

Oxygen diffusion in garnet: Experimental calibration and implications for timescales of metamorphic processes and retention of primary O isotopic signatures

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ABSTRACT

Knowledge of oxygen diffusion in garnet is crucial for a correct interpretation of oxygen isotope signatures in natural samples. A series of experiments was undertaken to determine the diffusivity of oxygen in garnet, which remains poorly constrained. The first suite included high-pressure (HP), nominally dry experiments performed in piston-cylinder apparatus at: (1) $T = 1050\text{--}1600\text{ }^{\circ}\text{C}$ and $P = 1.5\text{ GPa}$ and (2) $T = 1500\text{ }^{\circ}\text{C}$ and $P = 2.5\text{ GPa}$ using yttrium aluminum garnet (YAG; $\text{Y}_3\text{Al}_5\text{O}_{12}$) cubes. Second, HP H_2O -saturated experiments were conducted at $T = 900\text{ }^{\circ}\text{C}$ and $P = 1.0\text{--}1.5\text{ GPa}$, wherein YAG crystals were packed into a YAG + Corundum powder, along with ^{18}O -enriched H_2O . Third, 1 atm experiments with YAG cubes were performed in a gas-mixing furnace at $T = 1500\text{--}1600\text{ }^{\circ}\text{C}$ under Ar flux. Finally, an experiment at $T = 900\text{ }^{\circ}\text{C}$ and $P = 1.0\text{ GPa}$ was done using a pyrope cube embedded into pyrope powder and ^{18}O -enriched H_2O . Experiments using grossular were not successful.

Profiles of $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$ in the experimental charges were analyzed with three different secondary ion mass spectrometers (SIMS): sensitive high-resolution ion microprobe (SHRIMP II and SI), CAMECA IMS-1280, and NanoSIMS. Considering only the measured length of ^{18}O diffusion profiles, similar results were obtained for YAG and pyrope annealed at $900\text{ }^{\circ}\text{C}$, suggesting limited effects of chemical composition on oxygen diffusivity. However, in both garnet types, several profiles deviate from the error function geometry, suggesting that the behavior of O in garnet cannot be fully described as simple concentration-independent diffusion, certainly in YAG and likely in natural pyrope as well. The experimental results are better described by invoking O diffusion via two distinct pathways with an inter-site reaction allowing O to move between these pathways. Modeling this process yields two diffusion coefficients (D values) for O, one of which is approximately two orders of magnitude higher than the other. Taken together, Arrhenius relationships are:

$$\log Dm^2s^{-1} = -7.2(\pm 1.3) + \left(\frac{-321(\pm 32)\text{ kJ mol}^{-1}}{2.303RT} \right)$$

for the slow pathway, and

$$\log Dm^2s^{-1} = -5.4(\pm 0.7) + \left(\frac{-312(\pm 20)\text{ kJ mol}^{-1}}{2.303RT} \right)$$

for the fast pathway. We interpret the two pathways as representing diffusion following vacancy and interstitial mechanisms, respectively. Regardless, our new data suggest that the slow mechanism is prevalent in garnet with natural compositions, and thus is likely to control the retentivity of oxygen isotopic signatures in natural samples.

The diffusivity of oxygen is similar to Fe-Mn diffusivity in garnet at $1000\text{--}1100\text{ }^{\circ}\text{C}$ and Ca diffusivity at $850\text{ }^{\circ}\text{C}$. However, the activation energy for O diffusion is larger, leading to lower diffusivities at P - T conditions characterizing crustal metamorphism. Therefore, original O isotopic signatures can be retained in garnets showing major element zoning partially re-equilibrated by diffusion, with the uncertainty caveat of extrapolating the experimental data to lower temperature conditions.

Keywords: Oxygen isotopes, diffusion; piston-cylinder experiments, gas mixing furnace, garnet, SIMS

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