

SPECIAL COLLECTION: MECHANISMS, RATES, AND TIMESCALES OF GEOCHEMICAL TRANSPORT PROCESSES IN THE CRUST AND MANTLE

Kinetics of deuteration in andradite and garnet†

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ABSTRACT

The hydrogen mobility in andradite single crystals from an iron-skarn deposit was investigated through H-D and D-H exchange experiments. Thin slices were annealed in a horizontal furnace flushed with a gas mixture of Ar/D_{2(10%)} and Ar/H_{2(10%)} at ambient pressure between 400 and 700 °C. FTIR analyses were performed before and after each annealing run. Between 15 and 35% of the original OH content remained in the crystal structure at the end of the deuteration experiments. This contrasts with the results of similar experiments performed in other NAMs, where all hydrogen atoms are replaced by deuterium in the structure. However, because a steady state was reached at the end of the experiments, the diffusion law for the exchange process was determined as: $D_{\text{H-D}} = D_0 \exp[-(96 \pm 11) \text{ kJ/mol/RT}]$, with $\log D_0 = -5.9 \pm 0.7$ (in m²/s). The activation energy is similar to that for hydrogen diffusion in grossular, but H diffusivity is more than two orders of magnitude faster. Our results demonstrate that, because major element composition has a major effect on H-D diffusion laws, it must be considered in any discussion of δD signatures in garnets. In andradite-rich garnets, hydrogen isotope data can only be used to record short, low-grade metamorphic or metasomatic events, at temperatures lower than 400 °C.

Keywords: Hydrogen, andradite, FTIR, diffusion, deuterium, garnet