

EXPERIMENTAL DETERMINATION OF THE RATE AND ISOTOPE FRACTIONATION OF Li DIFFUSING INTO AUGITE AND CONSTRAINTS ON THE COOLING RATE OF MARTIAN METEORITE MIL 03346. F.M. Richter<sup>1,2</sup>, E.B. Watson, M. Chaussidon<sup>4</sup>, R.A. Mendybaev<sup>1,2</sup> and D. M. Ruscitto<sup>3</sup> <sup>1</sup>University of Chicago, <sup>2</sup>Chicago Center for Cosmochemistry <sup>3</sup>Rensselaer Polytechnic Institute, <sup>4</sup>CRPG-CNRS, Nancy University (richter@geosci.uchicago.edu).

**Introduction.** It is by now well established by experiments that mass transport by diffusion in molten silicates results in easily measured isotopic fractionation due to the greater mobility of the lighter isotope [1, 2]. Similar isotope fractionations have been recently found in various natural settings [3,4,5]. As a general rule, the correspondence between the kinetic isotope fractionations found in laboratory diffusion experiments and in a natural sample is the best way to establish whether an observed concentration gradient is the result of diffusion rather than some other process such as magma mixing, or in the case of a mineral, crystallization from an evolving melt. With this in mind, we present the results of a laboratory experiment showing isotopic fractionation of lithium as it diffused into augite, which we compare to the lithium concentration and isotope zoning in an augite crystal from Martian meteorite MIL 03346 reported by Beck et al. [5]. The specific goals of such experiments are to determine the diffusion coefficient of lithium in augite and the mass-dependence of the lithium diffusion coefficient that results in isotopic fractionation, and to provide analogues of natural zones minerals.

**Experimental method.** We used a standard method called the powder-source technique (see [6] for details) to diffuse lithium into a natural augite crystal. The method as used by us involved embedding an oriented and polished augite crystal in a fine powder of natural spodumene that acts as the source for the lithium to diffuse into the mineral grain. The augite with surrounding powder is placed in an evacuated silica ampoule along with a Ni-NiO oxygen buffer and placed in a one-bar furnace. The specific experiment reported here (LiPx7) was run at 900°C for 279 hours. Figure 1 shows a backscattered image of the sample.

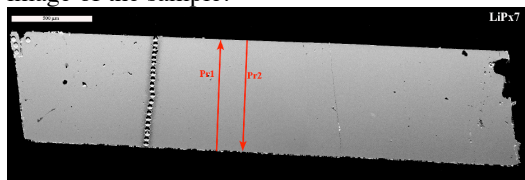


Figure 1. Backscattered image of augite sample LiPx7 showing the laser ablation pits used for lithium concentration measurements and two lines along which lithium isotopic measurements were made. White scale bar is 500 microns long.

**Chemical and isotopic analyses.** The major element composition of the augite (Templeton, QUE, Canada NMNH #R-15162-1) was measured along two profiles across the sample using JEOL JSM-5800LV SEM equipped with Oxford Link ISIS-300 energy dispersive analytical system. The major element composition of the augite is 54 wt% SiO<sub>2</sub>, 23 wt% CaO, 17 wt% MgO, 4 wt% FeO, 1 wt% Al<sub>2</sub>O<sub>3</sub>, and 1 wt% Na<sub>2</sub>O. Lithium concentration measurements were made using a Varian 820 quadrupole ICP-MS coupled with a Photon-Machines, Inc. 193 nm excimer laser. The lithium isotopic composition was measured along two lines shown in Fig. 1 using the Cameca 1280 SIMS at CRPG-CNRS.

**Results.** Figure 2 shows lithium concentration data from experiment LiPx7 (the highest temperature and longest duration and experiment we have so far run) along with a calculated profile based on the complementary error function solution to the diffusion equation. The calculated curve results in an estimate of the diffusion coefficient  $D_{Li}=3.2 \times 10^{-11} \text{ cm}^2/\text{s}$  for Li in augite at 900C and oxygen fugacity at the Ni-NiO. Figure 3 shows the lithium isotopic data taken along two parallel lines across sample LiPx7 and the calculated <sup>7</sup>Li/<sup>6</sup>Li fractionation using the ratio of the isotope diffusivities as

$$D_{7Li}/D_{6Li} = (6/7)^\beta \text{ with } \beta = 0.300.$$

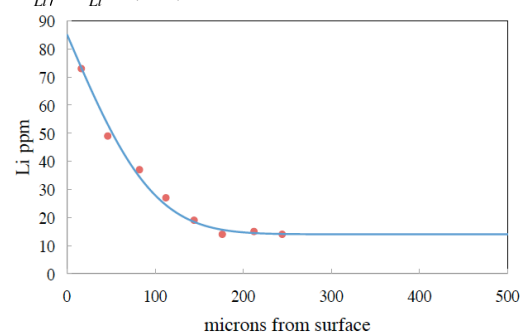


Figure 2. Lithium concentration data versus distance from the polished augite surface from sample LiPx7 compared to a complementary error function solution.

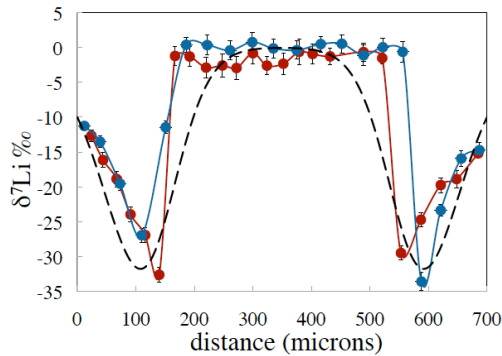


Figure 3. The circles show the lithium fractionation measured along two profiles in laboratory sample LiPx7. The fractionations are measured relative to the average of the unaffected core blue data points 200 microns from the boundaries. The dashed curve is the result of a diffusion calculation where the ratio of the diffusivity of  ${}^7\text{Li}$  relative to  ${}^6\text{Li}$  is given by  $D_{{}^7\text{Li}}/D_{{}^6\text{Li}} = (6/7)^{0.3} = 0.9548$

**Lithium isotopic fractionation in MIL 03346.** Figure 4 shows the wt% lithium reported by Beck et al. [5] at selected points across an augite crystal from Martian meteorite MIL 03346. Also shown is a calculated total lithium concentration profile that more or less fits the boundary layers at each end of the crystal ignoring, as was done by [5] the point shown as an unfilled circle. Figure 5 shows the data from [5] for the  ${}^7\text{Li}/{}^6\text{Li}$  across the same crystal. Also shown in Fig. 5 is the calculated isotopic fractionation of  ${}^7\text{Li}/{}^6\text{Li}$  that is associated with the lithium diffusion profile in Fig. 4 using the same  $D_{{}^7\text{Li}}/D_{{}^6\text{Li}} = (6/7)^{0.3} = 0.9548$  as was used for laboratory sample LiPx7.

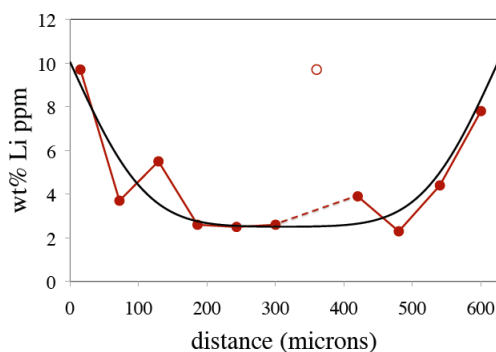


Figure 4. Red circles show the lithium concentration from [5] as a function of distance in an augite crystal from Martian meteorite MIL 003346. The black curve is a calculated diffusion profile of lithium diffusing into the grain.

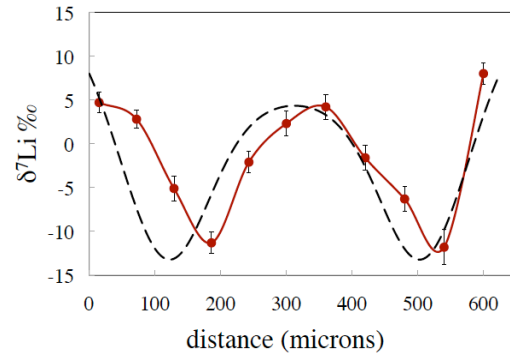


Figure 5. Lithium isotopic fractionation at selected points in the same augite as in Fig. 4 from [5]. The dashed curve is the calculated lithium isotopic fractionation associated with the calculated lithium concentration profile shown in Fig.4 assuming the same  $\beta=0.3$  as was used to model the results in the laboratory sample LiPx7.

**Discussion** The qualitative agreement of the general shape (aside from the larger unaffected interior of LiPx7) and amplitude of the lithium isotopic fractionation in the boundary layer at each edge of the laboratory augite sample LiPx7 and the augite grain from Martian meteorite MIL 03346 makes a strong case for the Beck et al. [5] interpretation that the boundary layers in the Martian augite grain they measured are indeed dominantly the result of lithium diffusion into the augite. In detail, there are some obvious misfits between our calculated lithium fractionation profiles and the data from both the laboratory sample and the natural augite that we do not yet understand. The diffusion coefficient we estimated from our laboratory sample ( $D_{\text{Li}}=3.2 \times 10^{-11}$  cm<sup>2</sup>/s at 900°C) yields an estimate for the cooling rate of MIL 03346 of about 1°C/hr, which is in good agreement with previously estimated rates based on the petrology of MIL 03346. The much faster cooling rate of 50°C/hr estimated by [5] was derived using a much larger value for the diffusivity of lithium reported by [7] for diffusion into clinopyroxene.

**References.** [1] Richter et al. (2003) *GCA* **67**, 3905-3923. [2] Richter et al. (2008) *GCA* **72**, 206-220. [3] Teng et al. (2006) *EPSL* **243**, 701-710. [4] Teng et al. *EPSL* **308**, 317. [5] Beck et al. 2007 *GCA* **70**, 4813-4825. [6] Watson and Dohmen (2010) *RiMG* **72**, 61-106. [7] Coogan et al. (2005) *EPSL* **240**, 415-424.