The potential for aqueous fluid-rock and silicate melt-rock interactions to re-equilibrate hydrogen in peridotite nominally anhydrous minerals

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Abstract
Hydrogen is a rapidly diffusing monovalent cation in nominally anhydrous minerals (NAMs, such as olivine, orthopyroxene, and clinopyroxene), which is potentially re-equilibrated during silicate melt-rock and aqueous fluid-rock interactions in massif and abyssal peridotites. We apply a 3D numerical diffusion modeling technique to provide first-order timescales of complete hydrogen re-equilibration in olivine, clinopyroxene, and orthopyroxene over the temperature range 600–1200 °C. Model crystals are 1–3 mm along the c-axis and utilize H⁺ diffusion coefficients appropriate for Fe-bearing systems. Two sets of models were run with different boundary compositions: (1) “low-H” models are constrained by mineral-melt equilibrium partitioning with a basaltic melt that has 0.75 wt% H₂O, and (2) “high-H models,” which utilize the upper end of the estimated range of mantle water solubility for each phase. Both sets of models yield re-equilibration timescales that are identical and are fast for all phases at a given temperature. These timescales have strong log-linear trends as a function of temperature (R² from 0.97 to 0.99) that can be used to calculate the expected re-equilibration time at a given temperature and grain size. At the high end of the model temperatures (1000–1200 °C), H⁺ completely re-equilibrates in olivine, orthopyroxene, and clinopyroxene within minutes to hours, consistent with previous studies. These short timescales indicate that xenolith NAM mantle water contents are likely to be overprinted prior to eruption. The models also resolve the decoupled water-trace element relationship in Southwest Indian Ridge peridotites, in which peridotite REE abundances are reproduced by partial melting models whereas the relatively high NAM H₂O contents require later re-equilibration with melt.

At temperatures of 600–800 °C, which correspond to conditions of hydrothermal alteration of pyroxene to amphibole and talc, H⁺ re-equilibration typically occurs over a range of timescales spanning days to years. These durations are well within existing estimates for the duration of fluid flow in oceanic hydrothermal systems, suggesting that peridotite NAM water contents are susceptible to diffusive overprinting during hydrothermal alteration. Thus, diffusion during aqueous fluid-rock interactions may also explain NAM H₂O contents that are too high to reflect residues of melting. These relatively short timescales at low temperatures suggest that the origin of water contents measured in peridotite NAMs requires additional constraints on sample petrogenesis, including poro-graphic and trace element analyses. Our 3D model results also hint that H⁺ may diffuse appreciably during peridotite serpentinization, but diffusion coefficients at low temperature are unconstrained and additional experimental investigations are needed.

Keywords: Nominally anhydrous minerals, peridotite, diffusion, hydrogen; Volatile Elements in Differentiated Planetary Interiors

Introduction
The water contents of olivine, orthopyroxene, and clinopyroxene in peridotites have been used to constrain the water content of the upper mantle, a value that is important for many mantle properties, including melting depth and viscosity (e.g., Mackwell et al. 1985; Hirth and Kohlstedt 1996; Ingrin and Skogby 2000; Peslier 2010). The hydrogen incorporated in these nominally anhydrous minerals (NAMs) is sometimes referred to as “water” or “hydroxyl” because of its chemical bond with oxygen within the olivine structure, but here we refer to this species as hydrogen or H⁺. Hydrogen is a rapidly diffusing monovalent cation (Fig. 1), and its re-equilibration in response to silicate melt-rock interactions quickly modifies NAM water contents (e.g., Mackwell 1990; Kohlstedt and Mackwell 1998; Ingrin and Skogby 2000; Stalder and Skogby 2003; Ingrin and Blanchard 2006).

Diffusion in igneous minerals is now widely used to quantify the timescales of geologic processes operating in diverse tectonic settings (e.g., Costa and Dungan 2005; Shea et al. 2015a; Ruth et al. 2018). Hydrogen diffusion chronometry has classically been applied at high temperatures (e.g., 1000–1200 °C), where it records short-lived processes such as magma ascent (Demouchy et al. 2006; Peslier and Luhr 2006; Denis et al. 2015; Lloyd et al. 2016) and melt inclusion re-equilibration during degassing/decompression of melts (e.g., Le Voyer et al. 2014). Yet it has the strong potential to be applied to lower temperature geologic processes such as hydrothermal fluid-rock interactions, which can

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