

Hydrogen incorporation and the oxidation state of iron in ringwoodite: A spectroscopic study

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ABSTRACT

Ringwoodite [(Mg,Fe)₂SiO₄] is the high-pressure polymorph of olivine stable in the upper mantle between ~525 to 660 km. Information on its temperature-dependent water content and Fe-oxidation state bears important implications on the hydrogen cycle and oxidation state of the Earth's interior. We conducted several multi-anvil experiments to synthesize iron-bearing ($0.11 \leq x_{\text{Fe}} \leq 0.24$) hydrous ringwoodite under oxidizing and reducing conditions. The experiments were performed at 1200 °C and pressures between 16.5 and 18.3 GPa. The incorporation of hydrogen and iron in ringwoodite was studied using Fourier transform infrared (FTIR), Mössbauer (MB), ultraviolet-visible (UV-VIS), and electron energy loss (EEL) spectroscopy. For MB spectroscopy, ringwoodite enriched in ⁵⁷Fe was synthesized. The IR spectra of ringwoodite show a broad OH band around 3150 cm⁻¹ and two shoulders on the high-energy side: one intense at 3680 cm⁻¹ and one weak at around 3420 cm⁻¹. The water content of the samples was determined using FTIR spectroscopy to have a maximum value of 1.9(3) wt% H₂O. UV-VIS spectra display a broad band around 12 700 cm⁻¹ and a shoulder at 9900 cm⁻¹ representing the spin-allowed dd-transitions of ^{VI}Fe²⁺. The weaker band around 18 200 cm⁻¹ is a distinct feature of Fe²⁺-Fe³⁺ intervalence charge transfer indicating the presence of Fe³⁺ in the samples. EEL spectra yield Fe³⁺ fractions ranging from 6(3)% at reducing conditions to 12(3)% at oxidizing conditions.

We performed heating experiments up to 600 °C in combination with in situ FTIR spectroscopy to evaluate the temperature-dependent behavior of ringwoodite, especially with respect to hydrogen incorporation. We observed a color change of ringwoodite from blue to green to brown. The heat-treated samples displayed hydrogen loss, an irreversible rearrangement of part of the hydrogen atoms (FTIR), as well as oxidation of Fe²⁺ to Fe³⁺ evidenced by the appearance of the spin-forbidden dd-transition band for Fe³⁺ and the ligand-metal (O²⁻-Fe³⁺) transition band in the optical spectra. An increased Fe³⁺ fraction was also revealed by EEL and MB spectroscopy (up to 16% Fe³⁺/ΣFe). Analyses of MB data revealed the possibility of tetrahedral Fe³⁺ in the annealed ringwoodite.

These results lead to a reinterpretation of the broad OH band, which is a combination of several bands, mainly [V_{Mg}(OH)₂]^δ, a weaker high-energy band at 3680 cm⁻¹ ([V_{Si}(OH)₄]^δ) and a shoulder at 3420 cm⁻¹ ([V_{Si}(OH)₂]^δ).

Keywords: Ringwoodite, water, iron, oxygen fugacity, hydrogen location, spectroscopy