

## 高温高圧下におけるブルーサイト中の水素同位体の振る舞い Behavior of hydrogen isotopes in brucite at high pressures and temperatures

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Hydrogen plays important roles in chemical and physical properties of hydrous minerals such as rheology, electrical conductivity, and diffusivity. Brucite  $\text{Mg}(\text{OH})_2$  is one of the representative hydrous minerals occurring in the earth's crust and mantle. It has a  $\text{CdI}_2$  structure (S.G.  $P-3m1$ ), which is consisted of edge-sheared  $\text{MgO}_6$  octahedra where OH-bonds are bound along  $c$ -axis (Zigan and Rothbauer 1967). The brucite layer is a fundamental building unit of hydrous phyllosilicate including micas, serpentines, clay minerals and dense magnesium hydrous silicates (DMHS). OH-bond possibly largely affects the nature of interlayer forces and the stability of such hydrous phases under geological pressure and temperature conditions. In the present study, we have performed X-ray powder diffractometry, micro-Raman spectroscopy and high pressure-temperature interdiffusion experiments of hydrogen isotopes in brucite to understand their behaviors at high pressures and high temperatures.

Protonated and deuteriated water were mixed to be desired D/H ratios, and then added to MgO powder. The starting materials encapsulated in an autoclave were heat at 250 degC and under autogenic pressure as high as 40 bars for 168 h. The grain size of recovered brucite is smaller than 10 micron in diameter. In order to determine isotope effects on lattice parameters, the brucite powders were examined by X-ray powder diffractometer. In diffusion experiments, two semi-circular disks of pure  $\text{Mg}(\text{OH})_2$  and  $\text{Mg}(\text{OD})_2$  were compressed in a diamond anvil cell and heated at 300 degC for 740 hours in a furnace in argon atmosphere. The pressures of the samples after cooling were  $\sim 1$ -2 GPa. H-D diffusion profiles of recovered samples were obtained on the basis of the intensity ratios of OH and OD stretching peaks by a micro-Raman spectroscopy.

An isotope effect on lattice parameters of brucite could be successfully recognized by precise XRD measurements in the present study. The  $a$ -axis of brucite is nearly constant with respect to the D/H ratio. However, the  $c$ -axis of  $\text{Mg}(\text{OH})_2$  linearly decreases down to 99.7 % with increasing deuterium content. This tendency suggests that the OH- and OD-bonds oriented along  $c$ -axis constrain the spacing of basal plane of the brucite structure. Smaller amplitude of the stretching vibration of OD than that of OH causes the shrinkage of  $d_{0001}$ . Diffusion profile measurements of the recovered sample from 1.8 GPa and 300 degC tentatively clarified that the H-D interdiffusion coefficient ( $D_{H-D}$ ) is  $10^{-15}$   $\text{m}^2/\text{s}$  order. This value tends to be much larger than those of other cations in silicates. For instance, the  $D_{H-D}$  of brucite is more than ten orders of magnitude larger than the Si-self diffusion coefficient in forsterite estimated considering the same temperature and grain size with those in the present study (Brady 1983, Hallwig et al. 1982). It was also clarified that the  $D_{H-D}$  in  $\text{Mg}(\text{OH})_2$  is faster than that in  $\text{Mg}(\text{OD})_2$ . This fact is inconsistent with that small distance between nearest-neighboring hydrogen isotopes in  $\text{Mg}(\text{OD})_2$ , which is deduced from its  $c$ -axis length, could enhance exchange of hydrogen isotopes. The width of hydrogen-bearing layers is not simply related to the  $D_{H-D}$ . Higher frequency ( $3650 \text{ cm}^{-1}$ ) of OH stretching vibration than that of OD ( $2693 \text{ cm}^{-1}$ ) is a plausible explanation of high  $D_{H-D}$  in proton-rich brucite. OH-bond which is a majority of hydroxyl bonds in proton-rich brucite would cause high probability of hydrogen isotope exchange.

キーワード: ブルーサイト, 水素同位体, 拡散, ダイヤモンドアンビルセル, 格子定数  
Keywords: brucite, hydrogen isotopes, diffusion, diamond anvil cell, lattice parameters