

論文 / 著書情報  
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## 論文要約

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In order to understand behavior of hydrogen in the Earth's upper mantle (reviewed in Chapter 1), water partitioning experiments have been carried out at pressures of 1.5–6 GPa and a temperature of 1573 K using Kawai-type multi-anvil and piston-cylinder apparatus (Chapter 2). DFT (density function theory) calculations of hydrogen substitution in enstatite were carried out and the results were compared with the IR spectra obtained by experiments (Chapter 3). In-situ IR high pressure experimental method was developed using diamond anvil cell that are applicable for upper mantle nominally anhydrous minerals with very small amount of water (100~1000 ppm). Using this technique, polarized IR spectra parallel to crystal axis of synthesized forsterite were obtained under high pressure for the first time (Chapter 4). Substitution mechanisms of hydrogen in mantle minerals and its bearing on the deformation mechanism of mantle rocks were discussed on the basis of high pressure experimental results and DFT calculations (Chapter-5).

In Chapter 2, I carried out high-pressure experiments to investigate the partition coefficient of water between orthopyroxene and olivine ( $D_{\text{Opx/Ol}}$ ) under low-water

concentrations similar to the Earth's mantle conditions.  $D_{(\text{Al-free Opx/Ol})}$  is  $\sim 1$  at all pressure conditions. However, the water contents of Al-bearing Opx are significantly larger than those of Ol at the same conditions. In addition, the effect of Al concentration in Opx on  $D_{(\text{Opx/Ol})}$  becomes larger with increasing pressure.  $D_{(\text{Opx/Ol})}$  in the Earth's mantle drops sharply at the pressure where garnet stabilized and Al concentration in Opx decreases dramatically in the Earth's mantle.

In Chapter 3, I calculated the electronic state in pure-enstatite and Al-bearing enstatite using the DFT to determine hydrogen positions in enstatite. In pure-enstatite, principle hydrous mechanisms are the substitution  $(4\text{H})_{\text{Si}}$  and  $(2\text{H})_{\text{Mg}}$ . In Al-bearing enstatite, it was found that dominant hydration mechanisms change to the substitution  $(\text{Al}+\text{H})_{2\text{Mg}}$  and  $(4\text{H})_{\text{Si}}+(\text{Al}+\text{H})_{\text{Si}}$ . These results indicate that hydrogen prefers substitutions along with  $\text{Al}^{3+}$  and this must be the reason why Al in enstatite enhances the water solubility of Opx found in Chapter 2.

In Chapter 4, to investigate behavior of hydrogen under high pressure conditions, in-situ IR high pressure experimental methods for low water content upper mantle nominally anhydrous minerals were developed. In-situ IR spectra at high pressures for forsterite single crystal using diamond anvil cell to investigate pressure effect of hydrogen positions was obtained. Large shift of some OH bond above 4 GPa and separation of OH

band were observed. In addition, I have calculated the electronic state in forsterite using the DFT to explain observed peak shifts during compression. Hydrogen substitution mechanism in Si site can explain observed IR spectra shift by first-principle calculation. It was found that when changes in O-H...O angle occur, very large and abrupt band shift should takes place. For simple decrease in O-O bond length, band shift should be quite small and gradual.

Finally in Chapter 5, I discussed the behavior of hydrogen in the Earth's upper mantle based on the results in the preceding Chapters. From direct comparison of the vibrational frequencies measured by the FT-IR methods (in Chapter 2) and simulated by the first-principles methods (in Chapter 3), I developed a method to determine hydrogen positions in nominally anhydrous minerals. Based on determined hydrogen position of forsterite together with all experimental and theoretical inferences obtained through preceding chapters, I tried to explain why water changes the slip system of olivine. Also I tried to estimate water effect on the slip systems of orthopyroxene from the hydrogen substitution mechanisms determined in Chapter 3.