Crystal chemistry of hydrogen and water storage in planetary interiors

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The crust and mantle of the Earth are made of oxygen minerals. Hydrogen solubility in these minerals controls the abundance of water on the surface and hence the possibility of life on terrestrial planets. Hydrogen can be incorporated in nominally hydrous minerals such as Phase B, superhydrous phase B, phase D, and phase H, or in nominally anhydrous minerals. In the upper mantle and transition zone, the nominally anhydrous minerals may be the principal host phases for H and are capable of incorporating many times the amount of water in the surface oceans.

In the nominally anhydrous minerals at the atomic scale H does not behave like any other cationic substituent. It bonds to a single oxygen with an inter-nuclear distance of less the nominal radius of the oxygen anion to form a hydroxyl anion. Although it does require charge balance, typically a cation vacancy, it does not substitute at cation sites. This has significant impact on elastic properties. The cation vacancies increase the molar volumes and decrease density as well as bulk and elastic moduli. By measurement of the effects of hydration on elastic properties of the nominally anhydrous major minerals of various regions of the mantle it possible to estimate the presence of water. The velocity structure of the Earth is consistent with significant hydration in the upper mantle and transition zone.

In nominally hydrous minerals, with a few notable exceptions, the hydroxyl does not bond to Si, or other high-charge cations, such as C, N, P, or S. In nominally anhydrous minerals, oxygen sites that can be partially protonated to form the hydroxyl can be predicted from Madelung electrostatic site energy calculations. These calculations predict significant hydration in wadsleyite and ringwoodite and limited hydration in olivine. They also predict potential limited hydration in bridgmanite.

Keywords: Water, Crystal Chemistry, Earth's interior

Role of water in subduction zone magmatism

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Arc magmas are hydrous reflecting water from the subducted oceanic plate and subsequent hydrous melting of the mantle. Both water and water-mobile elements are rich in the arc magmas which exert formation of the arc's crust thus the Earth's continent. Arc magmatism is a complex process occurring in such the dynamic system with the enigmatic water-bearing chemical reactions. This presentation aims to describe the processes of arc magma genesis based on chemical mass balance between the magmas and their source materials. The petrology/geochemistry-based mass balance model uses elemental-isotopic compositions and explores intensive-extensive parameters which control the chemistries. The determined parameters are then used to constrain the genetic conditions of the arc magmas and the dynamics of both the liquids and solids. The examinations focus on the contrasting NE and SW Japan arcs where the globally coldest and the hottest endmember subductions are taking place.
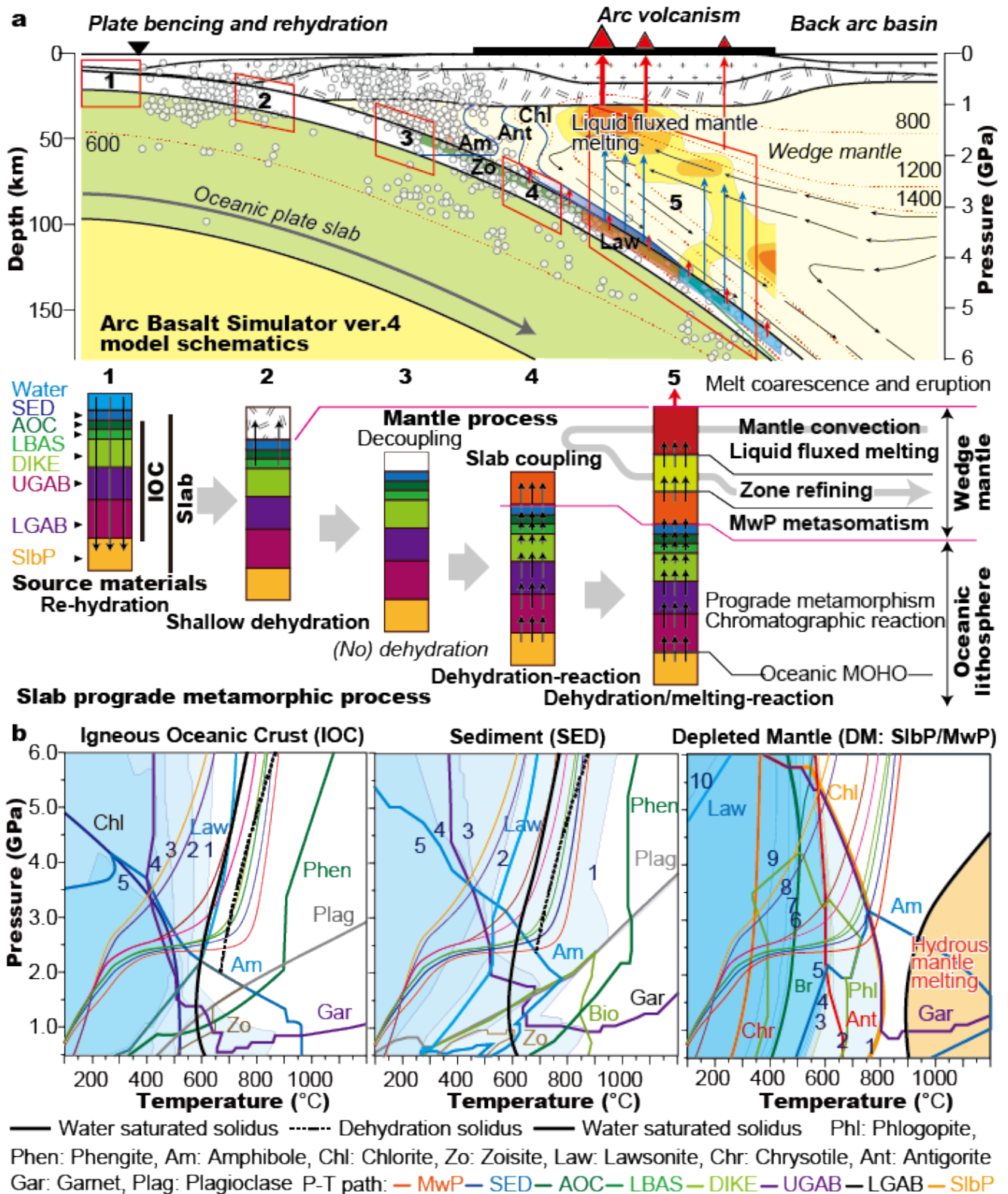
Keywords: Subduction zone, Water, Magma

a

Plate bencing and rehydration ▼   Arc volcanism   Back arc basin

1

2

600

3

Oceanic plate slab

4

Chl
Ant
Am
Zo
Law

Liquid fluxed mantle melting

5

800

Wedge mantle

1200

1400

Depth (km): 0, 50, 100, 150

Pressure (GPa): 0, 1, 2, 3, 4, 5, 6

Arc Basalt Simulator ver.4 model schematics

1   2   3   4   5   Melt coarescence and eruption

Water
SED
AOC
LBAS
DIKE
UGAB
LGAB
SlbP

IOC   Slab

Source materials
Re-hydration

Mantle process
Decoupling

Shallow dehydration

(No) dehydration

Slab coupling

Mantle convection
Liquid fluxed melting
Zone refining
MwP metasomatism

Wedge mantle

Prograde metamorphism
Chromatographic reaction

Oceanic MOHO

Oceanic lithosphere

Dehydration-reaction

Dehydration/melting-reaction

Slab prograde metamorphic process

b

Igneous Oceanic Crust (IOC)

Chl, Law, Phen, Plag, Am, Zo, Gar

Sediment (SED)

Phen, Plag, Law, Am, Gar, Bio, Zo

Depleted Mantle (DM: SlbP/MwP)

Law, Chl, Am, Hydrous mantle melting, Gar, Chr, Br, Phl, Ant

Pressure (GPa): 6.0, 5.0, 4.0, 3.0, 2.0, 1.0

Temperature (°C): 200, 400, 600, 800, 1000

—— Water saturated solidus   ---- Dehydration solidus   —— Water saturated solidus   Phl: Phlogopite,
Phen: Phengite, Am: Amphibole, Chl: Chlorite, Zo: Zoisite, Law: Lawsonite, Chr: Chrysotile, Ant: Antigorite
Gar: Garnet, Plag: Plagioclase P-T path: — MwP — SED — AOC — LBAS — DIKE — UGAB — LGAB — SlbP

Fig. 4.4.1 Schematic cross section of a subduction zone and the Arc Basalt Simulator ver.4 model description (panel a). Phase relations and maximum bound water in igneous oceanic crust, sediment, and depleted peridotite (panel b), modified from Kimura et al. (2012). Acronyms of the slab layers are MwP: mantle wedge peridotite, SED: sediment, AOC: altered oceanic crust, LBAS: lower basalt, DIKE: dike, UGAB: upper gabbro, LGAB: lower gabbro, and SlbP: slab peridotite.

Mantle melting and volatiles: Redox-controlled solution behavior in silicate-COH magmatic systems

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The behavior of hydrogen-bearing fluids and magmatic liquids is at the core of understanding formation and evolution of the Earth, its oceans, and atmosphere. To advance this knowledge, infrared and Raman spectroscopy has been employed for melt structural characterization and for determination of hydrogen and carbon isotope partitioning within and between melts and fluids in alkali aluminosilicate–C-O-H systems contained in externally-heated diamond anvil cells. The measurements were carried out in-situ under equilibrium conditions while the samples were at the temperatures, pressures, and redox conditions corresponding to those of the Earth's upper mantle and deep crust.

Hydrogen as H_2O is the major component of the silicate Earth. Its solubility in magma can reach >30 wt% under crustal and upper mantle conditions. The CH_4 and H_2 solubility is in the 0.1-1 wt% range, and CO_2-solubility typically 1-5 wt%. These variations reflect bulk chemical and, therefore, structural control of solubility. Water dissolved in magmatic liquids to form predominantly Si-OH and Al-OH bonding together with molecular H_2O. The OH/H_2O ratio is positively correlated with SiO_2 and Al_2O_3 concentrations in melts. The carbon solution equilibria are, $2CH_4+Q^n=2CH_3+H_2O+Q^{n+1}$ and, $2CO_3+H_2O+2Q^{n+1}=HCO_3+2Q^n$, under reducing and oxidizing conditions, respectively. In the Q^n-notations, the superscript, n, in the Q^n-species denotes number of bridging oxygen in the silicate species (Q-species). The abundance ratios, CH_3/CH_4 and HCO_3/CO_3, increase with temperature.

The resulting structural changes result in hydrogen and carbon isotope fractionation factors between melt, fluid, and crystalline materials significantly different from 1 even at magmatic temperatures. The D/H and fractionation between aqueous fluid and magma are also temperature dependent with a small enthalpy change near -5 kJ/mol. In silicate-C-O-H systems, the enthalpy-values for $^{13}C/^{12}C$ fractionation factors are near -3.2 and 1 kJ/mol under oxidizing and reducing conditions, respectively. These differences reflect different energetics of O-D, O-H, O-^{13}C, and O-^{12}C bonding environments governed by different solution mechanisms in melts of the individual volatile components.

From experimentally-determined temperature- and pressure-dependent D/H fractionation between fluids and melts, it is suggested suggest that (C-O-H)-saturated partial melts in the upper mantle can have dD-values 100%, or more, lighter than coexisting silicate-saturated fluid. This effect is greater under oxidizing than under reducing conditions. Analogous relationships exist for $^{13}C/^{12}C$ with $\partial^{13}C$-differences between silicate melts and coexisting CO_2+H_2O (oxidizing) and $CH_4+H_2O+H_2$ (reducing) fluid and at magmatic temperatures in the Earth's upper mantle increases with temperature from about 40 to > 100‰ and 80 –120 ‰under oxidizing and reducing conditions, respectively. The use of hydrogen and carbon isotopes of mantle-derived magma to derive isotopic composition of upper mantle source regions, therefore, is discouraged as these are affected by temperature, bulk composition, and redox conditions during melting, crystallization, and degassing events.

Keywords: Stable isotopes, melting, structure, fluid, melt, spectroscopy

Importance of being salty: Elemental partitioning between melts and aqueous fluids and salinity of fluid inclusions from subduction channels and mantle wedges

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In order to understand seawater recycling in subduction zones, we determine the salinity of natural fluid inclusions in harzburgites from the mantle wedge (Kawamoto et al., 2013, PNAS, Kumagai et al., 2014 CMP) and jadeitites from serpentine mélanges of Southwest Japan and Dominican Republic.

High-pressure and high-temperature experiments suggest that saline fluids can effectively transport large-ion-lithophile elements (Kawamoto et al., 2014, Earth Planets and Space) and carbonate (Newton and Manning, 2002, American Mineralogist). In natural specimens, subduction-zone fluids contain more or less amounts of salt. The salinity of aqueous fluids in the mantle wedge seems to decrease from trench side to back-arc side: from 5.1 wt% NaCl equivalent in harzburgite xenoliths of the Pinatubo, a frontal volcano of the Luzon arc, the Philippines [Kawamoto et al., 2013 Proc Natl Acad Sci USA] to 3.7 wt% NaCl equivalent in lherzolite xenoliths of the Ichinomegeta, a rear-arc volcano of the Northeast Japan arc [Kumagai et al., Contrib Mineral Petrol 2014]. Abundances of chlorine and H_2O in olivine-hosted melt inclusions also suggest that frontal basalts have higher Cl/H_2O ratios than rear-arc basalts in the Guatemala arc [Walker et al., Contrib Mineral Petrol 2003]. In addition to these data, quartz-free jadeitites contain fluid inclusions composed of aqueous fluids with 7 ±0.3 wt% NaCl equivalent and quartz-bearing jadeitite with 4.6 ± 1.2 wt% NaCl equivalent in supra-subduction zones in the Southwest Japan arc [Mori et al., 2015, International Eclogite Conference] and quartz-bearing jadeitites contain fluid inclusions composed of aqueous fluids with 4.3 ±1.3 wt% NaCl equivalent in Rio San Juan Complex, Dominica Republic [Kawamoto et al., 2015, Goldschmidt Conference]. Aqueous fluids generated at pressures lower than conditions for albite=jadeite+quartz occurring at 1.5 GPa, 500 °C may contain aqueous fluids with higher salinity than at higher pressures. All of these salinity data in natural fluid inclusions have values similar to or slightly greater than the value of seawater (3.5 wt% NaCl equivalent) and show decreasing salinity from trench to back-arc side in the mantle wedge and subduction channels.

Keywords: saline fluids, aqueous fluids, subduction zone, fluid inclusions, mantle wedge, magma

Serpentinized oceanic mantle and global water budget

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Hydration of oceanic mantle can occur along outer-rise faults that relate to the plate bending at close to the trench (Faccenda et al. 2009). This contributes an additional source of water into the Earth's interior, which might have larger water flux than that transported by hydrated oceanic crust. Recent seismic reflection survey has shown that seismic velocity in the oceanic lithosphere decreases at where bending-related faults are observed (e.g., Ranero et al. 2003; Fujie et al. 2013). Although these seismic data is not enough to image what extent of hydration occurs along the outer-rise faults, we modeled the thickness of serpentinization based on fluid percolation. When the reaction kinetics is much faster than the fluid access to the reaction front, the reaction rate is controlled by permeability through the hydrated layer (Macdonald and Fyfe 1985). Using laboratory measured permeability, the reaction thickness of serpentinization is estimated as thick as 18 km for a period from the initiation of outer-rise fault to the trench axis assuming a plate velocity of 10 cm/year. If outer-rise faults occur at depths shallower than 12 km, subduction water flux is estimated to be 2.5 x 10^{12} kg/year by hydrated oceanic mantle lithosphere, which is approximately twice as larger as that carried by hydrated oceanic crust. Since the subduction water flux is markedly larger than the output flux through magmatic degassing, the amount of present-day ocean is now decreasing and might be disappeared within 100 million years.

Keywords: serpentinite, oceanic mantle, water budget

Experimental investigations into the fate of water in Earth's transition zone

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The transition zone differs from the upper or lower mantle in that its major constituent minerals wadsleyite and ringwoodite can accommodate a significant amount of hydrogen in the crystalline structures. Translated into water storage capacities, hydrous wadsleyite or ringwoodite may contain several weight percent water, whereas the dominant minerals above or below the transition zone are nominally dry. The recent discovery of hydrous ringwoodite brought to the surface by a super-deep diamond indicates that transition zone is likely a sub-surface hydrosphere containing a comparable amount of water to the surface oceans. As a result of large contrast in water storage capacities, a wet transition zone is expected to dehydrate and form partially molten layers near its upper and lower boundaries when the interfaces are pushed downwards by descending slabs or upwards by rising plumes. Convection-induced dehydration of a wet transition zone may explain the seismically detected low-velocity zones near 410 and 660 km depths. In this study we test the hypothesis that dehydration is not limited to the interfaces but can take place in the interior of the transition zone following incipient melting of carbon-bearing materials that are carried to mid-mantle by subducted slabs. Experiments have been conducted using a multi-anvil apparatus to investigate the partitioning of hydrogen between hydrous wadsleyite or ringwoodite and coexisting carbonates or iron-carbon mixture at relevant high pressures and high temperatures. The results will be applied to understand the sources and sinks of water in Earth's transition zone and to elucidate the connections between the surficial and internal hydrospheres.

Keywords: transition zone, water, hydrous wadsleyite and ringwoodite, carbonates, iron-carbon mixture, melting

"Hydroxylation spectroscopy" of olivine tested on synthetic forsterite

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Olivine $(Mg,Fe)_2SiO_4$, the most abundant phase in the upper mantle, can incorporate a few ppm to
tens or even hundreds of ppm of water as hydroxide anions in its structure. Even at such low
concentrations, the presence of H^+ in the structure of olivine has a profound influence on its
physical properties and, consequently, geologic processes such as mantle convection and partial
melting. The incorporation of H^+ in olivine is mediated by a variety of hydrous point defects,
related to Si^{4+} and Mg^{2+} vacancies, or coupled substitution with Ti^{4+} or trivalent cations (*e.g.*, Al^{3+}
). These different types of hydrous point-defects can be fingerprinted using infrared spectroscopy.
The point defect chemistry of olivine depends on parameters such as silica activity or oxygen
fugacity, which are inherent to the last equilibrium conditions of the olivine. If the relaxation
of the high-temperature point defect structure is slow compared to the rapid diffusion of H^+ into
the crystal, then "decorating" the existing point-defect structure of an olivine by experimentally
diffusing H^+ into it potentially makes its point-defect structure visible to identification using
infrared light, thus revealing information about its geologic history. Here we present experimental
results to test whether we can illuminate the pre-existing point defect structure of synthetic
forsterite (Mg_2SiO_4) prepared under controlled conditions of temperature, silica activity and
oxygen fugacity, as a first step towards seeing how effective this technique of "hydroxylation
spectroscopy" may be in illuminating the point defect chemistry of natural mantle olivine crystals.
Experiments were performed with cubes of synthetic forsterite in a piston cylinder apparatus. The
forsterite cubes were annealed at temperatures ranging between 1100 and 1500 °C for 8 days, in
contact with Forsterite-Enstatite (Fo-En) or Forsterite-Periclase (Fo-Per) silica activity buffers.
Annealed and un-annealed cubes were then loaded in silver capsules along with liquid water and a
combination of silica activity and oxygen fugacity buffers. Hydroxylation of the cubes was done at
900°C and 1.5 GPa. Unpolarized and polarized infrared spectra were acquired along the principal
axis of the crystals, along profiles of a few hundred micrometers. From those spectral profiles,
diffusion coefficients were quantified and the diffusion mechanisms inferred, using the unique
infrared signature of each type of defect.
Results show that H^+ diffuses faster than expected in [Si] vacancies, such that this mechanism may
contribute as much as H^+ diffusion in [Mg] vacancies to the global diffusion of "water" in
Forsterite. The hydroxylation experiments further allow us to assess how the initial annealing
conditions of the crystals influence the diffusion mechanism of H^+.

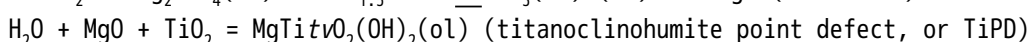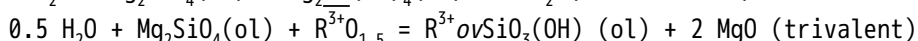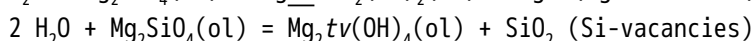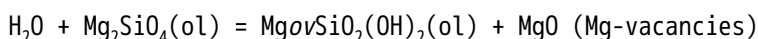Keywords: Olivine, Water, Diffusion, Hydroxylation, Infrared spectroscopy

Hydrogen incorporation in olivine

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The main silicate phases of the Earth's upper mantle, namely olivine, pyroxenes and garnet, do not
have hydrogen as an essential component of their crystal structures, but they can contain
geologically significant amounts of hydrogen as a trace element, substituting by point-defect
mechanisms. In the context of hydrogen storage, these phases have therefore become known as
"Nominally Anhydrous Minerals" or NAMs. The good correlations of H with incompatible trace elements
like the light Rare Earth Elements (e.g., Ce) in suites of mid-ocean-ridge and ocean-island basalts
(MORBs and OIBs) confirms the essentially trace-element-like behaviour of H. The H in NAMs occurs
bonded to the oxygen anions (O^{2-}) in their crystal lattices, forming hydroxyl species (OH^-), and
charge-balanced by cation vacancies with or without the coupled substitution of cations with
different charge to those in the stoichiometric crystals. The presence of the OH^- anions is readily
detected by infra-red spectroscopy, due to the good absorbance of the O-H stretching modes in the
infra-red. Moreover, the O-H stretching modes are sensitive to next-nearest-neighbour effects,
which may be used to deduce the nature of the H substitution mechanisms.

For Mg_2SiO_4-rich olivine, the most abundant phase in the upper mantle, experiments show that four
different substitution mechanisms are commonly encountered, each identifiable by its characteristic
infra-red fingerprint: those associated with Mg and Si vacancies, with 3+ cations, and with Ti^{4+}.
Note that other H substitution mechanisms in olivine may exist under special circumstances, e.g.,
in olivines containing boron. The four main substitution mechanisms can be represented by the four
equilibria:

$H_2O + Mg_2SiO_4(ol) = Mg\underline{ov}SiO_2(OH)_2(ol) + MgO$ (Mg-vacancies)

$2\ H_2O + Mg_2SiO_4(ol) = Mg_2\underline{tv}(OH)_4(ol) + SiO_2$ (Si-vacancies)

$0.5\ H_2O + Mg_2SiO_4(ol) + R^{3+}O_{1.5} = R^{3+}\underline{ov}SiO_3(OH)\ (ol) + 2\ MgO$ (trivalent)

$H_2O + MgO + TiO_2 = MgTi\underline{tv}O_2(OH)_2(ol)$ (titanoclinohumite point defect, or TiPD)

where $\underline{ov}$ and $\underline{tv}$ stand for octahedral and tetrahedral cation-site vacancies, respectively.
The H concentrations controlled by each of these four equilibria will in principle respond
differently to temperature and pressure, and to chemical environment, specifically, to the activity
of silica (a_{SiO2}), and the availability of trivalent cations and Ti. Importantly, the stoichiometry
of the substitution mechanisms implies that they may also respond differently to $f(H_2O)$, if
short-range ordering maintains the local charge balance implied by the substitution formulae; such
short-range ordering seems required by the distinctiveness of the infra-red fingerprints. With
short-range order, the concentration of H associated with trivalent cations would depend on $f(H_2O)^{1/2}$, with Mg-vacancies and TiPD on $f(H_2O)$, and with Si-vacancies on $f(H_2O)^2$. New experiments on H
incorporation in $Mg_2SiO_4(ol)$ doped with Sc and Ti at 15 kb and 1050ºC, with $f(H_2O)$ controlled at
different values using H_2O-NaCl mixtures, confirm this hypothesis. This means that results from
experiments at high $f(H_2O)$ (e.g., with $p(H_2O)$ = P_{total}) cannot be applied directly to natural
situations where $p(H_2O)$ << P_{total}.The different substitution mechanisms are also associated with very
different diffusion rates of H through olivine, and it is likely that they affect physical
properties differently too.

Keywords: Hydrogen, Olivine, Nominally Anhydrous Minerals, Mantle

Hydrogen mobility in transition zone silicates

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Hydrogen defects in mantle silicates adopt a variety of charge-balanced defects, including $V_{Mg}''+2(H*)$, $V_{Si}''''+4(H*)$, and $V_{Si}'+(Mg+2H*)$. Constraining the defect mechanism experimentally can be quite difficult, as it relies almost entirely on vibrational spectroscopy whose interpretation can often be controversial. Here we use a computational alternative: we study the above-mentioned defect mechanisms using molecular dynamics simulations based on the density-functional theory, in the VASP implementation. We perform isokinetical NVT simulations at 2000 and 2500 K using supercells containing 16 equivalent formula units of Mg_2SiO_4.

Our results show that temperature has a tremendous effect on mobility. H is significantly more mobile when incorporated as $V_{Mg}''+2H*$ defects than as hydrogarnet defects and that $V_{Mg}''+2H*$ defects are more mobile in wadsleyite than ringwoodite. This result is the opposite from the proton conductivity inferences of Yoshino et al. [2008] and Huang et al [2006], as well as the observed increase in electrical conductivity with depth through the transition zone [e.g. Kuvshinov et al, 2005; Olsen 1998].

Over the simulation time of several tens of picoseconds the H travel over several lattice sites. However, during its path it spends a considerable amount of time pinned in the defect sites. The lowest mobility is for the $V_{Si}''''+4(H*)$ defect, where the H atoms remain inside the octahedron from which they replaced the Si.

Keywords: diffusion, molecular dynamics, mantle silicates

Sound velocities of delta-AlOOH up to lowermost mantle pressures; Implications for the seismic anomalies in deep mantle

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It is widely recognized that the presence of water in the deep Earth's interior, which may be transported to such depths by various hydrous minerals in subducting slabs, can significantly affect the physical and rheological properties of the mantle. Most hydrous minerals become thermodynamically unstable under the pressure-temperature conditions corresponding to the upper part of the upper mantle (e.g., Ohtani, 2006). However, recent experimental data indicate that the hydrous mineral delta-AlOOH can be stable throughout the lowermost mantle (Sano et al., 2008; Ohira et al., 2014; Ohtani et al., 2014). This phase is, therefore, a possible carrier and host of water in the deep mantle. To uncover the physical properties of delta-AlOOH under deep mantle pressure conditions, we have conducted high-pressure acoustic wave velocity measurements of delta-AlOOH by using Brillouin spectroscopy combined with high-pressure Raman spectroscopic measurements in a diamond anvil cell up to pressures of 134 GPa. There is a precipitous increase by ~14% in the acoustic velocities of delta-AlOOH from 6 to 15 GPa, which suggests that pressure-induced O-H bond symmetrization occurs in this pressure range. The best fit values for the high-pressure form of delta-AlOOH of K_0 = 190 (2) (GPa), G_0 = 160.0 (9) (GPa), $(\partial K/\partial P)_0$ = K_0' = 3.7 (1), and $(\partial G/\partial P)_0$ = G_0' = 1.32 (1) indicate that delta-AlOOH has a 20–30% higher V_S value compared to those of the major constituent minerals in the mantle transition zone, such as wadsleyite, ringwoodite, and majorite. On the other hand, the V_S of delta-AlOOH is ~7% lower than that of bridgmanite under lowermost mantle pressure conditions. By comparing our results with seismic observations, we can infer that delta-AlOOH could be one of the potential causes of a positive V_S anomaly observed at ~600 km depth beneath the Korean peninsula and a negative V_S jump near 2800 km depth near the northern margin of the large low-shear-velocity province beneath the Pacific.

Keywords: delta-AlOOH, Brillouin scattering, seismic anomaly, transition zone, lower mantle

In-situ observation of hydrogen-bond symmetrization in δ-AlOOH and its isotope effect

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Hydrogen bond is unique compared to the other covalent bond that makes a framework of minerals. Generally hydrogen bonds covalently to one side of oxygen while it forms hydrogen bond with the other side of oxygen, which is longer and soft bond. Applying pressure to this asymmetric geometry induces the decrease of O...O distance and results in various interactions with surrounding atoms. These changes are unquenchable to ambient pressure thus *in-situ* neutron diffraction experiment is indispensable to shed the light on hydrogen bond under high-pressure.

Aluminus hydrous mineral δ-AlOOH [1] has a strong hydrogen bond in its distorted rutile type structure at ambient conditions. Its stability field expands in wide pressure and temperature range, from 18 GPa to 134 GPa, and up to 2300 K [2] and considered as an important water carrier into the lower mantle. Ab-initio calculations pointed out that the hydrogen locates at the center between two oxygen atoms at high-pressure, which is so-called "symmetrization" of hydrogen bond [e.g. 3]. It is also suggested that the increase of bulk modulus is induced by the symmetrization. Subsequent X-ray diffraction study found that the bulk modulus increases at around 10 GPa for δ-AlOOH and 12 GPa for δ-AlOOD. Neutron diffraction study was conducted to 9.2 GPa but the hydrogen bond remains asymmetric in this pressure range [4].

To observe pressure-induced hydrogen-bond symmetrization directly, we conducted high-pressure neutron diffraction experiments to 18.1 GPa. The samples of δ-AlOOH and δ-AlOOD were synthesized at 18 GPa and 800-900 °C using a multi-anvil press. The synthesized sample and deuterated methanol-ethanol pressure-transmitting medium were loaded into a TiZr gasket in a Paris-Edinburgh press. Neutron diffraction patterns were corrected at the high-pressure neutron diffractometer "PLANET" in the MLF, J-PARC. The crystal structure including a hydrogen and deuterium position was refined by Rietveld method.

In δ-AlOOH, the disappearance of 021 reflection was observed at high-pressure. This observation can be attributed to the transition from the space group of $P2_1nm$ with asymmetric hydrogen bond to that of $Pnnm$ with disordered or symmetric hydrogen bond. The transition pressure of 8.4 GPa is consistent with our previous single crystal X-ray diffraction experiment. On the other hand the transition pressure of δ-AlOOD was determined to be 12.1 GPa, which is higher than that of δ-AlOOH. The O...O distance of hydrogen bond decreases significantly compared to other O...O distances below the transition but it becomes less compressible above the transition pressure. The result reveals that the small change of hydrogen position can induce the significant change of compression behavior. To discuss the detail hydrogen distribution in the $Pnnm$ structure, the difference Fourier map was obtained from the difference between the observed diffraction pattern and the refined model without hydrogen. The result will be presented in the paper.

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Keywords: hydrogen bond, neutron diffraciton experiment, high pressure, isotope effect

Hydrogen solubility into Fe-alloys under high pressure

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Hydrogen, the most abundant element in the solar system, is known to incorporate into Fe and form FeHx above 3 GPa. The solubility of H in Fe is closely linked to light element in the terrestrial core and H reservoir in the planet interiors. In order to understand more realistic case of H in planet interiors, H solubility into Fe-alloys (such as Fe-Si, Fe-C, and Fe-S) needs to be clarified.
In this study, we have performed in situ X-ray diffraction measurements combined with Kawai-type multianvil press under high pressures and temperatures to study H solubility in FeSi and Fe3C. H solubility can be estimated from a volume expansion associated with hydrogen incorporation into metal. The lattice volumes and phase relations of FeSi-H and Fe3C–H systems were measured up to 19 GPa and 1973 K.
H starts to dissolve in FeSi and form FeSiHx (x=0.07-0.22) above 10 GPa, suggesting that presence of Si in metal increases the minimal pressure for H incorporation. H incorporation into Fe3C does not occur and H is unlikely to coexist with C in Fe-alloy up to 14 GPa (Terasaki et al. 2014). Therefore, hydrogenation pressures of Fe-alloys are different from that of pure Fe and more pressure is required for H incorporation into the Fe-alloy core.

Keywords: Hydrogen, Fe-alloy, core

Effect of pressure on water solubility in aluminous bridgmanite

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We have conducted a sequence of high pressure experiments to study water solubility in aluminous bridgmanite as a function of pressure at 1900°C. The experimental high pressures were generated using multi-anvil presses at Bayerisches Geoinstitut (BGI) for pressures up to 28 GPa and at Geodynamics Research Center (GRC) for pressures above 30GPa. The starting material for these experiments was a mixture of oxides ($Mg(OH)_2$, Al_2O_3 and SiO_2) with equivalent of about 5 mol % of Al_2O_3 and 15 wt % of H_2O. The structure and composition of the bridgmanite sample after high P/T syntheses were examined using x-ray diffraction (XRD) and electron probe microanalysis (EPMA). Water concentration in the sample was measured using secondary ion mass spectroscopy (SIMS) and Fourier transform infrared spectroscopy (FTIR). The measurements yield that the aluminous bridgmanite with about 2 wt% of Al_2O_3 may take as much as 0.13 wt % of H_2O at the P/T condition of the top of the Earth's lower mantle and this solubility increases significantly with pressure. At the bottom of Earth's lower mantle, bridgmanite may take nearly a couple of weight percent of water according to simple extrapolation of the experiment result, indicating that the capacity of water reservoir of the lower mantle can be as large as a few to ten oceans of water.

In-situ X-ray diffraction studies of hydrous phases up to ~50 GPa

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Recent experimental and theoretical studies suggest the high-pressure forms of hydrous minerals, phase H and delta-AlOOH, play important roles in transportation of water into the deep Earth's interior via subduction of oceanic slabs. Phase H forms a solid solution with delta-AlOOH by the substitutions of Mg^{2+} + Si^{4+} <-> $2Al^{3+}$ because of their similar crystal structure and volume. Since epsilon-FeOOH is also istostructural to $MgSiO_4H_2$ phase H and delta-AlOOH, delta-AlOOH likely form partial solid solutions with epsilon-FeOOH. However, experimental study shows that FeOOH component in delta-AlOOH is limited (~20 mol%) because of the much larger unit-cell volume of epsilon-FeOOH, in contrast to the complete solid solution between phase H and delta-AlOOH. On the other hand, spin transition of Fe in epsilon-FeOOH at ~50 GPa likely reduce its volume significantly, which may cause the compositional change of hydrous phase in the lower mantle. Thus, the unit-cell volume of hydrous phases at high pressures is important to understand the chemical composition of hydrous phase in the mantle.

Here, we report new experimental results on the X-ray diffraction studies of Phase H, delta-AlOOH, epsilon-FeOOH, and their solid solutions up to 50 GPa. In-situ X-ray diffraction measurements were performed using a multianvil apparatus (SPEED-Mk.II) at BL04B1, SPring-8. The unit-cell volume of $MgSiO_4H_2$ phase H is ~3% larger than those of pure delta-AlOOH and ~15% smaller than those of epsilon-FeOOH up to 50 GPa. However, the large volume reduction of epsilon FeOOH due to the spin transition of Fe was observed above ~50 GPa, resulting in the similar unit-cell volume with delta-AlOOH and phase H. Based on these experimental results, the chemical composition of hydrous phase in the lower mantle will be discussed.

Keywords: phase H, mantle, water

Reaction of MORB and water under the lower mantle

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High-pressure hydrous phases are considered to play important role for possible water reservoir in the Earth. The reaction between water and down welling slab into the lower mantle region containing mid-ocean ridge basalt (MORB) and surrounding minerals are important to understand water cycle in the mantle. Among the known hydrous minerals, Phase H has a deepest stability field up to ~60GPa in the $MgO-SiO_2-H_2O$ system (Ohtani et al., 2014) and ~128GPa in the $MgO-Al_2O3-SiO_2-H_2O$ (MASH) system (Ohira et al., 2014), suggesting possible transportation of water into the deep Earth.
Here we report the results of the direct reaction of the MORB + H_2O system under high-pressure and high-temperature to investigate the effect of iron and aluminum. We carried out in-situ X-ray diffraction experiments at High Energy Accelerator Research Organization (KEK), Photon factory (PF-AR). High pressure and temperature experiments were conducted using laser-heated diamond anvil cell installed at the station NE1A. Starting materials of glass MORB powder and pure water were confined in rhenium gasket. The pressure was measured using the equation of state of ice VII (Frank et al., 2013). The double-sided heating with Nd:YAG laser to heat, the reaction temperature was estimated from spectroradiometry of the high temperature portion of the sample. X-ray diffraction measurements to identify phases were performed using monochromatic x-ray with about 30keV and imaging plate detector at each step of elevated temperature to about 1000K. We identified the crystalline phases and the reaction products up to 35GPa under laser-heating condition. Ca-Perovskite, Stishovite and Phase D were observed as the reaction product in all runs. The results indicate an expanding of stability field to high pressure in Phase D than that of $MgO-SiO_2-H_2O$ system, we will present further results of SEM-EDS analysis of the recovery sample.

Keywords: MORB, DAC, water

Stability field of Phase D in hydrous basaltic system at the mantle transition zone

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The distribution of water in the mantle and its effects on mantle dynamics are significant to understand the evolution of the Earth. It's believed that the water is transported from the surface into deep mantle via a variety of hydrous minerals in the subducting oceanic slabs (Ohtani, 2015). However, stability of hydrous mineral(s) in basaltic system at the pressure temperature conditions equivalent to cold slabs in the transition zone, remains unclear.

High-pressure and high-temperature experiments were conducted in a hydrous basalt similar to primitive MORB composition (JB-2 basalt plus brucite, water content=3.5wt.%) at 17–25 GPa, and 800–1200°C using multi-anvil apparatus (SAKURA in Magma Factory) at Tokyo Institute of Technology. We used Au/Pt double capsules as sample containers. In runs below 20 GPa, the sample was loaded into an Au inner capsule and the oxygen fugacity was buffered at ~NNO by NiO + Ni + Ni(OH)$_2$ powder, which stuffed in the space between Pt outer capsule and Au inner capsule. Simple Au capsule was used in higher pressure runs. The run products were analyzed by FE-EPMA (JEOL-JXA8530F, ELSI Tokyo Institute of Technology). The water contents in hydrous phases were estimated from total deficits in FE-EPMA analyses.

The phase assemblages of the run products include majorite, stishovite, Ca-Ti perovskite, hollandite, silicate melts and hydrous phase(s). The hydrous phase is Fe-Ti hydroxide at pressures lower than 18GPa or Al-bearing phase D at pressures higher than 18GPa. These two hydrous phases coexisted in one experiment (18GPa, 900°C). Our results show that the phase D (containing 46–51 wt.% SiO_2, 19.1–20.6 wt.% MgO, 7.3–16.0 wt.% Al_2O_3, 3.8–5.1 wt.% FeO, 11–14 wt.% H_2O) is stable in wide pressure ranges of the mantle transition zone at pressures of 18–20 GPa and temperatures of 800–1000°C. In our experiments, the Al_2O_3 content and (Fe+Mg)/Si ratio of phase D increase with increasing pressure while MgO and FeO content remains constant, relatively. It is important to note that wadsleyite coexisting with Al-bearing phase D seemed to be nearly anhydrous in our experiment suggesting the importance of the subducting basaltic crust as a water carrier in mantle transition zone.

Consequently, we propose that the phase D is one of major water reservoir in cold subducting oceanic crust at the mantle transition zone. Moreover, if the subducting slabs stagnate at the bottom of the transition zone and warmed up, the water would be released from phase D in the subducting crusts, which may be the dominant way to hydrate the transition zone or to cause magmatism in back arc hot spots. Experiments at 25 GPa and 1000°C show coexisting bridgemanite, stishovite, Ca-perovskite, ferropericlase and very Al-rich phase D indicating that subducting clod MORB crust could be the major carrier of water from transition layer to the lower mantle by the Al-bearing phase D.

Keywords: water transportation to deep Earth, subducting oceanic crust, phase D

The stability of Topaz-OH II in the mantle transition zone

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Topaz-OH is one of the hydrous phases which would exist in the sedimentary layer of subducting slab. Kanzaki (2010) showed that Topaz-OH transforms to a high-pressure phase, Topaz-OH II, which was reported to be stable at least 13-14 GPa and 1300-1500 ℃. However, the stable conditions of Topaz-OH II are not determined well. Here, we report on the results of high-pressure and high-temperature experiments on the stability field of Topaz-OH II.
The starting material was prepared in the $MgO-Al_2O_3-SiO_2-H_2O$ system with the bulk composition of 4.27 wt.% MgO, 52.95 wt.% Al_2O_3, 28.47 wt.% SiO_2 and 14.30 wt.% H_2O. Experiments were carried out using a 1000-ton Kawai type multi-anvil press at Tohoku University. Semisinterd zirconia and platinum were used as pressure medium and sample container, respectively. The pressure was calibrated by the β-γ phase boundary of Mg_2SiO_4. In order to identify synthesized phases, X-ray diffraction measurements and Micro-Raman spectroscopy measurements were carried out at the Photon Factory in KEK, Tsukuba, Japan and at Tohoku University, respectively. Compositions of the recovered samples were determined using an electron probe microanalyzer (EPMA) at Tohoku University.
We found that hydrous phases of δ-AlOOH and phase egg were stable in the pressure range of 18-20 GPa and the temperature range of 1000-1300 ℃. Topaz-OH II was stable at 18 GPa and 1400 ℃, which is higher-pressure and -temperature condition than that reported previously. The composition of Topaz-OH II was 2.23(7) wt.% MgO, 55.24(13) wt.% Al_2O_3 and 31.46(21) wt.% SiO_2, (88.93(23) wt.% total) and its Al / Si ratio was 2.50(4). The lattice parameters of Topaz-OH II at ambient condition was a= 4.719(9) Å, b= 8.922(23) Å, c= 2.777(6) Å, and V_0=116.7(5) Å^3, which is consistent with the parameters reported by Kanzaki (2010).
Our results indicate that Topaz-OH II would be a potential candidate of the water carrier at the middle of the mantle transitions zone.

Keywords: Topaz, synchrotron X-ray diffraction, mantle transition zone, subducting slab

Stability of Phase H –δ-AlOOH solid solution in a hydrous peridotite and water cycle in the Earth's mantle.

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A number of high pressure and temperature (high P - T) experiments have been showing that various hydrous minerals can survive in a broad range of P - T conditions such as the conditions of slabs subducted in the deep mantle. A subdcuting slab consists of three rock layers; peridotite, oceanic crust (MORB) and sediment. A hydrous peridotite layer includes various dense hydrous magnesium silicates (DHMS), which can carry water as OH^- or proton in their structures but all of them decompose at the uppermost lower mantle (e.g., Ohtani, 2005). However, the new phase called Phase H ($MgSiO_4H_2$; space group, $Pnnm$ (Bindi et al., 2014)) was predicted to be stable at pressures up to 50 GPa and was synthesized by high P - T experiment (Tsuchiya, 2013; Nishi et al., 2014), suggesting that water stored in Phase H formed in a slab can be transported into the middle region of the lower mantle.

The stability field of Phase H depends strongly on Al content (Nishi et al., 2014, 2015; Ohira et al., 2014; Walter et al., 2015). Ohira et al. (2014) conducted *in-situ* high P - T experiments using a laser-heated diamond anvil cell (LHDAC) in $MgO-Al_2O_3-SiO_2-H_2O$ system simplified MORB composition. Their experiments indicated that Phase H –δ-AlOOH solid solution coexisted with Al-poor bridgmanite, and water stored in this solid solution may be transported to the lowermost mantle because of the broad stability field of δ-AlOOH (space group, $Pnnm$ above 8.2 GPa (Kuribayashi et al., 2014)) extending from the transition zone to the core-mantle boundary (CMB) conditions (Sano et al., 2008).

However, the possible existence of H –δsolid solution in realistic complex systems such as hydrous peridotite and MORB compositions has been unknown.

Here, we demonstrate the phase relations in hydrous peridotite system obtained from *in-situ* high P - T synchrotron X-ray diffraction measurements at BL10XU, SPring-8.

We used the gel-sample having the same composition as hydrous peridotite (bulk water content was 1.0 wt.%). LHDAC and YAG (Nd) or fiber laser were used for generation of high P - T conditions. In the first run, we only used the gel-sample without laser absorbers and pressure mediums. In the second run, the sample plate was sandwiched between Ir foils, and NaCl plates were put on the outer sides of Ir foils. *In situ* X-ray diffractions were measured at the pressure and temperature ranges of 69-84 GPa and 1910-2260 K in the first run and of 49-53 GPa and 1550-2210 K in the second run. Above 69 GPa, the coexistence of major anhydrous minerals in the lower mantle, bridgmanite (Brg), ferropericlase (Fp) and $CaSiO_3$-perovskite (Ca-Pv), was observed, while none of hydrous phases such as H –δsolid solution existed. On the other hand, the diffraction patterns of H –δsolid solution together with those of Brg, Fp and Ca-Pv were observed at pressures between 49 and 53 GPa, suggesting that the stability field of H –δsolid solution formed in a hydrous peridotite only extends up to the pressure conditions between 53 and 69 GPa. This decomposition boundary was consistent with the stability of pure phase H (Tsuchiya, 2013; Ohtani et al., 2014), implying that the composition of H –δsolid solution formed in a hydrous peridotite may be very close to pure-$MgSiO_4H_2$ Phase H.

Our results suggest the difference of water transport mechanisms between a peridotite layer and a MORB layer in a hydrous slab subducted in the lower mantle. Al-poor H –δsolid solution formed in a

hydrous peridotite layer may decompose and release H_2O-rich liquid at the middle of the lower mantle, while Al-rich H –δsolid solution formed in a hydrous MORB layer can be transported to the lowermost mantle.

Keywords: hydrous minerals, water cycle, in-situ XRD, Phase H, δ-AlOOH

Decomposition of hydrous phase D by the formation of Fe-bearing aluminous bridgmanite

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It has been considered that a certain amount of water is transported as hydrous minerals into the mantle through subduction of slab. Recent discovery of hydrous ringwoodite inclusion in a diamond suggests that the mantle transition zone is hydrous at least locally (Pearson et al. 2014). Next open question is whether the lower mantle can accommodate water or not. Although the major constituent minerals can host significant amounts of water in the upper mantle, most of the lower mantle minerals (e.g. bridgmantite (Brm) and ferropericlase (fPc)) can incorporate only a limited amounts of water. Therefore, if water is transported into the lower mantle, water must be hosted by dense hydrous minerals (DHMs) such as hydrous phase D. However, it is not clear whether DHMs can exist in the lower mantle because temperature of slab subducted into the lower mantle is not constrained well. Brm contains significant amounts of Fe^{3+} ($Fe^{3+}/\Sigma Fe > 0.1$) even in coexistence with metallic iron (Frost et al. 2004). The amounts of Fe^{3+} increase with increasing Al_2O_3 content in Brm, and the $Fe^{3+}/\Sigma Fe$ ratio exceeds 0.5 in the lower-mantle Brm (Frost et al. 2004; Frost and McCammon, 2008). Since the $Fe^{3+}/\Sigma Fe$ ratios are only 0.01-0.03 and 0.10-0.14 in the upper-mantle peridotite and MORB, the formation of Brm would extract oxygen from other minerals by the deposition of Fe metal. In other words, Brm should work as a reducing agent against other minerals. Therefore, we expect the breakdown of DHMs by reduction of OH to H_2 through the Brm formation. On the basis of this background, we conducted the following experiment using a Kawai-type multianvil press. A starting materials were used sintered Al-free and aluminous phase D pre-synthesized at 27 GPa and 1100 K, an natural olivine single crystal (Olv) and pyroxene aggregates with bulk composition of pyrolite minus fPc (Pyr-fPc) and $(Mg_{0.9}Fe_{0.1})(Si_{0.9}Al_{0.1})O_3$ (FeAl-En) synthesized at 1300 K in a controlled oxygen fugacity ($PO_2 \approx IW$) and ambient pressure. Pyroxene samples were packed in Mo capsule and sintered at 2 GPa and 1500 K. Sintered phase D was directly attached with Olv, sintered Pyr-fPc or FeAl-En in Au sample capsule. The samples were pressurized to 27 GPa and heated at 1100 K for 1 or 10 hours. Analyses of recovered samples were made with FE-SEM and ATEM.
No reaction between Al-free phase D and Brm + fPc aggregate formed from Olv was found in the SEM observation. The existence of 2-4 μm thick SiO_2-rich fine-grained layers were discovered on the boundary between Al-free / aluminous phase D and Brm formed from Pyr-fPc or FeAl-En. TEM observation indicated amorphous phases with Brm composition in fine SiO_2 stishovite. These observations strongly indicate that the decomposition of phase D accompanied by the formation of Fe-bearing aluminous Brm. The present result suggests that, although water can be transported into the top of the lower mantle due to the formation of phase D through subduction of slab, phase D will decompose by reduction at the depth to 720 km. The produced H_2 should come back to the upper mantle. Thus, water cannot be transported through slab subduction to the majority of the lower mantle.

Keywords: hydrous phase D, lower mantle, bridgmanite, subducting slab, water transportation, ferric iron

Compressibility of Al-bearing hydrous bridgmanite

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Water is the most important volatile component on the Earth, because it has significant influences on the chemical and physical properties of mantle minerals (e.g., melting temperature, electrical conductivity, and so on). The nominally anhydrous minerals (NAMs) can contain small amount of water. In particular, wadsleyite and ringwoodite which are the major constituent minerals in the mantle transition zone can contain ~2-3 wt% water (e.g., Inoue et al., 1995; Kohlstedt et al., 1996). Recently, hydrous ringwoodite contained ~1.5 wt% water was discovered by Pearson et al. (2014) as inclusion in ultra deep diamond. This observation implies that the mantle transition zone contains some water at least locally. On the other hand, water solubility of bridgmanite which is the most abundant mineral in the lower mantle, is a matter of debate (e.g., Bolfan-Casanova et al., 2000, 2003; Murakami et al., 2002; Litasov et al., 2003). In this situation, Al-bearing hydrous bridgmanite contained ~0.8 wt % water with 4.7 wt% Al_2O_3 was synthesized by Inoue et al., (in prep). The dominant substitution mechanism was suggested to be $Si^{4+} \rightarrow Al^{3+} + H^+$. However, the physical properties of Al-bearing hydrous bridgmanite under high pressure are unknown. In this report, the compressibility of Al-bearing bridgmanite is tried to determine.
 In situ P-V-T experiments of Al-bearing hydrous bridgmanite were conducted up to 50 GPa and 900 or 1500 K, using multi-anvil high pressure apparatus (SPEED-Mk.II) with sintered diamond 2nd stage anvil at SPring-8 BL04B1. Al-bearing hydrous bridgmanite was softer than $MgSiO_3$ bridgmanite below 27 GPa. Then with increasing pressure up to 40 GPa from 27 GPa, The drastic softening was observed. Above 40 GPa, it become the steady state as below 27 GPa. This phenomenon looked like the symmetrization of hydrogen bond in the case of iceVII - iceX transformation (Sugimura et al., 2008). In this presentation, we will report the compressibility of Al-bearing hydrous bridgmanite in detail.

Keywords: lower mantle, bridgmanite, water, compressibility

Water solution mechanisms in magmas: insights from *ex situ* piston-cylinder and *in situ* hydrothermal diamond anvil cell experiments.

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The global cycle of water on Earth involves different reservoirs in the solid Earth (Earth's crust, mantle, and potentially core) and its surface (atmo-, hydro- and biospheres). Exchanges of water between them occur in specific geological settings, such as subduction zones, mid-ocean ridges or intraplate volcanisms. Each of those settings implies magmatic activity, in which silicate melts play a determining role as they carry water from depth to surface. Furthermore, magmas rheological and thermodynamic properties are strongly affected by dissolved water that, hence, influences transfers of matter and heat in the crust and in superficial volcanic systems. However, the mechanisms of water incorporation in silicate melts are still not well understood, and, in particular, their dependence to melt chemistry, temperature and pressure remain to be fully assessed.

To address those issues, we investigated alkali (Li^+, Na^+, K^+) silicate, and sodium and calcium aluminosilicate melts containing various quantities of dissolved water. The melts were hydrated with a given amount of water in piston-cylinder apparatus, and studied *ex situ* after quenching using ^1H, ^2H and ^{29}Si Nuclear Magnetic Resonance, Infrared and Raman spectroscopy. Furthermore, using Raman spectroscopy, we probed *in situ* melts at equilibrium with aqueous fluids in hydrothermal diamond anvil cells (HDACs). While the *ex situ* data allow us to observe the melt structure and water environment at conditions corresponding to the glass transition, *in situ* data allow us to gather knowledge at higher P-T conditions, relevant to the Earth crust and upper mantle.

Results show that the environment of water in quenched melts is deeply affected by the melt composition. For instance, in silicate melts, increasing alkali ionic radius promotes water reaction with the silicate network, while the protons reside in environments with smaller volumes. The comparison of *ex situ* data for two sodium and calcium alumino-silicate melts further substantiates this dependence to melt composition, but also suggest that aluminum might help stabilizing the H^+ local environment. At temperatures much higher than the glass transition, Raman data from HDAC experiments show that the O-H stretching vibration, and hence the O-O distances around H^+, becomes more similar between the sodium and calcium alumino-silicate melts. Deconvolution and peak fitting analysis of the Raman peaks assigned to T-O stretching in TO_4 tetrahedral units in the glasses and melts further show a strong depolymerisation of the melts, which depends on melt temperature and initial composition. This complex environment of water in hydrous silicate melts induces non-linear variations of their transport properties as a function of water content, major element composition and temperature. Such knowledge can be integrated in models of magma mobility in the Earth crust, and of possible extrusive mechanisms at the Earth surface.

Keywords: water, magma, silicate melt, diamond anvil cell, NMR spectroscopy, Raman spectroscopy