

Hydrogen incorporation mechanisms in forsterite: ^1H NMR measurement and first-principles calculation

X. XUE^{1*}, M. KANZAKI¹, D. TURNER² AND D. LOROCH³

¹Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193 Japan
(*correspondence: xianyu@misasa.okayama-u.ac.jp)

²Institute of Geoscience, University of Jena, Burgweg 11, Jena 07749 Germany

³Institute for Mineralogy, Universität Münster, Corrensstrasse 24, Muenster, D-48149 Germany

Olivine is known to accommodate significant amount of OH defects under high pressure and temperature. Most of the studies of hydrogen (H) incorporation mechanisms in olivine relied on infrared spectra, which have been interpreted in terms of substitution of H for either Mg or Si or both.

Here, we present ^1H static and MAS NMR data (obtained using a 400-MHz spectrometer) on a Mg_2SiO_4 forsterite sample containing ~ 0.5 wt% H_2O (synthesized at 12 GPa and 1200°C), as well as first-principles GIPAW calculation results, which shed new light on this issue.

The ^1H static and MAS NMR spectra (10-30 kHz spinning rates) both revealed two main components, one experiencing strong ^1H - ^1H homonuclear dipolar couplings and contributing to a broad peak centered near 2.4 ppm, and another with weaker dipolar couplings and contributing to a narrower peak near 1.2 ppm in the MAS spectra. 2D ^1H NOESY experiment confirmed that the two components belong to the same phase (forsterite). In addition, there is a very weak, narrow MAS NMR peak near 7.2 ppm (contributing to $< 0.1\%$ of the total intensity).

First-principles GIPAW calculations (geometry optimization and NMR parameters) were performed on several model forsterite structures (2x1x2 supercell) with 1Si replaced by 4H or 1Mg replaced by 2H using the Quantum-ESPRESSO package. The lowest-energy models for the 4H = 1Si substitution have one H pointing away from the center of the tetrahedron, and can well reproduce the observed features (chemical shift & dipolar couplings) for the two main components in the ^1H NMR spectra. The lowest-energy model for the 2H=1Mg (in M1 site) substitution can account for the observed very weak and narrow ^1H NMR peak near 7.2 ppm.

Thus, this study has unambiguously confirmed that the dominant H substitution mechanism in forsterite synthesized at 12 GPa is 4H=1Si (hydrogarnet-like, but with different H_4O_4 configurations), with only very minor H substituting for Mg (in M1 site).