

The infrared signature of water associated with trivalent cations in olivine

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The most common and intense hydroxyl infrared stretching bands in spinel peridotite olivine (at 3572 and 3525 cm^{-1}) derive from water at defect sites associated with the trace element Ti [1]. This was shown by experiments in which these bands could only be reproduced in olivines grown under upper mantle conditions from compositions containing Ti. Other bands at 3355 and 3325 cm^{-1} have been attributed to water associated with Fe^{3+} since they occur experimentally only in Fe-bearing compositions, in particular when oxidation is likely to have occurred. To test the possibility that other trivalent trace elements in olivine may be involved in hydroxyl substitutions we have investigated the effect of a large number of trivalent cations on the infrared spectra of hydrous olivine.

Forsterite crystals were synthesised from an oxide composition corresponding to $\text{Mg}_2\text{SiO}_4 + 10 \text{ wt\% SiO}_2 + 7 \text{ wt\% H}_2\text{O} + 1 \text{ wt\% M}_2\text{O}_3$, where $M = \text{B, Al, Sc, V, Cr, Mn, Fe, Co, Ga, Y, Sm, Gd, Dy, Tm, or Lu}$, at 1400 °C and 1.5 GPa. The experiments were buffered by various techniques at the appropriate oxygen fugacity to stabilise the trivalent oxidation state. Run products consisted of olivine in equilibrium with hydrous melt. Concentrations of the dopants were determined by LA-ICPMS and were found to vary systematically with the trivalent ionic radius; deviations from the trend for some elements perhaps indicate different or additional valence states.

The infrared spectra of all samples exhibit the bands typical of buffering at a high silica activity [1] and are essentially identical except for the region between 3300 and 3400 cm^{-1} . This region is characterised by one or more bands with the energy of the most intense feature being correlated linearly with the trivalent ionic radius. The area of these hydroxyl peaks also correlates with the concentration of the trivalent metal. This is unambiguous evidence that these peaks correspond to water at defect sites associated with trivalent cations.

The occasional appearance of "trivalent bands" in natural samples corresponds to water associated with Fe^{3+} . The water at these sites is unlikely to be incorporated under mantle conditions and should not be included in estimates of the water capacity of mantle olivine.

References

[1] Berry A.J. *et al.* (2005) *Geology* 33, 869-872.