

# Proton conduction in hydrous forsterite aggregate at different buffered (MgO or SiO<sub>2</sub>) conditions

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Hydrogen in magnesium site is expected to be the most active type in dominating hydrogen lattice diffusion and thus proton conduction in nominally anhydrous minerals (NAMS) (e.g. olivine) in past decades. However, an unexpected small amount of hydrogen in magnesium site pointed out by a growing number of researchers put it into question (e.g. Ingrin et al., 2013; Xue et al., in press). Even if it is not that case, water effect on electrical conductivity quantified by total water content has been inaccurate given the hypothesis that hydrogen diffusion rate was site-specific in forsterite (Padron-Navarta et al., 2014). Therefore, a further evaluation on proton conduction in olivine is required. To clarify the contribution of hydrogen in different sites, we measured the electrical conductivity of hydrous forsterite as a function of water content at different buffered conditions (MgO-buffered and SiO<sub>2</sub>-buffered).

Forsterite aggregate with various water contents were synthesized at MgO- and SiO<sub>2</sub>-buffered conditions from 4 GPa to 8 GPa, 1373 K in a multi-anvil apparatus. Water content was determined by FTIR using Paterson calibration and occasionally SIMS. Absorption peaks of FTIR were assigned to different sites and water contents in each specific site were calculated. Electrical conductivity measurements were performed at the same pressure from 500 to 800 K.

The maximum water content in MgO-buffered sample (1500 wt. ppm) at 4 GPa was found to be near 10 times that of SiO<sub>2</sub>-buffered sample, indicating its superior water storage capacity. Compared with water content calibrated by Paterson method, SIMS measurement usually gives more than 3 times and more than 1.5 times amount of water for MgO-buffered sample and SiO<sub>2</sub>-buffered sample respectively at 4 GPa. FTIR spectra in the former shows extremely high intensity of peaks at wavenumbers higher than 3500 cm<sup>-1</sup>, while broad and noisy peaks at lower wavenumbers dominate in the latter. Peak assignment shows a dominance of hydrogen associated with silicon site in MgO-buffered sample and magnesium site in SiO<sub>2</sub>-buffered sample. With increasing pressure, difference in FTIR spectra in these two buffered conditions minimized. Both samples were dominated by peaks at wavenumbers higher than 3500 cm<sup>-1</sup>, indicating an increasing preference of hydrogen for silicon site at 8 GPa even in SiO<sub>2</sub>-buffered forsterite. Water content measured by SIMS in one SiO<sub>2</sub>-buffered sample is more than 3 times that of FTIR calibration, similar to the situation of MgO-buffered at lower pressure.

For electrical conductivity measurement, high resistance of forsterite close to the background insulation at low temperature and dehydration at relatively higher temperature prohibited us to obtain good spectra. Preliminary results show that for MgO-buffered sample at 4 GPa, electrical conductivity increases with increasing water content (from 760 wt. ppm to 1470 wt. ppm) while their activation enthalpies decrease from 0.79 eV to 0.61 eV. For SiO<sub>2</sub>-buffered sample, activation enthalpy is 1.23 eV for the only one sample. And its extrapolated conductivity to lower temperature crosses with that of MgO-buffered sample containing about 800 wt. ppm water at around 675 K. Combined with the FTIR peak assignment, such coincidence is probably caused by a different contributing factor of hydrogen in different sites. To verify our speculation, more experiments are needed, both at 4 GPa and 8 GPa. To prevent early dehydration during conductivity measurement, new setups aimed at controlling water fugacity will be tried.

Keywords: Proton conduction, Hydrous forsterite, Hydrogen position, Incorporation preference, Peak assignment and deconvolution

