Is orthopyroxene really a reliable recorder of mantle water signatures? Insights from an experimental study

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Experiments have been conducted to assess the effects of temperature, oxygen fugacity, crystallographic orientation, silica activity and chemical composition on the diffusivity and substitution mechanisms of hydrogen in orthopyroxene (opx). Axially oriented ~cuboids of natural Tanzanian opx were dehydrated at 1 bar in a gas mixing furnace (H₂-CO₂ mix) at three different oxygen fugacities (~QFM-1, ~QFM+1, ~QFM-7), and two different silica activity buffers (olivine+pyroxene or pyroxene+quartz) between 700°C and 1000°C. Profiles of hydrogen content versus distance were extracted from experimental samples using Fourier-Transform Infrared (FTIR) spectroscopy, with diffusion coefficients extracted using relevant analytical solutions and numerical approximations of Fick's second law. Diffusion is the fastest along [001] (D[001]>D[010]>D[100]). Fitting the diffusion coefficients to the isobaric Arrhenius relationship (logD=logD₀+(-Q/(2.303RT))) gives activation energies (Q) and pre-exponential factors (logD₀) between 127 to 162 kJmol⁻¹ and -4.29 to -5.42 m²s⁻¹, respectively, for ~QFM-1.

The extracted hydrogen diffusivities are faster than previously measured by 0.5 to 5 orders of magnitude at ~1000 °C and ~700°C, respectively (Carpenter (2003), Stalder and Skogby (2003), Stalder and Behrens (2006), Stalder and al. (2007)) and are slightly slower, but strikingly close, to those of the fastest experimentally-determined diffusivity of H in olivine (Kohlstedt and Mackwell, 1998), suggesting a mechanism akin to proton-polaron exchange. This presents a paradoxical decoupling between natural and experimental observations. In most cases for mantle xenoliths, natural olivine has low water contents (<35 ppm), or are dry, and show H diffusive loss of water, where natural opx contains between 10 and 460 ppm and rarely show H diffusive loss (Demouchy and Bolfan-Casanova (2016), suggesting opx is more capable of recording the mantle water signature. With hydrogen diffusivities of olivine and opx being quite similar, however, both minerals should suffer from the same rate of dehydration during ascent, thus show low or zero water content in natural settings, which is not the case. Therefore, the inference that pyroxenes are better recorder of water in the mantle (e.g. Warren et Hauri (2014), Peslier (2010)) cannot be a simple function of diffusivities. A case study on an opx crystal showing a dehydration profile from a spinel-peridotite xenolith, hosted in an alkaline magma, from Patagonia supports this. Using the H diffusion coefficients from this study, the calculated rates of ascent of the mantle xenolith in alkaline magma are comparable to those associated with kimberlite magmas. The two suggestions we present are the following: i) Changing the boundary conditions may modify the hydrogen
diffusive flux through the xenolith history and ii) The measured diffusivities would be apparent diffusivities as there might be different pathways or mechanisms of diffusion.