

Incorporation of Fe³⁺ in ringwoodite studied via EELS, FTIR-, and Mössbauer spectroscopy

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Ringwoodite is the most abundant mineral in the lower transition zone between 520 and 660 km in the Earth's mantle. It is the high-pressure γ -polymorph of $(\text{Mg,Fe})_2\text{SiO}_4$ and occurs in spinel structure. Although it is nominally anhydrous it can incorporate up to 3 wt % water as OH via point defects (e.g. Inoue et al., 1995). In general the OH-incorporation depends quali- and quantitatively on pressure, temperature, composition, and oxygen fugacity.

The latter parameter controls the fraction of ferric to ferrous iron. McCammon et al. 2004 reported on Fe³⁺ in ringwoodite synthesized under different f_{O_2} with the ferric iron content increasing with increasing oxygen fugacities reaching up to 18 (4) %. They also stated that there is a correlation between ferric iron and OH incorporation in phases of the upper mantle.

We conducted several Multi-Anvil-experiments to synthesize iron-bearing ($0.10 \leq x_{\text{Fe}} \leq 0.19$) hydrous ringwoodite under oxidizing (Re/ReO₂ buffer) and reducing (Fe/FeO buffer) conditions. The experiments were performed at constant temperature of 1200°C and pressures between 16.5 and 18.3 GPa. For ⁵⁷Fe-Mössbauer spectroscopy ringwoodite enriched in ⁵⁷Fe was synthesized.

The FTIR spectra in the OH stretching region of the different samples show a broad OH band around 3150 cm⁻¹ and two shoulders on the high-energy side: one intense at 3675 cm⁻¹ and a weak one at around 3460 cm⁻¹. The water content of the samples was determined using FTIR spectroscopy to a maximum value of app. 2 wt.% H₂O.

The analyses of EEL-spectra yield Fe³⁺ fractions ranging from 10 (4) at reducing to 19 (7) % at oxidizing conditions. According to the Mössbauer spectrum the ⁵⁷Fe-enriched sample contains 5 (2) % Fe³⁺ that - on the basis of the measured spectrum - could solely be assigned to the octahedral site.

High-temperature FTIR spectra were collected in-situ up to 700°C in 100°C steps. At about 500°C a dramatic change in the OH-spectra occurs. In addition to an overall decrease of the main broad IR-band around 3150 cm⁻¹ due to hydrogen loss, a strong increase of both shoulders can be observed indicating a rearrangement of a part of the hydrogens. On progressive heating to 700 °C a strong dehydration is characterized by a clear intensity loss of OH-bands in the complete IR-spectrum but the sample is still ringwoodite. The EEL-spectra taken on a FIB-foil of the quenched crystal reveal an oxidation of Fe²⁺ as the fraction of ferric iron increases from 15 (7) in the untempered sample to 28 (3) % in the sample annealed to 500 °C. X-ray diffraction analyses of the quenched samples show an increase of the lattice constant a from 8.096 (4) (ambient) to 8.112 (3) (500 °C) up to 8.134 (5) Å (700 °C) and reflects the expanding of the structure induced by heating.

References:

Inoue, T., Yurimoto, H., Kudoh, Y. (1995), *Geophysical Research Letters*, 22, 117-120.

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