

Fingerprints for coupled substitutions of H and trivalent elements in olivine from polarized infrared spectroscopy

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Infrared spectroscopic measurements of olivines from mantle xenoliths commonly reveal evidence for the presence of trace amounts of H₂O. The complexity of infrared spectra in the OH-stretching region shows that several competing substitutional mechanisms for H can operate at the same time. Previous work has shown convincingly that peaks appearing in the region between 3250 and 3400 cm⁻¹, the so-called group 2 bands, arise from OH groups that form a defect complex with an M-site vacancy and a trivalent element, such as Fe³⁺ or Al. These group 2 bands are commonly observed in olivines from mantle xenoliths, and are frequently attributed to a coupled substitution that involves Fe³⁺. However, the positions of the various peaks associated with coupled substitutions with different trivalent elements are similar, so an unambiguous assignment was not previously possible.

I will show that polarized transmission infrared spectroscopy can be used to fingerprint the different elemental substitutions. Olivines were synthesized in hydrothermal multianvil experiments at 6 GPa and 1400 °C, with added Fe₂O₃, Al₂O₃, or Cr₂O₃. The orientations of OH dipoles for forsterites doped with Fe³⁺, Al, and Cr are distinct and provide fingerprints for the different possible substitutions. Iron-bearing olivines synthesized without oxygen buffer and without Cr or Al show limited group 2 bands, indicating that under these conditions a small proportion of the H in olivine is associated with Fe³⁺. With the addition of Cr₂O₃ to the starting material, on the other hand, a good match for the group 2 bands of natural olivine is obtained.

Without performing polarized analysis of oriented samples, it was not previously possible to differentiate between the infrared fingerprints for different coupled substitutions involving trivalent elements. Group 2 bands were sometimes, but not always, observed in previous experimental studies where natural olivines were used as starting materials. This inter-study variation is likely owing to variations in Cr concentrations in the starting materials. The f_{O_2} dependence of the group 2 bands in olivine observed in previous studies is likely attributable partly to changes in f_{H_2O} and partly to a redox reaction that consumes Cr³⁺ and creates Cr²⁺ with decreasing f_{O_2} .