



## Hydrogen diffusion in forsterite and implications for determining the water content of the mantle

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The retention of mantle hydrogen concentrations in “nominally anhydrous” minerals in mantle peridotites depends on the rates of exhumation versus diffusion. The infrared spectra of the hydroxyl stretching band in olivine of spinel lherzolite xenoliths are dominated by the substitution mechanism associated with trace  $\text{Ti}^{4+}$  (Berry *et al.*, 2005), suggesting the possibility that hydrogen diffusion rates may be dependent on Ti concentration and valence in these olivines.

A single slab of synthetic forsterite was doped with ca. 400ppm Ti by annealing at 1500°C, 1atm, QFM-5.6 in the presence of an  $\text{MgTiO}_3$ - $\text{Mg}_2\text{Ti}_2\text{O}_5$  mix. This forsterite then served as the target for hydrogen diffusion-in experiments, with the point defect population homogenous, elevated, and defined by Ti concentration and the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio in the high-temperature pre-annealed experiments.

The doped forsterite was then cut into cubes, which were placed inside a mix of forsterite+enstatite or forsterite+periclase in a thick walled silver capsule along with a saturating quantity of water and an oxygen fugacity buffer assemblage (Re- $\text{ReO}_2$ ), and taken to run conditions (15kbar, 650-950°C) in an end-loaded piston cylinder.

The crystals were recovered from the capsules and analysed by FTIR. Progressive ‘decoration’ of the homogenous titanium defect population, from crystal rim to core, yielded diffusion profiles of hydrogen associated to different defects. The spectra show that Ti occurs as both as  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . The ratio of OH associated with each of these Ti species remains constant along the diffusion pathways. There is no evidence for re-equilibration of the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio with the external Re- $\text{ReO}_2$  oxygen buffer, which would be expected to eliminate  $\text{Ti}^{3+}$ .

In all cases, hydrogen diffusion was anisotropic, fastest along the c-axis and slowest along a-axis. Hydrogen diffusion is slightly faster than in previous studies considering hydrogen diffusion-in (Demouchy & Mackwell, 2006), but significantly faster than hydrogen diffusion-out associated with titanium in forsterite (Padron-Navarta *et al.*, in press). Thus, the relative hydration states of olivines versus their surrounding assemblage must be considered when determining whether olivine water contents represent true mantle values after exhumation; diffusion-in of hydrogen will alter olivine significantly faster than diffusion-out.

Our results show that at typical conditions for spinel lherzolite xenoliths in the lithospheric mantle of 950°C, 15kbar, an anhydrous Ti-doped forsterite cube 1x1x1mm would be fully hydrated by an external hydrous fluid in a matter of hours.

The effect of Ti on H diffusion (either in or out) during exhumation must be considered when using mantle olivines to yield information regarding the water content of the mantle.

References: Berry, A.J., Hermann, J., O'Neill, H.St.C., Foran, G.J., 2005. Fingerprinting the water site in mantle olivine. *Geology* 33, 869-872; Demouchy, S., Mackwell, S., 2006. Mechanisms of hydrogen incorporation and diffusion in iron-bearing olivine. *Physics and Chemistry of Minerals* 33, 347-355; Padrón-Navarta J.A., Hermann, J., O'Neill, H. St. C. Site-specific hydrogen diffusion rates in forsterite. *Earth and Planetary Science Letters* (in press).