

Comparisons between fluoride and hydroxide incorporation in nominally anhydrous and fluorine-free mantle minerals.

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The importance of water to the behaviour of the mantle is now widely recognised. A substantial body of data on the solubility of water in nominally anhydrous minerals has been obtained, and a range of constraints on the distribution of water in the mantle have been proposed. In contrast, the solubility of fluorine in nominally fluorine-free minerals (NFFMs) and the consequences for the global fluorine budget, the effects of fluorine on mantle properties and volatile recycling in subduction zones are all completely unexplored. Very few measurements of the F concentration in NFFMs have been reported (Hervig and Bell, 2005).

In this study, the solubility of fluorine in NFFMs was determined under shallow mantle conditions, by equilibrating forsterite and enstatite with fluorides, fluoro-clinohumite or fluorine rich silicate melts. Experiments were performed in piston-cylinder apparatus at pressures of 1-2 GPa and 1350-1600°C, and the phases present in the quenched samples were determined using SEM and EPMA. The concentration of F in olivine was measured using EPMA with a beam current of 100-200nA and an accelerating voltage of 15-20 kV.

Extraordinarily high solubilities up to 0.45 wt% F have been observed in olivine in the system Mg_2SiO_4 - MgF_2 . There is no apparent correlation between F and Mg concentrations in the olivine, implying that the high F concentrations are not simply due to inclusions or lamellae of MgF_2 or clinohumite. The fluorine solubilities observed in the Mg_2SiO_4 - CaF_2 and Mg_2SiO_4 - NaF systems are lower, for reasons which will be discussed. ^{19}F NMR and TEM studies are underway in order to definitively establish whether the high apparent solubility of F in forsterite is influenced by the incorporation of clinohumite lamellae in the structure, or is entirely associated with point defects such as oxygen vacancies.

The implications of a high solubility of F in NFFMs in the mantle could be wide ranging. For example the low recycling efficiency for F in subduction zones (Straub and Layne, 2003), could be explained by retention of F in NFFMs rather than by incorporation in hydroxyl-bearing minerals such as amphibole and serpentine. The differing partitioning and diffusion behaviour of OH and F imply that measurements of both F and OH concentrations in mantle-derived rocks could help constrain the mantle water cycle.

References

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Water in the mantle: The effect of olivine and orthopyroxene composition and fO_2

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Hydroxyl defects dissolved in olivine and orthopyroxene dramatically affect the physical, chemical and mechanical properties of the Earth's upper mantle. Understanding the processes governing the incorporation of these species is also essential before the total hydrogen contents of the Earth can be constrained. Here, we investigate hydroxyl speciation and solubility in both natural and experimentally re-equilibrated single crystals using polarised IR spectroscopy.

Our IR spectra demonstrate that the particular hydroxyl defects dissolved in olivine and orthopyroxene are strongly influenced by sample chemistry and experimental fO_2 . As a result, extreme caution must be exercised when developing models for solubility in both these phases in the upper mantle, particularly if models are based on data extrapolated from samples synthesised in chemically simple systems and/or experiments conducted under thermodynamic regimes not relevant to mantle conditions.

Experiments on olivine and orthopyroxene crystals from subduction-related, amphibole-bearing Ichinomegata xenoliths show that hydroxyl solubility in both phases increase with pressure and temperature. However, if all other variables remain constant (P, T, and aSiO₂), the effect of fO_2 on hydroxyl solubility in olivine contrasts sharply with orthopyroxene. Water contents in olivine crystals re-equilibrated at QFM and QFM -4 decrease from 65 to 50 ppm respectively, whilst the concentration in coexisting orthopyroxene increases from 550 to 640 ppm. Partitioning of hydrogen between these two phases will, therefore, vary as a function of oxidation state in the upper mantle.

Comparing spectra for a whole range of experimentally re-equilibrated samples with those in natural phases from Ichinomegata demonstrates that hydroxyl defect species and concentrations dissolved in natural crystals of olivine and orthopyroxene were inherited at near water-saturated conditions, similar to those of major element re-equilibration in the upper mantle (1.5 GPa, 950°C, QFM, enstatite buffered aSiO₂). Both the hydroxyl stretching modes and dissolved water contents are reproduced in the experimental samples. Water solubilities are lower than current solubility models would suggest, but do not appear to be the result of low pressure equilibration with the host magma during ascent.