

## **“Hydroxylation spectroscopy” may reveal the history of olivine crystals**

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Olivine ( $\text{Mg,Fe}_2\text{SiO}_4$ ), the most abundant phase in the Earth's upper mantle, can incorporate a few parts per million (ppm) to tens or even hundreds of ppm of water as protons  $\text{H}^+$  bound to oxygen 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  $\text{H}^+$  in olivine is mediated by a variety of hydrous point defects, related to  $\text{Si}^{4+}$  and  $\text{Mg}^{2+}$  vacancies, or coupled substitution with  $\text{Ti}^{4+}$  or trivalent cations (*e.g.*,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$ ), which can be identified using infrared spectroscopy. The point-defect chemistry of olivine depends on variables such as temperature, pressure, silica activity and oxygen fugacity, which are inherent to the last equilibrium conditions of the olivine. If the diffusive relaxation of the high-temperature point defect structure is slow compared to the rapid diffusion of  $\text{H}^+$  into the crystal, then “decorating” the existing point-defect structure of an olivine crystal by experimentally diffusing  $\text{H}^+$  into it makes this structure visible to infrared light, thus revealing information about its geologic history.

Here we present a feasibility study using synthetic forsterite ( $\text{Mg}_2\text{SiO}_4$ ) crystals, which demonstrates the potential of this new technique of “hydroxylation spectroscopy”. The forsterite crystals were first equilibrated under controlled conditions of temperature, silica activity and oxygen fugacity. After this *annealing stage*, crystals are hydroxylated in a piston-cylinder apparatus at 900°C and 1.5 GPa during an *hydroxylation stage*. After hydroxylation, polarized IR spectra are acquired along the principal axis of the crystals, along profiles of a few hundred micrometers.

Results show that, under the same hydroxylation conditions (900 °C and 1.5 GPa, forsterite-enstatite silica activity buffer, Re-ReO<sub>2</sub> oxygen fugacity buffer), crystals with different annealing history have different concentrations of H in the different point defects. Systematic relationships between H content in the point defect, silica activity and temperature of the annealing stage are observed. As a result, hydroxylation of a forsterite crystal allows its previous equilibrium conditions to be revealed. Extended to natural olivine, this approach promises to uncover novel information about the history of olivine crystals and their host rocks.