Hydrogen diffusion in orthopyroxene: experimental determinations and timescales of magmatic processes

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Structurally-bound OH (colloquially referred to as water) located in crystalline defects of Nominally Anhydrous Minerals (NAMs), such as olivine (ol), clino- or orthopyroxene (opx), can comprise a few to a few hundred parts per million (ppm) H_2O. This is sufficient to affect the phase equilibria and rheological properties of the mantle, and to make NAMs a signicant contributor to the total mantle water budget. Orthopyroxene, being the second most abundant phase of the upper mantle, has a greater water storage capacity compared to the volumentrically more abundant olivine, 10 to 650 ppm of water for orthopyroxene in comparison to 10-140 ppm for olivine (Ingrin & Skogby 2000; Demouchy & Bolfan-Casanova 2016), making it the dominant host of water in the upper mantle. Water also tends to partition in orthopyroxene instead of olivine (Dol/opx = 0,04-0,11 (Auband et al. 2004; Tenner et al. 2008). The relationship between hydrogen incorporation and diffusion mechanisms in orthopyroxene remains poorly constrained. We undertook a combined experimental and petrological study with two aims – firstly to better understand relationships between substitution and diffusion mechanisms and rates, and secondly to assess the applicability of H diffusion in orthopyroxene as a tool for diffusion chronometry.

Axially oriented ∼cuboids of natural tanzanian orthopyroxene were experimentally dehydrated in a gas mixing furnace (H2-CO_2 mix). The experiments were conducted at 1 bar, at near-mantle redox conditions (∼QFM-1), with 2 different silica activity buffers (olivine+pyroxene or pyroxene+quartz), from 700°C to 1000°C. Profiles of hydrogen content against distance were extracted from experimental samples using Fourier-Transform Infrared Spectroscopy (FTIR). Diffusion coefficients were then extracted using relevant analytical solutions and numerical approximations of Fick's second law. Fitting the diffusion coefficients to the isobaric Arrhenius relationship (logD=logD0+(-Q/(2.303RT))) gives activation energies (Q) from 90 to 120 kJmol-1, and pre-exponential factors (logD0) from -5.5 to -7.5 m2s-1.

The rate of H diffusion is strikingly similar to that determined for the fastest diffusivity of H in olivine (Kohlstedt and Mackwell, 1998), suggesting a mechanism akin to proton-polaron exchange. Thus, the observation that mantle orthopyroxenes appear to be more reliable recorders (than olivine) (e.g. Tian et al., 2017) of original water contents cannot be a simple function of relative maximum diffusivities.

We applied these diffusion coefficients to natural orthopyroxene grains from mantle xenoliths collected in the Sierra Baguales, in Southern Patagonia, in lava flows related to back-arc volcanism, aiming to extract timescales of magmatic events. The applicability of this method, including the relevance of our diffusion coefficients, will be discussed.

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