“Hydroxylation spectroscopy” of olivine tested on synthetic forsterite

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Olivine $(Mg,Fe)_2SiO_4$, the most abundant phase in the upper mantle, can incorporate a few ppm to tens or even hundreds of ppm of water as hydroxide anions in its structure. Even at such low concentrations, the presence of H^+ in the structure of olivine has a profound influence on its physical properties and, consequently, geologic processes such as mantle convection and partial melting. The incorporation of H^+ in olivine is mediated by a variety of hydrous point defects, related to Si^{4+} and Mg^{2+} vacancies, or coupled substitution with Ti^{4+} or trivalent cations (*e.g.*, Al^{3+}). These different types of hydrous point-defects can be fingerprinted using infrared spectroscopy. The point defect chemistry of olivine depends on parameters such as silica activity or oxygen fugacity, which are inherent to the last equilibrium conditions of the olivine. If the relaxation of the high-temperature point defect structure is slow compared to the rapid diffusion of H^+ into the crystal, then “decorating” the existing point-defect structure of an olivine by experimentally diffusing H^+ into it potentially makes its point-defect structure visible to identification using infrared light, thus revealing information about its geologic history. Here we present experimental results to test whether we can illuminate the pre-existing point defect structure of synthetic forsterite (Mg_2SiO_4) prepared under controlled conditions of temperature, silica activity and oxygen fugacity, as a first step towards seeing how effective this technique of “hydroxylation spectroscopy” may be in illuminating the point defect chemistry of natural mantle olivine crystals.
Experiments were performed with cubes of synthetic forsterite in a piston cylinder apparatus. The forsterite cubes were annealed at temperatures ranging between 1100 and 1500 °C for 8 days, in contact with Forsterite-Enstatite (Fo-En) or Forsterite-Periclase (Fo-Per) silica activity buffers. Annealed and un-annealed cubes were then loaded in silver capsules along with liquid water and a combination of silica activity and oxygen fugacity buffers. Hydroxylation of the cubes was done at 900°C and 1.5 GPa. Unpolarized and polarized infrared spectra were acquired along the principal axis of the crystals, along profiles of a few hundred micrometers. From those spectral profiles, diffusion coefficients were quantified and the diffusion mechanisms inferred, using the unique infrared signature of each type of defect.
Results show that H^+ diffuses faster than expected in [Si] vacancies, such that this mechanism may contribute as much as H^+ diffusion in [Mg] vacancies to the global diffusion of “water” in Forsterite. The hydroxylation experiments further allow us to assess how the initial annealing conditions of the crystals influence the diffusion mechanism of H^+.

Keywords: Olivine, Water, Diffusion, Hydroxylation, Infrared spectroscopy

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