Hydrogen diffusion in Ti-doped forsterite and the preservation of metastable point defects

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Abstract

The effect of trace concentrations of Ti on the rate and mechanism of hydrogen diffusion in pure forsterite was investigated experimentally. Forsterite doped with 350–400 ppm Ti (predominantly octahedral Ti^{3+}, minor tetrahedral Ti^{4+}) was prepared by diffusing Ti into pure synthetic forsterite at high temperature (1500 °C), very low oxygen fugacity (~QFM-5) at atmospheric pressure. The Ti-doped forsterite was then diffusively hydroxylated in a piston-cylinder apparatus at much lower temperatures (650–1000 °C) and higher oxygen fugacities, at 1.5–2.5 GPa, with chemical activities buffered by forsterite-enstatite or forsterite-periclase and partial pressure of H_2O equal to total pressure. This produced hydrogen concentration-distance profiles of several hundred micrometers in length. Diffusion of hydrogen through the Ti-doped forsterite, even at very high f_{O_2}, does not lead to redox re-equilibration of the high $Ti^{3+}/\Sigma Ti$ ratio set during the synthesis of the starting material at extremely reducing conditions—the metastable point defects are partially preserved.

Three main hydroxylated point defects are observed; hydroxyl is associated with Ti^{4+} (titano-clino-humite point defects), Ti^{3+} (and possibly other trivalent cations), and M-site vacancies. Concentration-distance profiles represent an interplay between diffusion and reaction (i.e., site rearrangement) to form the observed point defects. In all experiments, the concentration-distance profiles of the hydroxylated Ti defects coincide with the concentration-distance profiles of the M-site vacancy substitution, with the same crystallographic anisotropy. This suggests that the macroscopic movement of hydrogen through the crystal is due to one diffusion mechanism (the diffusion of hydroxylated M-site vacancies). The net H diffusion coefficient [$\log D(\Sigma H)$], between 650–1000 °C, is

$$\log D(\Sigma H) = \log D_0(\Sigma H) + \left(\frac{-223(\pm 8)\,\text{kJ/mol}}{2.3 R T} \right)$$

where the values of $\log D_0(\Sigma H)$ parallel to [100] and [001] directions are -3.0 ± 0.4 and -2.2 ± 0.4, respectively; diffusion is therefore around one order of magnitude faster along the *c* axis than along the *a* axis. The diffusion of hydrogen is slightly faster in Ti-doped forsterite than in pure forsterite. There is no effect of chemical activity or oxygen fugacity on the rate of diffusion. Hydrogen diffusion profiles represent a complex interplay between the movement of H through the crystal lattice and point-defect reactions to maintain charge balance.

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