

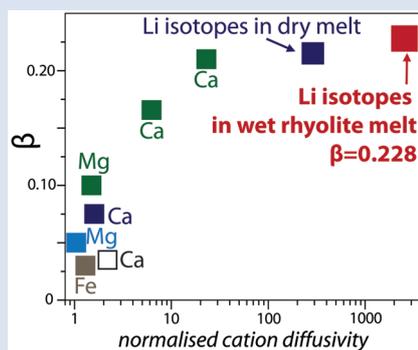
Diffusive fractionation of Li isotopes in wet, highly silicic melts

M.E. Holycross^{1,2*}, E.B. Watson¹, F.M. Richter³, J. Villeneuve⁴



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Abstract



The discovery of large lithium isotopic gradients in geologic media has motivated recent work examining the kinetic fractionation of Li isotopes in silicate materials. Here, piston-cylinder experiments were used to determine Li diffusivities in rhyolitic melts containing ~6 wt. % H₂O at 1 GPa pressure and 790–875 °C. Lithium transport in wet rhyolitic melt is almost an order of magnitude faster than diffusion in dry obsidian glass over the investigated temperature range. Li isotope profiles collected by ion microprobe show that the kinetic exponent $\beta = 0.228$ for diffusive fractionation of Li isotopes in wet rhyolite. This value is very close to $\beta = 0.215$ determined by Richter *et al.* (2003) for Li isotope diffusion in a dry basalt-rhyolite couple at 1350 °C. The similarity of the two values indicates little or no dependence of β_{Li} in silicate melts on either temperature or melt composition. The new data confirm a very high potential for diffusive fractionation of ⁶Li from ⁷Li and can be confidently used to model deviations in $\delta^7\text{Li}$ to determine the

time-temperature histories of natural rhyolite samples.

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Introduction and Experimental Approach

The detection of large lithium isotope variations in variety of terrestrial and planetary materials has driven significant advancements in Li isotope geochemistry over the past two decades (see recent reviews by Tomascak *et al.*, 2016 and Penniston-Dorland *et al.*, 2017 for details). The ~17 % mass difference between the two isotopes of lithium (⁶Li and ⁷Li) can lead to considerable equilibrium and kinetic fractionation in Earth systems. Experimental demonstrations have shown that Li diffusion in melts and minerals is subject to a large mass effect (Richter *et al.*, 2003, 2014, 2017; Dohmen *et al.*, 2010). In natural samples, diffusive fractionation of Li isotopes has been recorded at the μm to m scale (*e.g.*, Barrat *et al.*, 2005; Lundstrom *et al.*, 2005; Teng *et al.*, 2006; Jeffcoate *et al.*, 2007; Gao *et al.*, 2011). The relative diffusivities of the two isotopes of Li are expressed by the empirical constant β in the equation

$$\frac{D_{7\text{Li}}}{D_{6\text{Li}}} = \left(\frac{6}{7}\right)^\beta \quad \text{Eq. 1}$$

where D is the diffusivity of the individual isotopes (Richter *et al.*, 1999); the larger the value of β , the more sensitive the diffusivity is to isotope mass.

Lithium's small ionic radius and +1 valence make it an exceptionally fast diffuser in silicate melts (Jambon and Semet, 1978; Lowry *et al.*, 1981; Cunningham *et al.*, 1983; Richter *et al.*, 2003). In recent years, lithium diffusion gradients in silicate rocks have been increasingly used as geospeedometers of short-lived heating events (*e.g.*, Coogan *et al.*, 2005; Parkinson *et al.*, 2007; Charlier *et al.*, 2012; Richter *et al.*, 2016). Quantitative application of Li-geospeedometry requires that the gradients used for this purpose are demonstrably due to diffusion along with knowledge of Li kinetic isotope behaviour (*i.e.* β factors). Richter *et al.* (2003) reported $\beta = 0.215$ for the diffusive fractionation of Li isotopes in a dry basalt-rhyolite diffusion couple in a single experiment at 1350 °C. It was unclear if this β value applies to Li isotope fractionation in hydrous, silicic magmatic systems in which the behaviour of Li has drawn particular attention. In view of the widespread interest in the Li geochemistry of such systems, there is a compelling need for constraints on β in pertinent melt compositions and temperatures. Additionally, the work of Watkins *et al.* (2009, 2011, 2017) showed significant compositional dependence of β for isotope diffusion in simple silicate liquids, providing further motivation for determining the kinetic isotope fractionation of Li in a common but not previously studied molten silicate system.

To address the question of the general applicability of the earlier result of Richter *et al.* (2003), we performed piston-cylinder experiments to measure the relative diffusivities

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of Li isotopes in a melt composition and temperature range directly relevant to highly silicic volcanism (790–875 °C). Lithium diffusion couples were fabricated in Ag containers from two polished and juxtaposed cylinders of pre-synthesised hydrous rhyolite glass with different amounts of Li (Table S-1). The couples were placed in ¼" NaCl-Pyrex®-MgO assemblies, cold pressurised to ~12 kb and allowed to settle for 1 hr in the piston-cylinder before heating to the desired run temperature. This necessitated only minimal adjustments to the sample pressure once the run had reached the final temperature. A two-part ramping routine was used to heat the experiments quickly without significantly overshooting the desired temperature (see Supplementary Information). Experiment conditions are recorded in Table 1.

Table 1 Experiment conditions for diffusion couple runs and measured ^7Li diffusion coefficients.

experiment	T (°C)	t (s)	$D^7\text{Li}$ (m^2/s)	2σ SE
LiDiff2	875	492	7.40E-10	~7.4 E-11
LiDiff3	850	261	6.50E-10	~6.5 E-11
LiDiff4*	810	266	5.74E-10	7.53E-11
LiDiff5	790	205	5.25E-10	5.02E-11
LiDiff6*	830	133	6.28E-10	1.14E-10

*SIMS analysis

Lithium Diffusion Coefficients in Wet Rhyolitic Melt

Experimental glasses were analysed for ^7Li using the laser ablation ICP-MS at Rensselaer Polytechnic Institute. ^7Li diffusivities were derived by fitting the concentration profiles obtained from LA-ICP-MS measurements (Fig. S-2) with the time-dependent solution for diffusion in an infinite diffusion couple

$$C_{(x,t)} = C_{+\infty} + \left(\frac{C_{-\infty} + C_{+\infty}}{2} \right) \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) \quad \text{Eq. 2}$$

Resulting ^7Li diffusivities are listed in Table 1. All diffusion couples were ramped to the final temperature as quickly as possible to limit Li diffusion in the melt during run-up. However, it is inevitable that some Li diffusion occurred during the heating interval. The effects of diffusion during ramp up are accounted for in our data reduction scheme (see Supplementary Information). In two instances where the rapid diffusivity of Li resulted in an increase in Li concentrations at the end of the diffusion couple (experiments LiDiff2 and LiDiff3), an explicit finite-difference method was used to determine Li diffusion coefficients in a confined rhyolite melt system with zero-flux boundaries.

Calculated diffusion coefficients are fit to the Arrhenius equation to demonstrate the temperature dependence of Li transport in silicate melt (Fig. 1). A linear regression fit to D_{Li} vs. T^{-1} yields the Arrhenius parameters $\log(D_0, \text{m}^2/\text{s}) = -7.35 \pm 0.14$ and $E_a = 39.31 \pm 2.91$ kJ/mol for Li diffusion in hydrous rhyolitic liquid. Figure 1 shows the Arrhenius relationship for Li diffusion in hydrous rhyolite melt compared to Li diffusivities in rhyolite glass and various silicate melt compositions. Lithium diffusion is very fast even in dry rhyolite glass and the significant decrease in viscosity that occurs across the glass transition and from the addition of 6 wt. % H_2O to the melt network increases Li diffusivities by ~10x over the investigated T^{-1} range (cf. Jambon and Semet, 1978). As water is added to silicate liquid, OH^- molecules break bridging oxygen bonds, decreasing melt viscosity and increasing cation diffusivities

(e.g., Watson, 1979, 1981; Zhang *et al.*, 2003 and many others). The rapid diffusion of Li in hydrous, highly silicic melts implies that any gradients in total Li in rhyolite magma systems will be quickly homogenised while other trace element concentration gradients may persist (Hollycross and Watson, 2016a).

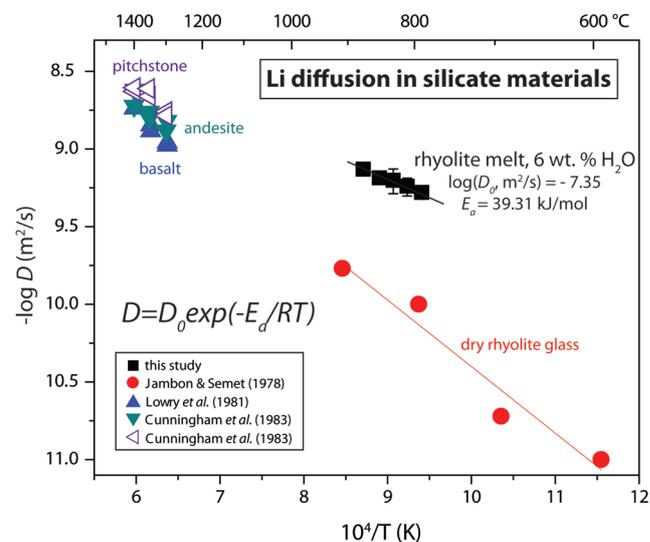


Figure 1 Arrhenius plot showing temperature dependence of Li diffusion in silicate materials. Lithium diffusion in wet rhyolite melt is significantly faster than in dry obsidian glass due to the decrease in viscosity from glass to liquid and from the addition of 6 wt. % dissolved H_2O to the melt.

Lithium Isotope Fractionation in Wet Rhyolitic Melt

To assess possible effects of melt composition on β_{Li} , we determined the relative diffusivities of the two Li isotopes in our hydrous rhyolite melts for comparison with the results of Richter *et al.* (2003). Lithium isotopic analyses were carried out on a Cameca IMS 1270-E7 ion probe at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Nancy, France. Information about the data collection routine is listed in the Supplementary Information. Lithium isotope fractionation profiles for two experiments are presented in Figure 2. Ion probe analyses revealed the two glasses used to form the diffusion couples had different $^7\text{Li}/^6\text{Li}$ compositions. Diffusion between the two glasses with different $^7\text{Li}/^6\text{Li}$ produced a somewhat unconventional $\delta^7\text{Li}$ profile characterised by a pronounced shoulder in the diffusion couple.

The β value for Li isotope diffusion in rhyolite was determined by generating individual model concentration profiles of ^7Li and ^6Li and then comparing the model $^7\text{Li}/^6\text{Li}$ values to the SIMS data. Model Li isotope profiles for experiments LiDiff4 and LiDiff6 were calculated using the solutions given by Equations 1 and 2. ^7Li diffusion coefficients obtained from least-squares fits to measured LA-ICP-MS profiles were kept constant while the diffusivity of ^6Li was varied so that the output of the $^7\text{Li}/^6\text{Li}$ model profile best matched the $^7\text{Li}/^6\text{Li}$ SIMS profile, as evaluated by obtaining the smallest χ^2 parameter for each ratio profile (Hollycross and Watson, 2016b).

In Figure 2, the Li fractionation data from experiment LiDiff4 is compared to profiles calculated with various β factors showing that $\beta = 0.23$ is the best fit. When $\beta \neq 0$, the different diffusivities of ^7Li and ^6Li create a shoulder or reversal in the $\delta^7\text{Li}$ profile near the couple interface. In the present experiments a $\delta^7\text{Li}$ sigmoidal profile is superimposed on the gradient due to the two end members having different $\delta^7\text{Li}$. The overall good



fit of the calculated Li fractionation profiles to the measured data confirms that ^7Li and ^6Li diffuse at different rates. Kinetic fractionation profiles from LiDiff4 and LiDiff6 are best fit when ^6Li diffuses $\sim 3.5\%$ faster than ^7Li in the melt (*i.e.* $D_{\text{Li}}^{7/6} = 0.965$), corresponding to an average β of 0.228.

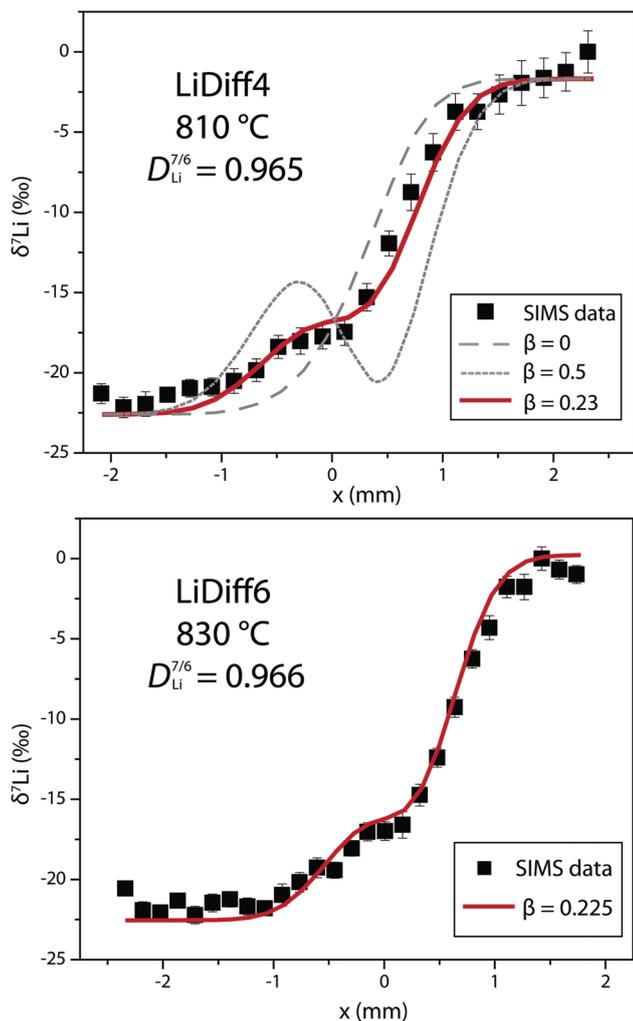


Figure 2 $\delta^7\text{Li}$ profiles produced from SIMS analyses. ^6Li diffuses into the “low” Li glass ($x > 0$) faster than ^7Li , fractionating the isotopes in the melt. If the Li isotopes were diffusing at the same speed in rhyolitic melt ($\beta = 0$), a smoothly varying isotope gradient would be present near $x = 0$. When $\beta \neq 0$, calculated profiles show a shallow or reversed slope near the diffusion couple interface at $x = 0$, as is seen in the data in both panels. The kinetic fractionation of Li isotopes in hydrous rhyolitic melt is best fit by an average $\beta = 0.228$.

The global dataset of experimentally-determined β values ($\beta > 0$) for fractionation in silicate liquids spans $\beta_{\text{Ca}} = 0.035$ to our new value of $\beta_{\text{Li}} = 0.228$ (compiled by Watkins *et al.*, 2017). The β_{Li} determined here for diffusion in hydrous obsidian melt at 790–875 °C is close to the value of Richter *et al.* (2003), who found $\beta = 0.215$ for Li isotopes in dry silicate melt in a single experiment at 1350 °C. It is unclear if our new value and that of Richter *et al.* (2003) are statistically different by a small amount given the difficulty of assigning realistic uncertainties for such a small number of experiments. Regardless, the key point is that the β_{Li} values are remarkably similar despite very different system compositions and temperatures.

The similarity of β_{Li} for both systems may be a consequence of Li decoupling from the silicate melt network during diffusion. Watkins *et al.* (2009, 2011, 2017) proposed that the β factor for isotopic fractionation of an element i in simple silicate melt may be a function of its Si-normalised diffusivity,

D_i/D_{Si} (Fig. 3). Faster diffusing elements may be moving as single atoms in the melt network and thus show a greater isotope mass discrimination because their diffusion is not correlated with the mobilities of other network elements. At very large values of D_i/D_{Si} , changes in β_i in different melt compositions are minimal. This is observed comparing our new data to that of Richter *et al.* (2003). At 810 °C in a rhyolite melt with 6 wt. % H_2O , $D_{\text{Li}}/D_{\text{Si}} \approx 2560$ (Si value from Baker and Bossányi, 1994), roughly an order of magnitude greater than $D_{\text{Li}}/D_{\text{Si}}$ in the experiment of Richter *et al.* (2003) and yet they have very similar values of β_{Li} . The high diffusivity of Li in wet rhyolite and the insensitivity of β_{Li} to liquid composition indicates Li isotope diffusion is independent of melt structure. This suggests that Li may jump primarily between coordinated sites in the melt network, perhaps not unlike the fast diffusion of Li *via* an interstitial mechanism in crystalline mineral phases (*e.g.*, Mullen, 1961; Dohmen *et al.*, 2010; Richter *et al.* 2014, 2017).

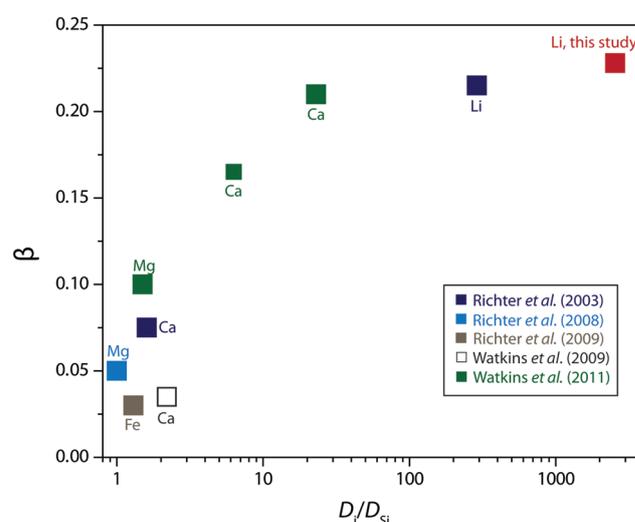


Figure 3 The reported β factors for isotopes of an element i vary with its Si-normalised diffusivity, D_i/D_{Si} . Data point in red is for rhyolitic melt containing 6 wt. % H_2O at 810 °C. Silicon is an extremely slow diffuser in rhyolite while Li is extremely fast. This suggests diffusion of Li may be decoupled from the melt network and exhibit a greater mass discrimination. Figure after Watkins *et al.* (2017).

The vital aspect of our measurements is that they can be confidently applied to Li isotope diffusion profiles in rhyolitic rock specimens to determine the timescales of rapid heating events in highly silicic volcanic systems. Diffusive fractionation of Li isotopes in our experiments demonstrate the potential for creating considerable variations in the $\delta^7\text{Li}$ of natural magmas during kinetically controlled growth of bubbles or crystalline mineral phases (Koga *et al.*, 2011; Watson, 2017). This raises the possibility that the isotopic composition of Li in rhyolitic rock systems may record significant kinetic fractionation, which can be modelled using β_{Li} derived from the experiments reported here.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1807>.



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■ Supplementary Information

The Supplementary Information includes:

- Experimental Methods
- Analytical Methods
- Table S-1
- Figures S-1 and S-2
- Supplementary Information References

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.* $^7\text{Li}/^6\text{Li} = 12.16$) to create a Li_2CO_3 mix with $^7\text{Li}/^6\text{Li} \approx 1.3$. 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 $^7\text{Li}/^6\text{Li}$ values of the melts were as similar as possible, both the “high” Li and “low” Li mixes were fused in the box furnace simultaneously. However, SIMS analyses later revealed the $^7\text{Li}/^6\text{Li}$ compositions of the glass starting materials differed by 0.2 % (*i.e.* $\delta^7\text{Li} = 20$ ‰; 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 $\frac{3}{4}$ ” 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 ⁷Li 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 ²⁹Si 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 Géochemiques (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 $M/\Delta M = 2500$. 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 ⁶Li and ⁷Li 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 ⁷Li/⁶Li 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.* $t = \text{duration at } T + \text{duration of run-up after } T = 700$ °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 ₂ O ₃	13.07
FeO	0.64
MgO	0.03
CaO	0.50
Na ₂ O	4.70
K ₂ O	3.39
MnO	0.07
H ₂ O	6.0



Supplementary Figures

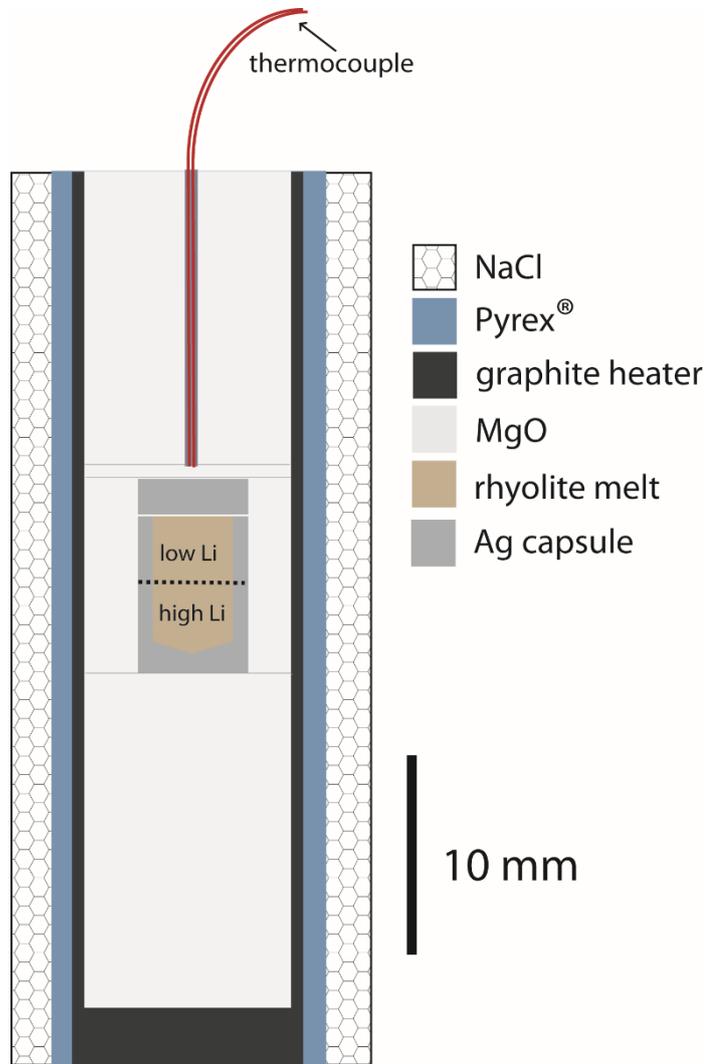


Figure S-1 3/4" piston-cylinder assembly used to investigate Li diffusion and fractionation in wet rhyolitic melts.

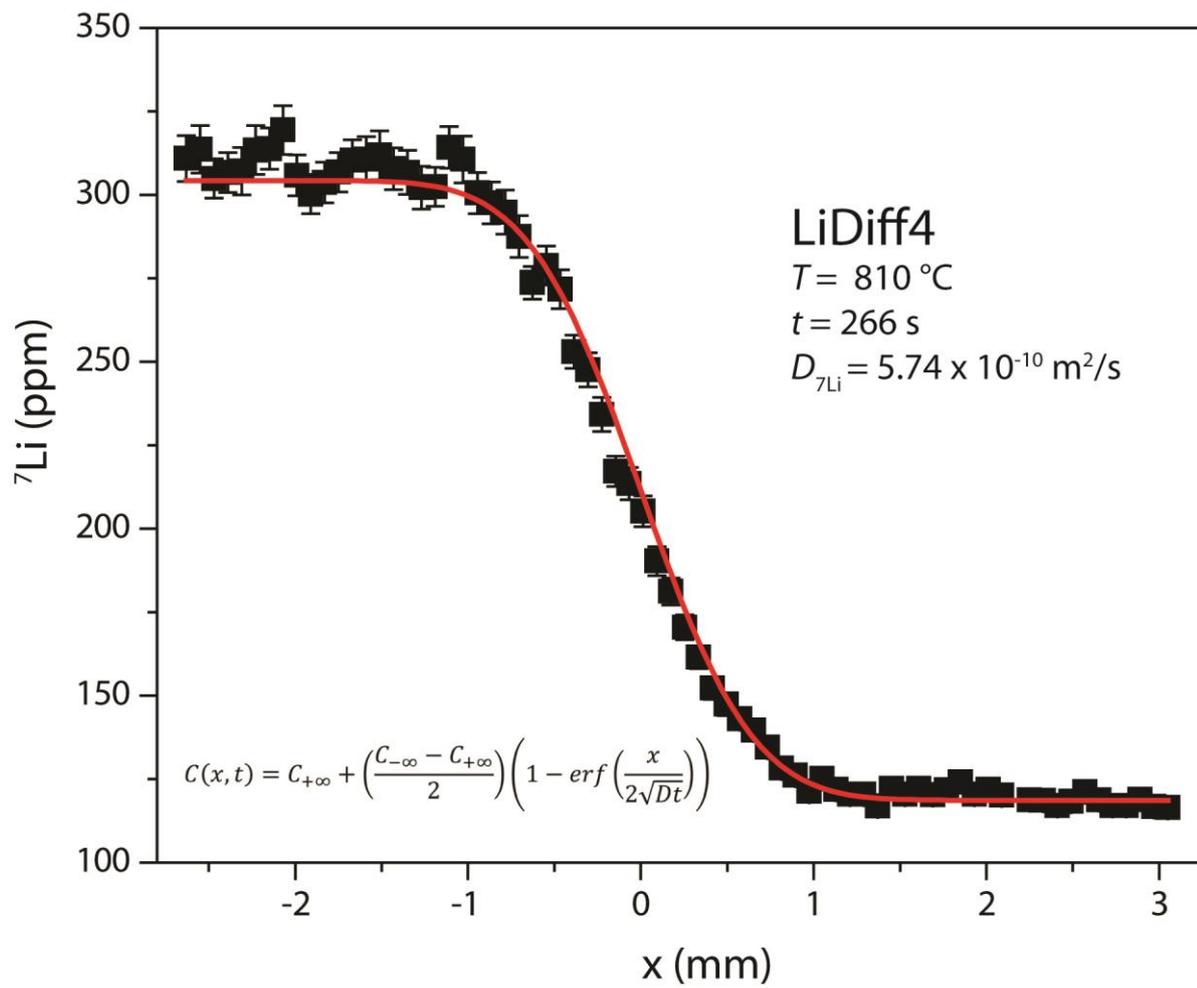


Figure S-2 Concentration profile from experiment LiDiff4 showing diffusion of ${}^7\text{Li}$ at $810\text{ }^\circ\text{C}$ in wet rhyolitic melt. ${}^7\text{Li}$ concentration gradient was collected via LA-ICP-MS.

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