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The effect of dissolved water on the intracrystalline partitioning of Al in orthopyroxene

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It has been suggested previously that the partitioning of Al between the tetrahedral and octahedral sites in orthopyroxene might be sensitive to the dissolution of water, and it was proposed that this phenomenon could provide a geohygrometer for mantle xenoliths. To test this idea, a series of samples of aluminous orthopyroxenes were synthesised and the aluminium coordination was studied using ²⁷Al MAS NMR.

Wet and dry samples were synthesised at 2 GPa and 1200°C in the stability field of orthoenstatite using run times of 1-4 days. Additional syntheses were performed at 1 atm. pressure in the field of protoenstatite. Samples were characterised using scanning electron microscopy and powder X-ray diffraction and ²⁷Al MAS NMR spectra were obtained at fields of 9.4T, 14.1T and 16.45 T.

The peaks for tetrahedral aluminium are extremely broad at 9.4 T, and even a field of 14.1T is not sufficient to fully resolve the tetrahedral and octahedral components of the spectra. This results from an unusually large electric field gradient for the Al^[4]. The measurements made at 16.45 T are therefore the most useful for quantifying the relative amounts of the different species. No change in the relative concentrations of Al^[4] and Al^[6] was seen when comparing dry and hydrous opx samples. The apparent concentrations of Al in the different coordinations was 40±2% Al^[4] and 60±2% Al^[6], however the tetrahedral Al has a much larger quadrupole coupling constant than the octahedral Al, so these numbers require a correction which probably brings them into agreement with the 50:50 ratio expected for Tschermak's substitution.

Despite the lack of change in the partitioning of Al between tetrahedral and octahedral sites, there are substantial differences in the nature of the Al sites between wet and dry samples. In the wet samples a new, relatively narrow, tetrahedral component is present which corresponds to between 10 and 20% of the total tetrahedral Al. An analogous peak for octahedral aluminium also appears to be present in wet samples, but is less striking because of overlap with the normal octahedral aluminium peak. The concentration of these new aluminium peaks is comparable with the expected dissolved H₂O concentration (on a molar basis), and a quantitative understanding of the relationship between the new Al species and the H₂O dissolution mechanism is currently being developed.

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The water site in mantle olivine

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Nominally anhydrous minerals (NAMs) such as olivine contain trace amounts of water and may accommodate the entire water budget of the Earth's upper mantle. This water is identified and quantified from the hydroxyl stretching region of infrared spectra. The spectra contain numerous bands which differ in number and intensity between samples. These bands are representative of different defect sites although there is no relationship between the bands and the tectonic setting. The nature of the defects and the mechanism of water incorporation remains unclear. In particular, the experimental synthesis of olivine samples under mantle conditions has hitherto not reproduced the hydroxyl spectrum characteristic of natural samples. This questions whether natural samples retain the water content corresponding to equilibrium conditions in the mantle.

In piston-cylinder experiments simulating upper mantle conditions we have successfully reproduced the first-order hydroxyl features of mantle olivines. Intense, characteristic peaks at 3572 and 3525 cm⁻¹, which appear in essentially every natural sample, are associated with the presence of Ti. These Ti point defects are the lowest energy hydrated defect in olivine. Further experiments have allowed additional bands to be attributed to Ti-clinohumite like defects, Si vacancies, Mg vacancies, and the effects of Fe oxidation. This provides a means of fingerprinting natural samples for the conditions of water incorporation. Samples exhibiting complex spectra, which are frequently the most hydrous, do not reflect mantle chemistry or water content.

We suggest that the Ti content of mantle olivine provides a control or upper limit on the water solubility. The resulting maximum water content of olivine in spinel peridotite is ~30 ppm, and in garnet peridotite ~100 ppm. This is in agreement with the finding that olivines from spinel peridotites have significantly lower water contents than those from garnet peridotites. High water contents observed in some samples (~200 ppm) are anomalous and these values can not be extrapolated to the entire upper mantle. While it is likely that NAMs in garnet lherzolite are able to accommodate the expected mantle water budget, this may not be the case for spinel peridotites for which we estimate a water storage capacity of only 90-130 ppm. The decreasing capacity to store water from garnet to spinel peridotite suggests that H₂O may occur as either a fluid, melt, or mineral phase in the spinel peridotite field.