Water in the mantle: The effect of olivine and orthopyroxene composition and fO₂

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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 fO₂ on hydroxyl solubility in olivine contrasts sharply with orthopyroxene. Water contents in olivine crystals reequilibrated 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 reequilibrated 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 disolved 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.