

Diffusion-driven extreme lithium isotopic fractionation in country rocks of the Tin Mountain pegmatite

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Abstract

Lithium concentrations and isotopic compositions in the country rocks (amphibolites and schists) of the Tin Mountain pegmatite show systematic changes with distance to the contact. Both Li and $\delta^7\text{Li}$ decrease dramatically along a $\sim 10\text{m}$ traverse from the pegmatite into amphibolite, with Li concentration decreasing from 471 to 68 ppm and $\delta^7\text{Li}$ decreasing from +7.6 to -19.9 . Rubidium and Cs also decrease from the pegmatite contact into the country rock, but only within the first 2 m of the contact, after which their concentrations remain constant. Neither mixing between pegmatite fluids and amphibolite, nor Li isotope fractionation by Rayleigh distillation during fluid infiltration is a likely explanation of these observations, due to the extremely light isotopic composition required for the amphibolite end-member in the mixing model ($\delta^7\text{Li} = -20$) and the similarly extreme isotopic fractionation required in a Rayleigh distillation model. Rather, these variations are likely due to isotopic fractionation accompanying Li diffusion from the Li-rich pegmatite (Li=450 to 730 ppm) into amphibolites (Li=20 ppm). The fact that other alkali element concentrations vary only within 2 m of the contact reflects the orders of magnitude faster diffusion of Li relative to heavier elements.

Quartz mica schists in contact with the pegmatite also show large variations in both Li and $\delta^7\text{Li}$ as a function of distance from contact ($\sim 1\text{ wt.}\%$ to $\sim 70\text{ ppm}$ and +10.8 to -18.6 , respectively), but over a longer distance of $>30\text{ m}$. Lithium concentrations of the schist decrease from $\sim 1\text{ wt.}\%$ adjacent to the contact to $\sim 70\text{ ppm}$ 300 m from the contact; the latter is a typical concentration in metapelites. The nature of the $\delta^7\text{Li}$ variations in the schists is different than in the amphibolites. Schists within the first 2 m of the contact have nearly identical $\delta^7\text{Li}$ of +10, which mimics that of the estimated bulk pegmatite (+8 to +11). At a distance of 30 m the $\delta^7\text{Li}$ reaches the lowest value in the schists of -18.6 (similar to the lowest amphibolite measured). At a distance of 300 m the $\delta^7\text{Li}$ climbs back to +2.5, which is within the range of $\delta^7\text{Li}$ of other schists in the region and metapelites worldwide. The behavior of Li in the schists can also be modeled by Li diffusion, with the effective diffusion coefficient in the schist being ~ 10 times greater than that in the amphibolite. The effective diffusion coefficients of Li in the amphibolite and schist are >2 orders of magnitude greater than those in minerals, which implicates the importance of fluid-assisted grain-boundary diffusion over solid-state diffusion in transporting Li through these rocks.

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1. Introduction

Lithium is a fluid-mobile, moderately incompatible element having two stable isotopes with $\sim 17\%$ relative

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mass difference. This large mass difference gives rise to significant isotopic fractionations in different geological environments, especially those involving fluid–rock interactions [see review of [1]]. These characteristics result in distinct Li concentration and isotopic composition in the hydrosphere, continental crust and mantle. In general, the hydrosphere is isotopically heavy ($\delta^7\text{Li}$ of seawater = +32), the mantle is intermediate at +4, whereas the weathered, upper continental crust is isotopically light (~ 0) [1,2].

Equilibrium Li isotope fractionation, like other stable isotope systems [3], is due to differences in bond energies between different phases for the two isotopes (e.g., mineral and fluid), with heavy Li (^7Li) preferring the higher-energy bond. Bond energy is, in turn, related to coordination number, with lower coordination number sites having higher bond energy [4]. Thus Li substituting for Mg in octahedral mineral sites (e.g., pyroxenes) will be isotopically lighter than Li found in fluids, which is believed to be in tetrahedral coordination [4,5]. Recent studies using both laboratory experiments and natural rocks have demonstrated the existence of another type of Li isotopic fractionation, produced by the different diffusivities of ^6Li and ^7Li in silicate melts and solids. Diffusion couple experiments have reported $\sim 40\%$ Li isotopic fractionation between juxtaposed molten rhyolite and basalt, with an initial Li concentration ratio of ~ 15 [6]. Large Li isotopic variation ($> 10\%$) was also observed along a $\sim 2\text{ m}$ Li concentration gradient in peridotite adjacent to discordant dunites (former melt channels), and explained by Li isotopic fractionation during a combined process of diffusion and melt extraction [7]. Compared with equilibrium isotopic fractionation produced by bond-energy differences, diffusion-driven (kinetic) isotopic fractionation is controlled by the concentration gradient and the relative mobility of isotopes. Thus, it can occur at high temperatures where equilibrium fractionation diminishes [8].

In this paper we report Li concentrations and isotopic compositions of country rocks adjacent to the Li-rich Tin Mountain pegmatite, Black Hills, South Dakota. Emplacement and crystallization of this pegmatite produced a large Li concentration gradient between the pegmatite and country rocks and led to Li diffusion into the country rocks. Our results demonstrate that up to 30% fractionation of Li isotopes was produced in this manner.

2. Geological background and samples

Samples studied here are from the country rocks of the ca. 1.7 Ga Tin Mountain pegmatite, Black Hills,

South Dakota, which crops out $\sim 12\text{ km}$ to the southwest of the main body of the Harney Peak Granite [9]. The Li-rich, Tin Mountain pegmatite discordantly intruded both schists and a tabular amphibolite unit, which are the focus of this paper. The pegmatite consists of five major structural/mineralogical zones, with the wall zone forming a shell that encloses inner zones. Fracture fillings are compositionally similar to the core and traceable from the core into the surrounding zones [10]. The estimated formation pressure is $\sim 0.3\text{ GPa}$ [9] with crystallization temperature varying from ~ 600 down to 340°C [10–12]. Lithium isotopic compositions of minerals and whole rocks from the different zones of the Tin Mountain pegmatite, as well as the Harney Peak Granite, associated simple pegmatites and representative country rocks are reported elsewhere [13]. All samples measured here have been characterized in previous investigations [14,15] and previously published chemical data are provided in the electronic supplement (see Appendix).

2.1. Amphibolites

The amphibolite is similar in composition to tholeiitic basalt. It overlies much of the wall zone of the pegmatite, and reached amphibolite facies prior to the intrusion of the pegmatite [9]. The Li isotopic variation within the amphibolite was determined for eight samples collected along a 10 m vertical traverse above the pegmatite body, where the outcrop ends at the cliff top. An additional sample, collected from a different amphibolite body 300 m away from the pegmatite, was also analyzed.

The amphibolite is a medium-grained rock composed predominantly of hornblende and plagioclase with minor amounts of quartz and biotite. Significant amounts of calcite (2–7%) are present in two samples (samples 12-2 and 12-3). The amphibolite is layered, with segregations of oriented hornblende alternating with layers of crystalloblastic plagioclase [14]. Most major and trace elements have relatively constant concentration along the traverse (Fig. 1), which suggests that modal variations are insignificant. Some fluid-mobile elements, however, show large variations in amphibolites near the contact (Fig. 1). Relative to the mean of the other samples, the sample taken from the contact (sample 12-8) is significantly enriched in K_2O , Rb, Cs, Sb, $\delta^{18}\text{O}$ and depleted in Na_2O [14,15]. By comparison, sample 12-7, taken 0.5 m from the contact, shows considerably less enrichment/depletion of these elements.

Feldspars show little compositional variation along the traverse, and range from An_{30-40} , except for the

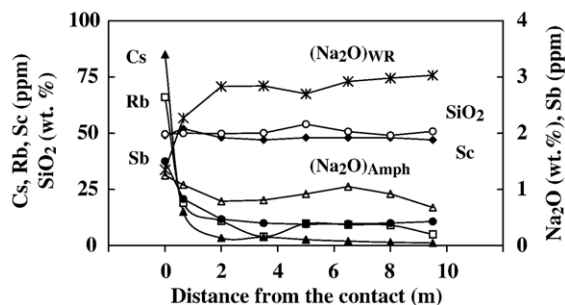


Fig. 1. Concentration profiles of SiO_2 , Sc, Cs, Rb, Sb, Na_2O in the amphibolite and Na_2O in the amphibole vs. distance from the contact with the Tin Mountain pegmatite. Data from Walker [14] and Laul et al. [15] and are provided in the electronic supplement.

sample at the contact, which is more anorthite-rich ($\sim\text{An}_{50}$). Amphibole compositions vary on the scale of a thin section, but, except for Na, no systematic change is observed along the traverse [14]. FeO contents range from 12.3 to 19.9 wt.% and MgO contents range from 7.6 to 12.4 wt.%. Amphibole at the contact contains more Na than amphiboles elsewhere along the traverse, a trend that is different from that observed from whole rock samples [14].

2.2. Quartz mica schists

Schists are the dominant country rocks in this area. Their protolith was shale that was metamorphosed to the sillimanite zone during regional metamorphism prior to the intrusion of Tin Mountain pegmatite [9]. Compared with the amphibolites, fresh outcrops of the schists are limited and it thus proved difficult to collect systematically along a traverse away from the pegmatite. Consequently, a variety of schists were sampled in and around the pegmatite in order to determine the extent of a metasomatic halo on a lateral scale. These samples include an inlier of schist enclosed by the wall and third intermediate zones of the pegmatite (13-1), three samples collected near the lower contact of the pegmatite (9-3, 9-1 and 9-4), and two samples taken from scattered outcrops to the northwest and southwest ends of the pegmatite at distances of 30 (23-4) and 300 m (23-2). In order to characterize any compositional variation within the Black Hills terrane, three more schist samples were taken in this region far away (e.g., >8 km) from known granite and pegmatite outcrops.

The schists are composed of quartz, biotite, plagioclase and minor muscovite. Both modal mineralogy and major element composition vary considerably. The variations are probably due to the original sedimentary layering of the protolith [14]. Trace element concentra-

tions do not generally correlate with modal biotite + muscovite abundances. Relative to regional schists, the inlier sample (13-1) is extremely enriched in Rb, Cs, and Zn and depleted in $\delta^{18}\text{O}$. Lesser amounts of alkali enrichment are found in two samples taken within 0.5 m of the pegmatite (i.e., 9-1 and 9-3) and no discernable enrichments are seen in samples taken from over a meter from the contact (9-4, 23-4 and 23-2) [14].

3. Analytical methods

Sample powders were the same as those used in previous studies [14–17]. Procedures for sample dissolution and column chemistry are described in Rudnick et al. [18] and the method of instrumental analysis is found in Teng et al. [2].

Table 1
Lithium isotopic composition and concentration of samples from the Tin Mountain pegmatite

Sample ID	$\delta^7\text{Li}^a$	Li ^b (ppm)	Distance (m)
<i>Amphibolites</i>			
14-1	+0.9	20	300
12-1	-19.5	72	9.5
12-1 replicate ^c	-19.9		
12-2	-14.2	68	8
12-3	-13.7	98	6.5
12-4	-8.3	140	5
12-4 replicate	-7.5		
12-5	-0.9	209	3.5
12-6	+6.5	260	2
12-7	+7.5	438	0.5
12-8	+7.6	471	0.03
12-8 replicate	+7.3		
<i>Quartz mica schists</i>			
40-1A	-3.1	62	>8000
WC-4	+1.6	79	>8000
26-2	+2.3	150	>8000
23-2	+2.5	68	300
23-4	-18.0	124	30
23-4 replicate	-18.6		
9-4	+10.0	960	1.5
9-1	+8.9	1607	0.3
9-3	+9.0	1179	0.1
13-1	+10.8	~10,000	0
<i>Wall zone whole rock of Tin Mountain pegmatite</i>			
10-3	+11.1	453	
9-2	+7.5	504	
43-1	+11.1	735	

^a Analytical uncertainty is $\pm 1\%$ (2σ), based on both pure Li solutions and natural rocks (see text for details).

^b Li measured by comparison of signal intensities with 50 or 100 ppm L-SVEC.

^c Replicate: repeat column chemistry from the same sample solution.

The external precision of Li isotopic analyses, based on 2σ of repeat runs of pure Li standard solutions and rock solutions, is $<\pm 1.0\text{‰}$. For example, pure Li standard solutions (IRMM-016 and UMD-1) always yield values falling within previously established ranges ($-0.1\text{‰}\pm 0.2\text{‰}$ and $+54.7\text{‰}\pm 1\text{‰}$) [2]; in-house rock standard AO-12, a shale from the Amadeus Basin (part of the PAAS group of Nance and Taylor, [19]), gives $\delta^7\text{Li}=+3.5\pm 0.6$ (2σ , $n=36$ runs with 4 replicate sample preparations); and BCR-1 gives $\delta^7\text{Li}=+2.0\pm 0.7$ (2σ , $n=10$ runs). The uncertainty of Li concentration measurement, determined by the comparison of signal intensities with that measured for the 100 or 50ppb L-SVEC standard and then adjusting for sample weight, is $<\pm 10\%$. The accuracy of this method has been established in Teng et al. [2] to be $<\pm 5\%$ as based on isotope dilution methods.

4. Results

Lithium concentration and isotopic composition for both schists and amphibolites are reported in Table 1 and plotted in Fig. 2 as a function of distance from the contact. The Li concentration and isotopic composition

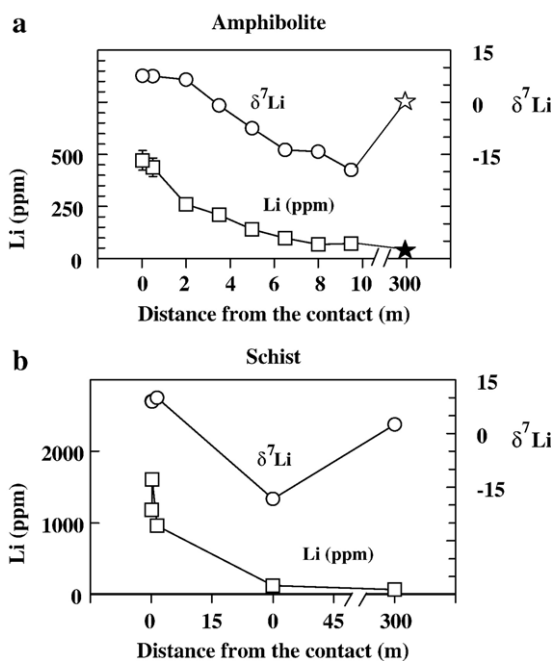


Fig. 2. Plots of Li and $\delta^7\text{Li}$ versus distance from the contact for a) amphibolite samples taken along a vertical profile and b) schist samples taken at different distances to the contact, but not along a single profile. Stars in a) represent Li (filled) and $\delta^7\text{Li}$ (open) of the regional amphibolite taken from another unit, 300m from the contact. Data from Table 1.

of the Tin Mountain pegmatite and related igneous rocks have been reported in Teng et al. [13]. Data for three wall zone whole rock samples that represent the average composition of the Tin Mountain pegmatite are presented for comparison in Table 1.

4.1. Amphibolite

Both Li and $\delta^7\text{Li}$ decrease with distance from the contact (Fig. 2a). The amphibolite near the pegmatite contact is isotopically heavy (+7.6), similar to wall zone samples of the pegmatite (+7.5 to +11.1), and it has the highest Li concentration (471 ppm). The sample at the end of the traverse, 10m away from the contact, has the lowest Li concentration (70ppm) and the lightest isotopic composition (-19.9). The regional amphibolite, taken 300m from the Tin Mountain pegmatite, has a Li concentration (20ppm) and isotopic composition (+0.9) comparable to typical upper crustal lithologies [2].

4.2. Quartz mica schist

Lithium concentrations and isotopic compositions of schists are also highly variable (Fig. 2b). The schist enclosed by the pegmatite (13-1) is extremely rich in Li (~1 wt.%) with pegmatite-like $\delta^7\text{Li}$ (+10.8). Three samples within 1.5m of the pegmatite also show pegmatite-like Li isotopic compositions and high Li concentrations, with the furthest one (9-4, 1.5m from the contact) showing no discernable enrichments in other fluid mobile elements. A sample collected 30m from the pegmatite has a very light Li isotopic composition (-18.6) and a Li concentration of 124ppm. Samples collected much further from the contact show typical shale-like Li concentrations (~70ppm) and isotopic compositions (-3 to +2.5) [2].

5. Discussion

The Tin Mountain pegmatite is extremely enriched in isotopically heavy Li [13] relative to typical amphibolites and schists [20–22]. Thus, the compositional variations observed within the country rocks as a function of distance from the pegmatite must have resulted from mass transfer of elements enriched in the pegmatite into the country rocks. This transfer may have occurred by fluid infiltration and/or solid-state diffusion.

Crystallization of the Tin Mountain pegmatite exsolved a large amount of fluids [10,14]. Since Li is fluid-mobile [23], infiltration of these fluids into the country rocks would have carried Li, which could then equilibrate with the country rocks. This process can be

considered as simple mixing between pegmatite fluids and country rocks if no isotopic fractionation occurred, or modeled as Rayleigh Distillation if Li isotopic fractionation occurred during fluid infiltration. Alternatively, the large compositional contrast between pegmatite and country rocks could have led to diffusion of Li from the pegmatite into country rocks [24]. Such diffusion can produce large Li isotopic fractionations, as demonstrated by previous studies [6,7]. Below we model each process and evaluate their potentials for explaining the Tin Mountain data. While all processes could have modified the Li concentrations and isotopic compositions of country rocks, we show that diffusion is the most likely process to have produced the trends we observe.

5.1. Modeling the Li profile in amphibolite country rocks

Amphibolites show a ten-fold decrease in Li concentration and a $\sim 30\%$ drop in Li isotopic composition along the 10m traverse. Variations in both Li and $\delta^7\text{Li}$ values do not correlate with either the modes of amphibole or plagioclase or the amphibole or plagioclase compositions. They therefore likely reflect interactions between the amphibolites and the Tin Mountain pegmatite.

5.1.1. Mixing model

If no Li isotopic fractionation during fluid-rock interactions occurred, then fluid infiltration can be modeled as two-end-member mixing between isotopically heavy Li from the pegmatite and lighter Li in the original amphibolite. Using amphibolites at either end of the transect as end-members, the mixing model fits the data well (Fig. 3).

The high Li concentration and $\delta^7\text{Li}$ of the amphibolite at the contact is similar to the Tin Mountain pegmatite, and suggests that Li in this sample is dominated by a component coming from the pegmatite. The other amphibolite end-member, however, is richer in Li (70 ppm) and isotopically lighter (-19.9) than regional amphibolite (sample 14-1) or amphibolites from other regions [20,21]. The regional amphibolite was likely not affected by the intrusion of this pegmatite or other plutons, and can be considered as representative of unaltered amphibolites in this area. The large difference in Li and $\delta^7\text{Li}$ between the amphibolite end-member used in these mixing calculations and typical amphibolites suggests that the end-member has been substantially affected by Li infiltration from the pegmatite, and thus this simple mixing model cannot explain the data.

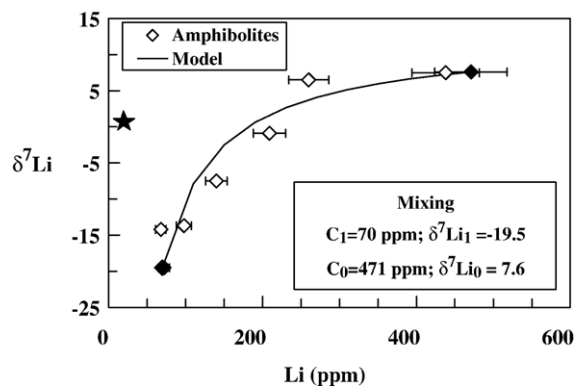


Fig. 3. Plots of Li and $\delta^7\text{Li}$ for amphibolites and two end-member mixing model. Mixing equation used: $\delta^7\text{Li} = (\delta^7\text{Li})_1 \times f_1 + (\delta^7\text{Li})_0 \times (1 - f_1)$, f_1 = fraction of Li in end member 1. End-members are shown as solid symbols and represent the measured values of amphibolites at either end of the transect. Star represents composition of the regional amphibolite taken from another unit, 300m from the contact (Table 1).

5.1.2. Rayleigh distillation model

Previous studies have shown that Li isotopes can be strongly fractionated during low-T fluid-rock interactions, with isotopically heavy Li partitioning into fluids relative to rocks [18,25,26]. Although fluid infiltration of amphibolite country rocks occurred at relatively high temperature ($T > 340^\circ\text{C}$) [10–12], Li isotopes may still be fractionated (the isotopic exchange between amphibole, plagioclase and fluids has not yet been quantified as a function of temperature). Therefore, we explore fluid infiltration accompanied by isotopic fractionation using a Rayleigh fractionation law, which is considered as an extreme end-member process that fractionates isotopes in the most effective way.

A series of Rayleigh distillation curves can be calculated to fit most of the data (Fig. 4), assuming that the Li isotopic fractionation factor between fluids and minerals (α) is $\sim 1.013 \pm 0.002$, i.e., there is $\sim 13\%$ difference between fluids and amphibolites. Since, in reality, fluid infiltration may not perfectly obey a Rayleigh distillation process, which is the most effective process at fractionating isotopes, these estimated α values are considered to be minimum values. Although experimentally measured fractionation factors between hydrothermal fluids and amphibolites are not currently available, data for α determined for seafloor alteration can be used for comparison. At $\sim 2^\circ\text{C}$, the Li isotopic fractionation factor between seawater and clays produced by alteration of basalts (α) is inferred to be 1.019 [25]; while at 350°C , α between hydrothermal fluids and basalts decreases to 1.003–1.007 [27,28]. Given a minimum crystallization temperature for this system of

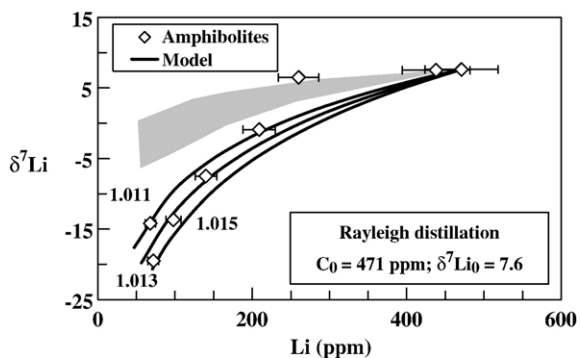


Fig. 4. Plots of Li and $\delta^7\text{Li}$ for amphibolites and Rayleigh distillation model. Rayleigh distillation equation: $\delta^7\text{Li}_{\text{amph}} = (\delta^7\text{Li}_0 + 1000) f^{(\alpha-1)} - 1000$; α : Li isotopic fractionation factor defined as ${}^7\text{Li}/{}^6\text{Li}_{\text{fluid}}/{}^7\text{Li}/{}^6\text{Li}_{\text{amph}}$; f : the fraction of Li remaining in the rock, calculated from $\text{Li}_{\text{amph}}/\text{Li}_0$; 0: amphibolite at the contact. The gray field represents the area where data would plot for a Rayleigh distillation model that uses more appropriate empirical α values (1.003 to 1.007). The greater α values (on lines) compared with those empirically observed in similar conditions rule out this process as a mechanism explaining the data.

~ 340 °C [10–12], the fractionation factor required to fit the data (1.013) is significantly greater than those observed at comparable temperatures in the oceanic environment. Therefore, this process is unlikely to explain the data.

5.1.3. Diffusion model

The above discussions suggest that fluid infiltration, with or without isotopic fractionation, is unlikely to produce the Li profile observed in the amphibolite country rocks. Instead, we explore the likelihood that diffusion of Li played an important role in producing the extreme isotopic fractionation observed. The importance of diffusion in producing the Li variations is consistent with the differences in scales observed in chemical modification of the country rocks for Li versus other elements. All other elements that change systematically within the amphibolite transect show concentration variations only within 2 m of the contact (Fig. 1). The much larger scale of Li variation (≥ 10 m) may reflect greater Li diffusivity relative to the other elements examined. Although Li diffusivity in amphibole is unknown, studies of other silicate minerals and melts demonstrate that Li diffusion is orders of magnitude faster than other elements [6,29–31]. For example, Li diffuses more than four orders of magnitude faster than other alkali elements in plagioclase feldspar [30] and 100 times faster than most trace elements in a liquid basalt [6].

To model the data, the pegmatite is considered as an infinite Li reservoir relative to the country rocks;

therefore, the diffusion model used to fit the data is a one-dimensional diffusion model with the boundary conditions of a constant Li concentration at the contact and uniform initial Li concentration in the country rocks. Using these boundary conditions, the solution to the Fick's second law of diffusion is [32]:

$$[(C_x - C_1)/(C_0 - C_1)] = \text{erfc}[x/2(Dt)^{1/2}]$$

where here, x = distance from the contact; C_x = element concentration at distance x from the contact; C_0 = element concentration at the contact at $x=0$; C_1 = element concentration in unaffected country rocks; D = diffusion coefficient; t = duration of the diffusion process; erfc = complementary error function.

${}^6\text{Li}$ and ${}^7\text{Li}$ are treated as two different elements and each diffusion curve is modeled separately. The ${}^7\text{Li}/{}^6\text{Li}$ ratio or $\delta^7\text{Li}$ is calculated by combining concentrations at different distances. By using the regional amphibolite to represent the unaltered amphibolite country rock, and the pegmatite as representative of the concentration at the contact, the following parameters are derived: $C_1 = 20$ ppm and $\delta^7\text{Li} = +0.9$. This, with $C_0 = 471$ ppm and $\delta^7\text{Li} = +7.6$, allows $C_{1,6}$ (or $C_{1,7}$) and $C_{0,6}$ (or $C_{0,7}$) to be calculated. Since neither ${}^7\text{Li}$ and ${}^6\text{Li}$ diffusion coefficients in amphibolites, nor the duration of diffusion is known, the value of \sqrt{Dt} (characteristic diffusive transport distance) is calculated to best fit the Li concentration profile (Fig. 5a). The best value of $\sqrt{Dt} = 3.1$ (m) was determined by using the Microsoft Excel® solver function. The effective diffusion coefficient derived here corresponds to the transport of Li through a mixed phase material (amphibolite + fluid, see Section 5.3 for more details). Moreover, this diffusion coefficient is the average D of both ${}^7\text{Li}$ and ${}^6\text{Li}$, but since $>90\%$ of Li is ${}^7\text{Li}$, D is considered to represent D_7 and the Li concentration profile can be considered to be that of ${}^7\text{Li}$.

In order to model the $\delta^7\text{Li}$ profile, the diffusion profile for ${}^6\text{Li}$ is needed. If the relationship between D_7 and D_6 can be found, then the ${}^6\text{Li}$ diffusion curve can be modeled, followed by the $\delta^7\text{Li}$ curve. Here the assumption of Richter et al. [8] is used: the ratio of the effective diffusion coefficients of the isotopes 1 (light) and 2 (heavy) of element i are related to their mass by the following equation: $D_{i,1}/D_{i,2} = (m_{i,2}/m_{i,1})^\beta$, where β is an empirical parameter determined from experimental data. Given the same conditions (e.g., same concentration gradient, temperature etc.) but different diffusion media, the larger the β , the stronger the isotopic fractionation. For ideal gases, β is equal to 0.5, while in condensed matter and fluids it is <0.5 . For example, a

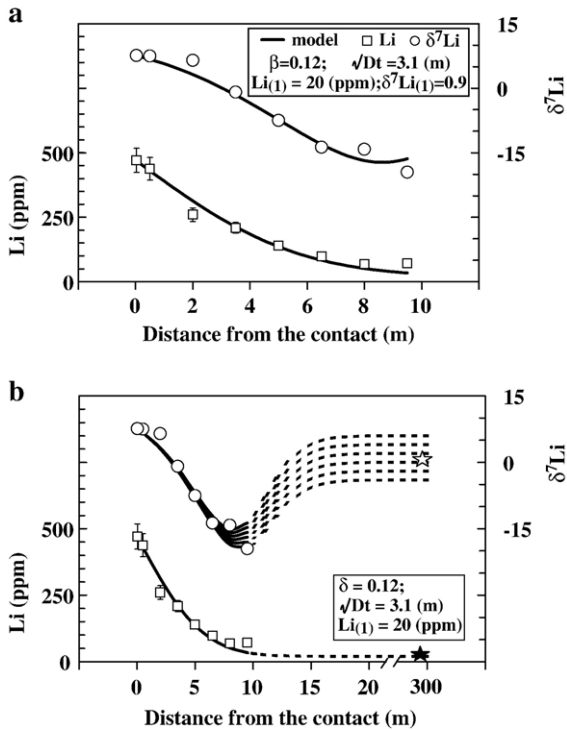


Fig. 5. Diffusion calculations (curves) compared to data (symbols) for Li and $\delta^7\text{Li}$ of amphibolites vs. distance from the contact, a) diffusion model for the amphibolite profile and b) shows how varying the initial Li isotopic composition of the unaltered amphibolite has little effect on outcome. Star in b) represents the Li (filled) and $\delta^7\text{Li}$ (open) of the regional amphibolite, which is used as the initial Li and $\delta^7\text{Li}$ values in the diffusion model in a); see text for details.

β value of ~ 0.215 was determined experimentally for Li diffusion in silicate melts [6] and 0.071 [33] and 0.015 [34] were reported for Li diffusion in water.

The effective diffusion coefficients depend on temperature, pressure and matrix (composition, mineralogy, fluid, etc.) [35]. The estimated crystallization temperature of the Tin Mountain pegmatite varied from ~ 600 to 340°C [10–12] at an intrusion depth of $\sim 10\text{ km}$ [9]. At a normal geothermal gradient of $\sim 35^\circ\text{C/km}$ [36], the country rocks at this depth should have had a temperature of $\sim 350^\circ\text{C}$, similar to that at the final stages of pegmatite crystallization. Therefore, the temperature gradient produced by the intrusion in the country rocks should be small. Moreover, both the major element composition and the mineralogy of the amphibolites along the traverse change little, so the effective diffusion coefficients of both ^6Li and ^7Li in the amphibolite are assumed to have remained constant, i.e., $D_6/D_7 = (m_7/m_6)^\beta = \text{constant}$, which means β is constant. The β value yielding the best fit to the data is 0.12 (Fig. 5a) and the corresponding ratio of $D_6/D_7 = 1.018$. This β value is

smaller than that measured in silicate melt [6] but greater than those measured in water [33,34]. This suggests that the difference in the effective diffusion coefficient between ^7Li and ^6Li is larger in fluid-infiltrated amphibolite than in pure water, which may result from different bonding environments for Li in pure water compared to supercritical fluids [13] and interactions of fluids with amphibolites. Furthermore, it is important to note that the initial Li isotopic composition of unaltered amphibolite is not important for this modeling (Fig. 5b). The calculated curves still fit the data well even if the $\delta^7\text{Li}$ values of the amphibolite are varied from -4 to $+6$.

In summary, the Li profile observed in the amphibolite country rocks cannot be explained by mixing between pegmatite fluids and amphibolite due to the extremely light $\delta^7\text{Li}$ required for the amphibolite end-member (≤ -20). Nor can Li isotope fractionation by Rayleigh distillation during fluid infiltration explain the trend due to the extreme fractionation factors required (≥ 1.013). Instead, these variations can be explained by isotopic fractionation accompanying Li diffusion from the pegmatite into amphibolites, assuming reasonable diffusion coefficients, β values and $\delta^7\text{Li}$ value for the unaltered amphibolite.

5.2. Modeling the Li profile in schist country rocks

The Li concentrations and isotopic compositions of schists taken from the inlier within the pegmatite and from near the contact with the pegmatite are dominated by Li from the Tin Mountain pegmatite. Samples taken far from the pegmatite ($>300\text{ m}$) have Li similar to schists and shales worldwide [2,22,37]. These distal schists may, therefore, represent samples that have not been affected by interactions with any pluton. The sample taken 30 m from the pegmatite, however, has

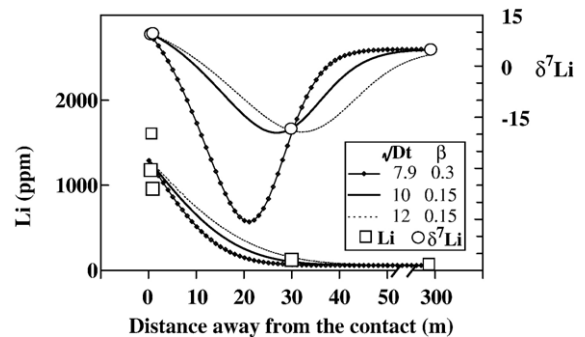


Fig. 6. Models of diffusion-induced lithium isotope fractionation for schists as a function of distance from the contact. Due to the limited sample numbers, the model is non-unique. See text for further details.

extremely light Li isotopic composition and was likely influenced by the pegmatite.

This isotopically light schist, like the isotopically light amphibolite, may also result from Li isotopic fractionation through diffusion-related processes. Applying the approach outlined above to the data for the schist provides a best-fit $\sqrt{Dt}=10$ (m) and $\beta=0.15$, although the lack of a well-constrained diffusion profile through the schist means that these values are not unique (Fig. 6). Nevertheless, the schist's relatively large \sqrt{Dt} value compared with that in amphibolite is consistent with earlier findings that demonstrated that Li can migrate to a greater distance in schist country rocks (the Etta pegmatite near the Harney Peak Granite) than amphibolite country rocks of the Tin Mountain pegmatite [15].

5.3. Implications for the nature of diffusion

Data from the country rocks of the Tin Mountain pegmatite demonstrate that Li isotopes can be strongly fractionated by diffusion at moderate temperature (down to 340°C) and over large length scales (>30m). This observation agrees well with the theoretical model, implying that diffusion-induced isotopic fractionation may be important and Li isotopic heterogeneity may exist at both large and small scales (e.g., zoned minerals or minerals that interacted with fluids). Moreover, results of this modeling can be used to constrain the effective diffusion coefficients in the country rocks and to constrain the type of diffusion: grain-boundary diffusion vs. volume diffusion.

Based on the best fits to the Li concentration profiles, the value for \sqrt{Dt} differs between the amphibolite and schist with $D_{\text{schist}}/D_{\text{amphibolite}} \sim 10$. Although neither the effective diffusion coefficient (D) nor the duration of the diffusion process (t) is known, the minimum D can be calculated by assuming that the maximum time of diffusion is equal to the age of the Tin Mountain pegmatite (1.7 Ga). As a result, the minimum $D_{\text{amphibolite}}$ for Li is calculated to be 2×10^{-12} cm²/s and the D_{schist} is accordingly ~ 10 times higher (Fig. 7). These estimated minimum D values are >2 orders of magnitude higher than those measured in silicate minerals (e.g., feldspar and pyroxene) [29,30], clearly ruling out the possibility of volume diffusion as the mechanism by which Li diffused through the country rocks, and suggesting that diffusion occurred in an interconnected fluid phase that interacted with mineral grains.

As discussed in Watson and Wark [38], the effective diffusion coefficient is related to the diffusion coefficient in the fluid, effective porosity and interactions

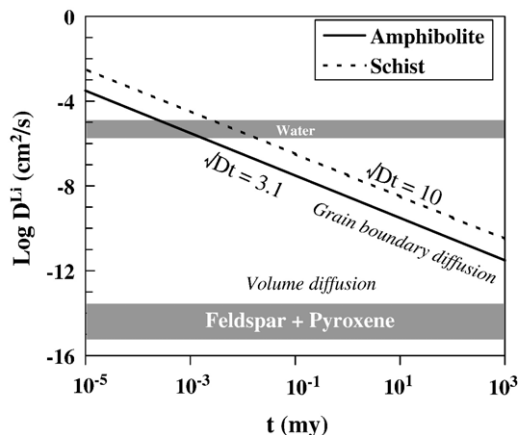


Fig. 7. Plot of D vs. t , assuming $\sqrt{Dt}=3.1$ and 10 in amphibolites and schists, respectively; D values for Li in water from Li and Gregory [39] and for Li in plagioclase and pyroxene from Giletti and Shanahan [30] and Coogan et al. [29], respectively.

between fluids and minerals. Whereas Li diffusivity in pure water has been measured [39], it is unknown in supercritical fluids (e.g., fluids exsolved during crystallization of the Tin Mountain pegmatite). It is likely that the different bonding environment for Li in pure water (Li coordinated with H₂O) is different from that in supercritical fluid (Li coordinated with Cl) [13]. Furthermore, the extent and nature of interactions between fluids and country rocks (e.g., fluid/rock ratios, Li partition coefficients between supercritical fluids and schist/amphibolite minerals) are not well characterized. In the simple case, if we assume that the diffusion coefficients in fluids are the same between amphibolites and schists and the partition coefficients for Li between the fluid and rock are not significantly different, the effective diffusion coefficient is mainly controlled by the effective interconnected porosity. In this case, the effective interconnected porosity in schists is thus ~ 10 times larger than in amphibolite, reflecting a greater permeability in the schist compared to amphibolite.

6. Conclusions

The country rocks of the Tin Mountain pegmatite exhibit $\sim 30\%$ Li isotopic change over a ~ 10 m traverse in the amphibolites and >30 m in the schist. These observations are unlikely to be due to either mixing between pegmatite and country rocks or Li isotope fractionation by Rayleigh distillation during fluid infiltration. Instead, they reflect extreme Li isotopic fractionation accompanying Li diffusion from the Li-rich

pegmatite into country rocks. These extreme fractionations are due to the large differences in diffusion coefficients between ^6Li and ^7Li , and in Li concentrations between the pegmatite and country rocks.

Lithium diffusion in the schists is inferred to be ~ 10 times faster than in the amphibolites. However, in both types of rocks, Li diffuses much faster than other alkali elements, as concentrations of these elements vary only within 2m of the contact. The effective diffusion coefficient of Li in both rocks are > 2 orders of magnitude greater than in minerals, which indicates Li diffusion in country rocks was dominated by fluid-assisted grain-boundary diffusion over solid-state diffusion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2006.01.036](https://doi.org/10.1016/j.epsl.2006.01.036).

References

- [1] P.B. Tomascak, Developments in the understanding and application of lithium isotopes in the Earth and planetary sciences, in: C. Johnson, B. Beard, F. Albarede (Eds.), *Geochemistry of Non-Traditional Stable Isotopes*, vol. 55, Mineralogical Society of America, Washington, DC, 2004, pp. 153–195.
- [2] F.-Z. Teng, W.F. McDonough, R.L. Rudnick, C. Dalpe, P.B. Tomascak, B.W. Chappell, S. Gao, Lithium isotopic composition and concentration of the upper continental crust, *Geochim. Cosmochim. Acta* 68 (2004) 4181–4192.
- [3] T. Chacko, D.R. Cole, J. Horita, Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geological systems, in: J.W. Valley, D.R. Cole (Eds.), *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry*, vol. 43, Mineralogical Society of America, Washington, DC, 2001, pp. 1–82.
- [4] M. Wenger, T. Armbruster, Crystal-chemistry of lithium—oxygen coordination and bonding, *Eur. J. Mineral.* 3 (1991) 387–399.
- [5] K. Yamaji, Y. Makita, H. Watanabe, A. Sonoda, H. Kanoh, T. Hirotsu, K. Ooi, Theoretical estimation of lithium isotopic reduced partition function ratio for lithium ions in aqueous solution, *J. Phys. Chem., A* 105 (2001) 602–613.
- [6] F.M. Richter, A.M. Davis, D.J. DePaolo, E.B. Watson, Isotope fractionation by chemical diffusion between molten basalt and rhyolite, *Geochim. Cosmochim. Acta* 67 (2003) 3905–3923.
- [7] C.C. Lundstrom, M. Chaussidon, A.T. Hsui, P. Kelemen, M. Zimmerman, Observations of Li isotopic variations in the trinity ophiolite: evidence for isotopic fractionation by diffusion during mantle melting, *Geochim. Cosmochim. Acta* 69 (2005) 735–751.
- [8] F.M. Richter, Y. Liang, A.M. Davis, Isotope fractionation by diffusion in molten oxides, *Geochim. Cosmochim. Acta* 63 (1999) 2853–2861.
- [9] J.A. Redden, J.J. Norton, R.J. McLaughlin, Geology of the Harney Peak granite, Black Hills, South Dakota, in: F.J. Rich (Ed.), *Geology of the Black Hills, South Dakota and Wyoming*, Amer. Geol. Inst., 1985, pp. 225–240.
- [10] R.J. Walker, G.N. Hanson, J.J. Papike, J.R. O’Neil, J.C. Laul, Internal evolution of the Tin Mountain pegmatite, Black Hills, South-Dakota, *Am. Miner.* 71 (1986) 440–459.
- [11] M.L.C. Sirbescu, P.I. Nabelek, Crystallization conditions and evolution of magmatic fluids in the Harney Peak Granite and associated pegmatites, Black Hills, South Dakota—Evidence from fluid inclusions, *Geochim. Cosmochim. Acta* 67 (2003) 2443–2465.
- [12] M.L.C. Sirbescu, P.I. Nabelek, Crustal melts below 400 °C, *Geology* 31 (2003) 685–688.
- [13] F.-Z. Teng, W.F. McDonough, R.L. Rudnick, R.J. Walker. Lithium isotopic systematics of granites and pegmatites from the Black Hills, South Dakota, *Am. Miner.* (In review).
- [14] R.J. Walker. The origin of the Tin Mountain pegmatite, Black Hills, South Dakota. PhD. dissertation, Univ. New York at Stony Brook, 1984.
- [15] J.C. Laul, R.J. Walker, C.K. Shearer, J.J. Papike, S.B. Simon, Chemical migration by contact metamorphism between pegmatite and country rocks: natural analogs for radionuclide migration, *Material Research Society Symposium Proceedings*, vol. 26, 1984, pp. 951–958.
- [16] R.J. Walker, G.N. Hanson, J.J. Papike, Trace-element constraints on pegmatite genesis—Tin Mountain pegmatite, Black Hills, South-Dakota, *Contrib. Mineral. Petrol.* 101 (1989) 290–300.
- [17] R.J. Walker, G.N. Hanson, J.J. Papike, J.R. O’Neil, Nd, O and Sr isotopic constraints on the origin of Precambrian rocks, southern-Black-Hills, South-Dakota, *Geochim. Cosmochim. Acta* 50 (1986) 2833–2846.
- [18] R.L. Rudnick, P.B. Tomascak, H.B. Njo, L.R. Gardner, Extreme lithium isotopic fractionation during continental weathering revealed in saprolites from South Carolina, *Chem. Geol.* 212 (2004) 45–57.
- [19] W.B. Nance, S.R. Taylor, Rare-earth element patterns and crustal evolution: 1. Australian Post-Archean sedimentary-rocks, *Geochim. Cosmochim. Acta* 40 (1976) 1539–1551.
- [20] F.-Z. Teng, W.F. McDonough, R.L. Rudnick, S. Gao, Lithium isotopic composition of the deep continental crust, *EOS* 85 (47) (2004) (Abstr. V51C-0597).
- [21] D.J. Bottomley, L.H. Chan, A. Katz, A. Starinsky, I.D. Clark, Lithium isotope geochemistry and origin of Canadian Shield brines, *Ground Water* 41 (2003) 847–856.
- [22] F.-Z. Teng, W.F. McDonough, R.L. Rudnick, B.A. Wing, Lack of lithium isotopic fractionation during progressive metamorphic dehydration in metapelite: a case study from the Onawa contact aureole, Maine. *Chem. Geol.* (in preparation).
- [23] J.M. Brenan, F.J. Ryerson, H.F. Shaw, The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium

- during subduction: experiments and models, *Geochim. Cosmochim. Acta* 62 (1998) 3337–3347.
- [24] W. Jost, *Diffusion in Solids, Liquids, and Gases*, Academic Press, New York, 1960. 558 pp.
- [25] L.H. Chan, J.M. Edmond, G. Thompson, K. Gillis, Lithium isotopic composition of submarine basalts: implications for the lithium cycle in the oceans, *Earth Planet. Sci. Lett.* 108 (1992) 151–160.
- [26] Y. Huh, L.-H. Chan, L. Zhang, J.M. Edmond, Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget, *Geochim. Cosmochim. Acta* 62 (1998) 2039–2051.
- [27] L.H. Chan, J.M. Gieskes, C.F. You, J.M. Edmond, Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California, *Geochim. Cosmochim. Acta* 58 (1994) 4443–4454.
- [28] L.H. Chan, J.M. Edmond, G. Thompson, A lithium isotope study of hot-springs and metabasalts from Mid-Ocean ridge hydrothermal systems, *J. Geophys. Res.-Solid Earth* 98 (1993) 9653–9659.
- [29] L.A. Coogan, S.A. Kasemann, S. Chakraborty, Rates of hydrothermal cooling of new oceanic upper crust derived from lithium-geospeedometry, *Earth Planet. Sci. Lett.* 240 (2005) 415–424.
- [30] B.J. Gilotti, T.M. Shanahan, Alkali diffusion in plagioclase feldspar, *Chem. Geol.* 139 (1997) 3–20.
- [31] C.C. Lundstrom, An experimental investigation of the diffusive infiltration of alkalis into partially molten peridotite: implications for mantle melting processes, *Geochem. Geophys. Geosyst.* 4 (2003) 8614, doi:10.1029/2001GC000224.
- [32] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975. 414 pp.
- [33] S.J. Fritz, Measuring the ratio of aqueous diffusion coefficients between ${}^6\text{Li}^+\text{Cl}^-$ and ${}^7\text{Li}^+\text{Cl}^-$ by osmometry, *Geochim. Cosmochim. Acta* 56 (1992) 3781–3789.
- [34] F.M. Richter, R.A. Mendybaev, J.N. Christensen, I.D. Hutcheon, R.W. Williams, N.C. Sturchio, J.A.D. Beloso, Kinetic isotopic fractionation during diffusion of ionic species in water, *Geochim. Cosmochim. Acta* 70 (2) (2006) 277–289.
- [35] D.R. Cole, S. Chakraborty, Rates and mechanisms of isotopic exchange, in: J.W. Valley, D.R. Cole (Eds.), *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry*, vol. 43, The Mineralogical Society of America, Washington, DC, 2001, pp. 83–224.
- [36] G.C. Brown, A.E. Mussett, *The Inaccessible Earth: An Integrated View of its Structure and Composition*, Chapman and Hall, London, 1993. 276 pp.
- [37] T. Moriguti, E. Nakamura, Across-arc variation of Li isotopes in lavas and implications for crust/mantle recycling at subduction zones, *Earth Planet. Sci. Lett.* 163 (1998) 167–174.
- [38] E.B. Watson, D.A. Wark, Diffusion of dissolved SiO_2 in H_2O at 1 GPa, with implications for mass transport in the crust and upper mantle, *Contrib. Mineral. Petrol.* 130 (1997) 66–80.
- [39] Y.-H. Li, S. Gregory, Diffusion of ions in sea water and in deep-sea sediments, *Geochim. Cosmochim. Acta* 38 (1974) 703–714.