

## Diffusion-driven Li isotope fractionation in Cpx: anisotropy and the influence of $f_{O_2}$

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Lithium (Li) is particularly useful for diffusion geospeedometry in volcanology, because of its exceptionally fast diffusivity in minerals and melts, giving access to processes that operate on time scales of seconds to years. The application of the Li speedometer is currently hampered by the restricted number of available experimentally determined diffusion data. In this study, Li diffusivity and diffusion-driven Li isotope fractionation in natural high-Ca clinopyroxene were experimentally determined as a function of  $T$ ,  $f_{O_2}$ , and crystallographic orientation. An evacuated silica-glass tube containing a sample capsule with orientated single-crystal Cpx embedded in a solid Li source (spodumene powder) and another capsule filled with solid oxygen buffers was heated at 0.1 MPa using a Deltech furnace. The chemical and isotope profiles of Cpx run products analyzed by SIMS can only be fitted by the multi-species diffusion model proposed for olivine by [1]. At the NNO buffer, Li concentration profiles display step-like shapes rather than simple error function-like patterns. Li isotope profiles show gradually decreasing trends at the rim, and dramatically jump back to the initial value closer to the crystal core. Our model simulations show that a high abundance of initial vacancies under oxidizing condition best explains the observed patterns. For these runs, the Arrhenius parameters obtained for interstitial Li diffusing parallel to the c-axis at 800–1100 °C are:  $D_0 = 3.7 \times 10^{-5}$  (m<sup>2</sup>/s) and  $E_A = 294$  (kJ/mol). We obtained a similar  $D_0$  but higher  $E_A$  than the values reported by [2]. The Li concentration profiles at the IW buffer are significantly different from the patterns observed at NNO, suggesting that Li diffusion in Cpx is rather sensitive to oxygen fugacity. For the reducing condition, high Li diffusivity and low vacancy concentration at the boundary are required to fit the observed patterns. Our results show that Li diffusivity is anisotropic, with the fastest transport along the c-axis and the slowest diffusion along the a-axis. Interestingly, the isotope fractionation parameter ( $\beta$ ) obtained along the c-axis is 0.25, while a smaller  $\beta$  value of 0.20 was obtained for diffusion parallel to the b- and a-axes.

[1] Dohmen *et al* (2010) *GCA*, **74**: 274–292; [2] Coogan *et al* (2005) *EPSL*, **240**: 415–424.