

Hydrogen positions in hydrous ringwoodite determined by pulsed neutron powder diffraction

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The transition zone in the Earth's mantle has been considered potentially large water reservoir. It was experimentally evidenced that its main constituent minerals can uptake significant amount of water as hydroxyl groups in their crystal structures. The ringwoodite $[(\gamma\text{-Mg,Fe})_2\text{SiO}_4]$ is one of the high pressure polymorph of olivine, which is the most major phase in the lower part of the transition zone, between 525 to 660 km in depth. It was reported that ringwoodite can incorporate up to 2.6 wt.% of water (Kohlstedt et al., 1996). The hydration of ringwoodite strongly affects its physical and chemical properties such as electrical conductivity, compressibility and seismic velocities. However, crystallographic sites of hydrogen and its incorporation mechanism are still unclear mainly due to insensitiveness of X-ray probe for hydrogen. The previous studies of its structure refinement by X-ray diffraction demonstrated that hydrous ringwoodite has cubic spinel structure with $Fd\text{-}3m$ space group (Kudoh et al., 2000; Smyth et al., 2003). Here we applied neutron diffraction for hydrous ringwoodite for the first time to analyze its hydrogen positions.

Deuterated ringwoodite powder samples were synthesized at 1300 °C and 18 GPa for 5 minutes using a scaled-up Kawai-type multi anvil apparatus. The run products were evaluated by micro-focused X-ray, Raman spectroscopy and powder X-ray diffractometer to confirm their purity.

Neutron powder diffraction patterns were taken at BL-19 (TAKUMI) at Materials and Life Science Experimental Facility, J-PARC. The two representative deuterated ringwoodite samples were with identical composition mixed and measured together in a sample holder made of TiZr "null" alloy. The obtained diffraction pattern has been analyzed by Rietveld refinement using the "Z-Rietveld" code in order to determine positions and site occupancies of deuterium atoms in the ringwoodite structure.

We can propose two possible models for the deuterium atomic positions, 96g and 192i. These refined models were given with almost identical R factors. They also gave similar site occupancies and temperature factors for the elements except for the deuterium. However, in terms of deuterium temperature factor, the 192i model is more preferable than the 96g model. The refinement results also showed that the (Mg+Fe)/Si ratio is lower than the ideal ratio of dry ringwoodite [(Mg+Fe)/Si = 2.0] while Si in T sites are fully occupied, which demonstrates that deuterium only substitutes Mg and Fe in M sites and Si in T sites is not affected.

References:

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Keywords: ringwoodite, neutron diffraction, Rietveld refinement

Stability of Hydrous phase H MgSiO₂(OH)₂ in the lower mantle

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Subducting slabs transport water to Earth's deep interior and its circulation on a global scale is the key to understanding the evolution of the planet. However, it is still a matter of debate how deep water can be transported. Therefore, there are many studies on phase relationships in hydrous minerals or MORB-H₂O systems. Most dense hydrous magnesium silicates (DHMS) are stable up to 50 GPa (e.g., Komabayashi et al., 2004). Recently, the synthesis of Mg- and Si- bearing δ -AlOOH, which is a solid solution between 2AlOOH-MgSiO₂(OH)₂, was reported and it might be transported with Mg-perovskite or Mg-post perovskite up to 135 GPa (Ohira et al., 2012, AGU). Tsuchiya (2013) theoretically reported Phase H, the end member of the system, was stable above 45 GPa and up to 55 GPa. And also it was experimentally synthesized at 50 GPa (Nishi et al., 2014). Although the previous studies claimed that Phase H was broken down above 55 GPa, it may be a host phase of water in the deep Earth interior. Here, we report the stability field of a new candidate phase of water reservoir at the lower mantle conditions by investigating the MgO-SiO₂-H₂O system up to 75 GPa and 2000 K.

A mixture of quartz and brucite (molar ratio 1 : 1) powders were used as starting materials. The high pressure and high temperature experiments were performed by using a double-sided Laser heated diamond anvil cell. A pellet with thickness of about 15 μ m was made by a cold compression technique. In situ XRD experiments in the MgO-SiO₂-H₂O system were performed at BL10XU, SPring-8. In this study we confirmed that hydrous phase H does exist in the MgO-SiO₂-H₂O system and its stability fields expands at least up to 75 GPa and above 2000 K in contrary with previous reports (Tsuchiya, 2013; Nishi et al., 2014).

If Phase H exists under high pressure conditions corresponding to the pressure of CMB, it may transport water to CMB and thus the core may contains hydrogen as a light element.

Keywords: hydrous phase, hydrous phase, subduction

Partitioning of carbon between metallic- and silicate-liquids in carbonaceous chondrite compositions at high pressure

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Major volatile elements in the terrestrial planets are oxygen, sulfur, carbon, hydrogen, and nitrogen. They are also candidates for light components in the earth's core which were incorporated into the core at terrestrial magma ocean stage. Partitioning behavior of carbon has not been determined well though it is one of the strong candidates for light elements in the earth's core. We investigated partitioning of carbon with sulfur and oxygen between metallic- and silicate liquids at 6 GPa and 2073 K in carbonaceous chondrite composition (Allende meteorite; CV3). Effect of nitrogen and water as accessory components were also examined. High pressure experiments were conducted with multi-anvil high pressure apparatus. Graphite was used as capsule material. Composition of coexisting metallic- and silicate liquids were measured by electron microprobe with wavelength dispersion type spectrometer except for carbon in silicate liquid. Carbon concentration of bulk recovered sample was measured by elemental analyzer. Then, carbon concentration in silicate liquid was obtained by subtraction of carbon amounts in metallic phase which obtained by electron microprobe and SEM image analyses. Present result suggests that in oxidized carbonaceous chondrite composition, partitioning coefficient of carbon [$D^{Metallicliquid/Silicateliquid} = C^{Metallicliquid}/C^{Silicateliquid}$; C is concentration of carbon in wt.%] is close to 1, and it may increase with increasing the Fe^{metal}/Fe^{oxide} ratio in the carbonaceous chondrite composition.

Microanalysis of H₂O and CO₂ in silicate melt using laser Raman spectroscopy

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<Introduction>

Water and carbon dioxide are the major volatile components in the crust and mantle. Development of microanalytical techniques of these volatiles has made it possible to investigate mechanisms of igneous and volcanic processes. FTIR has been used as a fundamental tool for this purpose, but its spatial resolution is too large ($\sim 30 \mu\text{m}$) to analyse small melt inclusions and micro-scale volatile distribution within a high-pressure experimental sample. In this study, we developed a new technique for volatile analysis in silicate glasses with $\sim 1 \mu\text{m}$ spatial resolution using laser Raman spectroscopy.

<Experimental and analytical procedure>

Standard glasses were synthesized by using a piston-cylinder apparatus in M. Nakamura's laboratory. Basaltic glass powder was loaded into a platinum-sleeved nickel capsule together with oxalic acid and run at 1473 K and 0.5-1.2 GPa. After quench, the H₂O and CO₂ (dissolved as CO₃²⁻) contents of the glasses were measured by using FTIR. The same glasses were then analysed with a Thermofisher DXR laser-Raman spectrometer. Wave length, power and diameter of the laser beam were 532 nm, 10 mw and 0.7 μm , respectively. We normalized the Raman spectra by the intensity of a peak at 500 cm⁻¹ (T-O-T bond) and subtracted the spectrum of the volatile-free glass. The intensities of peaks at 3550 cm⁻¹ (H₂O) and 1080 cm⁻¹ (CO₃²⁻) in the resulting spectra were compared with the H₂O and CO₂ contents determined by FTIR spectroscopy.

<Results>

The H₂O and CO₂ contents were determined to be 0.7-2.1 wt% and 0.05-0.82 wt%, respectively. Raman spectroscopy showed that the intensities of peaks at 3550 and 1080 cm⁻¹ increased with increasing H₂O and CO₂ contents, respectively. We fitted a linear equation to the data and obtained H₂O (wt%) = $(3.58 \pm 0.14) \times I_{3550}$ and CO₂ (wt%) = $(4.61 \pm 0.21) \times I_{1080}$.

<Application>

We applied this technique to volatile analysis of an experimentally-produced bubble-bearing basaltic glass. In the experiment, basaltic melt was first equilibrated with H₂O-CO₂ mixture fluid at 1473 K and 1 GPa, and then decompressed to 0.5 GPa and kept for 10 minutes. After quench, the H₂O and CO₂ contents around bubbles were measured along the radial direction at 2- μm intervals for a total of 50 μm . The CO₂ contents decreased on moving towards the bubble, indicating that CO₂ was diffusing into the bubble. Fitting the diffusion equation to this profile, we estimated the diffusivity of CO₂ to be $1.2 \times 10^{-12} \text{ m}^2/\text{s}$. This value is consistent with that reported by Zhang et al. (2007). In contrast to CO₂, H₂O showed a flat profile, suggesting that H₂O was already equilibrated with the fluid in the bubble. This is because the diffusivity of H₂O is one order of magnitude greater than that of CO₂. Such a diffusive fractionation was observed also in rhyolitic melt (Yoshimura and Nakamura, 2010).

Keywords: CO₂, H₂O, glass, Raman

Dynamic and cyclic process of carbon-bearing phases of the terrestrial interior

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The results of the present study are summarized as follows:

1) Carbon-bearing mineral phases of the terrestrial interior are discussed to elucidate dynamic change of material states (air, liquid and solid) on active Earth planet.

2) Samples used in this study are diamond (Congo,Africa), limestone (Akiyoshi, Japan), carbonatite (Lengai, Tanzania,Africa and Europe-North America), and shungite (Shunga, Russia) together with carbonate grains of Libyan glass (Africa) to observe micro nano-grains of carbon-bearing materials with the FE analytical SEM etc.

3) The present data indicate that micro carbon-bearing grains are easily changed and remained as the three materials states mainly as solidified glasses by high pressure shock waves of earthquake, volcano and impact events to the surface to the interior.

4) Local fluid-bearing depositions irregularly distributed on the surface and interior of active Earth are based on storages on the interior formed by solidified mixtures of multiple carbon-bearing material states originally triggered by impact process on primordial Earth and ocean floors of evolved Earth.

5) The primordial planet Earth with remained heterogeneous surface by original impact-related process is considered to produce dynamic cyclic system of three material states (air, liquid and solid) of carbon-bearing materials with macro-life activity which is formed by huge production from the interior triggered by huge collision process of the giant impact and followed inner movement of active Earth with complicate local reservoir.

Keywords: carbon, interior, cyclic process, shock wave event, irregular distribution, local deposit