



## **Hydrogen diffusion in garnets: Comparison between laboratory experiments and natural samples from high-pressure metamorphic rocks.**

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Garnet is a common high-pressure metamorphic mineral. Diffusion modelling in garnet offers an opportunity to constrain timescales of subduction and exhumation in high-pressure rocks. Hydrogen is the smallest element of the periodic table, and a fast diffusing species in minerals and glasses. The study of hydrogen diffusion in garnet could thus potentially help to constrain the duration of metamorphic processes in a temperature range of 300-600 °C for time spans of 100 000 years to 10 million years, where divalent cations in garnet do not show significant diffusion profiles.

Diffusion experiments on natural gem-quality spessartine (300 ppm H<sub>2</sub>O) and grossular (800 ppm H<sub>2</sub>O) cubes were conducted at 1 atm over a temperature range of 750-1050 °C under both air and various lower oxygen fugacities (QFM+8 to QFM-3). They reveal fast hydrogen diffusion rates in air, and slow diffusion rates at low oxygen fugacity. The strong dependency of hydrogen diffusion rates with oxygen fugacity can be explained by an oxidation related mechanism, in the form of

, where M is Fe or Mn. The activation energy (E<sub>a</sub>) evaluated for diffusion associated with this mechanism is rather low (158 kJ/mol) and consistent with a mechanism that does not involve metal vacancy diffusion. In contrast, the slow diffusion rates at low oxygen fugacity have a higher activation energy (286-410 kJ/mol) suggesting H loss associated with metal vacancy diffusion.

We measured various spessartine-rich and grossular-rich garnets from subducted oceanic crust present in the Alps by Fourier Transform Infrared spectroscopy (FTIR). All garnets display high water contents (300 to 5000 ppm H<sub>2</sub>O). The comparison between chemical maps of major and minor elements acquired by electron microprobe and water distribution maps reveals strong correlation of hydrogen content with growth and chemical zonings (Ca, Mn, and Ti), with no evidence of diffusive patterns. Diffusion models run at metamorphic temperatures cannot explain zoning patterns and water contents in these garnets considering the fast diffusion mechanism. The low hydrogen diffusion rates could be explained by the effect of pressure and/or the effect of low oxygen fugacity in these rocks, indicating that for the investigated conditions, hydrogen diffusion is not significantly faster than divalent cation diffusion.

Retention of hydrogen in garnet during high-pressure metamorphic pathways is thus more effective than expected, and water can be preserved at 550 °C over a few million years. Our study highlights the importance of evaluating experimentally obtained diffusion coefficients on natural samples in order to determine the dominant diffusion mechanism, before timescales of metamorphic processes are calculated.