Geochemical
Perspectives
Letters

Diffusive fractionation of Li isotopes in wet, highly silicic melts

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Supplementary Information

The Supplementary Information includes:

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Experimental Methods

Synthetic rhyolite composition powders were formed by grinding high purity silicate mineral and oxide powders under ethanol in an agate mortar and pestle. The rhyolite used in diffusion couple experiments is based on the composition of Lake County Obsidian (LCO; Table S-1). Rhyolite powders were doped with a mixture of two different lithium carbonates (Li_2CO_3), one containing 95 at. % ^6Li and one isotopically normal (*i.e.* $^7Li/^6Li$ = 12.16) to create a Li_2CO_3 mix with $^7Li/^6Li \approx 1.3$. One rhyolite powder was doped so that it contained 500 ppm total Li and a second aliquot of rhyolite was doped to 180 ppm total Li. The powders were deposited in Pt crucibles and decarbonated for 8 hrs in a box furnace at 1000 °C. After decarbonation, the temperature was increased to 1300 °C and the samples were left in the furnace overnight to form homogeneous silicate melts.

Lithium is a volatile element and Li isotopes may fractionate significantly during partitioning between the melt and vapor phase (Webster *et al.*, 1989; Koga *et al.*, 2011; Vlastélic *et al.*, 2011). To ensure the $^7Li/^6Li$ values of the melts were as similar as possible, both the "high" Li and and "low" Li mixes were fused in the box furnace simultaneously. However, SIMS analyses later revealed the $^7Li/^6Li$ compositions of the glass starting materials differed by 0.2 % (*i.e.* δ^7Li = 20 ‰; Fig. 3 of main text). This difference may be due to differing degrees of Li isotope fractionation between the two glasses during the fusion step, or may be due to contamination of isotopically normal Li in the mineral and oxide starting materials.

After overnight heat treatment, both glasses were quenched and ground under ethanol to powder consistency. Rhyolite powders were loaded into machined Ag capsules along with 6 wt. % distilled H_2O added *via* micrometric syringe. Previous experiments in Ag capsules have shown that they retain their added water throughout experimental duration (Holycross and Watson, 2016). Capsules were placed inside a standard ¾" assembly (Fig. S-1) and run in a piston-cylinder apparatus to create "high Li" and "low Li" glasses. Hydrous rhyolite glasses were synthesised at 1 GPa pressure and 920 °C over the course of 2-4 days. After run completion, the glass starting materials were depressurised, cut perpendicular to the long axis of the capsule and polished for use in a diffusion couple anneal. After the piston-cylinder synthesis step, the initial glass starting materials were analysed for ^7Li on the LA-ICP-MS to ensure their homogeneity before use in diffusion couple experiments.

Lithium diffusion experiments were formed by juxtaposing polished rhyolite glasses, "low Li" over "high Li", in a new

piston-cylinder assembly. Pre-compression diffusion couple capsules typically measured ~7 mm in length and fit well within the ~10 mm thermal "plateau" in the RPI piston-cylinders (Watson *et al.*, 2002); which is further flattened by the use of a massive metal capsule (Watson and Wark 1997). Lithium diffusion couples were cold pressurised to ~12 kb and allowed to settle for 1 hr in the piston-cylinder assembly before heat treatment. Experiments were over-pressurised so only minimal adjustments to the sample pressure were required once the run had reached the final temperature. All Li diffusion experiments were executed using a two-part ramping routine. Diffusion couples were run up to 50 °C below the final temperature in one min and then ramped at either 150 °C/min or 200 °C/min to the ultimate run temperature (*e.g.*, experiment LiDiff6 was run up at an initial ramp of 780 °C/min to 780 °C, followed by a ramp at 150 °C/min to the final *T* of 830 °C). The two-step run-up procedure heated the experiments quickly without significantly overshooting the desired temperature.

Analytical Methods

LA-ICP-MS

All experiments were analysed for ^{7}Li using the laser ablation ICP-MS at RPI. The LA-ICP-MS at RPI consists of a Bruker 820-MS inductively coupled plasma quadrupole mass spectrometer furnished with a Photon Machines Analyte ablation system and ATLEX-SI 193 nm ultra-short pulse excimer laser. Li concentration profiles were generated by stepping a 40 μm square laser spot at intervals of 80 μm across the long axis of all diffusion couples. NIST 610 glass was used as the standard and ^{29}Si as the internal standard to reduce the ICP-MS data in the Iolite for Igor Pro software package. The uncertainty of the LA-ICP-MS measurements are given by the 2σ counting statistics.

SIMS

Lithium isotopic analyses were performed on a Cameca IMS 1270-E7 ion probe in Nancy, France at the Centre de Recherches Pétrographiques et Géochimiques (CRPG). A 13kV O⁻ primary beam with intensity between 0.3 and 0.7 nA was set in Gaussian mode with a raster of 10 μm, producing a beam size of ≈15 μm. Another primary beam of 3 nA was used for surface cleaning during pre-sputtering. Lithium measurements were made in single-collection mode using the central electron multiplier (EM) with the mass resolution set at M/ΔM = 2500. One measurement consisted of 50 cycles with 2 min pre-sputtering, automatic mass and energy offset centering, and automatic centering of the secondary beam in both the field aperture and contrast aperture. Each cycle consists of 2 s counting of mass 5.8 for EM background correction followed by 5 s counting of ^{6}Li and ^{7}Li with 1 s waiting time. Because for present purposes we are only interested in the relative fractionation of the lithium isotopes along the diffusion profile, the isotopic fractionations are reported in per mil notation using the ^{7}Li/^{6}Li value of the high concentration rhyolite glass as the standard value. Errors are given by the 2σ counting statistics. No matrix corrections were required because the major element composition of the glass was uniform across the diffusion couple. A Li-doped synthetic glass named GB4 (a CRPG internal standard) was used at the beginning of the session to calibrate the dead time of the electron multiplier (EM) used to measure Li isotopes. The standard deviation of measurements on GB4 is typically 0.2-0.3 ‰, which is significantly smaller than the 2σ counting statistics (~0.5-1.5 ‰) of the instrument. A small drift of the EM (effect of 1-2 ‰) was accounted for during the analytical session.

Data reduction and effect of experiment ramp up

Diffusion of Li during heating may be significant for hotter experiments which experienced higher temperatures during run-up. To normalise the impact of differing run-up times and temperatures on calculated diffusion coefficients, the experiment time *t* (Equation 1; Table 1) represents the total time the diffusion couple was at *T* > 700 °C (*i.e. t* = duration at *T* + duration of run-up after *T* = 700 °C).

A more quantitative approach may also be used to determine the effect of ramping time on the resulting values of *D*. To quantitatively assess the effect of run-up duration on measured diffusivities, we plotted a curve representing the diffusivity of Li (as calculated from initially determined Arrhenius parameters) *vs.* time for a given diffusion experiment. The area under the curve is integrated according to

$$\int_{t_0}^{t_{end}} D(t)dt$$

where *dt* is the "effective time" of the diffusion experiment (*e.g,* Zhang and Behrens, 2000). The effective time values are roughly ~3 % longer than values calculated assuming significant diffusion only starts at 700 °C.

The Li concentration profiles generated by LA-ICP-MS analysis were then re-fit with the new *t* parameter from the integration. After executing this procedure to fit several Li profiles, we noted that the new values of extrapolated from this method only change by ~3-5 %, which is well within our 2σ SE of 0.1log*D* for the original fits.

Supplementary Table

Table S-1 Rhyolite melt composition used in Li diffusion couple experiments, as determined by EPMA.

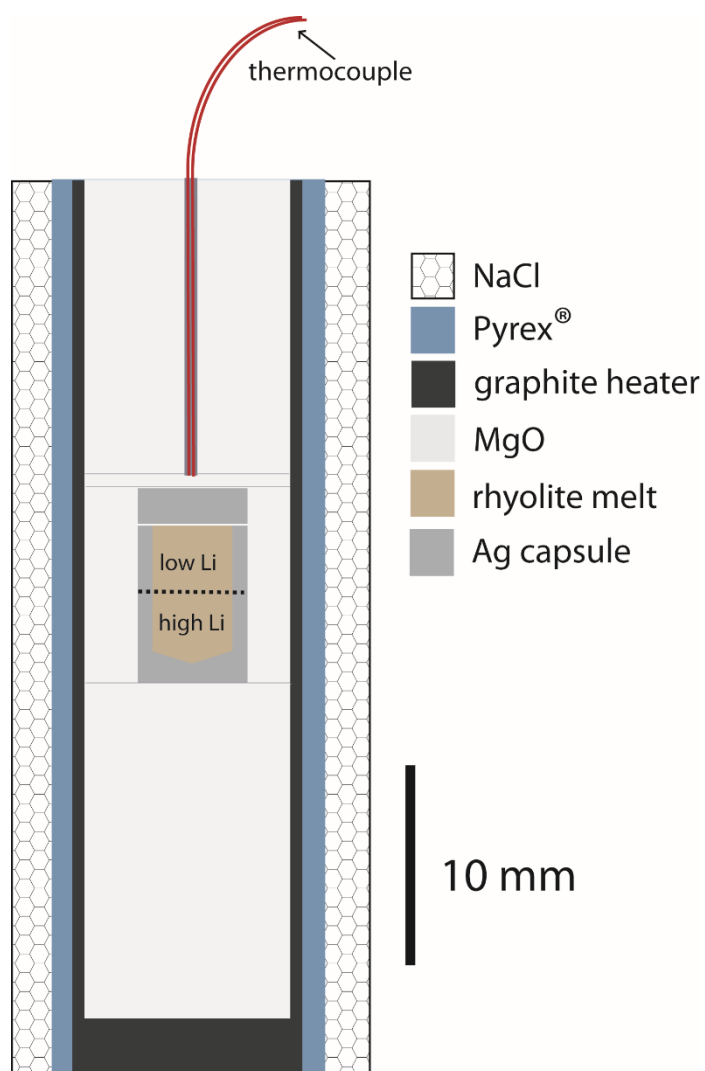| oxide	wt. %
SiO_2	72.05
TiO_2	0.13
Al_2O_3	13.07
FeO	0.64
MgO	0.03
CaO	0.50
Na_2O	4.70
K_2O	3.39
MnO	0.07
H_2O	6.0

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Supplementary Figures

Figure S-1   ¾" piston-cylinder assembly used to investigate Li diffusion and fractionation in wet rhyolitic melts.
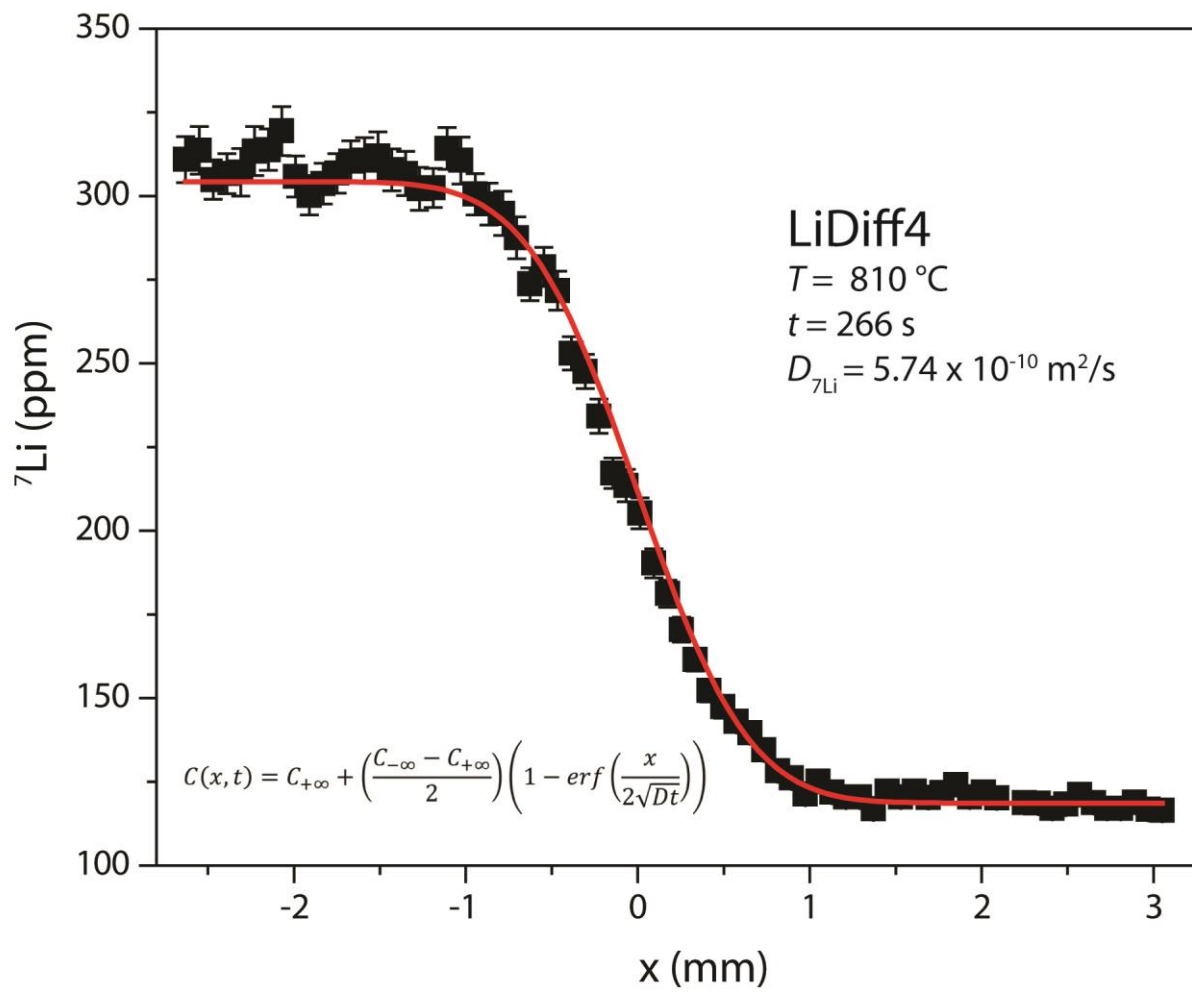
Figure S-2 Concentration profile from experiment LiDiff4 showing diffusion of [7]Li at 810 °C in wet rhyolitic melt. [7]Li concentration gradient was collected *via* LA-ICP-MS.

Supplementary Information References

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