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## D/H exchange in wadsleyite and ringwoodite: Implications for electrical conductivity D/H exchange in wadsleyite and ringwoodite: Implications for electrical conductivity

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Wadsleyite and ringwoodite, which are main constituent minerals of the mantle transition zone, can incorporate large amount of hydrogen in their structure (up to a few wt % H2O). A knowledge of hydrogen self-diffusion in these minerals and its relationship with their electrical conductivity is critical to estimate the real amount of water present in the transition zone. Although only the hydrogen incorporation experiments in wadsleyite was performed using polycrystalline samples, the obtained diffusion coefficients cannot rule out the influence of grain boundary diffusion (Hae et al. 2006). Therefore, we have to investigate hydrogen lattice self-diffusion of wadsleyite and ringwoodite using single crystal at high pressure.

To estimate proton conduction from hydrogen self-diffusion, large single crystals (>1mm) of hydrogen (H) and deuterium (D)-doped wadsleyite and ringwoodite were synthesized respectively at high pressure and high temperature in Kawai-type multianvil apparatus.

We applied H/D exchange method to determine hydrogen self-diffusion coefficients because this method (Du Frane et al. 2012) has advantage to distinguish between incorporation and self-diffusion, and provides more accurate hydrogen diffusion coefficients contributing to proton conduction than traditional incorporation method (Kohlstedt and Mackwell, 1998, Demouchy and Mackwell, 2003, Hae et al. 2006).

After determination of crystallographic orientation, a pair of H and D-doped wadsleyite or ringwoodite crystals aligned to the same axis was placed together in gold capsule. The polished surfaces were tightly contacted each other. The inter-diffusion experiments were conducted at different temperatures (900-1300K) and the same pressure as synthesis condition. H/D inter-diffusion profiles were obtained by SIMS in Hokkaido University.

Hydrogen volume diffusion coefficients in wadsleyite determined from each single crystal pair are ~1 order of magnitude lower than those obtained from polycrystal wadsleyite (Hae et al. 2006). The hydrogen self-diffusion coefficients in ringwoodite are characterized by lower enthalpy and hydrogen mobility than wadsleyite at the temperature of transition zone.

Electrical conductivities of wadslyite and ringwoodite estimated from the present diffusion coefficients based on the Nernst-Einstein relation. Our model suggests that hydrogen makes significant contributions to wadsleyite but insignificant contributions to ringwoodite due to large contribution of hopping conduction at the transition zone condition. Our proton conductivity values of wadsleyite are similar with those of Yoshino et al. [2012] at the transition zone condition but values of ringwoodite are lower especially at high water content. This model suggests that global average concentration of hydrogen in the transition zone of is ~1000 wt ppm H2O.

 $\neq - \neg - ec{r}$ : hydrogen, diffusion, wadsleyite, conductivity, ringwoodite Keywords: hydrogen, diffusion, wadsleyite, conductivity, ringwoodite