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学位論文の題目	H-D inter-diffusion in wadsleyite and ringwoodite: Implications for water content and distribution in the mantle transition zone (Wadsleyite と ringwoodite の H-D 相互拡散 : マントル遷移層の水の量と分布の解釈)
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学位論文内容の要旨

The mantle transition zone has considered to be a large water budget in the Earth's interior, because wadsleyite and ringwoodite, which are the major phases in the transition zone, can contain considerable amount of water in their crystal structure. To understand the water distribution and its absolute content, laboratory-based electrical conductivity measurement of wadsleyite and ringwoodite is a useful method when the data will be compared with the conductivity structure determined from electromagnetic surveys. However, the direct conductivity measurements provided large discrepancies among laboratories because of experimental difficulty.

In this study, proton conduction mechanism in wadsleyite and ringwoodite was investigated by high-pressure experiment of H-D inter-diffusion in H- and D-doped single crystal pair to constrain the electrical conductivity of hydrous wadsleyite and ringwoodite. H-D inter-diffusion coefficients were determined at various temperatures between 1000 and 1300 K and pressures of 16 and 21 GPa for wadsleyite with various Mg# and ringwoodite, respectively. To produce hydrogen self-diffusion data with high accuracy, H- and D-doped single crystals of wadsleyite and ringwoodite were synthesized at 16 and 21 GPa, respectively, by slow cooling method. H-D inter-diffusion experiments of ringwoodite and wadsleyite were performed with arbitrary crystallographic direction and three principle crystallographic direction, respectively. Diffusion profiles were obtained by secondary ion mass spectroscopy (SIMS).

H-D inter-diffusion profiles in both Fe-bearing wadsleyite and ringwoodite crystal pairs show symmetrical shape across the interface. Hydrogen self-diffusivities of Fe-bearing wadsleyite and ringwoodite are determined to be $D_H = 10^{-7.15 \pm 0.46} * \exp(-\frac{106 \pm 11 \text{ kJ/mol}}{2.303 * RT}) m^2/s$ and $D_H = 10^{-7.29 \pm 0.46} * \exp(-\frac{101 \pm 10 \text{ kJ/mol}}{2.303 * RT}) m^2/s$, respectively. The hydrogen self-diffusion coefficients of both phases are almost the same and about 1 order of magnitude higher than that of olivine determined at 2 GPa from *Du Frane and Tyburczy* [2012]. There is small anisotropy of hydrogen self-diffusion in Fe-bearing wadsleyite. In Fe-free wadsleyite, inter-diffusion profiles characterized by stagnating diffusion rate comparing with Fe-bearing condition and asymmetry indicate distinguish profile diffusion coefficients between hydrogen and deuterium in Fe-free condition. The multiple hydrogen model suggests that the dominant hydrogen migration mechanism changes from Mg sites at the condition with high partially-filled defect concentration to interstitial sites at the conditions with low unfilled defect concentration and jump probabilities from Mg sites to interstitial sites between deuterium and hydrogen are different.

Based on the Nernst-Einstein equation, electrical conductivities calculated from the present hydrogen self-diffusivities in Fe-bearing wadsleyite and ringwoodite are consistent well with those of *Yoshino et al.* [2008] at the transition zone condition except ringwoodite at high water content but about 1-2 orders of magnitude lower than *Dai et al.* [2009] and *Huang et al.* [2005]. The discrepancies between direct conductivity measurements and this study were probably caused by various degrees of dehydration during heating in the conductivity measurements. Estimated global average water concentration in the mantle transition zone is less than 0.1 wt.%. Beneath the northwestern China, only hydration of wadsleyite and ringwoodite cannot account for both high conductivity and fast seismic velocity anomalies. Generation of the supercritical fluid at the top of subducted stagnate slab by heating from the surrounding mantle could be the most plausible explanation for both high conductivity and fast seismic velocity anomalies in the wedge mantle.

論文審査結果の要旨

Ph. D defense of Mr. Wei Sun was held on 16th February.

Water plays an important role in the Earth's interior, such as triggering the volcanism and seismicity, enhancing plastic deformation and electrical conductivity, and reducing melting temperature and seismic velocities. To understand the water content and its distribution in the mantle transition zone, electrical conductivity of proton conduction in these minerals are essential to provide some constraints. However, measurement of proton conduction is experimentally difficult at high temperatures. This study took the other approach to determine the proton conduction.

This study is the first report on D-H exchange diffusion in wadsleyite and ringwoodite, which are thought to be dominant minerals in the mantle transition zone. New findings of this study are 1) Fe-bearing samples provides faster diffusion coefficient and the calculated electrical conductivity is consistent with previous work. 2) Fe-free wadsleyite has an asymmetric profile. The multiple hydrogen model indicates that the dominant hydrogen migration mechanism changes from Mg sites at the condition with high partially-filled defect concentration to interstitial sites at the conditions with low unfilled defect concentration, and jump probabilities from Mg sites to interstitial sites between deuterium and hydrogen are different. 3) Compared to the global average one dimensional conductivity-depth model, water concentration in the mantle transition zone is estimated to be less than 1000 ppmw. The characteristic distance for hydrogen self-diffusion in the mantle transition zone is estimated to be ~1.8 km after 100 Myr. The heterogeneity of water distribution in the mantle transition zone detected by geophysics observation could be maintained for geologically long time scale.

We considered that content of this thesis has a strong impact on the Earth science community. Therefore we concluded this thesis is proper to be accepted as PhD dissertation of Okayama University.