

Abstract volume

5th International Seminar on

High-Pressure Mineralogy

Conveners: Hiroyuki Kagi and Konstantin Litasov

Zoom online seminar (using Hiroshima University account)

Day-1: January 16th (Monday), 2023

9:00-12:25 (Moscow time) or 15:00-18:25 (Japan time)

<https://us06web.zoom.us/j/83165247614?pwd=QUdsK2lCTmdybnBEWdNjNDYwbGJ6dz09>

Meeting ID: 831 6524 7614

Passcode: 170492

Day-2: January 17th (Tuesday), 2023

9:00-12:35 (Moscow time) or 15:00-18:35 (Japan time)

<https://us06web.zoom.us/j/84408121700?pwd=S1Z3R3QrSWFKTTRucEoreHNLc0pUQT09>

Meeting ID: 844 0812 1700

Passcode: 252865

High-pressure new post-spinel phases in the MgO-Al₂O₃-Cr₂O₃ system

Iskrina A.V.^{a,b}, Bobrov A.V.^{a,b,c}, Spivak A.V.^b, Matrosova E.A.^c, Zakharchenko E.S.^b, Khasanov S.S.^d

^a*Lomonosov Moscow State University, Moscow, iskrina@iem.ac.ru*

^b*D.S. Korzhinskii Institute of Experimental Mineralogy RAS, Chernogolovka*

^c*Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow*

^d*Institute of Solid State Physics RAS, Chernogolovka*

Subducted slab enriches the mantle depths with crustal components such as SiO₂, Al₂O₃, CaO, FeO, Na₂O, K₂O. These oxides compose post-spinel-type phases, which are potentially stable in the deep Earth's geospheres and can be considered as host phases of crustal elements in the subduction zone. The series of experiments were carried out in the MgO-Al₂O₃-Cr₂O₃ system at 12, 14, 18, 22 and 24 GPa and 1600°C. As a result, several phases of solid solutions with a different MgAl₂O₄ and MgCr₂O₄ ratio were obtained. In this series of solid solution, a structural transition from the calcium ferrite post-spinel phase to the calcium titanate post-spinel phase is assumed. The post-spinel phases associate with Mg₂(Cr,Al)₂O₅ with a modified ludwigite-type (*mLd*) structure. The Mg(Cr,Al)₂O₄ phase has a calcium titanate-type structure and crystallizes with the *Cmcm* space group. It was studied up to 30 GPa in a diamond anvil cell. As a result, it was found that at 12-16 GPa, the color of the crystal changes from green to red, which persists even with a further increase in pressure. The above-described phases are undoubtedly stable up to the lower mantle conditions and be considered as hosts for crustal elements in the deep geospheres.

This study was supported by the Russian Foundation for Basic Research, project nos. 20-35-90095 and 21-55-50011. This study carried out within the scientific plan of the Laboratory of deep geospheres of the Lomonosov Moscow state University and within the Research Program of the D.S. Korzhinskii Institute of Experimental Mineralogy Russian Academy of Sciences (FMUF-2022-0001).

Clarification of the effect of high oxygen fugacity on melting temperature of wadsleyite by high-temperature and high-pressure experiments

Yamaguchi K^{1*}, Kawazoe T¹, Inoue T¹, Sakai T²

¹Hiroshima University, Higashi-hiroshima, Japan

²Ehime University, Matsuyama, Japan

* m213373@hiroshima-u.ac.jp

It is known that water is supplied into the Earth's interior by subduction of oceanic plates. Water is not the only component brought to the Earth's interior by subduction of the oceanic plates. Oxygen is also brought into the Earth's interior. For example, 205 kg/yr of oxygen is estimated to be brought to the Earth's interior at the Mariana subduction zone (Brounce et al. 2019). Some of the subducted oxygen are recycled to the Earth's surface by the island-arc and back-arc volcanisms, but most of the subducted oxygen are supplied to the deep mantle. The amount is estimated to be 171-200 kg/yr. In addition, $\text{Fe}^{3+}/\Sigma\text{Fe}$ in melt inclusions ejected from hot-spot volcanoes has been measured. From the measurements, the maximum $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt inclusions from the hot-spot volcanoes was found to be 0.40 (Moussallam et al. 2014). This value is higher than the global MORB average, indicating that the oxygen fugacities in the Earth's interior are heterogeneous. Moreover, seismological observations indicate the existence of a low-velocity layer of seismic waves around 410 km depth in the Earth's interior (Tauzin et al. 2010). This low-velocity layer is not localized but widely distributed. This low-velocity layer is likely to be caused by partial melting of the mantle. In this study, we investigated the effect of high oxygen fugacity on the melting temperature of wadsleyite.

A Kawai-type multi-anvil apparatus was used for the high-temperature and high-pressure experiments at Hiroshima University. The starting material was a powder of olivine from San Carlos. Temperature and pressure conditions were 1300°C to 1600°C and 13.7 GPa to 16.6 GPa, respectively. Re-ReO₂ and Mo-MoO₂ oxygen fugacity buffers were used to control oxygen fugacity. Au was used as a capsule material to enclose the olivine powder and the buffer materials. After keeping the target temperature for desired duration, the samples were quenched by turning off the heating power supply. Microstructural observations were made with a scanning electron microscope. Phase identification was performed by micro-Raman spectroscopy and micro-focus X-ray diffraction. Chemical composition was measured by EPMA. The water content of the samples was measured by FTIR. At 14.6 GPa and 1400°C, no quenched melt was observed in both samples buffered with the Re-ReO₂ and Mo-MoO₂ buffers. At 14.6 GPa and 1500°C, quenched melt was observed in the sample with oxygen fugacity controlled by Re-ReO₂ buffer. In contrast, no quenched melt was observed in the sample with oxygen fugacity controlled by Mo-MoO₂ buffer. The water content of the samples was 0.4 wt%. The solidus temperature of wadsleyite under low oxygen fugacity conditions is estimated to be about 2300°C (Ohtani et al. 1998). In the present experiment, wadsleyite melted under high oxygen fugacity condition at 1500°C. Therefore, the results of this study indicate that the melting temperature of wadsleyite was reduced by about 800°C. The sample contains 0.4 wt% water. It is estimated that this 0.4 wt% water lowers the melting temperature of wadsleyite by about 200°C (Litasov and Ohtani 2003). To constrain the effect of oxygen fugacity on the melting temperature of wadsleyite, single crystals of olivine were used as starting material. Use of single crystals minimizes the effect of surface adsorbed water. Experiments were performed at 14.6 GPa and 1500°C. As a result, no quenched melt was observed

in both samples buffered by the Re-ReO₂ and Mo-MoO₂ buffers at 14.6 GPa and 1500°C. We will continue to the experiments with single crystals to constrain the effect of oxygen fugacity on the melting temperature drop of wadsleyite.

In summary, we performed the experiments at the temperature conditions of 1300°C to 1600°C and the pressure conditions of 13.7 GPa to 16.6 GPa. The results of this study indicate that the melting temperature of wadsleyite was lowered by about 800°C with high oxygen fugacity and 0.4 wt% water.

References:

Brounce, M., Cottrell, E. and Kelly, K.A. (2019) The redox budget of the Mariana subduction zone. *Earth and Planetary Science Letters*, 528, 115859.

Moussallam, Y., Oppenheimer, C., Scaillet, B., Gaillard, F., Kyle, P., Peters, N., Hartley, M., Berlo, K. and Donovan, A. (2014) Tracking the changing oxidation state of Erebus magmas, from mantle to surface, driven by magma ascent and degassing. *Earth and Planetary Science Letters*, 393, 200-209.

Tauzin, B., Debayle, E. and Wittlinger, G. (2010) Seismic evidence for a global low-velocity layer within the Earth's upper mantle. *Nature geoscience* 3, 718-721.

Ohtani, E., Moriwaki, K., Kato, T. and Onuma, K. (1998) Melting and crystal-liquid partitioning in the system Mg₂SiO₄-Fe₂SiO₄ to 25 GPa. *Physics of the Earth and Planetary Interiors* 107, 75-82.

Litasov, K. and Ohtani, E. (2003) Stability of various hydrous phases in CMAS pyrolite-H₂O system up to 25 GPa. *Phys Chem Minerals* 30, 147-156.

In situ high pressure study Ga, Ge – analogues of important mineral phases for the Earth science

**Spivak A.V.¹, Setkova T.V.¹, Borovikova E.Yu., Iskrina A.V.^{1,2},
Zakharchenko E.S.¹, Kuzmin A.V.³**

¹*D.S. Korzhinskii Institute of Experimental Mineralogy RAS, Chernogolovka*

²*Lomonosov Moscow State University, Moscow*

³*Institute of Solid State Physics RAS, Chernogolovka*

The study of mineral phases, which are of great importance in the Earth sciences, especially their transformations at high pressures of the transition zone and lower mantle is one of the topical areas of experimental mineralogy. The solution of these scientific problems can be found on the basis of a systematic study of individual classes of compounds. Oxides, silicates, and aluminosilicates with various types of structural motifs, such as spinel, tourmaline, topaz, etc., were chosen as objects of this study. These minerals were synthesized in autoclaves with hydrothermal thermogradient conditions at $T = 600/650^{\circ}\text{C}$ and a pressure of 100 MPa as seed growth and spontaneous nucleation. The structural features of the crystals were analyzed in situ by Raman spectroscopy using DAC at pressures up to 30 GPa.

Based on the experimental data for Ga,Ge-rich tourmalines, we obtained correlation between the Raman band positions and the cation substitutions in the tetrahedral and octahedral sites at ambient conditions. A new band of Ge–O stretching vibrations, which is not common in natural tourmalines, occurs at $\sim 870\text{ cm}^{-1}$. Analysis of experimental and theoretical data reveals a possible phase transition at $\sim 18.4\text{ GPa}$ in the tourmalines with up to 10 wt. % Ga_2O_3 and 9 wt. % GeO_2 [1]. The Raman spectra of Fe_2GeO_4 crystal consist of an intense main band at 756 cm^{-1} and four less intense bands at $\sim 644, 472, 302,$ and $\sim 205\text{ cm}^{-1}$ at ambient conditions. All five bands inherent in the spectrum of cubic spinel are present and gradual change in high pressure spectra up to 30 GPa. The color of the crystal changes from brown-orange to reddish at the center at 22.7 GPa and became opaque black up to 30.2 GPa. Herewith, in the high pressure spectra, we observed the splitting of some bands and the appearance of additional bands in a wide pressure range (from 1.6 to 30 GPa). The factor group analysis with the lattice dynamics calculation of potential crystal structure distortions shows the decreasing of the structure symmetry to tetragonal or rhombohedral in this pressure range [2]. According to the data of Raman spectroscopy, it was revealed that kieselite does not undergo the phase transitions up to 30 GPa. The probable way of crystal structure distortion within the space group *Pnma* was proposed based on simulation of high-pressure Raman spectra [3].

This study carried out within the Research Program FMUF-2022-0001 of the D.S. Korzhinskii Institute of Experimental Mineralogy Russian Academy of Sciences, and was partially supported by the Russian Foundation for Basic Research (project no. 21-55-50011_YaF).

References:

1. Spivak A.V., Borovikova E.Yu, Setkova T.V. (2021) Raman spectroscopy and high pressure study of synthetic Ga,Ge-rich tourmaline. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 248, 119171. DOI: 10.1016/j.saa.2020.119171

2. Setkova T.V., Spivak A.V., Borovikova E.Yu., Voronin M.V., Zakharchenko E.S., Balitsky V.S., Kuzmin A.V., Sipavina L.V., Iskrina A.V., Khasanov S.S. (2022) Synthetic brunogeierite Fe₂GeO₄: XRD, Mössbauer and Raman high-pressure study. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 267(2), 120597. DOI: 10.1016/j.saa.2021.120597
3. Borovikova E.Yu., Spivak A.V., Setkova T.V., Kvas P.S., Kuzmin A.V., Zakharchenko E.S., Balitsky V.S., Khasanov S.S., Lazarenko V.A., Dorovatovskii P.V., Korshunov D.M., Aksenov S.M. (2023) Synchrotron single-crystal XRD, IR-, Raman spectroscopy and high pressure study of synthetic krieselite. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 288, 122137. DOI:10.1016/j.saa.2022.122137

Carbon isotopic analysis of microcrystalline diamond samples recovered from MA experiments by NanoSIMS

Kawamura H.¹, Takahata N.², Ishida A.¹, Sasaki K.¹, Shirai K.², Ohfuji H.¹, Suzuki A.¹

¹ *Department of Earth Science, Graduate School of Science, Tohoku University, Sendai, Japan*
kawamura.hideaki.q7@dc.tohoku.ac.jp

² *Department of Chemical Oceanography, Atmosphere and Ocean Research Institute, The University of Tokyo, Japan*

NanoSIMS is known as an effective method for isotope analysis and trace element analysis because it features high mass resolution and high sensitivity analysis with high spatial resolution. However, the analytical values (and their errors) are very sensitive to various factors, such as the state of the sample surface and other components in the sample. For accurate analysis, great care must be taken to maintain an extremely high vacuum in the sample chamber and extremely high smoothness and parallelness of the sample surfaces. Therefore, embedding in indium or resin with low volatile emissions is commonly used as a special sample treatment.

We have been investigating the interaction between magnesite and reduced C-H-O fluids by high-pressure experiments using a multi-anvil apparatus. To measure the carbon isotopic composition of diamond/graphite (several μm in size) produced by the decomposition of magnesite, we attempted NanoSIMS analysis. However, the standard procedure for NanoSIMS sample preparation could not be applied to the samples recovered by our multi-anvil experiments because they were brittle and difficult to polish mechanically due to the coexistence of volatile components. Furthermore, mechanical polishing causes contamination of samples with abrasives (diamond, SiC, etc.), which is a serious concern in carbon isotope analysis.

To solve these problems, we employed an Ar⁺ ion polishing method using a cross-section polisher (CP), which can provide polished cross-sections with less physical damage and virtually no contamination. However, ion polishing produces subtle unevenness as linear traces of the ion beam. Although such subtle unevenness is not a significant problem in routine SEM-EDS analyses, it may cause analytical errors and other issues in NanoSIMS analysis, which is very sensitive to the sample surface condition. In this talk, we present the sample preparation procedure and result of NanoSIMS analysis of ion-polished diamond/graphite samples recovered from high-pressure experiments.

Carbon isotope analysis was performed using a two-dimensional high-resolution secondary ion mass spectrometer (NanoSIMS NS50, CAMECA) installed at the Atmosphere and Ocean Research Institute, University of Tokyo. The sample surface was coated with Os to prevent charging by the ion beam during analysis. The Cs⁺ primary ion beam was adjusted to 200 pA during pre-sputtering and ~ 0.6 pA during analysis. $20 \times 20 \mu\text{m}^2$ area was manually pre-sputtered for 1 min 20 sec to remove surface contamination, and $5 \times 5 \mu\text{m}^2$ area was used for raster analysis. Fifteen cycles of measurements were performed per measurement point, switching between two different magnetic fields: 3 seconds for each ion in magnetic field [1] and 20 seconds for each ion in magnetic field [2]. The target ions were assigned to the electron multiplier detectors #2~#5 as follows.

magnetic field [1] - #2: $^{12}\text{C}^-$, #3: $^{12}\text{CH}^-$, #4: ^{16}O , #5: $^{12}\text{C}_2^-$
magnetic field [2] - #2: $^{13}\text{C}^-$, #5: $^{12}\text{C}^{14}\text{N}^-$

This makes it possible to measure ^{12}C and ^{13}C with the same detector and to ignore corrections due to differences in detector sensitivity. To correct for the effect of isotopic mass bias (SIMS instrument mass fraction: IMF), carbon isotope ratios of diamond and graphite standards were measured repeatedly at the beginning of each analysis. In addition, carbon isotope ratios were estimated by correcting for the counting loss of ^{12}C ions and IMF. The counting loss of secondary ions is known to be due to two factors: (1) detector dead time and (2) quasi-simultaneous arrival (QSA) of secondary ions to the detector (Slodzian et al., 2004; Nishizawa et al., 2010). Therefore, these corrections were calculated using the method described by Nishizawa et al. (2010).

The obtained carbon isotopic compositions of diamond/graphite produced in MgCO_3 – C-H-O fluid system range between $\delta^{13}\text{C} = 0$ and -20% , suggesting the interaction and assimilation of the two carbon sources. Since relatively large analytical errors ($2\sigma \sim 5$ to 10%) are expected due to various factors such as the effects of hydrogen bonded to carbon (e.g., Williford et al., 2016; Ishida et al., 2018) and area correction of the carbon distribution within the analyzed area ($5 \times 5 \mu\text{m}^2$), optimization of analytical conditions and correction calculations is necessary to improve the accuracy. Nevertheless, the result of the present study shows that NanoSIMS can analyze even tiny and fragile samples from multi-anvil experiments with extremely high spatial resolution and detection capability to obtain useful information such as carbon isotopes.

References:

- Slodzian, G., Hillion, F., Stadermann, F. J., & Zinner, E. (2004). QSA influences on isotopic ratio measurements. *Applied Surface Science*, 231, 874-877.
- Nishizawa, M., Maruyama, S., Urabe, T., Takahata, N., & Sano, Y. (2010). Micro-scale ($1.5 \mu\text{m}$) sulphur isotope analysis of contemporary and early Archean pyrite. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry*, 24(10), 1397-1404.
- Williford, K. H., Ushikubo, T. A. K. A. Y. U. K. I., Lepot, K. E. V. I. N., Kitajima, K. O. U. K. I., Hallmann, C., Spicuzza, M. J., ... & Valley, J. W. (2016). Carbon and sulfur isotopic signatures of ancient life and environment at the microbial scale: Neoproterozoic shales and carbonates. *Geobiology*, 14(2), 105-128.
- Ishida, A., Kitajima, K., Williford, K. H., Tuite, M. L., Kakegawa, T., & Valley, J. W. (2018). Simultaneous in situ analysis of carbon and nitrogen isotope ratios in organic matter by secondary ion mass spectrometry. *Geostandards and Geoanalytical Research*, 42(2), 189-203.

Diamond-forming fluids in coated diamonds from the Mirny kimberlite field (Siberian craton)

Dmitry A. Zedgenizov^{1,2} and Nikolai V. Gubanov^{1,3*}

¹ Zavaritsky Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russian Federation

² Ural state mining university, Ekaterinburg, Russian Federation.

³ Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation

Natural diamonds are unique time capsules of pristine mantle material, as they can contain inclusions which were captured at considerable depths and shielded from subsequent alteration processes. Traditional models of diamond formation suggest that diamonds can precipitate from high density fluids (HDFs) that interacted with surrounding deep-seated mantle rocks (Weiss et al. 2022). A suite of coated diamonds from the International'naya (n = 63) and Mir (n=5) kimberlite pipes (Mirny field, Siberian craton) was studied to track the most recent metasomatic events and the origin of diamond-forming HDFs in the subcontinental lithospheric mantle (SCLM).

The studied diamonds consist of two contrasting domains: an elder monocrystalline core, and a younger fibrous coat containing numerous microinclusions of diamond-forming HDFs. In the cores, nitrogen resided in A- and B-centers and showed advanced aggregation. In the coats, nitrogen resided only in C-centers and showed low aggregation. The limited range of nitrogen and low aggregation indicates the coats were formed shortly before the kimberlite eruption and within a single metasomatic event, in contrast to the cores.

Microinclusions in the coats contain silicic to low-Mg carbonatitic or high-Mg carbonatitic HDFs. Diamonds with high-Mg carbonatitic HDFs in the coats contain peridotitic mineral inclusions in the cores, and, compared to samples with silicic to low-Mg carbonatitic HDFs, both the cores and coats of these diamonds show higher aggregation states. This indicates storage in the mantle at higher thermal conditions and possibly deeper origin. The high-Mg carbonatitic HDFs show high concentrations of divalent cations (with a predominance of MgO) and are enriched in Na₂O, K₂O and CO₂. The PM-normalised trace element patterns show high levels of LREE, Th, U, Ba, Ta and Nb and are similar to patterns of host kimberlites of the Mirny field (Agashev et al. 2018). The chemistry of the high-Mg carbonatitic HDFs support the idea that they originated from the low-degree melting of a carbonated peridotite (Brey et al. 2008; Weiss et al. 2010).

Silicic to low-Mg carbonatitic HDFs are most common in the coated diamonds, and mineral inclusions in the cores of these diamonds suggest they were formed in eclogitic substrates. Silicic to low-Mg carbonatitic HDFs are enriched in SiO₂, Al₂O₃, CaO, K₂O, LREE, Th, U, Ba and water. Depletion of Ta and Nb in the most of HDFs indicate the presence of rutile in the parental eclogite. Radial compositional variations found in many of the samples reflect the evolution of the HDFs prior to kimberlite eruption. Although the composition of the HDFs in three diamonds display a trend from carbonatitic to more silicic, the composition of the HDFs in twenty-two diamonds

display a general trend from silicic to more carbonatitic. The scenario of both evolutions could have involved the passage of peridotite-derived carbonatitic HDFs into eclogites, which triggered their partial melting, followed by the appearance of immiscible, highly silicic and Ca-rich carbonatitic fluids/melts (Kiseeva et al. 2012). The immiscible fluids evolved toward a single silicate-carbonate melt, followed by the precipitation of silicate minerals upon cooling (Safonov et al. 2007).

This study was supported by the Russian Science Foundation (Grant № 22-17-00177).

References:

- Agashev A.M., Nakai S., Serov I.V., Tolstov A.V., Garanin K.V., Kovalchuk O.E. (2018) Geochemistry and origin of the Mirny field kimberlites, Siberia. *Mineralogy and Petrology* 112:597–608.
- Brey G.P., Bulatov V.K., Giris A.V., Lahaye Y. (2008) Experimental Melting of Carbonated Peridotite at 6–10 GPa. *Journal of Petrology* 49(4):797–821.
- Kiseeva E.S., Yaxley G.M., Hermann J., Litasov K.D., Rosenthal A., Kamenetsky V.S. (2012) An Experimental Study of Carbonated Eclogite at 3.5-5.5 GPa – Implications for Silicate and Carbonate Metasomatism in the Cratonic Mantle. *Journal of Petrology* 53(4):727-759.
- Safonov O.G., Perchuk L.L., Litvin Y.A. (2007) Melting relations in the chloride–carbonate–silicate systems at high-pressure and the model for formation of alkalic diamond–forming liquids in the upper mantle. *Earth and Planetary Science Letters* 253(1-2):112-128.
- Weiss Y., Czap J., Navon O. (2022) Fluid Inclusions in Fibrous Diamonds. *Reviews in Mineralogy and Geochemistry* 88(1):475–532.
- Weiss Y., Kiflawi I., Navon O. (2010) IR spectroscopy: quantitative determination of the mineralogy and bulk composition of fluid microinclusions in diamonds. *Chemical Geology* 275:26-34.

***In-situ* X-ray and neutron diffraction study on Fe_{0.95}Si_{0.05} hydrides**

Yuichiro Mori¹ (mori-yuichiro299@g.ecc.u-tokyo.ac.jp), Hiroyuki Kagi¹, Katsutoshi Aoki¹, Sho Kakizawa², Asami Sano-Furukawa³, Ken-ichi Funakoshi⁴

¹ The University of Tokyo, ² JASRI

³ J-PARC Center, JAEA, ⁴ CROSS

The density of the Earth's core estimated from seismic waves is notably lower than that predicted for pure iron [e.g., Dziewonski and Anderson, 1981 PEPI]. The reason for this density deficit is believed to be the dissolution of light elements in the core. Research have been widely conducted to identify these light elements. Among light elements, hydrogen is one of the plausible ones [e.g., Stevenson, 1977 Nature] that has attracted attention in recent years.

Hydrogen becomes highly siderophile under high pressure, it has been suggested that a large amount of hydrogen can be dissolved into liquid iron in the magma ocean. [Okuchi, 1997 Science; Tagawa+, 2021 Nat. Commun.]. On the other hand, it is known that hydrogen is released from iron hydrides when recovered to ambient pressure and room temperature. Hence, it is important to conduct *in-situ* diffraction experiments under high-pressure conditions to determine directly the actual amount of hydrogen in iron hydrides.

For *in-situ* diffraction experiments at high pressure, X-ray diffraction is a widely used technique. However, almost no change in scattering intensity can be observed when “light” hydrogen dissolves into “heavy” iron because the scattering intensity of X-ray diffraction depends on the number of electrons (atomic number). In contrast to X-ray, neutron interacts with atomic nuclei and their scattering intensity is independent of atomic number. Neutron diffraction under high-pressure conditions has been used to refine the crystal structure of iron hydrides to date.

The volume expansion of a unit cell caused by the dissolution of one hydrogen atom into an iron alloy is called the "*hydrogen-induced volume expansion coefficient*" (v_H). This value can be derived by dividing the difference between the unit cell volume of hydride (V_{MH_x}) and that of metal (V_M) at a certain *PT* condition by the amount of dissolved hydrogen x as follows.

$$\Delta v_H = \frac{V_{MH_x} - V_M}{Zx},$$

where Z is the number of host atoms in the unit cell ($Z = 2$ in hcp structure). Using this value (Δv_H), the amount of hydrogen (x) can be derived from the unit cell volume of hydride (V_{MH_x}).

As mentioned above, neutron diffraction under high pressure is the only method to quantify the amount of hydrogen in iron hydrides. To date, the hydrogen-induced volume expansion coefficients of Fe-H systems have been widely discussed using neutron diffraction under high pressure [e.g., Machida+, 2014 Nat. Commun.]. On the other hand, there are several candidates for light elements in the Earth's core, and there have been very few direct studies on the effects of other light elements on hydrogenation of iron.

Here, we focused on Si, one of the most promising candidates for light elements in the inner core [e.g., Lin+, 2003 Science; Antonangeli+, 2018 EPSL; Hasegawa+, 2021 GRL], we have performed neutron diffraction experiments on hcp-Fe_{0.95}Si_{0.05} deuterides under high temperature and high pressure. We have also performed *P-V-T* measurements of hcp-Fe_{0.95}Si_{0.05} using X-ray diffraction. Comparing those results, the obtained hydrogen-induced volume expansion coefficient of hcp-Fe_{0.95}Si_{0.05} was negligibly larger than that of pure iron. Accordingly, the dissolution of silicon may enhance the effect of density reduction caused by hydrogenation. If the results are adaptable to much higher-pressure environments such as the Earth's inner core, the obtained result suggests that the amount of hydrogen in the core has to be reconsidered if silicon is a major light element. This implies that the effect of the presence of other light elements in addition to hydrogen cannot be ignored when hydrogen dissolves into the Earth's core.

Interaction of upper mantle minerals with silicon carbide (SiC) at 6 GPa and 1100-1500 °C

Litasov KD¹ (litasov@hppi.troitsk.ru), Shatskiy A², Bekhtenova AE¹, Kagi H³

¹ Vereshchagin Institute for High Pressure Physics, Troitsk, Moscow, Russia

² Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia

³ Geochemical Research Center, University of Tokyo, Tokyo, Japan

One of the important methods that will help to solve the problem of the primary presence of SiC in rocks (e.g., di Pierro et al., 2003; Dobrzhinetskaya et al., 2018) is experimental studies. Experiments were carried out on the interaction of mantle rocks and minerals with SiC at 6 GPa and 1100-1500 °C. Studies at low pressures have not been performed, since Ballhaus et al. (2021) recently studied similar systems at pressure of 0.7 GPa.

Fine powders of natural peridotites and eclogites from kimberlites with the addition of 10 wt.% SiC, as well as monomineralic powders and crystals of chromite, olivine, and garnet were used as starting materials. The experiments were carried out on a 1500-tons multianvil apparatus.

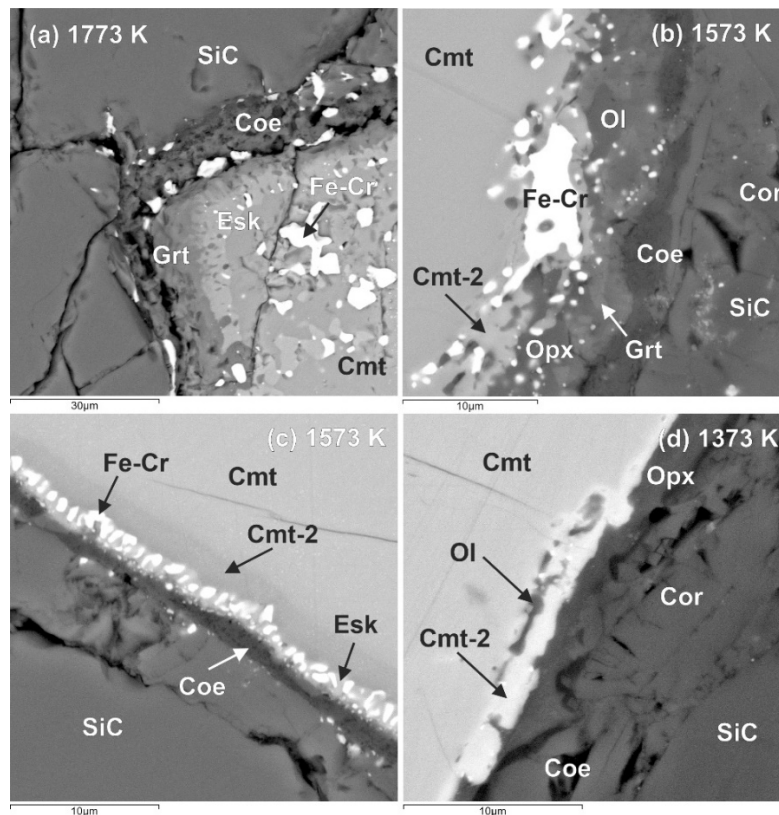


Figure 1. Reactionary rims at the contact between chromite and SiC at 6 GPa and 1773 K (a), 1573 K (b-c) and 1373 K (d). Cmt – chromite, Ol – olivine, Opx – orthopyroxene, Grt – garnet, Coe – coesite, Fe-Cr – metallic alloy, Cor – corundum, Esk – eskolaite.

In all experiments, the reduction of silicates and chromite was observed with an increase in the magnesium number (Mg#) of minerals to almost 100% and the precipitation of metallic phases

- alloys in the Fe-Si-Cr system. The most pronounced reactions were expressed at 1500 °C. Equilibrium was not achieved in all the studied systems. Instead, we observed reaction rims formed on the mineral grains (Fig.1) and finely dispersed iron alloys precipitated over the entire volume of the crystals. The reaction of SiC with chromite proceeds most rapidly. The Mg# of chromite changes from 57 (in the initial chromite) to 83.

It is shown that at 6 GPa, SiC reacts quickly with minerals and rocks of the mantle to form metal phases and high-magnesian silicates and chromite, which means that they cannot be in equilibrium, as was previously stated for a number of ophiolite peridotites and chromitites, and also volcanic rocks such as basalts and kimberlites.

This study was supported by the Joint project between Russian Science Foundation and Japan Society for Promotion of Science (project no. 21-55-50004).

References:

- Ballhaus, C., Helmy, H. M., Fonseca, R. O., Wirth, R., Schreiber, A., & Jöns, N. (2021). Ultra-reduced phases in ophiolites cannot come from Earth's mantle. *American Mineralogist*, 106(7), 1053-1063.
- Di Pierro, S., Gnos, E., Grobety, B.H., Armbruster, T., Bernasconi, S.M., Ulmer, P. (2003) Rock-forming moissanite (natural α -silicon carbide). *American Mineralogist*, 88: 1817-1821.
- Dobrzhinetskaya, L., Mukhin, P., Wang, Q., Wirth, R., O'Bannon, E., Zhao, W., Eppelbaum, L., Sokhonchuk, T., (2018) Moissanite (SiC) with metal-silicide and silicon inclusions from tuff of Israel: Raman spectroscopy and electron microscope studies. *Lithos*, 310: 355-368.

INVITED

Formation of Mn oxide nanowire on the surfaces of Fe oxide

Sayako Inoué¹ (inoue.sayako.nr@ehime-u.ac.jp)

¹ Geodynamics Research Center, Ehime University

Despite being the minor element in the Earth's crust, Mn (oxyhydr)oxides (Mn oxide) play a vital role in the geochemical cycling of elements in near-surface environments. Mn(II) is stable in solutions under relatively acidic and anoxic conditions without carbonate, sulfide and phosphate ions. In contrast, tri- and tetravalent Mn ions are unstable as aqueous species and precipitate as oxides under oxic conditions. Mn(II) oxidation proceeds very slowly, if at all, with no help from biotic or abiotic catalysts (Diem and Stumm, 1984). Fe (oxyhydr)oxide (Fe oxide) nanoparticles (NPs) are a common constituent of soils and sediments (Cornell and Schwertmann, 2003), and often coexist with Mn oxides (Jambor and Dutrizac, 1998). Numerous laboratory studies have been performed to characterize the adsorption and oxidation behavior of Mn(II) on various Fe oxides. It has been shown that the presence of Fe oxide NP surfaces accelerates the oxidation of Mn(II) in solution. The surface-catalyzed Mn(II) oxidation by Fe oxide NPs is linked to the semiconducting nature of Fe oxides, as described by the electron transfer (ET) process between Mn(II) and Fe oxide NPs. Previous studies mainly focused on the macroscopic characterization of product Mn oxide structures and trend in describing the structural transformations. Comparatively little attention has been paid to the direct observation of each single particle. In Inoué et al. (2019), we characterized the evolution of structure and morphology of product Mn oxide starting at the surfaces of nanoscale hematite catalyst. Although the ET process between Mn(II) and hematite NP is strongly suggested, how the catalytic properties of hematite influences the product Mn oxide is still ambiguous. In the present study, the ability of different Fe oxides to catalyze Mn oxide formation is compared to elucidate the influences of semiconducting properties of Fe oxide on the formation of Mn oxide NPs.

Synthesized hematite with different particle size and morphology and goethite were used in this study. The suspension of Fe oxides and 1 mL of 1M PIPES buffer were added to 50 mL of ultrapure water. The PIPES buffer, a classic biochemical buffer, was used to keep pH at 7.5. Then, A 50 μ L of MnCl₂ solution was added to the suspension under stirring. The reaction mixture was continuously stirred for two weeks. The Mn oxidation experiment was also conducted in the presence of cristobalite, insulating mineral, for comparison. The suspension was dialyzed as soon as the reaction was terminated. After the dialysis, the collected solids were examined by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

In the presence of hematite, wire-shaped manganite (γ -MnOOH) NPs were obtained regardless of particle size of hematite. The product manganite nanowires were elongated along [101] direction. Average particle size of manganite nanowires was 2192 nm in length and 47 nm in width for larger hematite and 906 nm in length and 21 nm in width for smaller hematite. Most of the product manganite nanowire were in contact with the hematite NP. On the other hand, no particulate Mn oxide was identified by TEM nor SEM in the product of Mn oxidation with goethite and cristobalite. Our preliminary data of band-structure analysis of Fe oxides indicated that the presence of manganite nanowire depends on the semiconducting properties of Fe oxide. The relationships between the product manganite nanowire and Fe oxide NPs will be discussed in the presentation.

Melting relations from the mantle transition zone to uppermost lower mantle in the MgO-SiO₂-H₂O system

Okumura K¹ (m214267@hiroshima-u.ac.jp), Inoue T¹, Kawazoe T¹,
Kakizawa S², Noda M³, Irifune T⁴, Shinmei T⁴

¹ Graduate School of Advanced Science and Engineering, Hiroshima University,
Higashi- Hiroshima, Japan

² Japan Synchrotron Radiation Research Institute (JASRI), Sayo, Japan

³ Physics, Delaware State University, Dover, United States of America

⁴ Geodynamics Research Center, Ehime University, Matsuyama, Japan

Recent seismic observations have revealed the existence of a low seismic velocity region just below the 660 km discontinuity (Schmandt et al., 2014), pointing to the possibility of magma formation near the uppermost lower mantle. Previous studies have shown that water not only lowers the melting point of minerals, but also significantly changes the chemical composition of the generated magma. Under hydrous conditions, Mg₂SiO₄ olivine melts incongruently above ~8 GPa, producing MgO-rich magmas with Mg/Si > 2 and MgSiO₃ clinoenstatite (Inoue 1994), and furthermore, above ~15 GPa under the mantle transition zone conditions, even MgSiO₃ clinoenstatite melts incongruently, producing MgO-rich magma and SiO₂ stishovite (Yamada et al., 2004). Since MgSiO₃ clinoenstatite melts congruently under anhydrous conditions, the composition of magmas formed under hydrous and anhydrous conditions are significantly different. However, it has not been clear about the chemical compositions of hydrous magma, especially including water content, formed near the uppermost lower mantle at 25 GPa. To answer these questions, we performed high-pressure melting experiments in the MgSiO₃ - H₂O system from the mantle transition zone to the uppermost lower mantle. Based on the results, we drew the melting phase equilibrium diagram in the MgO-SiO₂-H₂O system. In particular, we made various considerations for the determination of water content in magma precisely so that the present estimation could be more quantitative than the previous estimation.

Kawai-type 600-ton (Hiroshima University) and 3000-ton (Ehime University) high-pressure apparatuses were used for high-pressure experiments. The pressures were fixed at ~ 15.5 GPa and ~25 GPa to simulate the conditions from the mantle transition zone to the uppermost lower mantle, and the temperatures were in the range of 1200-1800°C. Two starting materials of the mixtures of SiO₂, MgO, and Mg(OH)₂ powders in the composition of MgSiO₃ with 8.2 and 15.2 wt% H₂O were prepared. The chemical compositions of magma and coexisting solid phases (except H₂O) were determined by EPMA. The degrees of melting were determined from the chemical compositions of the solid phases and magma (liquid phase) by mass balance calculations.

Figure 1 shows the cotectic lines at 15.5 GPa and 25 GPa for the hydrous magma produced in the $\text{MgSiO}_3\text{-H}_2\text{O}$ system. It can be understood that under high-pressure hydrous conditions, MgSiO_3 bridgmanite melts incongruently to produce MgO-rich liquid + stishovite, which is significantly different from the melting relationship under anhydrous conditions. The previous studies (Inoue, 1994; Yamada et al., 2004) reported that MgO-rich magma is formed above ~ 8 GPa, and this trend continues up to 15 GPa. This study indicates that MgO-rich magma is formed under hydrous condition with increasing pressure to 25 GPa, and the water content at ~ 25 GPa could be more than ~ 40 mol% because the mantle temperature would be below 1800°C .

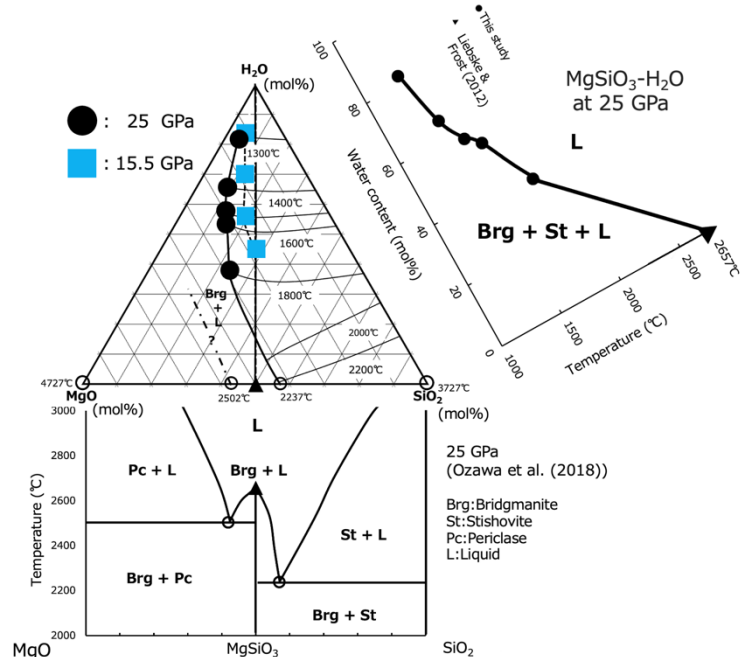


Fig.1. The cotectic lines in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system at 15.5 GPa (dotted line) and 25 GPa (solid line). Brg: bridgmanite, St: stishovite, Pc: periclase, L: liquid. Dry phase diagram is from Ozawa et al., (2018).

This study was supported by the PRIUS program, GRC, Ehime University.

References:

- Schmandt, B., Jacobsen, S.D, Becker, T.W, Liu, Z. Dueker, K.G. (2014) Dehydration melting at the top of the lower mantle. *Science*, 344, 1265-1268.
- Inoue, T. (1994) Effect of water on melting phase relations and melt composition in the system $\text{Mg}_2\text{SiO}_4\text{-MgSiO}_3\text{-H}_2\text{O}$ up to 15 GPa. *Physics of the Earth and Planetary Interiors*, 85, 237-263.
- Yamada, A., Inoue, T., Irifune, T. (2004) Melting of enstatite from 13 to 18 GPa under hydrous conditions. *Physics of the Earth and Planetary Interiors*, 147, 45-56.
- Ozawa, K., Anzai, M., Hirose, K., Shinmyo, R., Tateno, S. (2018) Experimental Determination of Eutectic Liquid Compositions in the MgO-SiO_2 System to the Lowermost Mantle Pressures. *Geophysical Research Letters*, 45, 9552-9558.

Hydrous phases as the key sign of crust-mantle interaction: Evidence from experiments up to lower mantle conditions

Bendeliani A.A.^{1,2}, Bobrov A.V.^{1,2}, Bindi L.^{3,4}, Eremin N.N.¹, Irifune T.^{5,6}

¹ *Moscow State University, Moscow, Russia*

² *Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS, Moscow, Russia*
a.bendeliani@outlook.com

³ *Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy*

⁴ *C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy*

⁵ *Geodynamics Research Center, Ehime University, 790-8577 Matsuyama, Japan*

⁶ *Earth-Life Science Institute, Tokyo Institute of Technology, 152-8550 Tokyo, Japan*

Hydrous phases in the deep geospheres attract the attention of an increasing number of researchers due to the significant role of water in many geodynamic processes. Our experimental studies were aimed at developing the idea of the crust-mantle interaction when the material of the oceanic crust subducts to different depths, which controls metamorphism and partial melting in the Earth's mantle. At the same time, the previous studies cover the PT range corresponding to the conditions of the upper mantle only [Bulatov et al., 2014; Brey et al., 2015; Woodland et al., 2018; Perchuk et al., 2019; 2020], while there are no results on the interaction under the conditions of the lower mantle and the transition zone. This is the reason for the goals and objectives of this work.

Experiments on the study of the interaction between peridotite and GLOSS [Plank, Langmuir, 1998] in the pressure range of 7–24 GPa, at 900–1400°C, using the successive loading of starting mixtures into an ampoule (“sandwich”-type) allowed us to detect a high degree of influence of large-scale chemical gradient on phase associations of products of experiments at low pressures (7, 12 GPa). It was shown that the chemical gradient at low pressures does not affect the redistribution of elements between the zones: the formation of high-calcium garnets and pyroxenes with elevated contents of TiO₂ and Na₂O was identified as a characteristic feature of the crustal (eclogitic) association. Under the conditions of the transition zone and uppermost lower mantle of the Earth (18 and 24 GPa), the main sign of the crust-mantle interaction is the formation of such high-alumina hydrous phases as phase D, δ , Egg, Mg-Egg [Bindi et al., 2020a], Si-Sur [Bindi et al., 2020b]. It is shown that the redistribution of Si and Mg controls the formation of the D phase in both zones at a pressure of 18 GPa. MgSiO₃ under the conditions of a water-saturated system (18, 24 GPa) will not contain significant concentrations of alumina, which will result in predominant accumulation of aluminum in the composition of hydrous: $(\text{Mg}_{1-x}\text{Al}_x)(\text{Al}_x\text{Si}_{1-x})\text{O}_3 + \text{H}_2\text{O} + (1-x)\text{SiO}_2 = (1-x)\text{MgSi}_2\text{O}_6\text{H}_2 + 2x\text{AlOOH}$. It is shown that the aluminum content in phase D is not controlled by the interphase distribution of the element between MgSiO₃ and DHMS phases, but is due to the influence of H₂O and SiO₂. At the same time, at 24 GPa, the bulk distribution of impurities between two substrates of the different composition does not correspond to their concentrations in the crustal (TiO₂) and mantle (Cr₂O₃) protolith, which is controlled by the bulk proportions of coexisting bridgmanite and hydrous phases (phases D, δ) in the considered zones. However, the chemical gradient does not affect the minor-element composition of bridgmanite, which allows the mineral to be a reliable indicator of the protolith. This fact can be used to distinguish the lower mantle diamonds into the paragenetic associations. In the studied system at low pressures (7, 12 GPa), mass crystallization of hydrous phases was not detected, which is due to the early disappearance of K-mica (phengite) even at low degrees of partial melting of oceanic sediment.

The composition of micas in inclusions in diamonds, which are the containers of OH, F, and Cl, has recently received an increasing attention. In this regard, two series of experiments on the crystallization of Cr and Ti-bearing micas in peridotite+/basalt+K₂CO₃+H₂O systems were

carried out, simulating the interaction of peridotite and eclogite with a potassium carbonate melt at 7 GPa and 900-1200°C [Bendeliani et al., 2023a]. It was shown that the presence of >1.3 wt.% TiO₂ in phlogopite is accompanied by a change in the mica composition to a lower Mg variety and introduces a limitation on high concentrations of Cr₂O₃ via the scheme $^{VI}(\text{Mg}^{2+}) + ^{IV}(\text{Si}^{4+}) = ^{VI}(\text{Cr}^{3+}) + ^{IV}(\text{Al}^{3+})$. This mechanism occurs in most of chromium-bearing phlogopites from inclusions in diamonds and those synthesized in various experimental systems. In addition, this mechanism is one of the most energetically preferable, according to the results of atomistic modeling [Bendeliani et al., 2023b]. This can explain the regularities in the composition of phlogopite from inclusions in natural diamonds, in which the content of Ti significantly exceeds the content of Cr.

It is shown that the crystallization of titanium-bearing phlogopite is possible with the participation of subduction crustal material at mantle depths. A high degree of enrichment of the mantle with titanium prevents the formation of high-chromium micas. However, crystallization of Ti-phlogopite requires predomination of mantle peridotite over basalt; otherwise, titanium would be accumulated in the composition of dioctahedral mica (aluminoceladonite) with $(\text{Mg}+\text{Fe})/^{VI}\text{Al} > 1$ via the scheme $2^{VI}\text{Al} = ^{VI}\text{Ti}^{4+} + ^{VI}(\text{Mg}+\text{Fe})$.

Thus, the results of our experiments confirm the idea of N.V. Sobolev (Sobolev et al., 2009) on the identification of paragenetic associations of diamonds by the composition of phlogopite and allow the mineral to be used as an indicator of the crust-mantle interaction.

This study was supported by the Russian Science Foundation (project no. 21-17-00147) and the Russian Foundation for Basic Research (project no. 21-55-50011).

References:

- Bendeliani A.A., Bobrov A.V., Bindi L., Eremin N.N. (2023a) Ti and Cr in High-Pressure Mica: Evidence from Experiments at 7 GPa and 900–1200°C. Petrology. V. 31. No. 1. P. 157-173*
- Bendeliani A.A., Eremin N.N., Bobrov A.V. (2023b) Mechanisms and Conditions of Ti and Cr Incorporation in Mantle Phlogopite: The Results of Atomistic Simulation. Physics and Chemistry of Minerals. In press.*
- Brey G.P., Girnīs A.V., Bulatov V.K., Gerdes A., Hofer H.E., Woodland A. (2015) Reduced sediment melting at 7.5-12 GPa: phase relations, geochemical signals and diamond nucleation. Contrib. Mineral. Petrol. V. 170 - 15.*
- Bulatov V.K., Brey G.P., Girnīs A.V., Gerdes A., Hofer H.E. (2014) Carbonated sediment-peridotite interaction and melting at 7.5-12 GPa. Lithos. V 200-201. P. 368-385.*
- Perchuk A.L., Serdyuk A.A., Zinovieva N.G. (2019) Subduction sediment-lherzolite interaction at 2.9 GPa: Effects of metasomatism and partial melting. Petrology. V. 27. P. 467-488*
- Perchuk A.L., Serdyuk A.A., Zinovieva N.G., Shur M.Yu. (2020) Melting and parageneses of global subducting water-enriched sediment in closed and open systems: Experiment and thermodynamic modeling. Russian Geology and Geophysics. V. 61, No. 5-6. P. 571-591*
- Plank T., Langmuir C.H. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. Chemical Geology. V. 145. P. 325-394.*
- Plank T., Langmuir C.H. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. Chemical Geology. V. 145. P. 325-394*
- Sobolev N.V., Logvinova A.M., Efimova E.S. (2009) Syngenetic phlogopite inclusions in kimberlite-hosted diamonds: implications for role of volatiles in diamond formation. Russian Geology and Geophysics. V. 50. P. 1234-1248*
- Woodland A.B., Bulatov V.K., Brey G.P., Girnīs A.V., Hofer H.E., Gerdes A. (2018) Subduction factory in an ampoule: Experiments on sediment-peridotite interaction under temperature gradient conditions. Geochimica et Cosmochimica Acta. V. 223. P. 319-349.*

Structure and speciation of hydrous sodium silicate melts under pressure

Ohashi T¹ (tomonori.ohashi.s8@dc.tohoku.ac.jp), Steinle-Neumann G², Sakamaki T¹,
Funakoshi K³, Hattori T⁴, Yuan L², Suzuki A¹

¹ Department of Earth Science, Tohoku University

² Bayerisches Geoinstitut, Universität Bayreuth

³ Neutron Science and Technology Centre, Comprehensive Research Organization for Science and Society (CROSS)

⁴ Materials and Life Science Division, J-PARC Centre

Silicate melts are generated and stabilized locally in Earth's mantle through the presence of volatiles. Determining the structure of hydrous silicate melts, which is largely different from anhydrous melts, is therefore important to acquire the microscopic insights into their properties such as density and viscosity. In addition, our understanding of the liquid state lags far behind that of solids and gases because of the difficulties in modelling and simplifying liquid structure with strong many-body correlations without long-range order, and experimental challenges for in situ experimental observation for hydrous silicate melts under pressure. Here, the structures of dry and hydrated (with H₂O and D₂O) Na₆Si₈O₁₉ melts, which is a typical hydrous ternary composition, were investigated by means of in situ X-ray and neutron diffraction experiments at 0–7 GPa, combined with ab initio molecular dynamics simulations. This study aims at obtaining a systematic view of the structural changes with pressure and water content and at understanding the chemical-bonding states.

On compression, the Na-Na distance rapidly decreases up to 1–2 GPa and then more moderately by shrinking the size of Na-O coordination polyhedra on further compression. The population of -O-H-O- bridging species increases by consuming -OH hydroxyl with increasing pressure with nearly constant abundance of molecular H₂O. Compression behaviour of chemical-bonding species is manifested by the increase in O-H-O and Si-O-Si bridges, which scavenges Na⁺ from its network-modifying role via $\text{Si-O-Na} + \text{Si-O-H} \rightarrow \text{Si-O-H-O-Si} + \text{Na}^+$ and $2 \cdot [^4\text{Si-O-Na}] \rightarrow [^4\text{Si-O-}][^5\text{Si}] + 2 \cdot \text{Na}^+$.

With increasing water content, the depolymerization degree (NBO/Si) increases and becomes more insensitive to compression. Even though the Si-O-Si linkage is largely modified by water via $\text{Si-O-Si} + \text{H}_2\text{O} \rightarrow 2 \cdot \text{Si-O-H}$, the Si-Si interatomic distances, Si-O coordination number, and Si-O-Si bond angle distribution do not show any clear structural changes with water content. Such depolymerization effects are clarified by using an orientational order parameter for the Si-(O-)Si arrangement, showing a tendency for disordering with increasing water content.

The effect of water on the phase transition in pyroxene - garnet system

Yasushi UENO¹ (m213942@hiroshima-u.ac.jp), Toru INOUE¹, Takaaki KAWAZOE¹,
Sho KAKIZAWA², Koji OHARA², Masamichi NODA³, Toru SHINMEI⁴, Tetsuo IRIFUNE⁴

¹ Hiroshima University, Higashi-hiroshima, Hiroshima, Japan

² JASRI, Sayo, Hyogo, Japan

³ Delaware State University, Dover, DE, USA

⁴ Ehime University, Matsuyama, Japan

It is generally believed that water exists in the Earth's interior as well as in surface seawater. The discovery of natural hydrous ringwoodite which includes ~1.5 wt% H₂O (Pearson et al., 2014) indicates that the mantle transition zone contains water at least locally. To date, many studies have been conducted under dry and wet conditions in the olivine system, which accounts for about 60% of the mantle composition. However, the studies under wet conditions in the pyroxene-garnet (Px-Gar) system, which accounts for the remaining 40%, have been scarcely. Therefore, in this study, experimental studies were conducted to clarify the effect of water on the phase diagram of the Px-Gar binary system. At the same time, since the dry samples in previous studies may have been slightly hydrated because of adsorbed water on the surface of the dry powder samples. So, to prevent hydration of the dry samples, a block of glass was used as the starting material to achieve nearly perfect dry conditions.

High-temperature and high-pressure experiment was conducted using a Kawai-type high-pressure apparatus, MAPLE600 at Hiroshima University and ORANGE3000 at GRC, Ehime University. The experimental conditions were 22-26 GPa, 1600-1700°C which are corresponding to the conditions from the lowermost mantle transition zone to the uppermost lower mantle. The four types of starting composition with Al₂O₃ contents of 5, 10, 15, and 20 mol% were prepared in the MgSiO₃-Al₂O₃ system in dry and wet samples. For the dry sample, a block of oxide glass was used as the starting material, and for the wet sample, a powder mixture of oxide glass and hydroxide was used as the starting material. The block of oxide glass was synthesized using a laser-heated levitation furnace apparatus installed at BL04B2 in SPring-8. The water content of the wet sample was fixed at 1 wt%. The starting materials for the high-pressure experiment were enclosed in AuPd capsule to prevent water leakage. The dry sample was partitioned inside the capsule with Au foil so that the two compositions could be conducted under the same conditions. The recovered samples were examined by XRD for phase identification and lattice parameter measurement, by SEM for microstructural observation, and EPMA for chemical composition analysis, after mirror polishing.

The results at 1700°C, 23 GPa showed that akimotoite (Ak) + Gar coexisted in the dry sample, while Brg + Gar coexisted in the wet sample. Thus, the phase transition boundary shifts to the lower pressure side due to the influence of water. On the other hand, Ak was observed instead of Brg even under higher pressure than 24 GPa, in the Al content higher than 15 mol%, under nearly perfect dry conditions. Since this result is different from the phase diagram of the conventional dry Px-Gar system, further investigation is underway.

References:

Pearson et al. (2014) *Nature*, 507, 221-224.

Kubo & Akaogi (2000) *Phys. Earth Planet. Inter.*, 121, 85-102.

Hydrogen-bonding configurations of fluorine-doped brucite under high pressure

Xuejing He¹ (xuejinghe@g.ecc.u-tokyo.ac.jp), Hiroyuki Kagi¹, Asami Sano-Furukawa², Jun Abe³, Ko Fukuyama⁴, Toru Shinmei⁴, Kazuki Komatsu¹

¹ Geochemical Research Center, Graduate School of Science, The University of Tokyo

² J-PARC Center, Japan Atomic Energy Agency

³ Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS)

⁴ Geodynamics Research Center, Ehime University

The circulation of halogens in the interior of the Earth, together with that of H, C, N, S, noble gases, etc., forms the deep volatile cycles which play an important role in the Earth's mantle. In particular, fluorine (F) is supposed to be the most abundant halogen in the mantle [1]. Hydrous minerals commonly contain F, and play an important role in transporting F into the mantle via subduction processes. F⁻ incorporates into hydrous minerals by substituting hydroxyls in the crystal structure, which leads to modifications of physicochemical properties and the formation of the O-H...F hydrogen bond (e.g., [2,3]). The high-pressure and high-temperature stability of hydroxyls in the mineral structure is strongly related to large-scale geological processes, such as slab dehydration, rock melting, and subduction earthquakes. Therefore, investigating the O-H...F hydrogen-bonding configuration under high pressure and high temperature is among the fundamental mineralogical issues.

The brucite [Mg(OH)₂] ($P\bar{3}m1$, $Z = 1$) structure is an archetype of hydrous minerals and phases. Miao et al. (2022) [3] have refined the proton site of F-doped hydrogenated brucite under ambient condition using the single-crystal XRD data. In this study, we have investigated the crystal structure and the hydrogen-bonding configuration of hydrogenated and deuterated F-doped brucite under ambient condition and at high pressure via neutron powder diffraction. The incorporation of fluorine shortens the a and c axes, resulting in smaller unit cell volumes. Under ambient condition, the proton site of Mg(OH)₂ can be refined by either the single-site model (the proton adopts the $2d$ site ($1/3, 2/3, z$), and the hydroxyl dipole is aligned parallel to the c axis) or the three-fold split-site model (the proton is in the $6i$ site ($x, 2x, z$), being disordered in three equivalent splitting sites around the three-fold axis with an equal occupancy of $1/3$), while the proton of Mg(OH)_{1.81}F_{0.19} tends to locate in the $2d$ site. Both Mg(OD)₂ and Mg(OD)_{1.79}F_{0.21} have the proton in the $6i$ site. The hydrogen-bonding geometry, i.e., $d(\text{O-H/D})$, $d(\text{H/D}\cdots\text{O})$, $d(\text{O}\cdots\text{O})$, and $\angle\text{O-H/D}\cdots\text{O}$, has been determined up to 6.9 GPa for Mg(OH)_{1.81}F_{0.19} and up to 10.1 GPa for Mg(OD)_{1.79}F_{0.21}. In Mg(OD)_{1.79}F_{0.21}, the incline of the O-D dipole increases steadily with increasing pressure, and the hydrogen-bonding interaction strengthens. Compared with Mg(OD)₂ [4], the substitution of F alleviates the pressure-induced hydrogen-bonding strengthening under compression.

References

[1] McDonough W. F., Sun S.-s. (1995) *Chem Geol*, 120:223-253. [2] Friedrich A., et al. (2002) *Am Mineral*, 87:931-939. [3] Miao Y., et al. (2022) *Am Mineral*, 107:2065-2074. [4] Parise J. B., et al. (1994) *Am Mineral*, 79:193-196.

Phase relation in a natural hydrous basalt under the lower mantle condition

Yuta Ishikawa¹ (j850002y@mails.cc.ehime-u.ac.jp), Tetsuo Irifune¹, Takehiro Kunimoto¹
¹ GRC, Ehime University

It has been believed that basaltic crust materials completely dehydrate at relatively low pressures and would not play any important roles in delivering water into deep mantle upon subduction of slabs (Litasov and Ohtani, 2005). Recently, however, the formation of some new hydrous phases, i.e., Fe-Ti oxyhydroxide, Al-rich phase D, and Al-rich phase H (Al-PhH, hereafter), in basaltic compositions was reported in hydrous basaltic compositions under the relatively low temperature and at pressures to 26 GPa, which shed light on the possibility of water transport to the mantle transition zone and uppermost lower mantle (Liu et al., 2019). It is important to understand precise phase relations in hydrous basalt compositions under the lower mantle conditions to address the possibility of transportation of water into the lower mantle.

In this study, WC and S.D. anvils were used in experiments at 27 and 30GPa, 1000-1600°C, and 40, 50GPa at 1600°C respectively, to reveal phase relations in a hydrous basalt composition using natural hydrous basalt (JB-1b with a water content of 2.59wt%). As a result, the formation of Al-rich bridgmanite, Al-rich stishovite, davemaoite, NAL phase, CF phase, K-rich hollandite, and Al-PhH was confirmed in the hydrous basalt composition, depending on the pressure and temperature conditions. As for the hydrous phase, the presence of Al-PhH is confirmed at 1200°C at 27GPa and at 1200 and 1400°C at 30GPa. No hydrous phases have been observed at 40 GPa and 50 GPa, at a temperature of 1600°C. Based on the obtained compositional data sets and mineral proportions evaluated by mass-balance calculations, it is shown that the hydrous basalt may retain 1.8wt% water as Al-PhH under the pressure and temperature conditions, close to those expected in cold slab subducted into the uppermost lower mantle. This indicates that the hydrous mineral may exist in cold subducting slabs under the lower mantle conditions, and when water is retained by hydrous minerals at low pressures, Al-PhH transports some amount of water into even deeper regions of the Earth's mantle.

Temperature dependence of nitrogen solubility in bridgmanite: Evolution of the nitrogen storage capacity of the lower mantle

Fukuyama K.¹(fukuyama.ko.ld@ehime-u.ac.jp), Kagi H.², Inoue T.³, Kakizawa S.⁴, Shinmei T.¹,
Sano Y.⁵, Deligny C.⁶, Fūri E.⁷

¹ Geodynamics Research Center, Ehime University

² Geochemical Research Center, Graduate School of Science, The University of Tokyo

³ Graduate School of Advanced Science and Engineering, Hiroshima University

⁴ Japan Synchrotron Radiation Research Institute (JASRI)

⁵ Center for Advanced Marine Core Research, Kochi University

⁶ Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden

⁷ Centre de Recherches Pétrographiques et Géochimiques, Université de Lorraine

Nitrogen occupies approximately 78% of the Earth's atmosphere and is one of the essential elements of life. The abundance of nitrogen normalized by carbonaceous chondrite in the bulk silicate Earth (BSE) appears to be depleted compared to other volatile elements and understanding the cause of this apparent depletion is a key to unraveling nitrogen behavior in the evolution of the Earth. Especially, nitrogen behavior in the deep parts of the Earth such as the lower mantle is not clearly understood.

In this study, we experimentally investigated the temperature dependence of nitrogen solubility in bridgmanite which occupies approximately 75 wt.% of the lower mantle. The experimental temperature ranged from 1400 °C to 1700 °C at 28 GPa in the redox state corresponding to the shallow lower mantle. In our research, ¹⁵N-substituted ammonium nitrate was used as a nitrogen source and all experiments were conducted in a nitrogen-saturated condition. The nitrogen content of the run products was analyzed using secondary ion mass spectrometry. The maximum nitrogen solubility in bridgmanite (MgSiO₃) increased from 1.8±0.4 to 5.7±0.8 ppm with increasing temperature from 1400 °C to 1700 °C. The nitrogen solubility in bridgmanite was not dependent on the Al₂O₃ content.

The nitrogen solubility in bridgmanite obtained in this study was not as high as that in the previous study by Yoshioka et al. (2018), where nitrogen solubilities in bridgmanite ranged from 5.8 ppm to 53.9 ppm. However, the nitrogen solubilities determined in this study are in good agreement with the minimum values previously reported. The difference in nitrogen solubility in bridgmanite between our study and the previous report could be caused by the coexistence of ringwoodite which has high nitrogen solubility up to 283 (±3.8) ppm (Yoshioka et al., 2018).

As bridgmanite was the first mineral to crystallize in a cooling magma ocean, our study suggests that it played an important role in preserving nitrogen through solidification of the Earth's magma ocean. The nitrogen storage capacity of Mg-endmember bridgmanite under the current temperature conditions is 3.4 PAN (PAN: mass of present atmospheric nitrogen). Furthermore, the nitrogen solubility of bridgmanite increases with increasing temperature, in contrast to the nitrogen solubility of metallic iron. Thus, the nitrogen storage capacity of bridgmanite can be larger than that of metallic iron during the solidification of the magma ocean. Such formation of a "hidden" nitrogen reservoir by bridgmanite in the lower mantle may have controlled the coevolution of the atmosphere and the mantle by lowering the apparent nitrogen abundance ratio of other volatiles in the BSE.

USING RAMAN SPECTROSCOPY TO CHARACTERIZE THE COMPOSITION OF MINERAL INCLUSIONS IN NATURAL DIAMONDS

Anastasiya D. Kalugina^{1,2} (anastaskalugina@gmail.com), Dmitry A. Zedgenizov^{1,3}

¹*Institute of Geology and Geochemistry UB RAS, Ekaterinburg, Russia*

²*Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia*

³*Ural State Mining University, Ekaterinburg, Russia*

Mineral inclusions in natural diamonds carry an important information about the chemical and physical parameters of the Earth's mantle. Most of inclusions in diamonds belong to either peridotite (P-type - olivine (forsterite), orthopyroxene (enstatite), garnet (Cr-rich pyrope), clinopyroxene (Cr-diopside)) or eclogite (E-type - garnet (pyrope-almandine-grossular), clinopyroxene (omphacite)) parageneses. Raman spectroscopy is a non-destructive technique often used to analyze the spectroscopic features of inclusions in diamonds. This study presents data on the Raman spectroscopic characteristics of the inclusions and links Raman features to their chemical composition.

The studied olivine inclusions show variations in chemical composition within the range: SiO₂ 40.0–42.2 wt.%, Cr₂O₃ <0.13 wt.%, MgO 48.2–51.5 wt.%, MnO <0.15 wt.%, FeO 6.30–9.43 wt.%, CaO <0.06 wt.%, Mg# 0.900–0.935. The most intense Raman peaks (DB1 and DB2) in the spectrum of studied olivine inclusions form a doublet consisting of five vibrational modes (2A_g + 2B_{1g} + B_{2g}). The frequencies position of these peaks vary between 822.4–824.9 cm⁻¹ (DB1) and 854.7–858.3 cm⁻¹ (DB2). Significant positive correlations were found between the shifts of these peaks and Mg# (r-correlation coefficient = 0.66 for the BD1, and r = 0.69 for the BD2). The observed correlations confirm that the shift of the DB1 and DB2 reflects forsterite-fayalite isomorphism. The chemical composition of the studied orthopyroxene inclusions in natural diamonds varies within the following ranges: SiO₂ 55.5–58.5 wt.%, MgO 33.6–36.7 wt.%, FeO 4.10–6.88 wt. %, Al₂O₃ 0.12–0.78 wt.%, Cr₂O₃ 0.13–0.45 wt.%, CaO 0.18–0.82 wt.%, Mg# 0.917–0.932. In the spectra of the orthopyroxene inclusions for the stretching vibration modes (ν₁₁, ν₁₂) the Raman shifts of 661.5–665.9 cm⁻¹ and 682.1–688.2 cm⁻¹ were observed. Positive correlations for the ν₁₁ and ν₁₂ modes was observed with the Mg# (r = 0.59 for ν₁₁ and r = 0.55 for ν₁₂). The revealed correlations testify to the influence of the enstatite–ferrosilite isomorphism on the mode shifts in the Raman spectrum of orthopyroxene. The studied P-type clinopyroxene inclusions are Cr-rich diopside (Cr₂O₃ 0.31–5.74 wt.%, CaO 12.81–22.9 wt.%, MgO 12.25–18.3 wt.%, FeO 1.81–3.45 wt.%, Al₂O₃ 0.31–5.41 wt.%, Na₂O 0.28–5.09 wt.%). The E-type clinopyroxene inclusions are omphacites (Na₂O 3.12–8.12 wt.%, Al₂O₃ 4.46–17.9 wt.%, CaO 9.81–17.2 wt.%, MgO 5.65–15.1 wt.%, FeO 2.22–11.4 wt.%, Cr₂O₃ < 0.3 wt.%). For studied clinopyroxene inclusion, the peak positions of the stretching O-Si_{br} mode vary in the range up to 23 cm⁻¹ (665.6–675.5 cm⁻¹ for the P-type inclusions, and 673.8–688.2 cm⁻¹ for the E-type inclusions). Several correlations for the Raman shift of the ν₁₁ mode were detected: two positive correlations with Na₂O (r = 0.95) and Al₂O₃ (r = 0.97) and two negative correlations with CaO (r = -0.88) and MgO (r = -0.92). The correlations reflect jadeite-diopside isomorphism and can potentially be applied to evaluate the chemical composition of mantle clinopyroxenes. Studied P-type garnet inclusions are Cr-rich pyropes (MgO, 16.1–23.9 wt.%, FeO, 5.92–8.44 wt.%, CaO,

0.92–9.75 wt.%, Cr_2O_3 3.91–17.1 wt.%). Studied E-type Garnets compositionally vary in the ranges (MgO 7.76–15.9 wt.%, CaO 3.93–13.4 wt.%, FeO 12.4–20.3 wt.%, Cr_2O_3 <0.19 wt.%). Raman spectra of garnets reveal several most intense peaks which can be assigned to stretching (ν_1) and bending (ν_2) vibrations of the Si-O bond. The P-type garnets show wavenumber ranges of 546.7–559.6 cm^{-1} for ν_2 , and 910.9–928.8 cm^{-1} for ν_1 . The E-type garnets have frequency ranges of 554.5–558.7 cm^{-1} for ν_2 , and 907.5–918.1 cm^{-1} for ν_1 . The shifts of intense modes for garnet inclusions generally correlated with chemical composition. The P-type garnets show a positive ($r = 0.83$) and negative ($r = -0.85$) correlations between position of ν_1 and MgO and CaO, respectively. Also for the P-type garnets ν_2 mode position correlates with Al_2O_3 ($r = 0.89$) and Cr_2O_3 ($r = -0.87$). The E-type garnets show similar correlations between ν_1 mode and MgO ($r = 0.86$) and CaO ($r = -0.97$) contents. The most expressed correlations may be used to evaluate garnet inclusions composition by Raman spectroscopy.

The work was supported by Russian Science Foundation (grant No. 22-17-00177).

In situ observation and Raman spectroscopic studies on the formations of hydrocarbon fluids under subduction zone conditions

Naoko Takahashi¹ (ntakahashi@eqchem.s.u-tokyo.ac.jp), Hiroki Kobayashi¹, Hiroyuki Kagi¹
¹ Graduate School of Science, The University of Tokyo

Carbon speciation in the Earth's interior is critical for understanding global carbon cycling. Recent theoretical models have predicted that most dissolved carbon may exist as organic carbon species such as acetate under specific redox and pH conditions in subduction zones (Sverjensky et al., 2014 [1]). Huang et al. (2017) [2] experimentally demonstrated that aqueous sodium acetate solution forms immiscible hydrocarbon fluids at 300 °C and 2.4–3.5 GPa. Furthermore, their theoretical calculations suggested that the immiscible hydrocarbon fluids are stable in the presence of silicate rock assemblages under subduction zone conditions, which could potentially play a role in carbon transport. Motivated by the previous experimental work and theoretical predictions, our experiments are underway to examine the formation of hydrocarbon fluids from aqueous sodium acetate solutions and their immiscibility in the absence and presence of silica at temperatures (T) up to 300 °C and pressures (P) up to 3 GPa. We carried out the experiments in a hydrothermal diamond anvil cell. In all the experimental series, no gas mixture with hydrogen was used because the permeation of hydrogen could affect the redox state in the sample chamber. Our experiments combined with Raman spectroscopy and optical microscopic observations under in situ and quenched conditions. For determining pressures at elevated temperatures using a zircon Raman pressure scale, we also attempted to optimize the zircon pressure scale as a consistent pressure determination standard by Raman scattering and synchrotron X-ray diffraction experiments at simultaneous high P – T conditions up to 9 GPa and from 300 to 773 K. Ruby and the equation of state of gold were used as internally consistent standards for the calibration.

We observed that aqueous sodium acetate solutions in the absence of silica minerals undergo the precipitation of Na_2CO_3 crystals upon heating and pressurization to the target conditions. In contrast to the earlier work, our results showed that a significant amount of optically visible immiscible fluids was not observed during the retention time of approximately three hours. Furthermore, the experiments with silica minerals showed no precipitation of Na_2CO_3 crystals and the absence of immiscible fluids during the retention time. Clear evidence for light hydrocarbons was not observed in all the Raman spectra under in situ conditions; however, the C-H stretching mode of methane molecules was detected in the gas bubbles generated during quenching and decompression. The present results, therefore, do not support the immiscibility of hydrocarbon fluids produced from aqueous acetate solutions in equilibrium with silica in deep subduction zone environments unless heavier hydrocarbons form through further specific reactions. In the presentation, the possible factors for controlling the immiscible hydrocarbon formations in the earlier work, the comparison between the existing thermodynamic modeling and the present experimental data, and the implications of the new data within the deep carbon cycle will be further discussed.

References: [1] Sverjensky *et al.* (2014) *Nature Geoscience*, 7(12), 909-913. [2] Huang *et al.* (2017) *Nature communications*, 8(1), 1-8.