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}) derived from water at defect sites associated with the trace element Ti (Berry, 2005). 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 $\mathrm{Mg_2SiO_4} + 10$ wt% $\mathrm{SiO_2} + 7$ wt% $\mathrm{H_2O} + 1$ wt% $\mathrm{M_2O_3}$, where M = 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 (Berry, 2005) 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.

Reference

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Geochemical characteristics of the Yao'an and machangqing Alkaline-rich intrusions in the Ailaoshan-Jinshajiang belt, western yunnan, China

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The NW-NNW trending Ailaoshan-Jinshajiang fault zone is one of the biggest strike-slip systems on Earth related to escape tectonics from the India-Eurasia collision since the early Himalayan orogeny. Numerous alkaline igneous rocks occur along or near the fault zone, forming the Ailaoshan-Jinshajiang alkaline intrusive belt over 1000 km long. In recent years numerous gold deposits and copper deposits have been discovered in the area, which are spatially related to and contemporaneous with these alkaline intrusions. The recent researches showed that there are genetic connections between alkaline magmatism and mineralzation.

The Yao'an and Machangqing alkaline-rich intrusions, form parts of the Ailaoshan-Jinshajiang alkaline-rich intrusive belt. The Yao'an intrusion consists mainly of syenite porphyry, and the Machangqing intrusion consists mainly of granite porphyry. Chemically these two intrusions are characterized by enrichment in alkaline and potassium. They enrich in LREE and LILE (such as Rb, Sr, Ba, Th, La etc.), deplet HFSE (such as Nb, Ta and Ti etc.), have high Rb/Sr, La/Nb, Ba/Nb and LREE/HREE ratios, and don't show obvious Eu anomalies. The $\mathrm{I_{Sr}}$ values of these two intrusions are relatively high, and ϵ_{Nd} values are relatively low. It is suggested that the intrusions were derived from partial melting of an enriched upper mantle (EMII), a mixture between normal mantle and subducted oceanic crust, in a continental arc of extension tectonic setting. Although these two intrusions share similar characteristics on tectonic setting in the Himalayan period, age and source region, they have some difference on lithology and chemical composition, which was probably related to the difference on physical-chemical condition (such as T, P and $f\mathrm{O_2}$ etc.) during magmatic crystallization, and on different melted degress of source rocks. Au mineralization is considered to be associated with the intrusions of alkaline series while Cu mineralization with the intrusions of alkaline-subalkaline series in Ailaoshan- Jinshajiang alkaline intrusive belt.

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