

Incorporation mechanisms of hydrogen in enstatite

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Water, even when present in trace amounts in ‘nominally anhydrous’ major mantle minerals, could have significant effects on mantle properties. As the effects of water on mineral properties strongly depend on how it is incorporated in the crystal structure, a fundamental understanding of the structure is indispensable. Most of the studies on hydrogen incorporation in ‘nominally anhydrous’ minerals have been carried out so far using infrared spectroscopy. The interpretations are, however, often controversial. Recently, we demonstrated on forsterite, endmember of the most abundant upper mantle mineral, olivine that a combined multi-nuclear (¹H, ²⁹Si) NMR and first-principles calculation approach is a very effective and revealed that the predominant H incorporation mechanism in forsterite at 12 GPa is (4H)_{Si}, with minor (2H)_{M1} (Xue et al. 2017, Am. Mineral. 102, 519-536).

The aim of this study is to apply a similar approach to gain insights into the hydrogen incorporation mechanisms in MgSiO₃ enstatite, endmember of the second most abundant upper mantle mineral, low-Ca pyroxene.

Samples studied include orthoenstatite containing nominally 0.05-0.1 wt% H₂O, synthesized at 7 GPa, 1200°C for 1 hr., and low-clinoenstatite with 0.3-0.5 wt% H₂O, synthesized at 14 GPa, 1200°C for 1 hr. using a multi-anvil press. The starting material was a mixture of MgSiO₃, Mg(OH)₂ and SiO₂. The respective phases were confirmed by Raman spectroscopy. Low-clinoenstatite likely formed from high-P clinoenstatite during recovery to ambient condition.

The ¹H MAS NMR spectra obtained at 10-30 kHz spinning rates and 400 MHz resonance frequency are markedly different for the two enstatite phases. The spectra for orthoenstatite (7 GPa) are dominated by two narrow peaks near 5.8 and 7.8 ppm of equal intensities, whereas those of clinoenstatite (14 GPa) are much broader with peak maxima (or shoulders) recognized near 0.3, 3, 5.8, 8 and 12 ppm, and the peak widths in general are narrower at higher spinning rates, suggesting strong ¹H-¹H dipolar interactions. First-principles DFT calculations (structural relaxation and NMR parameters) were performed on several orthoenstatite and low-clinoenstatite supercell (1x1x2) models that contain either 2H substituting for 1Mg in M1 or M2 site, or 4H substituting for 1Si in SiA or SiB site, similar to our previous study for forsterite. The results suggest that the ¹H NMR spectra for orthoenstatite (7 GPa) are consistent with (2H)_{Mg}; those of clinoenstatite (14 GPa) are consistent with (4H)_{Si} as the predominant substitute mechanism, with the strong ¹H-¹H dipolar interactions resulted from clustering of the 4H in the Si vacancy. The presence of ¹H NMR peak of large chemical shift (12 ppm) for the latter suggests that some of the protons have strong hydrogen-bonding. The latter is expected to yield low O-H stretching frequency (<3000 cm⁻¹) and may be complicated by Fermi resonance, rendering it difficult to detect and may have been overlooked in previous infrared studies (that only reported > 3000 cm⁻¹ region).

In conclusion, this study revealed a clear change of H substitution from (2H)_{Mg} in orthoenstatite (7 GPa) to (4H)_{Si} in clinoenstatite (14 GPa). Additional results for intermediate pressure range, as well as ²⁹Si NMR data, will be presented at the meeting. The study also suggests that previous vibrational spectroscopic studies may have failed to detect all the O-H stretching bands for enstatite, and thus need to be revisited.

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