The effect of Fe on olivine H\textsubscript{2}O storage capacity: Consequences for H\textsubscript{2}O in the martian mantle

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**Abstract**

To investigate the influence of chemical composition on the behavior of H\textsubscript{2}O in Fe-rich nominally anhydrous minerals, and to determine the difference between H\textsubscript{2}O behavior in the martian and terrestrial mantles, we conducted high-pressure H\textsubscript{2}O storage capacity experiments employing a wide range of olivine compositions. Experiments were conducted with bulk compositions in the system FeO-MgO-SiO\textsubscript{2}-H\textsubscript{2}O with Mg no. \((\text{Mg no.} = 100 \times \text{molar Mg/(Mg+Fe)})\) ranging between 50 and 100 at 3 GPa in a piston-cylinder and at 6 GPa in a multi-anvil apparatus. Experiments at 3 GPa were conducted at 1200 °C, with \(f_{\text{O}_2}\) buffered by the coexistence of Fe and FeO, and at 1300–1500 °C in unbuffered assemblies. Experiments at 6 GPa were conducted at 1200 °C without buffers. Experiments at 1200 °C produced olivine + orthopyroxene + hydrous liquid (liq), and higher \(T\) experiments produced olivine + liq. Additionally, we synthesized a suite of 7 olivine standards (Mg no. = 90) for low blank secondary ion mass spectrometry (SIMS) analysis of H in multi-anvil experiments at 3–10 GPa and 1250 °C, resulting in large (200–400 \(\mu\)m) homogeneous crystals with 0.037 to 0.30 wt% H\textsubscript{2}O. Polarized Fourier transform infrared (FTIR) measurements on randomly oriented grains from the synthesis experiments were used to determine principal axis spectra through least-squares regression, and H contents were calculated from the total absorbance in the OH stretching region. Using these olivines as calibrants for SIMS analyses, the H contents of olivines and pyroxenes from the variable Mg no. experiments were measured by counting \(^{16}\text{OH}\) ions. Ignoring any matrix effects owing to variation in Mg no., H contents of olivine and pyroxene increase linearly with decreasing Mg no. At 6 GPa and 1200 °C, olivine H contents increase from 0.05 to 0.13 wt% H\textsubscript{2}O (8360 to 23 900 H/10\(_6\)Si) as olivine Mg no. decreases from 100 to 68, and at 3 GPa and 1200 °C olivine H contents increase from 0.017 to 0.054 wt% (278 to 10 000 H/10\(_6\)Si) as Mg no. decreases from 100 to 55. The partition coefficient for H between pyroxene and olivine, \(D_{\text{H}\text{opx/ol}}\), decreases from 1.05 at 3 GPa and 1200 °C to 0.61 at 6 GPa and 1200 °C. The storage capacity of Fe-rich olivines with compositions expected in the martian mantle is \(\sim 1.5\) times greater than those in the terrestrial mantle, suggesting that the geochemical behavior of H\textsubscript{2}O in the mantles of the two planets are quite similar. If 50% of the K\textsubscript{2}O on Mars remains in its mantle (Taylor et al. 2006), then a similar or greater proportion of the H\textsubscript{2}O is also in the mantle. Given accretionary models of the total martian H\textsubscript{2}O budget (Lunine et al. 2003), this suggests concentrations of 100–500 ppm H\textsubscript{2}O in the martian mantle and 0.1–1.9 wt% H\textsubscript{2}O in primary martian basalts.

**Keywords:** Olivine, H\textsubscript{2}O storage capacity, Mars, infrared spectroscopy, ion microprobe

**Introduction**

Small concentrations of hydrogen dissolved in mantle minerals play a critical role in the dynamics of planetary interiors. Trace amounts of hydrogen dissolved in nominally anhydrous minerals have a substantial influence on the viscosity of convecting interiors (Karato and Wu 1993; Mei and Kohlstedt 2000a, 2000b) as well as the strength of planetary lithospheres (Kohlstedt et al. 1995; Mackwell et al. 1990), and thereby influence planetary tectonic evolution. Dehydration of nominally anhydrous peridotite may lead to hydrous partial melting in several tectonic environments (Hirth and Kohlstedt 1996; Asimow and Langmuir 2003; Hirshmann 2006), including those significantly deeper than the sources of planetary basalts (e.g., Bercovici and Karato 2003; Hirshmann et al. 2005). The storage capacity of hydrogen, considered as H\textsubscript{2}O, in planetary mantles is also a key parameter influencing the history of volatile fluxes from planetary interiors to the surface (Rüpke et al. 2004; Hirshmann 2006). Importantly, the H\textsubscript{2}O storage capacities of planetary interiors may differ substantially according to compositional and thermal differences between planets.

As in Earth, the upper parts of the martian mantle are composed chiefly of olivine and its higher pressure polymorphs, wadsleyite and ringwoodite. These phases are known to be