

論文の内容の要旨

Pressure Responses of Hydrogen Bonds in Hydrated Minerals

– Pressure-induced Phase Transition in $\text{Ca}(\text{OH})_2$ and Technical Development of High Pressure Neutron Experiments –

(含水鉱物中の水素結合の圧力応答についての研究

- $\text{Ca}(\text{OH})_2$ の圧力誘起相転移のその場観察と中性子回折用高圧装置の開発 -)

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A large amount of water exists in the interior of solid Earth as a form of hydroxyl ions or hydrogen in lattice defects. These minerals can play essential role as a host for H_2O transportation into the crust and mantle of the Earth. Therefore, it is important to investigate high-pressure responses of these minerals and to clarify the behavior of hydrogen. Among recent high-pressure studies of hydrated minerals, an attention has been focused mostly on layered silicates and hydroxides. As the simplest model of hydrated phases, brucite-type hydroxides $\text{M}(\text{OH})_2$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Co}, \text{Ni}$ etc.), which have hydrogen bonds in their layered structure, show diverse responses to pressure depending on cation size. These results will provide significant insights for understanding the high-pressure physical properties of hydrogen bond in solids for both geo-science and materials science.

In this thesis, high-pressure behaviors of $\text{Ca}(\text{OH})_2$, portlandite, as shown in Fig. 1, is focused on. To date, many studies have clarified the existence of pressure-induced phase transitions and/or amorphization of portlandite using variety of high-pressure cells, analytical methods and pressure-transmitting media (e.g., *Meade and Jeanloz 1990; Nagai et al., 2000; Ekbundit et al., 1996; Catalli et al., 2008*). However, there remain some difficulties in clarifying the phase transition at around 6-8 GPa, since the hydrostaticity of the applied pressure sensitively affects on this transition. Neutron diffraction is a powerful tool to clarify the crystal structures including hydrogen positions. In portlandite, however, no data on the structure of the high-pressure phase (**High-P phase**) has been reported in previous neutron diffraction studies (*Pavese et al., 1997; Xu et al., 2007*). In other words, the nature of the transition and the crystal structure of the High-P phase of portlandite remain unknown.

The main purposes of the present study are: (i) to clarify the pressure response of portlandite including the behavior of hydrogen bonds, (ii) to identify the crystal structure of the High-P phase of portlandite, and (iii) to improve experimental techniques for neutron diffraction measurements under high pressure to determine the hydrogen position in the High-P phase. This thesis consists of three following chapters.

In chapter 2, the pressure responses of portlandite were studied by single-crystal Raman and IR spectra, and powder XRD was investigated using diamond anvil cells (DACs). All the experiments were conducted under highly hydrostatic condition using a helium pressure-transmitting medium. The H–D isotope effect on the pressure response was also examined because deuterated samples are required in neutron diffraction studies to avoid large incoherent scattering from hydrogen. Moreover, similar experiments were repeated using a 4:1 methanol-ethanol pressure medium (Met/EtOH) to clarify the effect of the hydrostaticity on the pressure-induced phase transitions.

A reversible pressure-induced phase transition at around 6 GPa and room temperature was observed. The small H–D isotope effect was observed on the phase transition pressures (and partial amorphization); the transition pressure of $\text{Ca}(\text{OH})_2$ is slightly lower than that of $\text{Ca}(\text{OD})_2$ as shown in Fig. 2. In contrast, no isotope effect was found on the volume and axial compression of portlandite, as shown in Fig. 3. These results suggest that the H–D isotope effect is limited in the local environment surrounding H(D) atoms.

All the Raman and IR spectroscopic peaks disappeared at pressures greater than about 20 GPa, whereas the XRD peaks of the High-P phase were observed even at 28 GPa. This suggests that long-range ordering of Ca and O atoms is preserved even after the nature of the O–H bond has changed probably by the partial amorphization of H-sublattice.

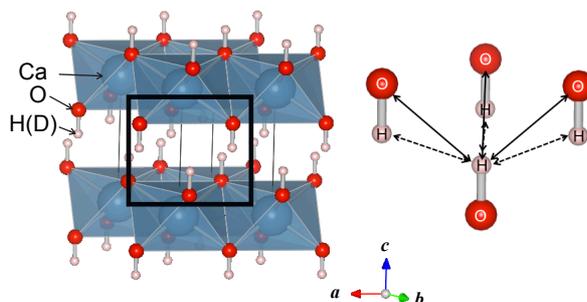


Fig. 1. (Left) Crystal structure of portlandite at ambient pressure. (Right) Partial structure of hydrogen bonding around the rectangle in the left figure. Solid lines indicate possible hydrogen bonds between H and O. Dotted lines indicate repulsive H...H interactions.

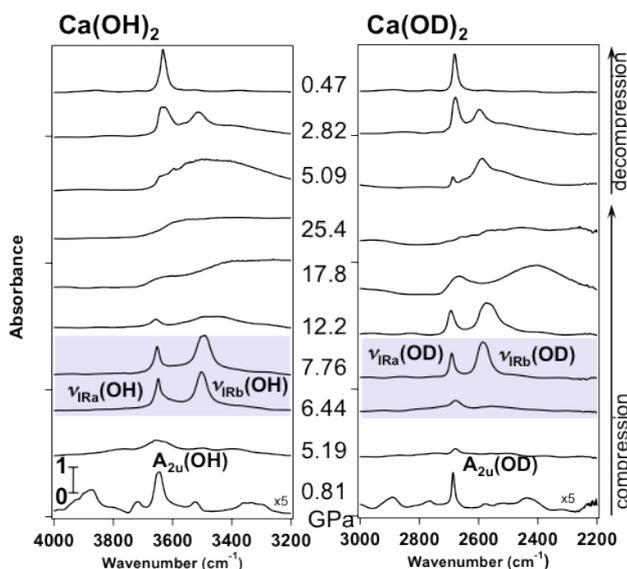


Fig. 2. IR spectra of $\text{Ca}(\text{OH})_2$ (left) and $\text{Ca}(\text{OD})_2$ (right) single crystals in helium in the regions of OH and OD stretching vibration modes. The shaded region indicates the phase transition toward the High-P phase.

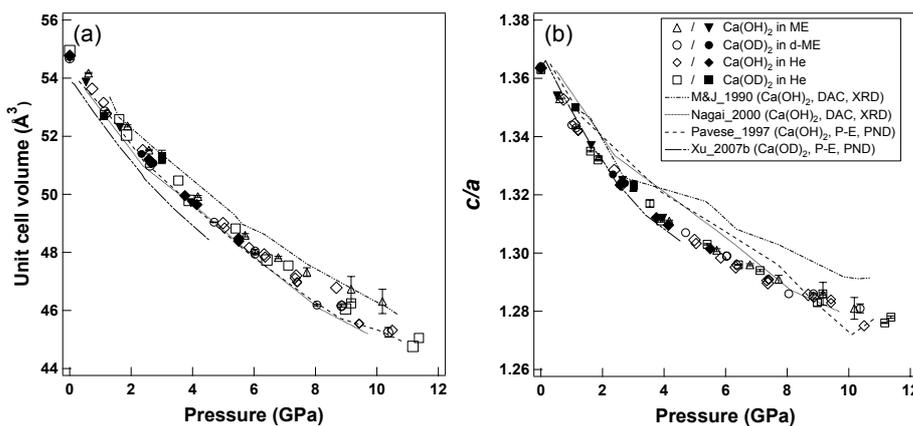


Fig. 3. Pressure dependences in (a) Unit cell volume and (b) the ratio of unit cell parameters of the a axis, c axis for powder $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OD})_2$ in various pressure-transmitting media. Open and closed symbols represent the data taken on compression and decompression, respectively. The three line plots from other previous studies are shown for comparison.

In Chapter 3, *in-situ* single crystal X-ray diffraction studies are presented to clarify the crystal structure of the High-P phase of portlandite. In order to overcome the difficulties in previous studies, some new experimental techniques were developed for single crystal X-ray diffraction measurements using DACs. Figure 4 shows a diamond anvil cell, which was improved in this study from "Radial-DAC" to have a wider aperture angle and lower background so as to obtain more reflections from the single crystal samples. Based on the clarified crystal structure of the High-P phase as shown in Fig. 5, the phase transition mechanism of portlandite was discussed. The phase transition is accompanied by the geometrical change in hydrogen bonds. Hydrogen atoms are expected to locate on at least two positions, which can be geometrically stable for hydrogen bonds. The identified crystal structure of the High-P phase will provide a valuable clue to determine H positions and state of hydrogen bonds in future neutron diffraction studies.

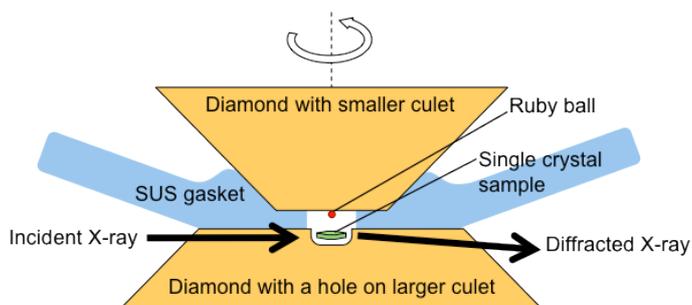


Fig. 4. Measurement geometry of single-crystal X-ray diffraction using the improved Radial-DAC.

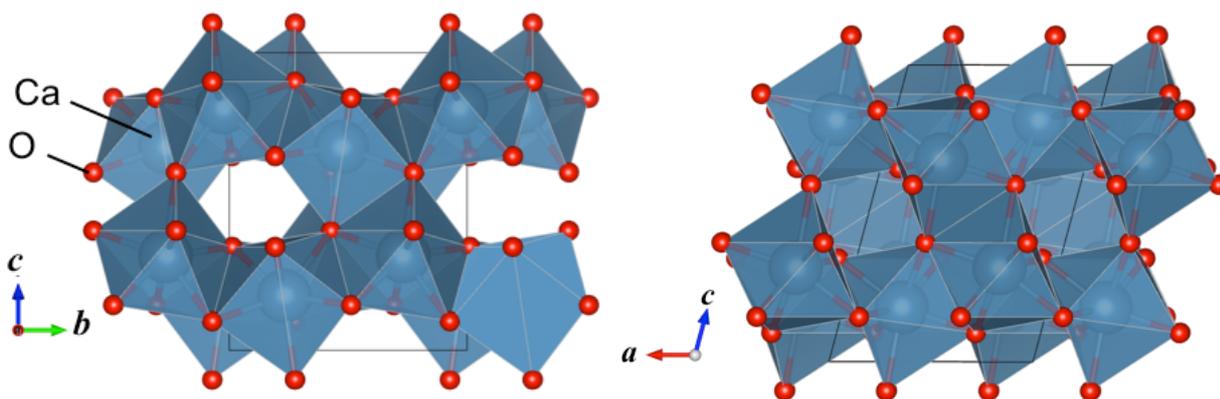


Fig. 5. Crystal structure of the High-P phase of portlandite at 8.5 GPa, from the perspectives of (left) the *a*-axis, and (right) the *b*-axis. Blue and red spheres indicate Ca and O atoms, respectively.

In Chapter 4, developments of a high-pressure experimental technique were described for studying the phase transition of portlandite using neutron diffraction. A newly designed cell-assembly was tested using a Paris-Edinburgh (P-E) press (Fig. 6 left), so as to increase the high-pressure capability and to obtain the high-intensity diffraction data. This will allow us to perform more reliable neutron diffraction measurements under higher pressures. In order to extend the pressure range of the P-E press without reducing the sample volume, following technical developments were made (Fig. 6 right): (1) New anvils were designed with a wide conical aperture

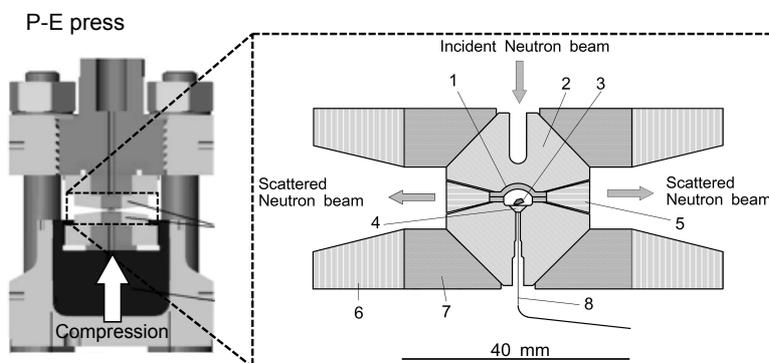


Fig. 6. Design of the new cell assembly loaded into a P-E press. (1) TiZr encapsulate and ring gasket, (2) Ni-binded WC anvil, (3) ruby chip, (4) moissanite anvil, (5) Al-alloy (A6061) disk, (6) SNCM439 support ring, (7) Ni-binded WC support ring, (8) Optical fiber.

to get higher signal intensity, (2) A hybrid gasket was developed by TiZr and Al-alloy for reducing absorption of neutron beam, (3) A new anvil with an optical window was designed for monitoring ruby fluorescence spectra to determine pressure and evaluate the hydrostaticity in a sample chamber. Pressure generation tests were repeated by measuring the electrical resistance of Bi and ruby fluorescence spectra at the same time. *In-situ* synchrotron XRD experiments were also carried out using NaCl pressure marker at Photon Factory-Advanced Ring (PF-AR), KEK. At present, maximum pressure of 13 GPa was achieved as shown in Fig. 7.

The performance of this newly developed system was tested at J-PARC using a pulsed neutron source. As a result, 2.5–3 times higher intensities were obtained compared with those of original "toroidal anvil" designs with the same initial sample volume using Pb as standard material. A preliminary high pressure experiment on powder $\text{Ca}(\text{OD})_2$ was carried out using the new cell at J-PARC. The neutron diffractions derived from the High-P phase of portlandite were observed for the first time as shown in Fig. 8. Further experiments will allow us to investigate structural information of hydrogen bond in portlandite and in various solid materials.

For summary of this study, high-pressure behaviors of portlandite were investigated from IR and Raman spectroscopic methods, and X-ray diffraction measurements. The crystal structure of the High-P phase and the phase transition mechanism of portlandite were clarified. New experimental techniques for neutron diffraction were developed. Future neutron diffraction measurements at J-PARC using the developed cell-assembly will play important roles to clarify the high-pressure behaviors of hydrogen bonds in various hydrogen-bearing materials.

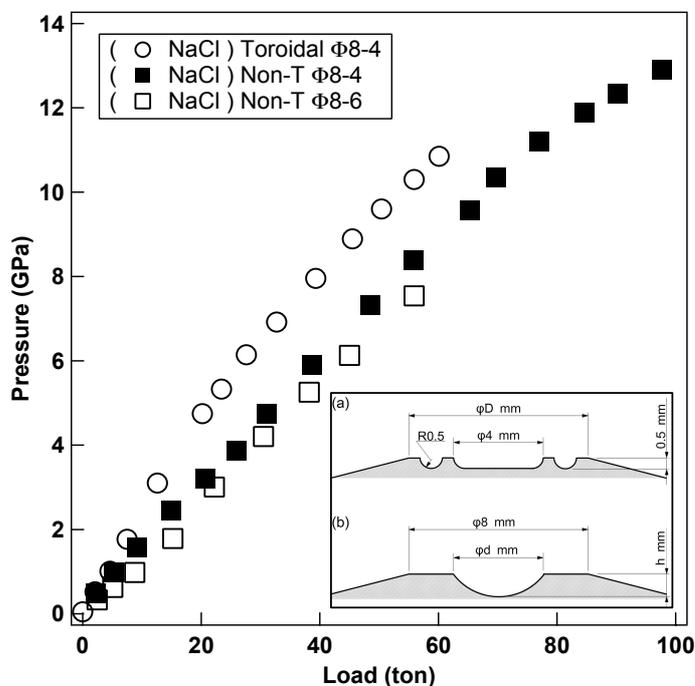


Fig. 7. Pressure generation curves for various types of anvils. (inset) Culet shapes of (a) Toroidal and (b) Non-Toroidal anvils.

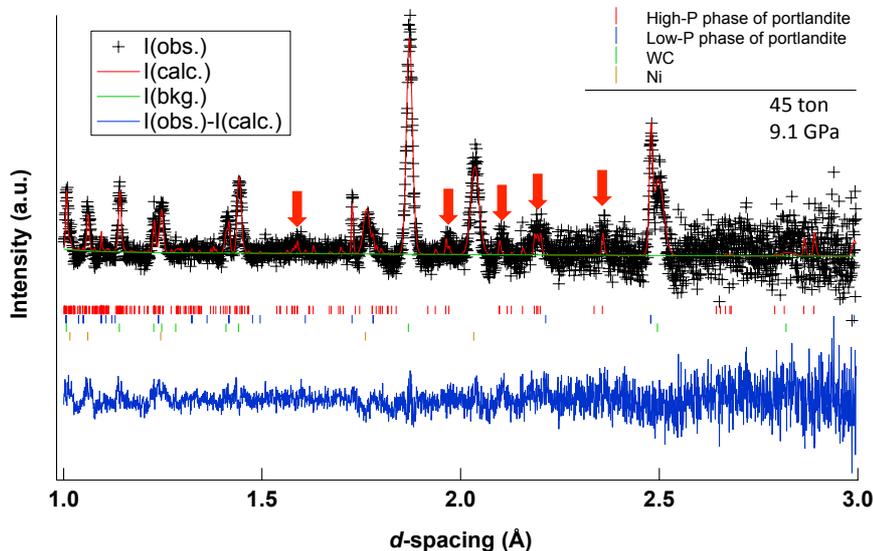


Fig. 8. Neutron diffraction pattern of $\text{Ca}(\text{OD})_2$ at 9.1 GPa. Red tick marks and arrows indicate the diffraction peak positions derived from the High-P phase.