basalt is considered to be a 2.77 Ga flood basalt, widely occurring in the northern Pilbara area of Western Australia. Less metamorphosed sedimentary rocks ($T < 300^\circ\text{C}$, $P < 3\text{ kb}$) are interbedded in the basaltic flows. Both detrital and authigenic sulfides occur in the continuous sedimentary layer.

To identify the sulfide minerals, chemical composition and crystal structure analyses were performed using an X-ray analysis microscope, an electron probe microanalyzer (EPMA) and a high-resolution transmission electron microscope (TEM) with analytical electron microscopy.

The detrital grain consists of quartz, metal-rich pyrrhotite with composition between FeS and Fe_7S_8 , and minor pentlandite. Authigenic sulfide minerals occur as complex mineral assemblages: metal-poor pyrrhotite (Fe_7S_8), smythite (Fe_9S_{11}), pyrite, pentlandite, chalcopyrite, and sphalerite. Notable feature of authigenic sulfides is the development of crystal defects in Fe-sulfides (composition between Fe_7S_8 and FeS_2), and their abnormally high nickel concentrations (~3 wt.%). These sulfides were crystallized under low-temperature condition ($< 100^\circ\text{C}$). Textures and chemical compositions of the sulfide assemblages suggest that they precipitated meta-stably in the sediment by 2.77 Ga diagenesis or 2.2Ga low grade metamorphism. It is difficult to constrain which was the case. In either case, this is the first report for the Precambrian metastable sulfides.



Authors Index

Bold: Communicating Author

Authors Index

A

Abart, Rainer	O12-04
	P18-13
	P18-23
Abbott, Jeffrey	O15-15
Abdelmonem, Ahmed	O25-10
Abduriyim, Ahmadjan	O32-08
Abe, Jun	O03-11
Abe, Masanao	O21-13
Abe, Natsue	O20-03
Abe, Takaaki	O08-12
	O23-16
	O37-07
Abe, Toshiya	P12-05
Abratis, Michael W.	P20-01
Abu El-Hassan, Mohamed M.	O26-16
Acerio, Patricia	O11-10
Adachi, Kouji	O26-01
Adachi, Mamoru	P30-12
	O36-07
Adachi, Satoshi	O11-04
Adachi, Yoshiko	O20-05
Agrosi, Giovanna	P12-14
Ahmad, Talat	P35-06
Ahrens, Thomas J.	O05-16
Aikawa, Nobuyuki	P03-11
	P25-03
Aizawa, Jun	P24-21
Akai, Junji	P26-12
	P08-22
	P16-12
	P16-15
	P36-05
	O37-06
	O37-08
Akaki, Takeshi	P21-09
Akamatsu, Tadashi	P04-03
Akaogi, Masaki	O01-03
	O01-08
	P01-04
	P05-07
Akasaka, Masahide	O08-16
	O16-03
	O16-05
Akatsuka, Takashi	P12-01
Akiko, Hokura	P31-19
Akiko, Ito	P26-11
Akimoto, Azusa	O20-05
Akune, Yasuhiro	P28-04
Alaabed, Sulaiman A.	P20-15
Ali, Mohd. Roushown	P08-02
Ali, Murad A.	P20-11
Allen, Jeremy	O04-06
Alnæs, Lisbeth	P29-01
Al-Qady, Gad M.	O26-16
Alterman, Michail	O24-01
Alvarez, Rebeca	O26-06
Amouric, Marc	P01-03
Amthauer, Georg	O04-13

Andal, Eric S.	O20-08
	O20-09
Andersen, Tom	O14-06
Anderson, Greg	O16-11
Ando, Jun-ichi	O10-06
Andrade, Marcelo B.	P31-12
Andrault, Denis	O01-13
	O02-06
	P02-02
	P02-12
Andreani, Muriel	P20-01
	O27-01
Andreozzi, Giovanni Battista	P08-14
Androne, Delia A-M	P18-25
Anikina, Elena Yu.	P16-13
Anna, Neubeck	O36-06
Anschutz, Amy J.	O37-02
Aoki, Masahiro	P30-04
Aoki, Takayuki	O37-08
Aoki, Tomoaki	P21-01
Aoya, Mutsuki	O35-13
Arai, Shoji	P19-07
	O20-08
	O20-09
	P20-02
	P20-03
	P20-05
	P20-06
	P20-08
	P20-09
	P20-10
	O35-06
Arai, Tomoko	O22-05
	O22-06
Arakawa, Yoji	O19-09
Araki, Tatsuro	P02-11
Aratake, Koji	O35-06
Aratani, Go	P20-12
Arima, Hiroshi	P02-02
	P02-13
	P28-08
	P33-04
Arima, Makoto	O07-05
	O18-07
	P18-15
Arita, Kazunori	P35-07
Armbruster, Thomas	P08-05
	O18-08
	O31-11
Armstrong, Richard	O16-15
Armstrong, Richard A.	O35-07
Arvidson, Rolf S.	O11-03
	O25-12
Asada, Ryuji	O24-05
	P24-01
	P24-08
Asahara, Yuki	O05-15
Asai, Atsushi	O26-14
Asakura, Etsuro	P11-01
Asimow, Paul D.	O05-16

Askhabov, Askhab M.	O13-02
Asogwa, Sachiko	O08-02
Asta, M. Pilar	O11-10
	P25-07
Atac, Ahmet	P16-14
Atake, Tooru	O01-08
Atanassova, Radostina	O12-15
	P13-02
Atencio, Daniel	O31-06
	P31-12
Atou, Toshiyuki	P02-11
	P09-06
Audetat, Andreas	O06-05
	O15-03
	O17-01
Auricchio, Carlo	O32-06
Auzende, Anne-Line	P04-05
Avedisyan, Anaid A.	O14-05
Ayumi, Katagiri	P26-11

B

Bae, Inkook	P27-10
Bai, Wenji	P05-02
Baikie, Thomas	O08-21
Baioumy, Hassan M.	O26-16
Baker, Don	O12-13
Bakirov, A.A.	P18-24
Bakirov, A.B.	P18-24
Bakirov, Apas B.	O19-11
Bakun-Czubarow, Nonna	O35-05
Balan, Etienne	O03-08
Balic-Zunic, Tonci	P02-03
	O04-14
Ballirano, Paolo	P08-14
Ban, Masao	O19-02
Banno, Shohei	P08-21
Banno, Yasuyuki	P30-04
	P31-07
Baronnet, Alain	O25-02
Baronnet, Alain J.	P04-05
	O27-01
Barz, Ralph-Uwe	P12-10
Baslakunov, J.U.	P18-24
Bass, Jay	O02-01
	O05-10
Baturin, Gleb	P16-11
Bauer, Andreas	O25-11
Baumgartner, Lukas P.	O11-08
	PL6
Baxter, Nichelle	O15-14
Bea, Fernando	O19-12
	P19-16
Beard, James S.	P20-01
Beckholmen, Monica	O14-06
Behrens, Harald	P09-04
	P12-02
Bekker, Tatyana B.	P12-10
Bellatreccia, Fabio FB	P31-18
Belmabkhout, Youssef	P01-03
Bente, Klaus	P08-15
Beppu, Yuki	P18-12

Bermanec, Vladimir	P08-20	Burke, Ernst A.J.	031-01	Cluzel, Nicolas	O23-15
	P24-09	Burrows, Debra	O29-08	Cocherie, Alain	035-11
Bernd, Lehmann	P16-08	Buseck, Peter R.	026-01	Cody, George D.	O09-04
Bihannic, Isabelle	P25-16	Butterworth, Anna	O21-11	Cody, George D.	036-05
	034-09	Buzgar, Nicolae	P18-25	Cohen, Ronald E.	004-03
Binh, Pham	O18-04	C			
Birch, William D.	O08-07	Cabaret, Delphine	O09-12	Coker, Victoria S.	O33-02
	O30-04	Calas, Georges	003-08	Collins, Alan	O32-02
	031-05		026-07	Comodi, Paola	005-03
Bizzarro, Martin	023-06		O28-02		P06-04
Blaess, Ulrich	P23-02		028-03	Connolly, James Alexander	P18-23
Blanchard, Marc	O06-07		O34-12	Cook, Nigel J.	O16-06
Bland, Phil	O21-11	Cama, Jordi	011-10		016-07
Bobrov, Andrey V.	001-03		P25-06	Cooke, David J.	O04-06
Bocek, Adrijana	P24-09		P25-07	Cookson, David	O02-04
Bocor, Nabil	O36-05	Camara, Fernando	P31-16	Cora, Ildiko	P16-16
Boiocchi, Massimo	P03-02	Cao, Ye	P24-23		P27-03
Boisen, Monte B.	O25-03	Caracas, Razvan	O04-03	Cordier, Patrick	002-03
Bolfan-Casanova, Nathalie	O01-13	Cardile, Vera	P26-01		P02-14
	O02-06	Carducci, Michael D.	O08-06	Cormier, Laurent	009-02
Bonaccorsi, Elena	O08-13	Carpenter, Michael A.	O03-05		O28-02
	P31-05		P03-01		O28-03
Bonev, Ivan K.	012-15		PL8		O33-06
	P13-02	Carrez, Philippe	O02-03		034-12
Bonev, Nikolay	P15-07	Carson, Christopher J.	O18-08	Coutinho, Jose	O31-06
Bonneau, Vincent	O18-15		P18-09	Cozar, Onuc	O32-04
Borch, Thomas	O24-13	Catalano, Jeffrey G.	025-09	Cozzupoli, Domenico	O16-14
Borg, Gregor	014-07	Celotto, Steve	O11-14	Crichton, Wilson	P33-09
	016-15	Cera, Fabio	O05-03	Crichton, Wilson A.	O02-05
Bortnikov, Nickolay S.	014-05	Ceuleneer, Georges	020-01		O01-10
	P16-13		O20-07	Crispini, Laura	O20-02
Borzdov, Yuri M.	O07-10	Chae, Soochun	P27-10	Cristina, Betti Maria	P10-01
Boscherini, Federico	P03-02	Chaerun, Siti K.	P24-01	Crowe, Sean A.	O24-11
Bose, Sankar	P18-01	Chakraborty, Subrata	O23-05	Cui, Weihua	O25-16
	P18-03	Chang, Qing	O19-07	Culea, Monica	O32-04
Botcharnikov, Roman	P12-02	Channer, Dominic M.DeR.	O07-01	D	
Bougerol, Catherine	O31-05	Charnock, John M.	O26-08	Da Pelo, Stefania	P25-07
Bourcereau, Laurence	O24-15		O33-02	Dachs, Edgar	P01-01
Bouvier, Pierre	P02-12	Chatellier, Xavier	024-15		P01-02
Boyle, Alan P.	016-02	Chen, Chun-Jung	025-17	Dai, Guoliang	O11-09
Bradley, John	O21-11		P26-10	Dai, Qun-wei	P24-22
Brearley, Adrian	O21-11	Chen, Honghan	P24-03	Dai, Zorong	O21-11
Brennan, Sean	O21-11		P24-04	Dal Negro, Alberto	P10-02
Bridges, John	O21-11	Chen, Jiuhua	P02-14	Dalconi, Maria Chiara	P03-02
Brodholt, John	O04-04	Cheng, Hao	019-14	Daliran, Farahnaz	O16-15
Brodtkorb, Milka	O16-08	Chernov, Alexander A.	011-01	Damian, Gheorghe	O16-07
	P16-01	Chiba, Hitoshi	O14-02	DaPelo, Stefania	P25-06
Brown, David	O25-14	Chihara, Hiroki	O23-10	Darling, Tim W.	O03-05
Brown, Michael	018-02	Chisato, Okamoto	P22-04		P03-01
Brownlee, Don	O21-11	Chong, Ryan K.K.	O24-16	Das Sharma, Subrata	O25-07
Brunelli, Daniel	O20-03	Chopin, Christian	031-10	Das, Kaushik	P18-01
Brunet, Fabrice	O10-08		P31-16		P18-03
	018-15	Christiansen, Eric H.	O15-15	Dasgupta, Somnath	P18-01
Bruni, Biagio Maria	P08-14	Christy, Andrew G.	P18-07		P18-03
	P26-01	Chukanov, Nikita V.	031-15	De Capitani, Christian	P18-23
	P26-02	Ciftci, Emin	O16-13	De Giudici, Giovanni	P25-07
Bryan, Nick	O26-06		P16-14	De ligny, Dominique	O33-06
Bryzgalov, Igor A.	P27-12	Ciobanu, Cristiana L.	016-06	De Villiers, Johan	O29-04
Bubnova, Rimma S.	O28-13		O16-07	De Vito, Caterina	016-14
Bunno, Michiaki	030-01	Clague, David A.	P09-02		O32-06
	P30-04	Claret, Francis	O27-11	De Weireld, Guy	P01-03
Burchard, Michael	O19-13	Clement, Alain	O25-02	Deakin, Michelle	O12-13
				DeGiudici, Giovanni	P25-06

Delacour, Adeline.....	P20-01	Enami, Masaki.....	O18-13	Fowle, David A.....	O24-11
Della Ventura, Giancarlo GDV.....	P31-18	Enderle, Ralph.....	O26-13	Fragneto, Giovanna.....	O34-09
Demé, Bruno.....	O34-09	Endo, Noriaki.....	P05-03	Francis, Arokiasamy J.....	O24-09
Deng, Jian-jun.....	P24-22	Endo, Yuji.....	O15-16	Francis, Arokiasamy Joseph.....	P24-18
Depmeier, Wulf.....	O24-17	Eng, Peter.....	O09-04	Francis, Carl.....	O30-03
DeRonde, Almar.....	O05-01	Engel, Annette S.....	O24-04	Fransolet, André-Mathieu.....	O31-04
Deutsch, Alexander.....	P23-02	Enjoji, Mamoru.....	P12-13	Franzolin, Ettore.....	O01-06
Devineau, Karine.....	P25-16		P17-05	Freed, Andrew M.....	O01-02
.....	O34-09		P17-06	Fritsch, Emmanuel.....	O32-02
Devouard, Bertrand.....	P04-05	Erbs, Jasmine.....	O37-02		P32-01
.....	O23-15	Erikawa, Wataru.....	P11-07	Fritz, Bertrand.....	O25-02
.....	O27-01	Essene, Eric J.....	P01-01	Frost, Bryce R.....	P20-01
DeYoreo, James J.....	O11-01	Etzel, Katja.....	O24-17	Frost, Daniel J.....	O01-09
Dilles, John H.....	O15-04	Evans, Jim R.J.....	O03-09		O06-06
Dimalanta, Carla B.....	P20-07	Evstigneeva, Tatiana L.....	O16-12	Frost, Daniel J.....	O05-15
Dingwell, Donald B.....	P09-02	F		Fryda, Jiri none.....	P24-10
Dittrich, Maria.....	O24-03	Fagan, Timothy J.....	O21-17	Fryer, Patricia B.....	P20-01
Dixon, Roger D.....	O16-01		P22-01	Fujibayashi, Norie.....	P19-09
Dobson, David P.....	O05-01	Fakih, Mohamad.....	O24-15	Fujii, Yasuhiko.....	O34-02
Dogomi, Daisuke.....	P08-10	Fanfani, Luca.....	P25-06	Fujimaki, Hirokazu.....	P14-01
Doi, Nobuo.....	P19-03		P25-07		P19-02
Donadio, Davide.....	O04-10	Fang, Qingson.....	P05-02		P19-04
Dong, Faqin.....	P24-22	Fanghaenel, Thomas.....	O25-11		O21-09
Dorais, Michael.....	O15-14	Fanghanel, Thomas.....	O25-10	Fujino, Kiyoshi.....	O01-11
Dorokhova, Galina I.....	O32-03	Fanning, Christopher Mark.....	O35-07		O05-06
Dove, Martin T.....	O34-03	Fanning, Mark C.....	O35-11		P05-06
Downs, Robert T.....	O03-13	Fehr, Karl Thomas.....	P11-11		O10-03
.....	O08-06	Fei, Yingwei.....	O06-04	Fujioka, Kantaro.....	O19-06
.....	P08-12		O09-04	Fujiwara, Kentaro.....	P08-10
.....	P08-21	Feig, Sandrin T.....	O20-04	Fujiwara, Takashi.....	P30-15
.....	P08-25	Feig, Sandrin T.....	P20-14	Fukuda, Chihiro.....	O16-05
.....	P34-01	Fendorf, Scott.....	O24-13	Fukuda, Junichi.....	P03-11
Drabek, Milan.....	P16-03	Fenter, Paul.....	O25-09	Fukuda, Tsuguo.....	O28-05
Drits, Victor A.....	O27-02	Fenter, Paul A.....	P24-13	Fukui, Hiroshi.....	O01-13
.....	O27-11	Ferraris, Cristiano.....	O05-05		P02-02
Drouin, Marion.....	P20-01	Ferraris, Giovanni.....	P08-01		O06-11
Du, Lin-Shu.....	O09-05		O31-13		P06-05
Dubinchuck, Viktor.....	P16-11	Ferre, Denise.....	O02-03		P28-08
Dubrovinsky, Leonid.....	O05-03	Ferrini, Vincenzo.....	O16-14		O33-09
Duchene, Stephanie.....	O12-11	Field, Cyrus W.....	O15-04		P33-04
Dunin-Borkowski, Rafal E.....	O24-16	Filatov, Stanislav K.....	O28-13	Fukuoka, Kiyoto.....	P02-11
Dunkley, Daniel J.....	P18-09		O31-14		P09-06
.....	O35-02	Finch, Katie J.....	O26-11	Fukura, Satoshi.....	O03-03
Durinck, Julien.....	P02-14	Finger, Friedrich.....	P35-04		O07-08
Dutrızac, John E.....	O26-05	Fiske, Richard S.....	O19-07	Fukushi, Keisuke.....	O26-15
Dutrow, Barb.....	O12-07	Flörsheimer, Mathias.....	O25-10	Fukushima, Sei.....	P03-03
Dymov, Inna.....	O29-07	Flank, Anne-Marie.....	O33-06	Fukuyama, Seijiro.....	O11-04
Dzierzanowski, Piotr.....	P31-10	Fleet, Mike E.....	O24-02	Fumagalli, Patrizia.....	O05-03
E		Fleming, Chris.....	O29-07	Fuminori, Sakamoto.....	O24-09
Ebata, Shingo.....	O21-17	Flemming, Roberta L.....	O03-07	Funakoshi, K.....	O33-08
Ebel, Denton.....	O21-11	Flynn, George J.....	O21-10	Funakoshi, Ken-Ichi.....	O01-13
Ebihara, Mitsuru.....	P22-04		O33-04		O02-02
Echeverri, Balmer.....	O15-13	Fockenber, Thomas.....	O19-13		P02-01
Echigo, Takuya.....	O14-09	Fois, Ettore.....	P10-01		P05-04
.....	P19-13	Fomina, Marina.....	O26-06		P09-09
Effenberger, Herta.....	O08-09	Fontan, François.....	O31-04		O33-10
Ehiro, Masayuki.....	P35-06	Fontan, Francois.....	O31-08		P33-06
EIMF, J.....	O07-10	Ford, J M.....	O12-03		P33-10
El Goresy, Ahmed.....	O01-05	Forneris, Juliette.....	O06-07	Funakoshi, Kennichi.....	O33-09
.....	O21-04	Fortin, Danielle.....	O24-06	Funamori, Nobumasa.....	P09-09
Ellis, David J.....	P18-07		O24-12	Furche, Markus.....	O25-18
Elzinga, Evert.....	P08-13	Fowle, David.....	O24-01	Furukawa, Asuka.....	O01-08

Furukawa, Noboru.....	P24-12	Graupner, Torsten.....	O25-18	Hatta, Tamao.....	P01-08
Furukawa, Yoshihiro.....	O36-02	Grew, Edward S.....	O18-08		P19-13
.....	O36-03	Grey, Ian.....	O31-05		P25-12
Furukawa, Yoshinori.....	O11-12	Grice, Joel D.....	O31-12	Hauzenberger, Christoph Anton.....	P18-13
Furukawa, Yuki.....	P33-04	Groat, Lee A.....	O32-05	Hawthorne, Frank C.....	O08-15
Furuno, Masanori.....	O15-05	Grodzicki, Michael.....	O03-09		O31-09
Furusawa, Miyuki.....	P15-05		O04-13	Hayakawa, Kazuichi.....	P26-08
Futakuchi, Katsuhito.....	P26-03	Grossman, Jeff N.....	O21-02	Hayakawa, Ken.....	P33-01
G					
Gabor, Rachel.....	O37-02	Gu, Ja Lang.....	P27-07	Hayakawa, Yasushi.....	P33-01
Gadd, Geoff.....	O26-06	Gu, Ying.....	O29-08	Hayashi, Ken-ichiro.....	P16-09
Gaidies, Fred.....	P18-23	Gucsik, Arnold.....	P03-08		P17-01
Gailhanou, Hélène.....	P01-03	Guggenheim, Stephen.....	O27-07		P20-13
Gajovic, Andreja.....	P08-20	Guignot, Nicolas.....	O01-13	Haydrich, Stephanie.....	O16-17
Gallego, Alba Nury.....	O16-03		O02-06	Hedenquist, Jeffrey W.....	O15-02
Galoisy, Laurence.....	O03-08	Gunter, Mickey E.....	P08-07	Hehlen, Marcus P.....	P34-01
.....	O28-02		O08-19	Heide, Klaus.....	P23-02
.....	O28-03	Guo, Guangjun.....	O04-05	Heidelberg, Florian.....	O05-01
Galuskin, Eugeny V.....	P08-05	Gurney, John J.....	O07-03	Heinrich, Christoph A.....	O17-01
Galuskin, Evgeny.....	P31-10	H			
Galuskina, Irina.....	P31-10	Hagiya, Kenji.....	P01-06		PL2
Gamyanin, Gennady N.....	P16-13		P02-01	Hejny, Clivia.....	O01-10
Ganguly, Jibamitra.....	O01-02		O08-14	Hellebrand, Eric.....	O20-03
Gao, Yonghua.....	P24-23	Hagni, Richard D.....	O16-13	Hellmann, Roland.....	O25-01
Garcia Ruiz, Juan Manuel.....	O13-05		P16-14		O25-14
.....	P13-02		O29-05	Henderson, Grant.....	O33-06
Garland, Mary L.....	O32-05	Haikawa, Masataka.....	P36-06	Henderson, Grant S.....	O09-12
Gaucher, Eric.....	P01-03	Hainschwang, Thomas.....	O32-02	Henry, Darrell J.....	O08-18
Gaudio, Sarah J.....	O09-03	Hajime, Sugita.....	P25-01	Henry, Dermot A.....	O30-04
.....	P09-07	Haloda, Jakub none.....	P24-10	Hernandez-Laguna, Alfonso.....	O04-10
Gault, Andrew G.....	O26-08	Halter, Werner E.....	O09-10	Herrmann, S.....	P21-04
.....	O33-02		O09-11	Herzog, Florian.....	O09-11
Gault, Robert A.....	P31-13	Hamane, Daisuke.....	O01-11	Hidaka, Hiroshi.....	O35-08
Geiger, Charles.....	P01-02		P05-06		P35-03
Geiger, Charles A.....	O27-06		O10-03	Hideki, Kanazawa.....	P08-07
Gen, Sazaki.....	P11-06	Hamane-Nishio, Daisuke.....	O05-06	Hiemstra, Tjisse.....	O25-08
Gena, Kaul.....	O14-02	Hamano, Yozo.....	O26-16	Higashi, Shoji.....	P27-06
Genin, Jean-Marie R.....	O31-16	Hamasaki, Satoshi.....	P19-13	Higo, Yuji.....	O02-02
Ghosh, Sujoy.....	O06-08	Hamel, Gerard.....	P33-09		O33-12
.....	P07-02		O34-03	Higuchi, Kensuke.....	O11-07
Gianfagna, Antonio.....	P08-14	Hammer, Julia E.....	O12-05	Hillier, Steve.....	O25-06
.....	P26-01	Hammouda, Tahar.....	P33-09	Hinrichs, Ruth.....	O17-03
.....	P26-02	Handley, Stephanie.....	O26-06	Hiraga, Takehiko.....	O05-04
.....	P31-08	Hansen, Heidi-Elisabeth.....	O20-03	Hirai, Hisako.....	O02-07
Giantomassi, F.....	P26-01	Harada, Akira.....	P31-11		P02-07
Gibbs, G V.....	O08-06	Haranaka, Akiko.....	P18-20	Hirai, Takeshi.....	P27-11
Gibbs, Gerald V.....	O25-03	Hariharan, G.N.....	P24-14	Hirajima, Takao.....	P08-21
Gilbert, Benjamin.....	O37-01	Harlow, George E.....	O18-12		P12-08
Gil-Crespo, Pedro P.....	P19-18		P19-17		O18-01
Glass, Colin W.....	O04-11		O30-03		O18-10
Goebbels, Matthias.....	O26-13	Harte, Ben.....	O07-01		P18-18
.....	O28-09		O07-03		P18-20
Goetz-Neunhoeffer, Friedlinde.....	O26-13		O07-10		P18-22
Golla-Schindler, Ute.....	O17-03		O07-11	Hirano, Naoto.....	P18-14
Gonzalez-Lodeiro, Francisco.....	P19-16	Haruna, Makoto.....	P30-04	Hirano, Nobuo.....	O03-11
Gorby, Yuri A.....	O24-10	Haruyama, Jun'ichi.....	O22-03		P25-14
Goto, Atsushi.....	P31-09	Hase, Hiroko.....	P27-14	Hirao, Naohisa.....	P05-05
Grady, Monica M.....	O21-07	Hasebe, Noriko.....	O35-06		P06-03
Graham, David.....	O24-01	Hashimoto, Takafumi.....	O06-11	Hirata, Daiji.....	P30-08
Grandjean, Agnes.....	O28-04	Hashimoto, Takahumi.....	P28-05	Hirata, Hikaru.....	P08-24
Grauby, Olivier.....	P04-05	Hasson, Sean.....	P15-07	Hirata, Naru.....	P21-06
.....	O27-01	Hatert, Frederic B.R.....	P16-06	Hirata, Takafumi.....	P18-14
.....			O31-04		O35-08

Hiroaki, Ohfuji.....	P24-02	Ihlen, Peter M.....	O28-14	Ishikawa, Hiromasa.....	P14-01
Hiroi, Yoshikuni.....	P12-08	Iida, Etsuko.....	O02-07		P19-02
.....	P18-16	Iida, Yoshihisa.....	P25-17	Ishikawa, Kenichi.....	P19-02
.....	O35-04		P25-18	Ishikawa, Kenji.....	P03-04
Hirokawa, Kazuo.....	P31-14	Iijima, Sumio.....	PL9	Ishikawa, Masamichi.....	O13-03
Hirono, Tetsurou.....	P27-01	Iishi, Kazuake.....	O28-11		P25-13
Hirose, Kei.....	O05-11	Iizuka, Tsuyoshi.....	O35-08	Ishikawa, Shin.....	P08-04
.....	O05-12	Ikeda, Yukio.....	O22-10	Ishikawa, Takehiko.....	P11-10
.....	O05-13	Ikegami, Yasuyuki.....	P27-11	Ishimaru, Satoko.....	O20-03
.....	P33-08	Ikorskii, Serafim V.....	O14-05		P20-09
Hirose, Tadayuki.....	O10-04	Ikuta, Daijo.....	P08-07	Ishiyama, Daizo.....	P14-02
Hiroshi, Ohmoto.....	O16-10		P08-21		P15-01
Hirota, Tomoe.....	O17-05	Imadate, J.....	P24-14		O16-09
Hirotsugu, Shihou.....	O19-02	Imae, Naoya.....	O22-10		P25-03
Hjelen, Jarle.....	P29-01	Imai, Akira.....	O15-05		P25-04
Hoashi, Masamichi.....	O36-09		O15-06	Ishizaki, Noriko.....	O21-03
Hodson, Mark E.....	O25-14		O15-11	Ishizeki, Hirota.....	P14-02
Hoebler, Hans-Joachim.....	O08-17		P15-02	Ishizuka, Osamu.....	O19-05
Hoeck, Volker.....	P16-17		P15-06		O19-07
.....	O32-04		P15-08	Islam, Farhana S.....	O33-02
Hokada, Tomokazu.....	O18-06		O19-04	Isobe, Hiroshi.....	P12-09
.....	O18-11	Imanishi, Hiroki.....	P24-16	Itakura, Yoshinori.....	P33-04
.....	P18-17	Inatomi, Yuko.....	O11-06	Itaya, Tetsumaru.....	O35-13
.....	O35-04	Ingrin, Jannick.....	O06-07		P35-04
Hokura, Akiko.....	P08-11	Inoue, Akane.....	P09-06		P35-05
Holden, Peter.....	O35-07	Inoue, Toru.....	O02-02		P35-06
Holl, Christopher M.....	O06-06		O06-09		P35-07
Holtz, Francois.....	P09-04		O08-04		P35-08
.....	P12-02		P09-09	Ito, Akiko.....	P25-15
Honma, Ushio.....	P19-10		O10-06	Ito, Eiji.....	P01-05
Horie, Kenji.....	O35-08		O33-12		P02-05
Horiuchi, Hiroyuki.....	O08-05	Inouye, Yasushi.....	O03-01		P02-08
Hoshida, Takashi.....	P12-01	Inui, Mutsuko.....	P12-07		P02-13
Hoshino, Kenichi.....	O17-05	IODP, Expedition 309&312 Scientific Parties.....	O20-02		P02-15
Hoshino, Kinichi.....	O15-16	Ionescu, Corina.....	P16-17		O06-11
Hoshino, Mihoko.....	O19-09		O32-04		P06-05
.....	P19-13	Irifune, Tetsuo.....	O02-02		P08-18
Houston, Robert A.....	O15-04		O05-02		P08-19
Howard, Christopher J.....	O10-02		O06-09		O33-09
Hu, Huan.....	O31-08		P09-09		PL3
Huang, Shanshan.....	O26-04		O10-06	Ito, Kanako.....	P31-14
Huang, Xinming.....	O28-06		O10-08	Ito, Kazuhiko.....	P08-07
Huang, Yuanying.....	O25-16		O18-15		P08-21
Huang, Zhenyu.....	P27-13		O33-10		O12-12
Huber, Harald.....	O24-17		O33-12		O25-03
Huber, Michael.....	P11-11		P33-10		P28-07
Hughes, John M.....	P08-13	Isao, Matsunaga.....	P25-01	Ito, Kenichi.....	P25-15
.....	O08-19	Ishibaashi, Hidemi.....	P09-03		P26-11
Hunter, Elizabeth O.....	O15-14	Ishibashi, Jun-ichiro.....	O14-02	Ito, Seturo.....	P04-06
Hunter, Jacob.....	O15-14		O14-04	Itoh, Shoichi.....	O21-17
Hur, Hor-Gil.....	P24-20	Ishida, Kiyotaka.....	P27-05		O23-09
Huss, Gary.....	O21-05	Ishida, Naoya.....	P01-08	Itou, Kazuhiro.....	O23-04
Hyodo, Hironobu.....	O35-12	Ishida, Naoyuki.....	P19-09	Ivanic, Tim J.....	O07-03
.....	O35-13	Ishida, Yoshito.....	P19-07	Iwahori, Keisuke.....	P24-06
.....	P35-02		O20-09	Iwai, Takamasa.....	O24-05
I			P20-10	Iwai, Yuichi.....	P36-03
Iai, Yutaka.....	O19-02	Ishihara, Shunso.....	O15-16	Iwamoto, Taku.....	P36-01
Iancu, Gabriel O.....	P02-10		P15-09	Izumi, Hiroyuki.....	O10-03
Ibaraki, Yosuke.....	P30-10	Ishii, Satoshi.....	P17-04	J	
Ibrahim, Hassan A.E.....	P35-04	Ishii, Shunsuke.....	P18-06	Jacobsen, Chris.....	O33-04
Ichiro, Sunagawa.....	O37-05	Ishii, Teruaki.....	P20-04	Jahn, Sandro.....	O04-07
Ida, Akihiro.....	P08-24				O09-13

Jambor, John L.....	O26-05	Kang, Il Mo.....	P27-07	Kawasaki, Masashi.....	P02-11
Jang, Hee-Dong.....	P24-20	Kani, Kouki.....	P21-06		P09-06
Jang, Yongnam.....	P27-10	Kanke, Nami.....	O20-06	Kawasaki, Masayuki.....	P11-03
Jia, Zhongpeng.....	O30-07	Kano, Kazuhiko.....	P25-03	Kawazoe, Takaaki.....	P05-04
Jiang, Wei-Teh.....	O25-17	Kanzaki, Masami.....	O06-04	Kayama, Masahiro.....	P03-06
.....	P26-10		O06-11	Kayanne, Hajime.....	O26-16
Jige, Mayumi.....	P27-01		P06-05	Kebukawa, Yoko.....	P21-05
Jin, Wei Qing.....	P11-09		O09-01		P21-08
Johnsen, Ole.....	O31-03		O33-07	Keiko, Nakamura.....	O21-06
Johnson, Kevin T.M.....	O20-03	Karamelas, Stefanos.....	P32-01	Keisuke, Fukushi.....	P26-11
Johnston, Cliff T.....	O04-09	Karato, Shun-ichiro.....	P06-08	Keith, Jeffrey D.....	O15-15
Jolliff, Bradley L.....	O08-19		O19-08		O15-14
Jones, John H.....	O22-07	Kargl, Florian.....	O34-11	Keith-Roach, Miranda.....	O26-06
JORAND, Frederic.....	O24-14	Karki, Bijay.....	O04-12	Keller, Lindsay P.....	O21-12
Jun-ichi, Ando.....	P24-02	Karmakar, Subrata.....	P18-01		O33-04
.....	K	Kasama, Takeshi.....	O24-16		O21-16
Kôsa, Ilona.....	O24-16	Kashiwaya, Kouki.....	P26-04		PL5
Kabashima, Nobusuke.....	O09-09	Kasper, Haino Uwe.....	P18-25	Keller, Lukas.....	P18-13
Kaden, Ronny.....	P08-15	Kassahun, Andrea.....	O25-18		O12-04
Kadoshima, Kazuyuki.....	P20-03	Katayama, Ikuo.....	O19-08	Kemp, Tony I.....	O35-10
Kagami, Hiroo.....	O18-06	Katayama, Shin-ichi.....	P02-11	Kent, Adam J.....	O15-04
.....	P19-09		P09-06	Keppler, Hans.....	O06-05
Kagi, Hiroyuki.....	O03-03	Katayama, Yoshinori.....	O09-17		O06-06
.....	O06-08		O11-07	Kerisit, Sebastien.....	O04-06
.....	O07-08		P28-08	Khalaf, Ibrahim M.....	P35-04
.....	O08-10		P33-04	Khobaer, T.M.....	P08-23
.....	P08-16	Kato, Akira.....	P30-08	Khomyakov, Alexander P.....	P31-15
.....	O34-06	Kato, Kazuyuki.....	P26-03	Kido, Osamu.....	P37-02
.....	O34-07	Kato, Koich.....	P11-08	Kihara, Kuniaki.....	P08-24
Kahlenberg, Volker.....	O08-03	Kato, Takenori.....	P35-01		O10-04
Kaito, Chihiro.....	O23-11	Kato, Takumi.....	O10-05	Kikegawa, Takumi.....	O02-07
.....	O37-05	Kato, Yasutake.....	P16-08		O05-14
.....	P37-02	Katsui, Yoshio.....	P16-05		P05-05
Kajino, Shigeo.....	O19-04	Katsura, Tomoo.....	P02-01		P06-03
Kakegawa, Takeshi.....	P26-06		P02-15		P09-09
.....	O36-02		P06-07		O10-05
.....	O36-03		O33-09		P10-04
.....	O36-04	Katsuta, Masanori.....	O06-09	Kikuchi, Masae.....	P02-11
.....	O36-08	Kausar, Allah B.....	P35-02		P09-06
.....	P36-03	Kawabata, Akiko.....	P19-14	Kikuchi, Minoru.....	P07-01
.....	P36-04	Kawabata, Hiroshi.....	O19-07	Kim, Jae-Il.....	O25-10
.....	P36-06		P19-06	Kim, Jean Y.....	O08-21
.....	P37-03	Kawadai, Yuta.....	P05-01	Kim, Yong Ui.....	O15-10
Kallai, Mariann.....	P27-08	Kawaji, Hitoshi.....	O01-08	Kim, Youn Joong.....	P27-07
Kameda, Jun.....	O27-03	Kawakami, Tetsuo.....	P18-07		P10-05
.....	O27-10		O35-13	Kimata, Mitsuyoshi.....	P01-08
Kamenskii, Igor L.....	O14-05	Kawame, Naoyuki.....	P08-07		O14-09
Kameo, Koji.....	P24-12		P08-21		O19-09
Kameshima, Yoshikazu.....	O29-03		P28-07		P19-13
Kamiya, Toshiaki.....	P31-07	Kawamoto, Tatsuhiko.....	O06-04		P19-15
Kanagawa, Kyuichi.....	P05-09		P06-02	Kimura, Hideo.....	P11-02
.....	P12-08		O33-07	Kimura, Jun-Ichi.....	O19-01
Kanai, Yohsuke.....	O37-06	Kawamura, Katsuyuki.....	P04-03	Kimura, Makoto.....	O10-05
Kanai, Yosuke.....	P16-15		P25-05		O21-02
Kanamori, Hiroshi.....	O22-06	Kawamura, Makoto.....	P30-19	Kimura, Yasuyuki.....	P19-02
Kanazawa, Hideki.....	O12-12	Kawamura, Taro.....	P02-07		P19-04
.....	P28-07	Kawano, Jun.....	P04-02	Kimura, Yuki.....	O23-05
Kanda, Hisao.....	P32-02		O32-07		O23-11
Kaneko, A.....	O33-08	Kawano, Motoharu.....	P24-07		P37-02
Kaneko, Katsuhiko.....	P26-04	Kawaragi, Chie.....	P26-04	Kinniburgh, David G.....	O26-08
Kaneko, Takeo.....	P26-03	Kawasaki, Haruka.....	O23-02	Kirwin, Douglas J.....	O15-01
.....	O36-06		P23-01	Kishikawa, Yuka.....	O26-03

Kitadai, Norio	P24-15	Kojonen, Kari K.	O16-17	Kumagai, Yoshitaka	P06-02
Kitade, Yuki	P19-02	Kolesov, Boris A.	O27-06	Kumatoriya, Mizuho	P28-07
Kitagaki, Toshiaki	P30-16	Kolitsch, Uwe	O08-07	Kung, Jennifer	O33-13
Kitagawa, Ryuji	O27-10		P28-01	Kunimoto, T.	O33-08
	P27-01		P31-02	Kuramoto, Kiyoshi	O23-07
Kitagawa, Yuka	P24-08	Komabayashi, Tetsuya	O01-07	Kuribayashi, Kazuhiko	O11-05
Kitakaze, Arashi	P16-07		O06-02		O11-07
	P31-03	Komata, Yuuki	P30-19	Kuribayashi, Takahiro	P04-04
Kitamura, Masao	P01-07	Komatsu, Kazuki	P08-23		O08-04
	P12-04		O34-07		O08-10
	P32-03	Komatsu, Ryuichi	P11-01		P08-06
Kitatani, Takeshi	P02-11	Komiya, Tsuyoshi	O35-08		P08-23
Kitawaki, Hiroshi	O32-08	Komuro, Kosei	P16-09		O34-07
Kiyonori, Michiba	P31-19		P35-09	Kurihara, Hironari	O36-06
Kiyota, Kaoru	O31-07	Kondo, Hiroko	P19-09	Kurisasi, Kousuke	P24-21
Kleebe, Hans-Joachim	O28-01	Kondo, Tadashi	O05-14	Kurka, Andreas	O06-07
	O28-01		P05-01	Kuroda, Masato	O26-15
Klementova, Mariana none	P24-10		P05-03	Kurosawa, Masanori	P17-04
Klotz, Stefan	P33-09		P05-05	Kurumada, Mami	O37-05
	O34-03		P05-10		P37-02
Knapp, Charles	O24-01		P06-03	Kusachi, Isao	P31-01
Knauf, Vladimir V.	O16-17	Koneev, Rustam	P37-01	Kusaka, Katsuhiro	O08-14
Kobatake, Hidekazu	O11-15	Konzelt, Juergen	O08-03	Kusiak, Monika A.	O35-02
Kobayashi, Katsura	O19-14	Kose, Tamon	O11-02		O35-05
Kobayashi, Kensei	O36-06	Koster van Groos, August F.	O27-07	Kuwada, Takao	P33-01
Kobayashi, Norihiko	P14-02	Kosuge, Yasuhiro	P31-11	Kuwahara, Yoshihiro	P25-09
Kobayashi, Ryo	O13-01	Kotova, Olga B.	P02-09	Kuwata, Akira	P02-01
Kobayashi, Sachio	O21-15	Kotova, Yevgeniya N.	P03-05	Kuzawa, Keiko	O25-03
	O21-17	Kouchi, Akira	O23-11		P28-07
Kobayashi, Shoichi	P25-10	Kovács Kis, Viktória	O26-02	Kuzmin, Dmitry V.	O07-02
	P25-11	Koyano, Mikio	P02-11	Kwak, Musun	O11-02
	P31-01		P09-06	Kyono, Atsushi	P08-08
Kobayashi, Tomoyuki	P18-11	Kozai, Naofumi	O24-09		
Kobayashi, Yusuke	O05-14		O26-09	Lábár, János	O26-02
	P05-10	Kozai, Yusuke	O07-05	Lüders, Volker	O16-08
Kocar, Ben	O24-13	Kozaki, Tamotsu	O26-09	Laetsch, Thomas A.	P08-25
Koehler, Melanie	O21-07	Kozlowski, Andrzej	O17-04	Lagarde, Pierre	O33-06
Koenigshof, Peter	P30-01	Krasnova, Nina	O27-01	Lalonde, Andre E.	P19-19
Koepke, Juergen	P09-04	Kreher-Hartmann, Birgit	P23-02	Langenhorst, Falko	O05-15
	O20-04	Krinov, Igor D.	O14-05		O22-11
	P20-14	Krishnan, Sajeev	O35-03		P23-02
Kogiso, Tetsu	P33-02	Krivovichev, Sergey V.	O31-11	Langhof, Nico	O28-09
Kogure, Toshihiro	O04-09	Kroll, H.	O22-11	Langley, Sean	O24-12
	P24-05	Krot, Alexander N.	O23-12	Lanson, Bruno	O27-02
	O27-03	Kruse, Krause	O25-10		O27-11
	O27-10	Krzeminska, Ewa	P12-12	Laporte, Didier	O23-15
	P31-07	Krzhizhanovskaya, Maria G.	O28-13	Lathe, Christian	O33-11
Koh, Shinji	O28-06	Kuba, Toshiko	P05-03	Lattanzi, Pierfranco	P25-06
Kohara, Shinji	O11-07	Kubo, Katsuyuki	P33-04		P25-07
Kohlstedt, David L.	O05-04	Kubo, Tomoaki	O10-05	Lawrence, Allard F.	O16-10
Kohno, Yasuyuki	O19-04		P10-03	Lawrence, Anovitz M.	O16-10
Koichi, Hashimoto	P26-11	Kudaikulova, Gulzhan A.	P27-02	Lazic, Biljana	O08-03
Koike, Chiyo	O23-10	Kudoh, Kentaroh	O21-09	Le Godec, Yann	P33-09
Koike, Wataru	P30-13	Kudoh, Yasuhiro	P04-04		O34-03
Koizumi, Haruhiko	O11-04		O08-04	Le Guillou, Corentin	O10-08
Kojima, Kenichi	O11-04		O08-10	Le Lannic, Joseph	O24-15
Kojima, Satoru	P35-06		P08-06	Le Page, Yvon	O08-21
Kojima, Tomoko	O26-03		P08-23	Le, Loan	O22-08
Kojitani, Hiroshi	O01-03		O34-07	Leblanc, Marc	O31-12
	O01-08	Kudryavtseva, Galina P.	P07-04	LeCheminant, Anthony N.	O32-05
	P01-04	Kulczycki, Ezra	O24-01	Lee, Bum Han	O27-08
	P05-07	Kumagai, Hidenori	P20-02	Lee, Ji-Hoon	P24-20

L

Lee, Jung-Hoo	P10-05	Lucey, Paul G	022-01	Marumo, Katsumi	014-03
Lee, Martin R	O12-06	Lukacs, Andrea	P27-08	Maruoka, Teruyuki	O14-09
.....	025-14	Luo, Junyan	P24-23	Maruyama, Mihoko	P11-06
Lee, Sang Soo	P24-13	Luo, Yun	P08-13	Maruyama, Shigenori	O35-08
Lee, Sung Keun	009-04	Lupulescu, Marian	P08-13	Maruyama, Takahiko	P30-06
.....	O27-08	Luttge, Andreas	011-03	Masaki, Kentaro	O15-05
Lee, Sungki	P27-10		O11-10	Masatake, Sato	P25-01
Lee, Won Pyo	P27-07		025-12	Mashima, Hiroki	P08-22
Lee, Yongjae	P27-07	Lysiuk, Andrey Y.	P18-26	Mashimo, Reina	P19-05
Lee, Young-Boo	P10-05	Lysiuk, Galina N.	P08-09	Massi, Laurent	O32-02
Lekki, Janusz	O35-05	M			O09-02
Lengke, Maggy F.	O24-02	Márton, István	P15-07	Masue, Yoko	024-13
Leopold, Nicolae	O32-04	M, Santosh	P18-02	Matas, Jan	O05-10
Lermi, Abdurrahman	O16-13		P18-06	Matsubara, Kazunari	O10-06
Leroux, Hugues	O23-15	Ma, Guobin	011-13	Matsubara, Satoshi	P08-11
Lesher, Charles E.	O09-03		P13-01		P30-05
.....	P09-07	Ma, Zhesheng	P08-03		P31-07
Li, Baosheng	033-13	Machida, Shin-ichi	P02-07		P31-09
Li, Guowu	P05-02	MacKenzie, Kenneth J.D.	O29-03		P31-11
.....	P08-03	MacKenzie, Maureen	O25-14		P31-14
Li, Li	P02-14	Mackwell, Stephen J.	O22-07		P35-03
.....	O05-01	Madden, Paul A	O04-07	Matsubaya, Osamu	P25-03
Li, Shengrong	P24-23	Madhusoodana, Chengala Damodara	O29-03		P25-04
Li, Xiaofeng	O15-07	Maeda, Jinichiro	P20-02	Matsuda, Jun-ichi	P02-13
.....	015-08	Maeda, Toshikatsu	P25-17	Matsue, Chisayo	P30-04
Li, Ye	P24-03		P25-18	Matsueda, Hiroharu	O15-12
.....	P24-04	Maekawa, Hirokazu	P18-21		P15-03
Li, Yuhua	030-07		P20-04		P15-04
Li, Zhaolin	017-02	Maglambayan, Victor B	O15-06		P16-10
Liao, Libing	P27-13	Maisonneuve, Vincent	O31-12		P17-08
Libourel, Guy	023-12	Maiwa, Koji	P11-02		P30-19
Lin, Jung-Fu	005-08	Majerus, Odile	O28-03	Matsui, Masanori	P01-06
Liou, Juhn G.	O18-12	Makino, Kuniaki	O08-16		P02-01
Litasov, Konstantin	P05-04		P08-10		O04-05
Litasov, Konstantin D.	006-08	Makishima, Junichi	O22-08		P04-01
.....	P07-02	Makita, Mitsuo	P19-07	Matsui, Takuro	O11-09
Lithgow-Bertelloni, Carolina	O01-01	Makovicky, Emil	P02-03	Matsui, Tomoyuki	P24-05
Litvin, Yuriy	O01-03	Malakhova, Nastya	O32-03		O27-03
Litvin, Yuriy A.	O07-07	Malfait, Wim J.	009-10	Matsukage, Kyoko N	O06-04
Litvin, Yury A.	O07-06		O09-11	Matsukura, Yukinori	P25-12
Liu, Fei	P24-03	Malvik, Terje	P29-01	Matsumoto, Ichiro	P20-12
.....	P24-04	Manara, Dario	O28-04	Matsumoto, Keisaku	P18-20
.....	025-16	Manceau, Alain	O27-02		P18-22
Liu, Lin-gun	001-05	Manjanna, Jayappa	026-09	Matsumoto, Naoko	023-02
Liu, Milan	P31-17	Manning, David AC	O26-12		O23-03
Liu, Rui	O26-04	Manuel, James R.	O29-01		P23-01
Liu, Wei	O33-13	Mao, Hokwang	005-07	Matsumoto, Takuya	P02-13
Liu, Xiang Yang	013-07	Mao, Ho-Kwang	O09-04	Matsunaga, Tsuneo	O22-03
Liu, Zheng	O27-04	Mao, Wendy L.	O05-07	Matsushita, Taishi	009-16
Livens, Francis	O26-06	Marchev, Peter	P15-07	Matsuyama, Fumihiko	O31-07
Lloyd, Jon	O26-06	Maresch, Walter V.	019-13	Matsuzaki, Takuya	P06-07
Lloyd, Jon R.	024-08	Marmier, Arnaud	O04-06	Matsukage, Kyoko	O33-07
Lloyd, Jonathon R.	O33-02	Marques Fernandes, Maria	O25-11	Mauk, Jeffrey L.	016-04
Lodeiro, Francisco G	O19-12	Marshall, William G.	O34-07		O16-16
Logar, Mihovil	O08-11		O34-03	Mauthner, Mark	O30-03
Logvinova, Alla M	O07-02	Martignago, Fedora	P10-02	Mazziotti Tagliani, Simona	P08-14
.....	O07-04	Martin, Chris	O29-07		P26-01
Lombardo, Laura	P26-01	Martin, Mark W.	O15-04		P26-02
Lorand, Jean-Pierre	O05-05	Martin, Robert F.	008-20		P31-08
Lorrai, Mario	P25-07		P31-13	McCaig, Andrew M	P20-01
Lu, Anhui	026-04	Martin, Svojka	P18-11	McCammon C.	PL1
Lu, Ren	P08-12	Martinez, Domingo	P33-09	McCarthy, Andrew C.	P08-12

McKay, Gordon	O22-09	Miyake, Akira	P01-07	Morita, Seiya	O15-05
McKay, Gordon A	O22-08		P04-02	Moritz, Robert	P15-07
McKnight, Ruth E.A	P03-01		P32-03	Morlok, Andreas	O21-07
Medenbach, Olaf	O18-08	Miyake, yuya	O28-11	Morotz, Inessa	O32-06
Medici, Cinzia	P10-01	Miyamoto, Masamichi	O22-09	Morris, Pete	O25-13
Meier, Roger	O29-06	Miyamoto, Tomoharu	O18-04	Motoyama, Muneyuki	P03-03
Mellini, Marcello	O08-11		P18-08	Motoyoshi, Yoichi	O18-09
Melone, Nicola	O12-17		P18-09		P18-08
	P12-14	Miyashita, Sumio	O20-05		P18-09
Mercier, Patrick H.J	O08-21		P20-02		P18-16
Meredith, Philip J	O05-01	Miyata, Naoyuki	P24-06		O35-04
Merkle, Roland	O16-01	Miyawaki, Masaaki	O05-14	Mouri, Takashi	O18-13
Merlino, Stefano	O08-13	Miyawaki, Ritsuro	P08-06	Mueller, Hans J	O33-11
	P31-05		P08-11	Mueller, Thomas	O11-08
Messenger, Keiko	O21-16		P18-15	Mugnaoli, Enrico	O08-11
Messenger, Scott R	O21-16		O27-03	Muhongo, Sospeter M	O24-05
Meyer, Andreas	O34-11		O27-10	Muller, Axel	O28-14
Mezouar, Mohamed	O02-06		P30-05	Mun, Hyang-Ran	P10-05
	P02-12		P31-07	Murai, Kei-ichiro	P28-04
	P33-09		P31-09		P28-08
Mibe, Kenji	O06-04		P31-11	Murakami, Hideki	P19-19
	O33-07		P31-14	Murakami, Hiroyasu	O15-16
Michalik, Marek	O25-19		P35-03		P15-09
	O25-20	Miyawaki, Riturou	P28-03	Murakami, Takashi	O25-07
Michau, Nicolas	P25-16	Miyazaki, Akimitsu	P11-02		P25-08
	O34-09	Miyazaki, Kazuhiro	O12-08	Murata, Keiko	P20-04
Michiba, Kiyonori	P08-11		O12-12	Murata, Keisuke	O23-10
Michihiro, Itoh	O14-04		P28-07	MUSTIN, Christian	O24-14
Michimasa, Koichi	P15-03		P35-02	Musu, Elodia	P25-06
Michot, Laurent J	P25-16	Miyoshi, Naoya	P25-03		P25-07
	O34-09	Mizuno, Akitoshi	O11-07	Mysen, Bjorn O	O09-04
Mierdel, Katrin	O06-06	Mizuno, Tsuyoshi	P25-17		O09-08
Mikouchi, Takashi	O22-08		P25-18		
	O22-09	Mizuta, Toshio	P14-02	N	
Miletich, Ronald	O01-10		P15-01	Naemura, Kosuke	O18-10
	P02-04		O16-09	Naemura, Kousuke	O18-01
Milke, Ralf	O12-04		P19-03	Nagahara, Hiroko	O23-01
Mills, Stuart J	O08-07		P25-03		O23-02
	O31-05		P25-04		O23-03
Minato, Hideo	O27-09	Moen, Kari	P29-01		P23-01
Mine, Tetsuro	O08-02	Mohan, Anand	O18-03	Nagai, Chisato	P19-01
Ming, Nai-Ben	O11-13	Molina, Jose Francisco	O01-06	Nagai, Takaya	O01-11
	O13-06	Molina-Montes, Esther	O04-10		O05-06
	P13-01	Momma, Koichi	P04-04		P05-06
Minh, Nguyen T	O18-04	Monno, Alessandro	P12-14		O10-03
Mio, Minato	P26-11	Montero, Pilar	O19-12		O34-06
Mitchell, Lyndon D	O08-21		P19-16	Nagai, Yuki	P15-02
Miura, Hiroyuki	P16-05	Moon, Hi-Soo	P27-07	Nagao, Keisuke	O21-14
	P18-03	Morard, Guillaume	O01-13	Nagasaki, Shinya	P26-03
	P30-19		O02-06	Nagasawa, Hiromichi	P24-05
Miura, Hitoshi	O23-13		P33-09	Nagase, Toshiro	P04-04
Miura, Yasunori	P02-10	Mori, Yasushi	P30-14		P30-17
	P10-06	Moriga, Toshihiro	P28-04		P37-03
Miura, Yoshinari	O09-06	Morii, Issei	P24-17	Nagaseki, Hiroki	P17-01
Miyagi, Yasuo	P18-19	Morimoto, Kazuya	P26-07	Nagashima, Kazuhide	O21-17
Miyahara, Masaaki	P05-03	Morin, Guillaume	O03-08		O23-09
	P05-09		O26-07	Nagashima, Ken	O11-15
	P05-10	Morishita, Tomoaki	P08-24		O21-18
Miyajima, Hiroshi	P30-10		P19-07	Nagashima, Mariko	O08-16
	P31-14		O20-08	Nagashio, Kosuke	O11-05
Miyajima, Nobuyoshi	O02-07		O20-09	Nagashio, Kousuke	O11-07
			P20-02	Nagatomi, Ai	O17-05
					P30-15

Nagy, Kathryn L.....	P24-13	Nakazawa, Hiromoto.....	O36-02	Nishihara, Yu.....	P06-08
Nakada, Setsuya.....	P12-02		O36-03	Nishikawa, Osamu.....	P30-06
Nakagawa, Masaharu.....	P24-14		O36-04	Nishimiya, Shinobu.....	P33-04
Nakagawa, Takeshi.....	O10-04	Nam, Tran N.....	O18-04	Nishimura, Ryo.....	P17-05
Nakagawa, Tatsuo.....	O03-03		O18-05		P17-06
.....	O07-08	Nambiar, C.G.....	P24-14	Nishimura, Yoshihiro.....	O11-11
Nakai, Izumi.....	P08-11	Nanba, Tokuro.....	O09-06		P11-05
.....	P31-19	Nankawa, Takuya.....	O24-09		P11-07
Nakai, Munenori.....	O03-03		P24-18		P11-08
Nakajima, Haruna.....	O21-02	Naoya, Miyoshi.....	P03-11	Nishimura, Yujiro.....	P35-05
Nakajima, Kazuo.....	O11-09	Nazzareni, Sabrina.....	O05-03	Nishiyama, N.....	O33-08
Nakajima, Takashi.....	P35-02		P06-04	Nishiyama, Norimasa.....	O02-04
Nakamoto, Taishi.....	P21-10	Nedachi, Munetomo.....	O14-08		P09-07
.....	O23-13		P15-05		P33-05
.....	O23-14		O36-09	Nishiyama, Tadao.....	O12-12
Nakamoto, Yuki.....	O08-02		P36-05		P12-03
.....	P10-04		P37-03		O18-13
Nakamura, Akiko.....	P21-06	Nedachi, Yoko.....	O14-08	Nishizaki, Chisa.....	P21-07
Nakamura, Daisuke.....	O01-04	Negi, Daisuke.....	P17-03	Nishizawa, Shotaro.....	P03-07
.....	O18-01	Negishi, Kumi.....	P25-18	Nitta, Eriko.....	P19-13
Nakamura, Eizo.....	O19-14	Neil, Banerjee R.....	O20-02	Niwa, Ken.....	P33-10
Nakamura, Hiroaki.....	P11-02	Nemoto, Seiko.....	P25-12	Noguchi, Kyoko.....	P33-01
Nakamura, Michihiko.....	O12-02	Nemoto, Takahiro.....	P09-08	Noguchi, Naoki.....	O03-12
.....	P12-06	Neo, Natsuki.....	P20-02		P03-09
Nakamura, Ryosuke.....	P22-03	Nespolo, Massimo.....	P08-01	Noguchi, Takaaki.....	P33-03
Nakamura, T.....	P21-04	Nestola, Fabrizio.....	O06-06		P33-07
Nakamura, Tomoki.....	P10-03	Neufeld, Heather L.D.....	O32-05	Noguchi, Takuro.....	O14-04
.....	O21-05	Neuville, Daniel R.....	O09-02	Noguera, Claudine.....	O25-02
.....	O21-14		O09-14	Nomura, Hiromu.....	P17-06
.....	P21-05		O09-15	Nomura, Masaharu.....	P08-16
.....	O23-04		O28-04	none, Widiasmoro.....	P27-09
.....	P33-07		O33-06	Nonogaki, Masatoshi.....	P12-04
Nakamura, Yusuke.....	P26-04	Ngô, Thanh Xuan.....	P35-06	Noshita, Kenji.....	P26-03
Nakamuta, Yoshihiro.....	P21-01	Nguyen, Nuong Dieu.....	P35-05	Nozaka, Toshio.....	P20-01
.....	P21-07		P35-08	Nozawa, Akifumi.....	P02-01
.....	O22-12	Nguyen, Trung Minh.....	P35-08		O33-09
.....	P30-03	Ngwenya, Bryne T.....	O25-06		P33-06
Nakano, Hideyuki.....	O23-11	Nichols, Alex RL.....	P09-02	Nozawa, H.....	O33-08
Nakano, Nobuhiko.....	O18-04	Nichols, Alexander RL.....	P17-02	Nozawa, Jun.....	O11-15
.....	O18-05	Nicola, Cayzer.....	O07-11		P13-03
.....	O18-06	Niida, Kiyooki.....	P20-12	Ntafos, Theodoros.....	P08-20
.....	P18-17		P30-19	Nuth, Joseph A.....	O23-05
Nakano, Satoshi.....	P12-11	Niitsuma, Sachiko.....	P37-03		O
Nakano, Tsukasa.....	O33-05	Niituma, Sachiko.....	P36-06	Obata, Masaaki.....	P12-01
.....	P33-03	Nilsen, Odd.....	O14-06		O20-10
Nakaseama, Miwako.....	O14-02	Ninagawa, Kiyotaka.....	P03-06	Obata, Masahiro.....	P01-06
Nakashima, Daisuke.....	P21-04		P03-07	Obayashi, Tatsuo.....	P30-09
Nakashima, Satoru.....	O03-02		P03-08	Oberti, Roberta.....	P03-02
.....	O03-10	Nishi, Fumito.....	P08-06		O31-09
.....	P03-04	Nishi, Masayuki.....	O10-05		P31-16
.....	P03-10	Nishibori, Eiji.....	P08-04	O'Brien, Rachel.....	O24-01
.....	P21-05	Nishida, Keisuke.....	P09-05	Obst, Martin.....	O24-03
.....	P21-08	Nishida, Norimasa.....	P01-08	Ofuji, Hiroaki.....	P02-05
.....	P24-15		P18-05	Oganov, Artem R.....	O04-02
.....	O25-15		O19-09		O04-11
.....	P36-01		P19-13		O05-09
.....	P36-02		P19-15	Ogasawara, Yoshihide.....	O07-09
Nakatsuka, Akihiko.....	O28-11	Nishido, Hirotugu.....	P03-06		P07-01
.....	P28-05		P03-07		P07-03
Nakaya, Hiroyuki.....	O11-12		P03-08	Ogata, Takeyuki.....	P15-01
Nakayama, Noriaki.....	O28-11		P35-09	Ogawara, Takahiko.....	O37-06
Nakayama, Shininchi.....	P25-17	Nishihara, Sho.....	O15-06		P16-12

Ogura, Eiki	P25-11	Ohtani, Eiji	O05-14	Olives, Juan	P01-03
Ohara, Shohei	O36-02		O05-17	Olsen, Lars A.	P02-03
.....	O36-04		P05-01	Omori, Soichi	O01-07
Ohara, Syohei	P26-06		P05-03	O'Neill, Andrew	O24-01
Ohara, Yasuhiko	O19-05		P05-04	O'Neill, Hugh St.C.	O05-11
.....	P20-01		P05-05	Ono, Ayano	P01-04
Ohashi, Fumihiko	P27-14		P05-09	Ono, Kanta	O04-09
Ohashi, Haruo	O03-07		P05-10	Ono, Shigeaki	O06-04
Ohba, Tsukasa	P14-01		O06-01		O33-07
.....	P19-02		O06-08	Onuma, Kazuo	P11-03
.....	P19-04		P06-03	Onuma, Kosuke	O08-16
Ohbuchi, Yukiko	O15-05		P07-02	Ooi, Takuya	O15-10
Ohe, Toshiaki	P26-03		O09-17	Oomori, Tamotsu	O14-04
Ohfuji, Hiroaki	O05-02		P09-05	Origlieri, Marcus J.	O08-06
.....	O10-08		P10-03	Orlandi, Paolo	P31-04
Ohguchi, Takeshi	P19-03	Ohtani, Tomoyuki	P35-06		P31-05
.....	P25-03	Ohtomo, Yoko	P36-04	Orme, Christine A.	O11-01
Ohi, Shugo	P01-07	Ohtomo, Yukiko	P20-02	Orozbaev, A.A.	P18-24
Ohira, Hiroto	O15-13	Ohuchi, Tomohiro	O12-02	Orozbaev, Rustam T.	O19-11
.....	P17-03		P12-06	Osada, Yukihiisa	P18-21
Ohishi, Yasuo	O01-12	Ohyama, Hiroyuki	P17-07	Osako, Masahiro	P02-08
.....	P02-02	Okada, Kiyoshi	O29-03	Osanai, Yasuhito	O18-03
.....	O05-12	Okada, Masashi	O11-09		O18-04
.....	O05-13	Okada, Taku	O05-06		O18-05
.....	P06-03		O08-02		O18-06
.....	P33-08	Okamura, Hidenobu	P20-03		P18-17
Ohkawa, Makio	P08-05	Okazaki, Ryuji	P10-03	Ota, Yosuke	P25-14
Ohkubo, Koichi	P08-04		O21-05	Ota, Yukie	P26-06
Ohkubo, Satoru	O14-02		O21-14		P26-08
Ohmasa, Masaaki	O08-14	Okazaki, Takahide	P33-03	Otake, Tsubasa	O16-10
Ohmoto, Hiroshi	O36-09	O'Keeffe, Michael	O08-08	Otani, Yusuke	P26-05
Ohnishi, I	O33-08<br	Okihara, Kohsuke	P36-02	Otarora, Fermin	O11-09
Ohnishi, Ichiro	O21-03	Okrugin, Victor M.	O15-12	Otsuka, Kazuhiko	P18-18
.....	O21-04	Okube, Maki	P02-13	Otsuka, Takahiro	P03-04
Ohnishi, Masayuki	P31-01		P08-04	Ott, Ulrich	O21-01
Ohnuki, Toshihiko	O24-09		P28-05		P21-04
.....	P24-18		P28-08	Ottolini, Luisa	O32-06
Ohsumi, Takashi	P25-13	Okubo, Tatsuya	O27-05	Owada, Masaaki	O18-04
Ohsuna, Tetsu	O27-04	Okudaira, Kyoko	P33-03		O18-05
Ohta, Atsuyuki	P08-16	Okudaira, Takamoto	P18-12		O18-06
Ohta, Kenji	O05-12	Okudera, Hiroki	P08-24		P18-17
Ohta, Yasushi	O19-10		P09-06	Ozaki, Takuo	P24-18
Ohtaka, Osamu	O01-13		O28-11	Ozawa, Akiko	P11-05
.....	P02-02		P28-02	Ozawa, Kazuhito	O23-02
.....	P02-12		P28-05		O23-03
.....	P28-08	Okui, Masato	P03-03		P23-01
.....	P33-04	Okumura, Satoshi	O25-15	Ozhogina, Elena	P16-11
Ohtake, Makiko	O22-03	Okumura, Tasuku	P03-06	P	
.....	O22-06		P03-07	Pósfai, Mihály	O26-02
Ohtaki, Sachio	P32-03		P03-08		O24-16
.....			P35-09	Pöllmann, Herbert	O28-12
.....		Okunishi, Eiji	O05-11	Paar, Werner H.	O16-08
.....		Okuno, Hideaki	O22-04		P16-01
.....			P22-03		P16-02
.....		Okuno, Masayuki	P02-11	Pacella, Alessandro	P26-01
.....			P09-06		P26-02
.....			P24-08	Paktunc, Dogan	O29-02
.....			O35-06	Palyanov, Yuri N.	O07-10
.....		Okuyama, Keita	P26-03	Pan, Yuanming	P08-13
.....		Okuyama, Muneyuki	O32-07	Paoletti, Luigi	P26-01
.....		Okuyama, Yasuko	P19-14		P26-02
.....		Okuyama-Kusunose, Yasuko	P30-04	Paquette, Jeanne	O12-13

Sasaki, Satoshi.....	P02-13	Sekiguchi, Hisashi.....	P12-13	Shiraishi, Kazuyuki.....	O35-04
.....	P08-04	Sekiguchi, Nozomu.....	P36-05	Shiraishi, Rei.....	P05-09
Sata, Nagayoshi.....	O01-12	Sekine, Toshimori.....	O21-06	Shiraki, Koichi.....	O24-05
.....	O05-12		O36-03		P24-01
.....	O05-13	Self, Peter.....	O16-06	Shirotori, Tatsuya.....	P24-19
.....	P33-08	Semeniuk, Trudi.....	O26-01	Shiryaev, Andrey A.....	O07-07
Sata, Naoyoshi.....	P06-03	Sen, Sabyasachi.....	O09-03	Shmakin, Boris M.....	O30-05
Satish-Kumar, Madhusoodhan.....	O18-09	Sereenen, Jargalan.....	O15-09	Shoji, Arai.....	P20-11
Sato, Aki.....	P15-04	Setijadji, Lucas D.....	O19-04	Shu, Da-jun.....	O13-06
Sato, Eriko.....	P31-19		P27-09	Shukuno, Hiroshi.....	O19-07
Sato, Hiroaki.....	P09-03	Seto, Koji.....	P20-12	Shushkanova, Anastasia V.....	O07-06
.....	P09-04	Seto, Yusuke.....	O01-11	Siebel, Wolfgang.....	P35-04
.....	P12-02		O05-06	Simon, Gilla.....	P12-10
Sato, Hiroki.....	O12-12		P05-06		P30-02
.....	P28-07		O10-03	Simon, Lindsey.....	O24-01
Sato, Hisako.....	O04-09		P32-03	Simonics, Renáta.....	O26-02
Sato, Isamu.....	P33-01	Seward, Gareth GE.....	O11-14	Simonov, Vladimir A.....	O14-05
Sato, Kei.....	P18-09	Seyama, Haruhiko.....	P24-06	Simpson, Edward T.....	O24-16
.....	P18-14	Sha, Xianwei.....	O04-03	Simpson, Mark P.....	O16-16
Sato, Seichi.....	O26-09	Shapiro, Alan H.....	P34-01	Sinmyo, Ryosuke.....	O05-11
Sato, Seigo.....	P24-11	Shatskiy, Anton.....	O33-09	Sinno, Isamu.....	O35-06
Sato, Tsutomu.....	P25-15	Shatskiy, Anton F.....	P02-15	Sisson, Virginia B.....	O18-12
.....	O26-14	Shelley, Michael.....	O12-06	Skinner, H. Catherine W.....	O26-10
.....	O26-15	Shi, Jinghua.....	P24-03	Sklavounos, Spyros.....	P32-01
.....	P26-06		P24-04	Skogby, Henrik.....	O06-07
.....	P26-07	Shi, Nicheng.....	P05-02		P06-06
.....	P26-08		P08-03	Skora, Susanne.....	O11-08
.....	P26-09	Shibata, Shuichi.....	O09-09	Smith, Caroline L.....	O25-14
Satoh, Hinako.....	P25-04	Shigley, James E.....	O32-01	Smith, Douglas.....	P20-10
Satoh, Hisao.....	O11-11	Shimamoto, Toshihiko.....	P27-01	Smyth, J. R.....	O22-11
.....	O11-15	Shimano, Sadayoshi.....	P17-04	Smyth, Joseph R.....	O06-06
.....	P11-05	Shimizu, Katsuya.....	P10-04	Snee, Larry W.....	O15-04
.....	P11-08	Shimizu, Marina.....	P16-08	Snow, Jonathan E.....	P20-14
.....	P13-03	Shimizu, Masaaki.....	P16-08	Sobolev, Alexander V.....	O07-02
.....	O21-18	Shimizu, Masahiro.....	P01-08	Sobolev, Nikolay V.....	O07-02
Satoshi, Matsubara.....	P31-19		O19-09		O07-04
Satybaev, M M.....	P18-24		P19-13	Soboleva, Svetlana V.....	O31-13
Sawada, Tsutomu.....	O13-04		P19-15	Sokolov, Maria.....	O08-20
Sawada, Yoshihiro.....	P20-12	Shimizu, Rentaro.....	P07-03	Sokolova, Elena.....	O08-15
Sawai, Takashi.....	P03-10	Shimizu, Tomoe.....	P27-11	Soldatos, Triantafyllos.....	P32-01
Saxena, Saxena K.....	O01-02	Shimizu, Toru.....	P15-04	Solomatov, Viatcheslav S.....	O12-01
Sazaki, Gen.....	O11-09		P16-10	Solozhenko, Vladimir L.....	P33-09
Scandale, Eugenio.....	O12-17	Shimobayashi, Norimasa.....	P01-07	Soma, Mitsuyuki.....	P24-06
.....	P12-14		P32-03	Sondi, Ivan.....	P24-09
Schüler, Dirk.....	O24-16	Shimoda, Keiji.....	P09-08	Song, Yungoo.....	P27-07
Scheffel, André.....	O24-16	Shimojuku, Akira.....	P10-03	Songo, Majura A. M.....	O24-05
Scherl, Hans-Peter.....	P30-02	Shimojyuku, Akira.....	P05-09	Sorai, Masao.....	P25-13
Schilling, Frank R.....	O33-11	Shimomura, Osamu.....	O33-01	Sorensen, Sorena S.....	O18-12
Schmalz, Gottfried.....	O24-17	Shimpo, Makoto.....	P18-02	Southam, Gordon.....	O24-02
Schmid, Daniel W.....	O12-10	Shimura, Toshiaki.....	O35-10	Spagnoli, Dino.....	O04-06
Schorr, Susan.....	O08-17	Shindo, Hitoshi.....	O11-02	Spivak, Anna V.....	O07-07
Schouwstra, Robert P.....	O29-09	Shindo, Kazuyasu.....	P20-13	Sreenivas, Bulusu.....	O25-07
Schreuer, Juergen.....	P03-01	Shinmei, Toru.....	O05-02	Stackhouse, Stephen.....	O04-04
Schreuer, Jurgén.....	O03-05		P06-08	Stalder, Roland.....	P06-06
Schuermann, Kay Uwe.....	P30-01		P33-10	Stamponi, Marco.....	P25-16
.....	P30-02	Shinoda, Keiji.....	O03-12	Stark, Alexander IR.....	O26-11
Schultz, Emmanuelle.....	P02-12		P03-09	Stavrova, Olga V.....	O14-05
Schulze, Daniel J.....	O07-01		P03-11	Stebbins, Jonathan F.....	O03-06
Schwandt, Craig.....	O22-08	Shinohara, Armando H.....	O28-07		O09-05
Schwendtner, Karolina.....	P28-01	Shinohara, Hiroshi.....	P19-13	Stein, Holly J.....	O15-04
Scordari, Fernando.....	P31-08	Shiota, Dai.....	P36-01	Steiner, Walter.....	O04-13
Seetharaman, Seshadri.....	O09-16	Shirai, Kyoko.....	P08-11		

Stixrude, Lars	001-01	Svojtka, Martin	P12-08	Tamada, Osamu	P08-07
.....	004-12		O18-01		P08-21
Strassle, Thierry	O34-03		O18-10		O12-12
Strukelj, Eozen	O09-15	T			025-03
Stumpf, Silvia	O25-11	Törnroos, Ragnar	O16-17		P28-07
Stumpf, Thorsten	025-11	Tabacchi, Gloria	P10-01	Tamada, Shinnosuke	O23-02
Sturchio, Neil C.	P24-13	Tachibana, Masaru	O11-04		P23-01
Sturm, Arne	O24-11	Tachibana, Shogo	O23-02	Tamamura, Shuji	P26-08
Su, Dangsheng	P08-20		023-03	Tamamura, Syuji	P26-06
Sueda, Yuichiro	P33-10		P23-01	Tamayo, Jr., Rodolfo A.	P20-07
Suemine, Kouich	P27-01	Tachibana, Yurika	P30-20	Tamura, Akihiro	P20-08
Suerte, Leilanie O.	015-06	Tachida, Yosuke	O05-02		O20-03
.....	P20-07	Tada, Ryuji	O26-16	Tamura, Ayako	P26-12
Sugaki, Asahiko	P16-07	Tadokoro, Hiroyuki	P18-04	Tamura, Kenji	P27-04
Sugawara, Naoyuki	P15-01	Taga, Masaru	P19-11	Tamura, Yoshihiko	019-07
Sugawara, Toru	P09-01	Tagai, Tokuheii	P30-20	Tanaka, Kimitoshi	P12-09
Sugimori, Hirokazu	P25-08	Tagiri, M.	P18-24	Tanaka, Masahiko	O08-10
Sugita, Hiroaki	P08-19	Tagiri, Michio	O19-11		P33-07
Sugita, Mitsuhiro	P02-01	Taguchi, Sachihiro	P17-03	Tanaka, Tadao	P25-17
.....	021-08		P17-08		P25-18
.....	O33-09		P18-17	Tanaka, Takayuki	O15-05
Sugiyama, Kazumasa	O03-03	Tahara, Takeshi	P08-11	Tanaka, Toshihiro	P17-03
.....	O28-07	Tait, Kimberly T.	P34-01	Tanaka, Toshinari	P33-01
.....	028-10	Takada, Morio	P26-09	Taner, Mehmet F.	P31-13
.....	P28-03	Takafuji, Naoto	P19-06	Tang, Ning	P26-08
Suko, Takeshi	O24-07	Takagi, Tetsuichi	015-17	Tange, Yoshinori	P05-04
Sunada, Daiki	P19-12	Takahashi, Eiichi	O33-10		033-10
Sunagawa, Ichiro	P11-03	Takahashi, Naoki	P30-18	Tangeman, Jean A.	P09-07
.....	012-14	Takahashi, Ryohei	015-12	Tani, Atsushi	P03-04
Sundblad, Krister L.	014-06		P30-19	Tani, Kenichiro	O19-07
Sunohara, Kenichi	P30-16	Takahashi, Yoshio	024-06		P19-08
Sureda, Ricardo J.	O16-08		033-03	Tani, Yukinori	P24-06
.....	P16-01	Takahata, Hiroyuki	O15-05	Tanida, Hajime	P02-02
Sutton, Steve R.	O02-04	Takai, Yasuhiro	P31-06	Taniguchi, Taketoshi	P04-06
Suzuki, Akiko	P21-05	Takakura, Takashi	O23-10	Tarkian, Mahmud	O16-17
.....	P22-03	Takaoka, Nobuo	O21-14	Tartarotti, Paola	O20-02
Suzuki, Akio	P05-04	Takashi, Okabe	P25-01	Tateno, Shigehiko	005-13
.....	P07-02	Takashima, Ryoichi	O08-12	Tatsumi, Yoshiyuki	P19-08
.....	O09-17		023-16		PL7
.....	P09-05	Takasu, Akira	P18-19	Taylor, Rex N.	O19-05
Suzuki, Hitoshi	P37-02		P18-24	Tazaki, Kazue	024-05
Suzuki, Katsuhiko	P33-02		O19-11		P24-01
Suzuki, Kazuhiro	035-01	Takaya, Yasuhiko	P25-12		P24-08
.....	O35-02	Takayama, Akiko	P21-02		P24-16
.....	O35-03	Takayama, Harumi	O01-08		P24-17
.....	O35-05	Takazawa, Eiichi	020-06		P24-19
Suzuki, Kenji	P20-05		O20-10	Teagle, Damon A.H.	O20-02
Suzuki, Michio	P24-05	Takeda, Hiroshi	022-06	Tejada, Maria Luisa G.	019-03
Suzuki, Norimichi	P26-12	Takemaru, Yasutaka	O28-10	Tempesta, Gioacchino	O12-17
Suzuki, Ryohei	O14-02	Takemoto, Yoshitoshi	P20-06		P12-14
.....	014-04	Takenouchi, Ko	P30-10	Terada, Kentaro	O35-09
Suzuki, Satoru	P25-05	Takeshi, Kakegawa	P24-11	Terada, Yasuko	P02-13
Suzuki, Toshiaki	P05-03	Takeshi, Miyata	O32-07		003-04
Suzuki, Toshihiro	P33-02	Takeuchi, Akihisa	O33-05	Terasaki, Hidenori	O05-17
Suzuki, Yohey	024-07		P33-02		P05-03
Suzuki, Yoshinori	O24-09	Takeya, Kei	P03-04		P05-04
.....	P24-18	Takumi, Kikegawa	P05-03		P07-02
Suzuki, Yoshio	O33-05	Takuo, Ozaki	O24-09		P09-05
.....	P33-02	Talavera, Cristina	O19-12		P33-05
Suzuki, Yukari	P20-02		P19-16	Terasaki, Osamu	027-04
Syafrizal	015-11			Terashima, Kazuya	O14-08
				Terazono, Junya	022-02

Teranya, Ekaterina O.....	O14-05	Tsuchiyama, Akira	O23-04	Ujike, Osamu	P19-05
Teresa, Jentzsch.....	O37-02		O23-10	Ullrich, Angela.....	O01-10
the Hayabusa Science Team.....	O21-13		O33-05		P02-04
Thiemens, Mark H.....	O23-05		P33-03	Umemoto, Koicro	O04-08
Thom, James.....	O16-11	Tsujimori, Tatsuki	O18-12	Umino, Susumu	O20-02
Thomm, Michael.....	O24-17		P19-17	Urabe, Testuro	O14-03
Thornto, Kristy	O12-13		O35-13	Urabe, Tetsuro	O14-01
Tillmanns, Ekkehart.....	P28-01	Tsukamoto, Katsuo.....	O11-09		O14-04
.....	P31-02		O11-11	Urakawa, Satoru.....	O09-17
Tingey, David.....	O15-14		O11-15		P09-09
Titisari, Anastasia Dewi	P27-09		P11-04		P33-05
Tobu, Yasuhiko	P09-08		P11-05	Urushihara, Makoto	O09-06
Togonbaeva, A A.....	P18-24		P11-06	Usurelu, Sorin.....	O32-04
Toh, Shoichi.....	P21-01		P11-08	Utsunomiya, Satoshi.....	O37-04
Tomasic, Nenad.....	P08-20		P13-03	Uyeda, Akira	P19-14
Tomatsu, Takashi.....	O20-05		O21-18	Uyeda, Chiaki	O08-12
Tomeoka, Kazushige	O21-03		P25-13		O23-16
.....	O21-04	Tsukimura, Katsuhro.....	O15-17		O37-07
.....	O21-06		O25-04	V	
.....	O21-08	Tsuno, Hiroshi.....	P08-16	Valley, John W	O07-01
.....	P21-02	Tsuno, Kyusei	O05-17	Van den Berg, G. J. K.....	P01-03
.....	P21-06	Tsunogae, Toshiaki	P17-07	Van Driessche, Alexander	O11-09
Tominaga, Aiko	O10-05		P18-02	Van Millenburg, J. C.	P01-03
Tomioka, Naotaka.....	P02-01		P18-05	Van Reenen, Dirk D.....	P18-10
.....	O10-06		P18-06	Van Riemsdijk, Willem H	O25-08
.....	O21-06		P18-10	Vandenkoornhuysse, Philippe.....	O24-15
.....	O33-09	Tsunogai, Urumu	O14-02	Vaughan, David J	O26-06
Tomita, Katsutoshi	P24-07	Tsushima, Norio.....	P15-03		O26-11
Tomita, Takeshi.....	P25-10	Tsutomu, Sato	P26-05	Velbel, Michael A.....	O25-05
Tong, Jinggui	P24-23		P26-11	Vennemann, Torsten.....	P15-07
Topa, Dan	O16-08	Tsutsumi, Yukiyasu	P30-05	Ventruti, Gennaro	P31-08
.....	P16-01		P31-09	Vergasova, Lidia P.....	O31-14
.....	P16-02		P35-03	Verryn, Sabine	O29-04
Toplis, Mikeal J.	O12-11	Tuba, Gyorgyi	P16-16	Vetere, Francesco	P09-04
Toporski, Jan	O24-17	Tucker, Matthew G.	O34-03	Vezzalini, Giovanna.....	P10-01
Torimoto, Junji	P17-08	Turchkova, Anna G.....	P27-12	Viliéras, Frédéric.....	O34-09
Toriumi, Mitsuhiro	O35-09	Turner, David	O32-05	Villiéras, Frédéric.....	P25-16
Tornos, Fernando	O14-07	Tycova, Patricie none	P24-10	Vinson, Michael D.....	O25-12
Torres-Ruiz, Jose.....	P19-18	U		Viti, Cecilia	O08-11
Toth, Erzsebet.....	P08-26	Ubukawa, Taro.....	P18-20	Vlaicu, Aurel Mihai	P03-03
.....	P08-27	Uchida, Akihito.....	P08-18	Vocadlo, Lidunka	O04-04
.....	P27-03	Uchida, T	O33-08	Von Dreele, R B.....	O33-08
Toth, Judit.....	P27-08	Uda, Satoshi.....	O28-06	W	
Touret, Lydie	O30-06	Uda, Yukihiro	O11-12	Wada, Keiji	P16-05
Tovar, Michael.....	O08-17	Ueda, Akira.....	O11-11	Wada, Shin-Ichiro	P27-14
Toyoda, Shin.....	P35-09		P11-04	Wada, Tomohito	P16-09
Tran, Nam N.	P18-17		P11-05	Wada, Tomoyuki	O06-09
Tran, Nam Ngoc	O35-09		P11-08	Wada, Yukari	P21-06
Trouw, Frans R.....	P34-01		P30-07	Wagner, Gerald	P08-15
Trudu, Alfonso	O29-01	Ueda, Masahiro	P37-02	Waizumi, Kenji	O13-08
Tschauner, Oliver D.....	O05-16	Uehara, Seiichiro.....	P08-17	Wajima, Takaaki.....	P27-11
Tsubomoto, Akihide	P27-06		P28-07	Wakihira, Toru.....	O27-05
Tsuchiya, Jun.....	O04-01		P30-03	Wakimoto, Rie	O24-05
.....	P05-08		P31-06	Wallis, Simon.....	O35-13
.....	O06-10	Uesugi, Kentaro.....	O33-05	Wallis, Simon R.....	P18-16
Tsuchiya, Nobutaka	P19-03		P33-02	Walsh, Joanna N	O03-05
Tsuchiya, Noriyoshi	O03-11		P33-03	Walther, Clemens	O25-11
.....	P25-14	Uesugi, Masayuki	P21-09	Wang, Mu	O11-13
Tsuchiya, Taku.....	O04-01	Ueta, Shinzo	O11-11		O13-06
.....	P05-08		P11-04		P13-01
.....	O06-10		P11-08	Wang, Rucheng.....	O31-08
.....		Ugolkov, Valeriy L.....	O28-13		

Wang, Yanbin	O02-04	Wogelius, Roy A	O25-13	Yanai, Keizo	P19-03
.....	P09-07		O26-08	Yang, Hexiong	P08-12
.....	O33-08		O33-02	Yang, Jian-Jun	O18-14
.....	P33-05	Wohlers, Anke	O11-08	Yang, Liangfeng	P24-23
Wang, Yufan	P24-04	Wysoczanski, Richard J	P17-02	Yang, Zhuming	P31-17
Warren, James A.	O13-01		P19-08	Yano, Hajime	P33-03
Warren, Michele C.	O26-11	X		Yano, Tetsuji	O09-09
Watanabe, Hiroaki	O24-05	Xiong, Ming	P08-03	Yashima, Masatomo	P08-02
.....	P24-01	Xu, Qi	P28-06		O28-08
Watanabe, Katsuaki	P24-02	Xu, Wenbo	O01-01		P28-05
Watanabe, Kenji	P32-02	Xue, Xianyu	O06-11		P28-06
Watanabe, Koichiro	O15-06		P06-05	Yasuaki, Ikuta	O28-11
.....	O15-11		O09-01	Yasuda, Seiji	P21-10
.....	P15-06	Y		Yasui, Maya	P03-03
.....	P15-08	Yabuuchi, Takahiro	P10-04	Yasunaga, Kentaro	O15-05
.....	O19-04	Yachi, Yusuke	P06-01	Yates, Martin G.	O18-08
.....	P27-09	Yagi, Takehiko	O02-07	Yavuz, Berna	P16-14
Watanabe, Makoto	O17-05		P02-07	Yazawa, Yuuki	O22-06
Watanabe, Masahito	O11-07		P05-01	Yoda, Shinichi	O11-04
Watanabe, Miho	P12-13		P33-10	Yoko, Ohtomo	O36-08
Watanabe, Takashi	P27-04	Yagishita, Keiichi	P36-05	Yokoshi, Sho	P02-01
Watanabe, Yasushi	O15-07	Yakovenchuk, Victor N	O31-11	Yokota, Yasuhiro	O22-03
.....	O15-08	Yamada, A	O33-08	Yokoyama, Elsuero	O11-12
.....	O15-09	Yamada, Akihiro	P09-09	Yokoyama, Kazumi	P30-05
.....	P15-09	Yamada, Akira	P18-05		P31-09
Watanabe, Yoshihiro	P14-02	Yamada, Fumika	P25-17		P31-14
Waters, John	O26-08		P25-18		P35-03
Wehrli, Bernhard	O24-03	Yamada, Hirohisa	O26-14	Yokoyama, Shingo	O26-15
Weidner, Donald	P02-14		P27-04		P27-04
.....	O05-01	Yamada, Maho	O23-03	Yokoyama, Tadashi	O25-15
Weisberg, Mike K.	O21-02	Yamada, Norikazu	P11-04		P36-01
Weiszbarg, Tamas	P27-03	Yamada, Ryoichi	P19-01		P36-02
Weiszbarg, Tamas G.	P08-26		P19-03	Yokoyama, Takushi	P15-08
.....	P08-27	Yamada, Shigeo	P31-07	Yoneda, Akira	P02-06
.....	P16-16	Yamada, Takashi	P31-11		P02-08
Welch, Mark D.	O02-05	Yamagishi, Akihiko	O04-09	Yoneda, Tetsuro	P26-04
.....	O34-05	Yamaguchi, Akira	P22-04	Yonezawa, Makoto	P11-07
Weng, Liping	O25-08	Yamaguchi, Tamami	O19-10	Yonezu, Kotaro	P15-08
Wentzovitch, Renata M.	O04-08	Yamaguchi, Tatsuaki	O22-06	Yong, Wenjun	P01-01
Wesolowski, David J.	O16-10	Yamaguchi, Tetsuji	P25-17	Yoo, Jung Ho	P05-10
Wesselsky, Andreas	O28-09		P25-18	Yoshiasa, Akira	P02-02
Wheeler, John	O11-14	Yamaguchi, Yoshiaki	O19-10		P02-13
.....	O12-03	Yamakawa, Junji	P31-01		O28-11
White, Maggie L.	O26-12	Yamamoto, Koshi	P18-21		P28-03
White, Timothy J.	O08-21	Yamamoto, Masatsugu	P25-03		P28-05
Whitehouse, Martin	P19-16	Yamamoto, Yoshitaka	P02-07		P28-06
Whitehouse, Martin J.	O19-12	Yamanaka, Takamitsu	O05-06		P28-08
Whitfield, Pamela S.	O08-21		O08-02		P33-04
Wicks, Fred J.	P08-17		P08-18	Yoshida, Hidekazu	P30-12
Wilczynska-Michalik, Wanda	O25-19		P08-19		O36-07
.....	O25-20		O10-01	Yoshida, Hideto	P16-08
Williams, Ian S.	O35-07	Yamanoi, Yuta	O03-10	Yoshida, Takahiro	O24-09
.....	P35-02		O22-04	Yoshida, Takeyoshi	P18-19
Williams, Ian S.	P12-12	Yamasaki, Toru	P20-02		O19-01
Willis, Michael J.	O05-16	Yamashita, Hiroyuki	P30-08		P19-01
Wincott, Paul L.	O26-11	Yamashita, Michiru	P03-03		P19-03
Wirick, Susan	O33-04	Yamashita, Shigeru	P06-07	Yoshida, Takuma	P26-03
Wirth, Richard	O07-04	Yamazaki, Daisuke	P02-05	Yoshihiro, Nishimura	P11-06
Wise, Matthew E.	O26-01		O05-02	Yoshikawa, Akira	O28-05
Wiszniewska, Janina B.	P12-12		O33-09	Yoshikawa, Masako	O20-08
.....	O17-04	Yanagawa, Hiroshi	O36-06	Yoshimura, Kazuhisa	P24-21
Withers, Anthony C.	P01-01	Yanagisawa, Norio	P25-01		

Yoshimura, Yasutaka	P18-04
.....	P18-08
.....	P18-09
.....	P18-14
Yoshimura, Yohei	P25-03
Yoshino, Takashi	P02-05
.....	P06-07
Yoshio, Saito	P37-02
Yoshitake, Miwa	023-08
Yoshizaki, Izumi	011-04
Yoshizuka, Kazuharu	P27-11
Young, Jason M	O29-01
Yu, Ping	O09-03
Yuguchi, Takashi	P12-03
Yukie, Ota	P26-11
Yumul, Jr., Graciano P	O15-06
.....	P20-07
Yurgenson, G	P18-26
Yurimoto, Hisayoshi	O06-09
.....	O21-15
.....	O21-17
.....	023-07
.....	O23-08
.....	O23-09
.....	P23-03
Yusa, Hitoshi	001-12
Yushkin, Nikolay	P18-26
Yushkin, Nikolay P	012-16
Yusoff, Zainuddin M	025-06
Z	
Zakaznova-Herzog, Valentina P	O09-10
.....	009-11
Zanazzi, Pierfrancesco	P06-04
Zangooi, Azin	O12-13
Zedgenizov, Dmitry A	O07-02
Zegeye, Asfaw	024-14
Zepeda, Salvador	O11-12
Zhai, Shuangmeng	P01-05
.....	O33-09
Zhang, Feiwu	004-02
.....	O05-09
Zhang, Li	O25-12
Zhang, Lihua	O15-04
Zhang, Ting	P13-01
Zhang, Yigang	004-05
Zhang, Zhan	O25-09
Zhao, Dapeng	O04-05
Zhao, Dongjun	O26-04
Zhao, Yusheng	034-04
.....	P34-01
Zhou, Joe	029-07
Zhu, Jianmin	O11-13
Zolensky, Michael E	021-11
.....	P21-08
.....	O21-16
Zolotarev, Andrey A	O31-11

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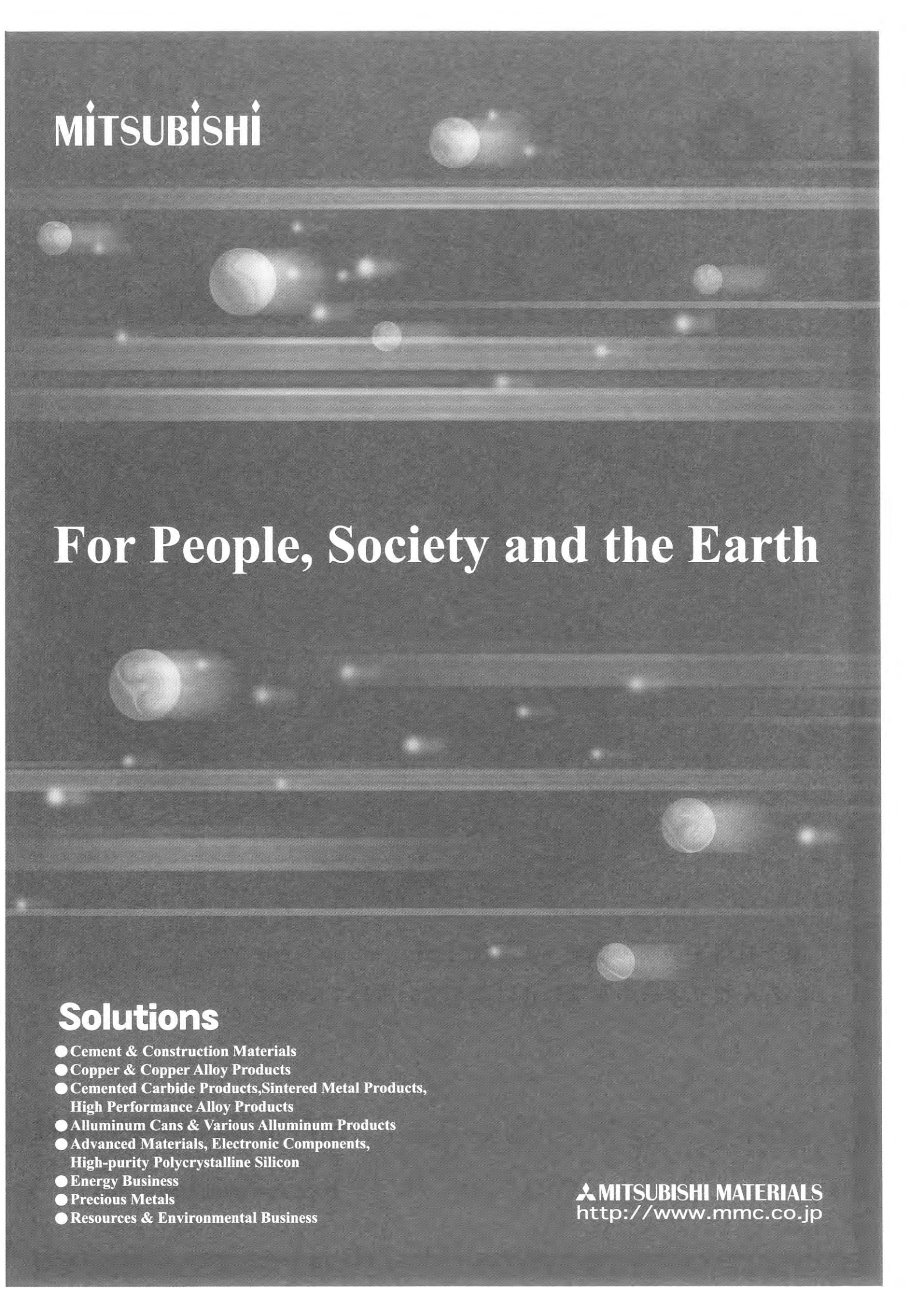
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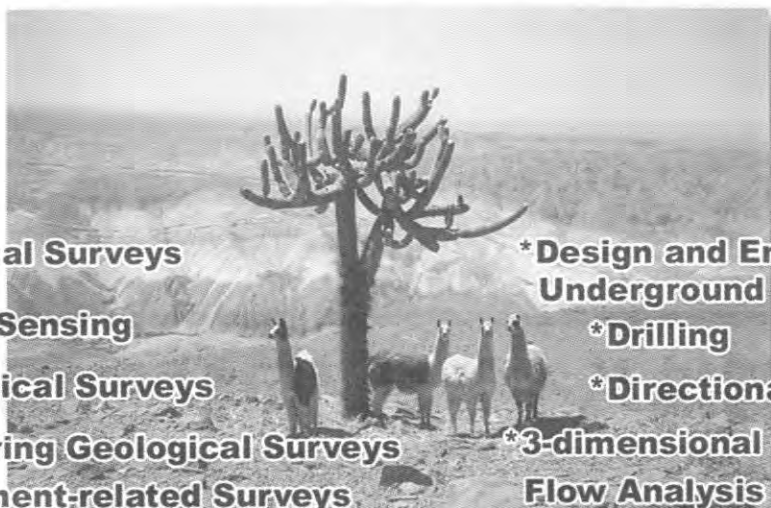
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大地の音色を聴く。

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砂漠の遊牧民は砂嵐の音で移動の可否を決め、

熱帯雨林に住む狩猟民族は枝の折れる音で動物を判断するといわれます。

そして音は、それぞれの風土、環境の中で、音楽という完成体を形成します。

それは、私たち人間が自然との関わりの中で築き、

磨きあげてきたひとつの結晶といえるでしょう。

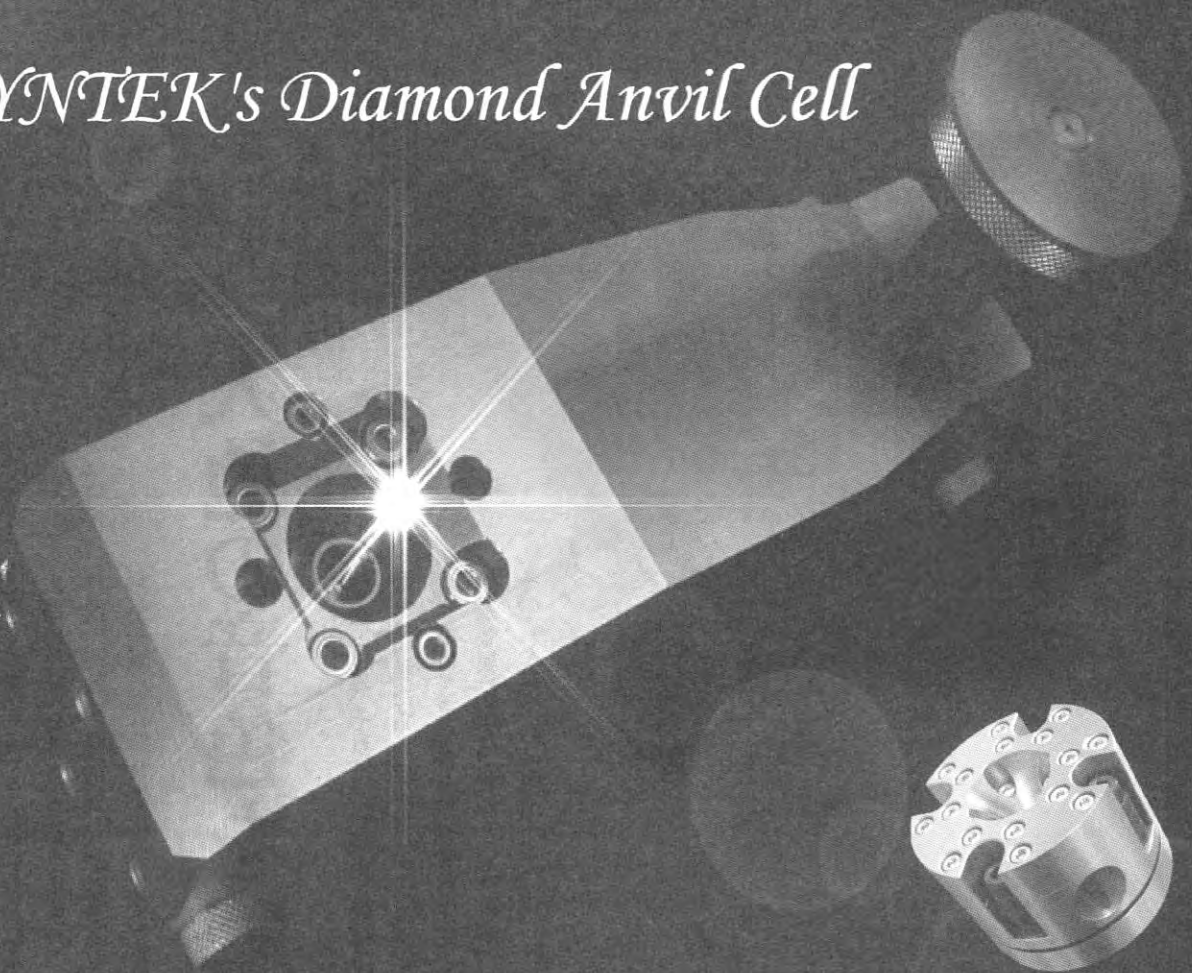
住友金属鉱山は、資源という自然の生みだすもうひとつの音に、しっかりと耳を傾け、その音を私たちの生活へ、大切に、そして確実につなげたいと考えています。



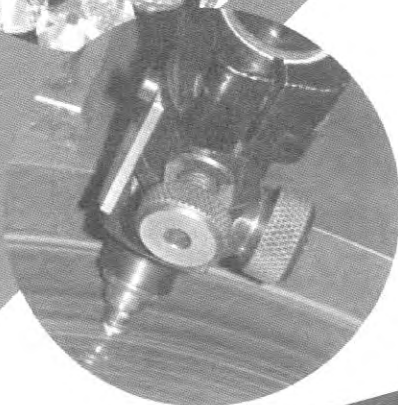
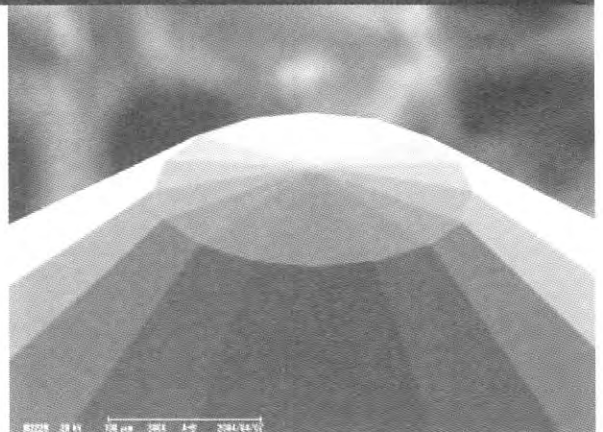
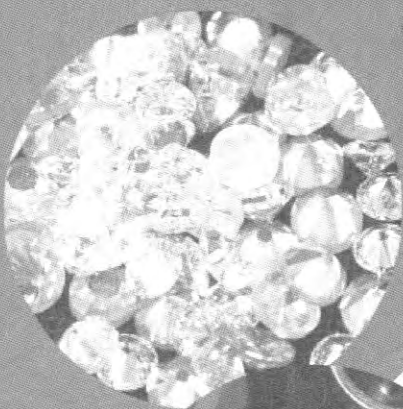
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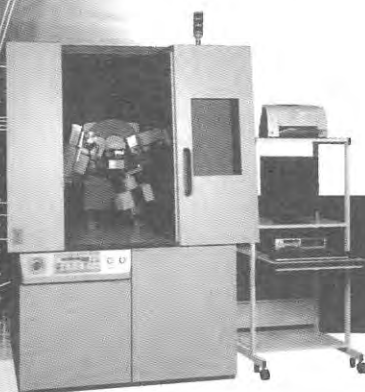
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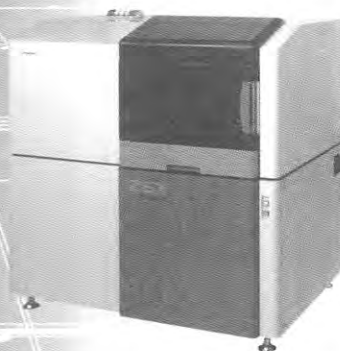
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