

## **K isotope fractionation in diffusion couples of molten basalts**

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Isotope fractionation during diffusion is a fundamental process with numerous applications, including the separation of isotopes, correcting for isotope fractionation in geochronology, understanding isotope fractionation during crystal growth or dissolution, magma interaction and crystal fractionation. In the last two decades, diffusive isotope fractionation has been discovered to be measurable for Li, Mg, Ca, and Fe [1-3]. Based on experimental data as well as studies of natural systems, diffusive isotope fractionation is rather large compared to equilibrium isotope fractionation at high temperature. Still diffusive isotope fractionation is found to be smaller than the Graham's law limit ( $\beta = 0.5$ ) for isotopes diffusing as atomic species. The measured  $\beta$  factor [1] in melts is  $\leq 0.23$  [3], suggesting diffusion as clusters or exchange. In previous experimental studies, except for Li, isotope ratio measurements were made by cutting or drilling pieces of samples from experimental charges, treating these pieces by conventional solutions and columns, and then analyzing them using TIMS or MC-ICP-MS. These analytical methods do not have high spatial resolution and related sample preparation is time consuming.

We are making effort to analyze K isotope ratio profiles in diffusion couple experiments [4] using SIMS, hoping to achieve a precision of 0.1‰ in isotope ratios. Preliminary data show that diffusive  $^{41}\text{K}/^{39}\text{K}$  fractionation can be as large as 10‰ when K concentration contrast in a diffusion couple is  $\sim 50$  at a temperature of 1260 to 1350°C. The data were fit using an effective binary diffusion model for each of  $^{39}\text{K}$  and  $^{41}\text{K}$ , resulting in a  $\beta$  factor of  $\sim 0.12$ , consistent with K diffusing in the melt as large clusters such as  $\text{KAlSiO}_4$ , or through exchange such as  $(1/2)\text{Mg}^{2+}$  with  $\text{K}^+$ . The significant fractionation suggests that diffusive K isotope fractionation during melt mixing is measurable under favorable conditions, and such fractionation may impact K-Ar dating, and can be used to infer the mixing time scale and cooling history. In addition, the preliminary data seem to indicate a slight increase of the  $\beta$  factor from  $\beta = 0.112 \pm 0.006$  at 1260°C to  $0.124 \pm 0.005$  at 1350°C, which warrants further examination of the temperature dependence of the  $\beta$  factor.

### **References**

1. Richter et al., 1999, GCA, 63, 2853.
2. Watkins et al., 2011, GCA, 75, 3103.
3. Holycross et al., 2018, Geochem. Persp. Lett., 6, 39.
4. Guo and Zhang, GCA, 228, 190.