Hydrogen incorporation in olivine

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The main silicate phases of the Earth’s upper mantle, namely olivine, pyroxenes and garnet, do not have hydrogen as an essential component of their crystal structures, but they can contain geologically significant amounts of hydrogen as a trace element, substituting by point-defect mechanisms. In the context of hydrogen storage, these phases have therefore become known as “Nominally Anhydrous Minerals” or NAMs. The good correlations of H with incompatible trace elements like the light Rare Earth Elements (e.g., Ce) in suites of mid-ocean-ridge and ocean-island basalts (MORBs and OIBs) confirms the essentially trace-element-like behaviour of H. The H in NAMs occurs bonded to the oxygen anions (O^{2-}) in their crystal lattices, forming hydroxyl species (OH^-), and charge-balanced by cation vacancies with or without the coupled substitution of cations with different charge to those in the stoichiometric crystals. The presence of the OH^- anions is readily detected by infra-red spectroscopy, due to the good absorbance of the O-H stretching modes in the infra-red. Moreover, the O-H stretching modes are sensitive to next-nearest-neighbour effects, which may be used to deduce the nature of the H substitution mechanisms.

For Mg_2SiO_4-rich olivine, the most abundant phase in the upper mantle, experiments show that four different substitution mechanisms are commonly encountered, each identifiable by its characteristic infra-red fingerprint: those associated with Mg and Si vacancies, with 3+ cations, and with Ti^{4+}. Note that other H substitution mechanisms in olivine may exist under special circumstances, e.g., in olivines containing boron. The four main substitution mechanisms can be represented by the four equilibria:

$H_2O + Mg_2SiO_4(ol) = Mg\underline{\mathit{ov}}SiO_2(OH)_2(ol) + MgO$ (Mg-vacancies)

$2\ H_2O + Mg_2SiO_4(ol) = Mg_2\underline{\mathit{tv}}(OH)_4(ol) + SiO_2$ (Si-vacancies)

$0.5\ H_2O + Mg_2SiO_4(ol) + R^{3+}O_{1.5} = R^{3+}\underline{\mathit{ov}}SiO_3(OH)\ (ol) + 2\ MgO$ (trivalent)

$H_2O + MgO + TiO_2 = MgTi\underline{\mathit{tv}}O_2(OH)_2(ol)$ (titanoclinohumite point defect, or TiPD)

where $\underline{\mathit{ov}}$ and $\underline{\mathit{tv}}$ stand for octahedral and tetrahedral cation-site vacancies, respectively.

The H concentrations controlled by each of these four equilibria will in principle respond differently to temperature and pressure, and to chemical environment, specifically, to the activity of silica (a_{SiO2}), and the availability of trivalent cations and Ti. Importantly, the stoichiometry of the substitution mechanisms implies that they may also respond differently to $f(H_2O)$, if short-range ordering maintains the local charge balance implied by the substitution formulae; such short-range ordering seems required by the distinctiveness of the infra-red fingerprints. With short-range order, the concentration of H associated with trivalent cations would depend on $f(H_2O)^{1/2}$, with Mg-vacancies and TiPD on $f(H_2O)$, and with Si-vacancies on $f(H_2O)^2$. New experiments on H incorporation in Mg_2SiO_4(ol) doped with Sc and Ti at 15 kb and 1050ºC, with $f(H_2O)$ controlled at different values using H_2O-NaCl mixtures, confirm this hypothesis. This means that results from experiments at high $f(H_2O)$ (e.g., with $p(H_2O) = P_{total}$) cannot be applied directly to natural situations where $p(H_2O) << P_{total}$.The different substitution mechanisms are also associated with very different diffusion rates of H through olivine, and it is likely that they affect physical properties differently too.

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