LITHIUM ISOTOPE FRACTIONATION BY DIFFUSION OF AUGITES IN LABORATORY EXPERIMENTS AND IN MARTIAN METEORITE MIL 03346.

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Introduction: Isotopic fractionations of ^{7}Li/^{6}Li by more than 10‰ have been found in igneous minerals from many different settings including mantle peridotites, arc volcanics, and Martian meteorites [1,2,3]. In many cases these fractionations have been interpreted as arising from the faster diffusion of ^{6}Li compared to ^{7}Li. The work described here was motivated by lithium isotopic fractionations in an augite grain from Martian meteorite Miller Range 03346 reported by Beck at al. [3]. MIL 03346 is a Nakhlite (~79% cpx, ~1% ol, and ~20% vitrophyric material) with a grain size distribution indicating a residence time of more than year in a crustal magma chamber [4]. In contrast to this, the properties of the intercumulus material was interpreted as indicating rapid cooling of about 3-6˚C/h at an oxygen fugacity near the Ni-NiO buffer [5]. Thus the inferred evolution of MIL 03346 involved crystal growth in a magma chamber followed by eruption onto the Mars surface and rapid cooling of a cpx-dominated cumulate. Beck et al. [3] added support to this view by interpreting the lithium concentration and isotopic zoning of an augite grain from MIL 03346 as indicating a cooling at 50˚C/h. Richter et al. [6] used an estimate of the diffusion coefficient of Li in augite to suggest that the lithium zoning indicated an even slower cooling rate of about 1 ˚C/h, a value that we now question given the complexity we have recently found in the behavior of lithium diffusion in augite. Here we report new experimental results on the diffusion and associated isotopic fractionation of lithium in augite. We also measured lithium concentration and isotopic profiles across a number of additional augite grains in MIL 03346 with the thought in mind that for lithium zoning to be a useful indicator of the cooling history of the cumulate as a whole, the different mineral grains must show a reasonable degree of consistency in their lithium concentration and isotopic zoning.

Lithium diffusion experiments. A powder-source technique (see [7] for details) was used to diffuse lithium from spodumene powder into grains of augite from Templeton, QUE, Canada (NMNH #R-15162-1). The experiments were run by placing an augite grain surrounded by spodumene powder in an evacuated silica ampoule along with a Ni-NiO oxygen buffer and holding the sample for a predetermined length of time in a one-bar furnace at 900˚C.

Chemical and isotopic analyses: The major element composition of the augite used in the diffusion experiments (54 wt% SiO_2, 23 wt% CaO, 17 wt% MgO, 4 wt% FeO, 1 wt% Al_2O_3, and 1 wt% Na_2O) was measured using JEOL JSM-5800LV SEM equipped with Oxford Link ISIS-300 energy dispersive analytical system and found to be uniform. Lithium concentration and isotopic profiles across the experimental samples and the augite grains from MIL 03346 were measured as ^{7}Li/^{30}Si and ^{7}Li/^{6}Li using the Cameca 1280 SIMS at CRPG-CNRS, Nancy, France.

Results. The new experimental data on lithium that diffused into augite grains show step-like concentration profiles and large isotopic fractionations (Figure 1) that we modeled in terms of two lithium species: fast diffusing interstitial lithium and a much slower diffusing lithium in metal sites. Model fits such as shown in Fig. 1 were used to derive an estimate of the diffusion coefficient for the interstitial lithium and the fractionation exponent β in the parameterization $D_{^7Li}/D_{^6Li} = (6/7)^{\beta}$.

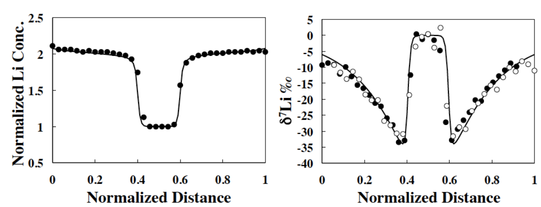

Figure 1. Li concentration (left panel, normalized to a value of one in the interior) and isotopic fractionation (right panel) across a 700 μm wide augite grain run at 900°C and Ni-NiO for 842 hours. The solid curve is a model calculated fit to the data.

Because lithium can exist as two or more distinct species, estimating the diffusion coefficient for the fast diffusing interstitial lithium is difficult and not very precise. The results of three experiments with Templeton augite gave D_{Li}~10^{-9} cm^2/s and one experiment with Dekalb diopside gave ~5x10^{-10} cm^2/s. The experiments are consistent in terms of the degree of isotopic fractionation (~30‰) and yield an estimate of β =0.27±0.01.

Lithium zoning in MIL 03346: Figure 2 shows the lithium concentration and isotopic fractionation data reported by Beck et al. [3] at selected points across an augite crystal from Martian meteorite MIL 03346. Also shown is our model fits to these data using a single-lithium species model and the experimental value β =0.27. The fact that the degree of lithium isotopic fractionation in this augite from MIL 03346 can be so well accounted for by the β from our experiments is the most compelling evidence that the isotopic fractionation is indeed due to diffusion of lithium into the grain.

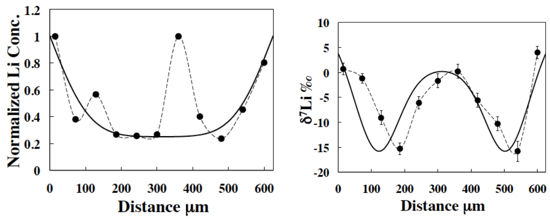

Figure 2. Filled circles show the data points for Li concentration normalized to a value of one in the interior (left panel) and isotopic fractionation (right panel) across the augite grain reported by [3] along with model profiles (solid lines) that require symmetry around the center of the grain. The isotopic fractionation was calculated using β =0.27. The thin dashed lines are an interpolation between the measured points to give the impression of a continuous profile for comparison with the calculated profiles.

Figure 3 shows our re-measurement of the same grain from MIL 03346 measured by [3]. Figure 4 show two further examples of data measured across other augite grain from MIL 03346.

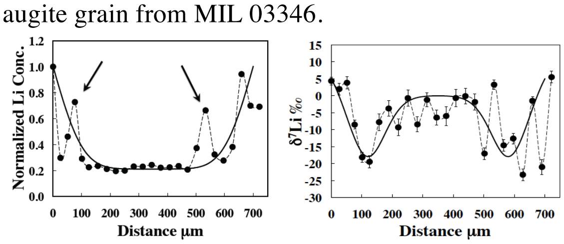

Figure 3. Same as Fig. 2 but for new data across the same grain measured by [3]. The arrows show two local high-Li concentration features in the grain interior that are also seen in many of the other augite grains we measured.

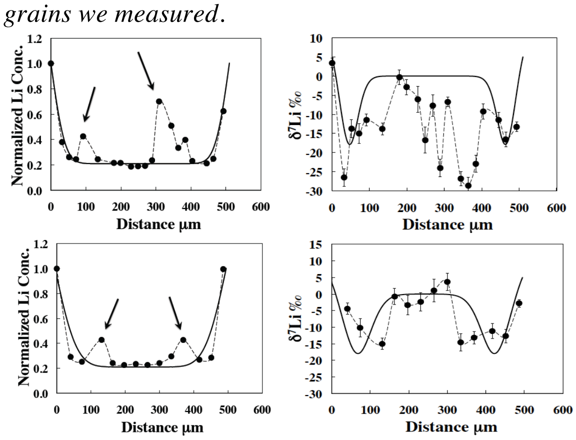

Figure 4 Same as Fig. 3 for two additional grains from MIL 03346.

Discussion: Our experiments (see Fig. 1 for an example) confirm that diffusion of lithium into augite results in large isotopic fractionation that require a relative mobility of the lithium isotopes given by $D_{^7Li}/D_{^6Li} = (6/7)^{\beta}$ with β=0.27±0.01. This makes it almost certain that the concentration profiles and isotopic fractionations shown in Figs. 2-4 are the result of lithium diffusion into the augite grains and thus that they can be used to estimate the cooling rate of MIL 03346 once it was erupted as a lava flow on the surface of Mars. Using a lithium diffusion coefficient of 10^{-9} cm^2/s we calculated cooling rates of 32 to 46 ˚C/h for four grains, 115˚C/h for one grain and 290 and 320˚C/h for two other grains. While these cooling rates cover a range of about a factor of ten, the general conclusion is that the cooling rate indicated by the lithium data is very fast compared to the time the system must have been molten to account for the grain size distribution. The range of cooling rates reflect the fact that the model fits shown in Figs. 2-4 are certainly not perfect but there is a general consistency among all the grains we measured in that they have steep concentration gradients at each boundary and W-shaped isotopic fractionation profiles. We believe some of the short length scale variations in the lithium concentration and isotopic composition seen in some parts of the crystals are likely due to numerous small shock fractures throughout the gains. We have independent evidence that even small fractures cause problems with the ion probe measurements and need to be avoided when possible. If on the other hand one were to assume that the short wavelength variations are real, perhaps resulting from contamination along fractures, then the existence of these short wavelength features would imply fast cooling for them not to have been smoothed out by diffusion. The more or less symmetric set of local regions of high lithium concentration (see arrows in Figs. 3 and 4) are seen in many of the grains, which leads us to believe they are conveying significant information, but we do not yet have a good explanation for these features.

References: [1] Jeffcoate et al. (2007) *GCA* **71**, 202-218. [2] Parkinson et al. (2007) *EPSL* **257**, 609-621. [3] Beck et al. (2006) *GCA* **70**, 4813-4825. [4] Day et al. (2006) *Meteor. Planet. Sci.* **41**,581-606. [5] Hammer and Rutherford (2005) abstract #1999, LPSC XXXVI. [6] Richter et al. (2012) abstract #2482, LPSC XLIII. [7] Watson and Dohmen (2010) *RiMG* **72**, 61-106.