

## Locating hydrogen in lower mantle transition zone hydrous ringwoodite

\*Narangoo Purevjav<sup>1</sup>, Takuo Okuchi<sup>1</sup>, Xiaoping Wang<sup>2</sup>, Christina Hoffmann<sup>2</sup>, Naotaka Tomioka<sup>3</sup>

1. Institute for Planetary Materials, Okayama University, 2. Neutron Scattering Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, 3. Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology

Water is one of the crucial components affecting the geochemical and geophysical evolution of the Earth. Besides its existence as surface oceans, it also presents in the Earth's interior as structurally bound hydroxyls (OH) within the hydrous minerals. The major constituent minerals of the mantle transition zone have been considered as the largest reservoirs of that structurally bound OH in the deep mantle region, which are wadsleyite [ $\beta$ -(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>] and ringwoodite [g-(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>]. These minerals are the two high-pressure polymorphs of olivine [ $\alpha$ -(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>]. By previous experimental studies, it has been confirmed that wadsleyite and ringwoodite accommodate up to a few weight percent of water in their crystal structures. The presence of hydrous ringwoodite in deep mantle has been discovered recently, which was containing about 1.5 weight percent of H<sub>2</sub>O in it.

By our previous powder neutron diffraction study, we first revealed that ringwoodite incorporates water by exchanging of hydrogen cations for magnesium, iron and also for silicon cations in its crystal structure (Purevjav et al., Geophys. Res. Lett., 2014). By our subsequent neutron diffraction study for a high-quality hydrous ringwoodite single crystal, we best-quantitatively determined its hydrogen site and occupancies (Purevjav et al., Acta Crystallogr. B, 2018). The high-quality single crystals of hydrous ringwoodite were synthesized by applying our established a slow-cooling method (Okuchi et al., Am. Mineral., 2015), which is the most effective for growing crystals free from twinning, inclusion and chemical heterogeneity of deep mantle hydrous minerals. The synthesized single crystal of hydrous ringwoodite with Mg<sub>1.895</sub>H<sub>0.208</sub>SiO<sub>4</sub> composition was measured at neutron time-of-flight single-crystal Laue diffractometer TOPAZ at Spallation Neutron Source facility at Oak Ridge National Laboratory, USA. Obtained reflection intensity dataset with a spatial resolution of 0.60 Å in minimum *d*-spacing was used for the structure refinement. By this single crystal study, the position of hydrogen cation having negative scattering length was accurately located in the ringwoodite crystal structure. We found that hydrogen cations were only at around the site MgO<sub>6</sub> octahedra, which compensated the reduced occupancies of both magnesium and silicon cations in the ringwoodite structure. The refined occupancies of these cations suggested that the hydration mechanism is that three hydrogen cations simultaneously occupy a MgO<sub>6</sub> octahedron, whereas four such hydrogenated octahedra surround a vacant SiO<sub>4</sub> tetrahedron. The hydration of MgO<sub>6</sub> octahedra were occurred in both of powder and single crystal samples of hydrous ringwoodite, while the hydration of SiO<sub>4</sub> tetrahedra was occurred only within hydrous ringwoodite powder sample (Purevjav et al., Geophys. Res. Lett., 2014). The reason of this difference between the powder and the single crystal samples should be due to their difference in synthesis environments, because except pressure difference by 2 GPa and synthesis duration difference by 10 hours the other parameters are almost the same for both samples. The single crystals were grown from the hydrous melt, which sustains hydrostatic environment (low stress). But powder sample was synthesized from the solid-state reaction, which cannot sustain hydrostatic environment (high stress). It means that high stress on powder sample is related to the extensive hydration of SiO<sub>4</sub> tetrahedra.

Keywords: hydrous ringwoodite, neutron diffraction, structure refinement