

## Multispecies Diffusion of Li in Olivine

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Olivines from terrestrial and lunar samples show a diversity of Li contents, isotopic compositions and concentration profiles (e.g., Rudnick and Ionov, 2007; Barrat et al., 2005). These are difficult to interpret unless reliable diffusion coefficients are available. Therefore, we have carried out experiments to study the diffusion of Li in olivine (along [001] of single crystals from San Carlos and Pakistan, at 800 °C – 1200 °C, 1 atmosphere total pressure and  $fO_2 \approx$  WM buffer). Oriented, polished cubes of the crystals were annealed surrounded by a powder mix of the same olivine and <sup>6</sup>Li enriched lithium silicate. Li concentration and isotopic profiles were measured using a Cameca IMS4f ion microprobe in the step scanning mode. The concentration profiles of Li show complex shapes with plateaus in between that are not amenable to treatment using standard solutions to the diffusion equation. The shape of the Li diffusion profiles change at higher temperature. However, these features are reproducible and evolve systematically with time, indicating that they are an intrinsic aspect of the diffusion behavior of Li. Analysis of the profiles in the framework of a point defect thermodynamic model (Dohmen and Chakraborty, 2008) reveals that the following mechanism explains the observations adequately and quantitatively: (i) Li is incorporated in olivine on octahedral metal sites ( $Li_{Me}$ ) as well as interstitials ( $Li_i$ ), as two different species (ii) a fast, homogeneous reaction involving metal vacancies ( $V_{Me}$ ) partitions Li between the octahedral site and interstitial positions:  $Li_{Me} = V_{Me} + Li_i$ . The equilibrium constant of this reaction is such that Li is preferentially incorporated in the octahedral site ( $Li_{Me} \approx 10 \times Li_i$ ), (iii) Diffusion of total Li occurs as the sum of fluxes of  $Li_{Me}$  as well as  $Li_i$ , at very different rates:  $D(Li_i) > D(V_{Me}) > D(Li_{Me})$ , ( $Li_i \approx 100 \times Li_{Me}$ ). The calculated profiles are also very sensitive to the boundary conditions that define the Li content of the olivine. The observed isotopic profiles are also well described by the model (<sup>6</sup>Li is about 2% faster than <sup>7</sup>Li on the interstitial site). To calculate diffusion fluxes for calculation of homogenization times of elemental or isotopic Li gradients in natural systems, it is necessary to consider the partitioning of Li between the two sites calculate diffusion coefficients appropriate for each concentration regime and boundary condition. This complexity arises because the transport of Li depends on the relative abundance of other defects, which in turn control how much each Li species contributes to the overall diffusion process. Examples will be shown to illustrate simplified recipes for calculation of Li transport in olivines from some well known (e.g. mantle, volcanic, lunar) settings.

### References

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