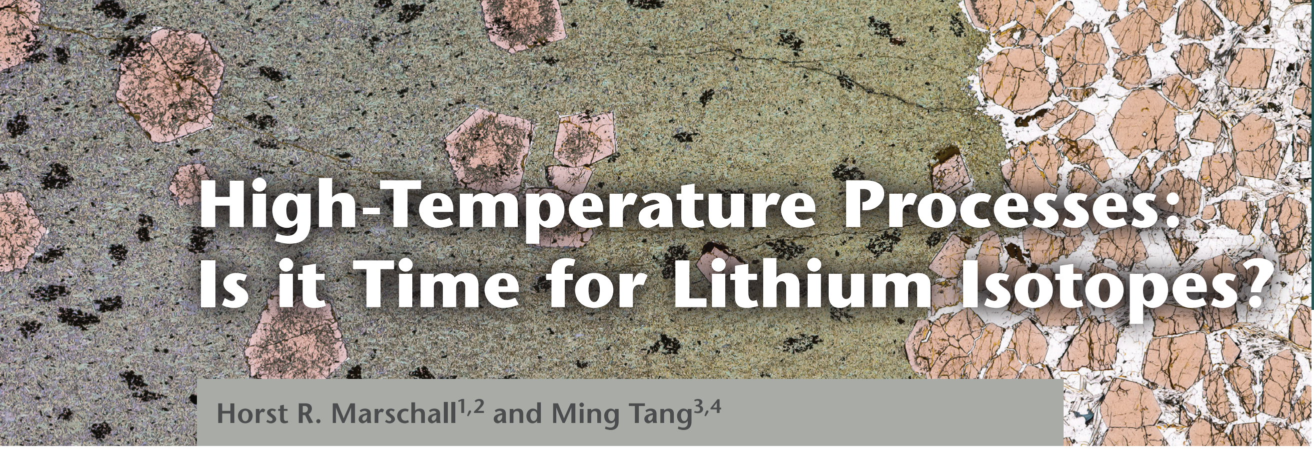

High-Temperature Processes: Is it Time for Lithium Isotopes?

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Microphotograph of high-pressure fluid vein (right side) consisting of garnet (red) and quartz (colorless) crosscutting an eclogitic host rock from New Caledonia (field of view 5 cm) (Taetz et al. 2018).

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The field of high-temperature Li isotope geochemistry has been rattled by major paradigm changes. The idea that Li isotopes could be used to trace the sources of fluids, rocks, and magmas had to be largely abandoned, because Li diffusion causes its isotopes to fractionate at metamorphic and magmatic temperatures. However, diffusive fractionation of Li isotopes can be used to determine timescales of geologic processes using arrested diffusion profiles. High diffusivity and strong kinetic isotope fractionation favors Li isotopes as a tool to constrain the durations of fast processes in the crust and mantle, where other geochronometers fall short. Time may be the parameter that high-temperature Li isotope studies will be able to shed much light on.

KEYWORDS: lithium isotopes, diffusion, geochronometry, timescales, isotope fractionation

INTRODUCTION

Elements at the low-mass end of the periodic table show large equilibrium isotope fractionation, especially at the low temperatures prevailing at the Earth's surface where rocks interact with the atmosphere and hydrosphere. For these reasons, the lightest of all metals, lithium (see "Lithium Facts Box"), would seem to be most suitable in tracing the recycling of surface materials into the deep mantle. Early work on Li isotopes, pioneered by Lui-Heung Chan, focused on the characterization of the marine environment, including seawater, sediments, and fresh and altered oceanic crust (e.g., Chan and Edmond 1988). Efforts then moved to identify the Li isotopic composition of the depleted upper mantle, as defined by mid-ocean-ridge basalts and mantle samples, and the differences between the depleted mantle and subduction-related and ocean-island volcanoes (Chan et al. 1992, 2002b; Tomascak et al. 2002). Disappointingly, the vast majority of samples from these settings revealed Li isotopic compositions that are indistinguishable from the depleted upper mantle, despite the unmistakable contribution of recycled materials to their magma sources, as evidenced by various other trace elements and isotope systems (e.g., Chan et al. 2002b; Tomascak et al. 2002). Nonetheless, some rock samples did display Li isotopic excursions, supporting a model in which subducted materials are heterogeneous in Li concentration (noted here as [Li]); specifically, it was suggested that Li isotopes, and the average bulk subducted slab, introduces isotopically heavy Li (i.e., high ^{7}Li/^{6}Li) into the mantle to create high-δ^7Li domains (Chan et al. 2002a, see "Lithium Facts Box" for the definition of δ^7Li).

The situation became more complex when the first high-pressure metamorphic rocks (i.e., eclogites and garnet mica schists) were investigated for their Li isotopic composition with the aim of constraining the composition of subducted, dehydrated slabs. These rocks displayed a large spread in δ^7Li with some very negative values that were interpreted to represent strong equilibrium Li isotope fractionation between minerals and fluids during slab dehydration (Zack et al. 2003). It was concluded that subducting slabs would be driven to very low δ^7Li values during metamorphic dehydration and, thus, introduce isotopically light Li into the mantle (Zack et al. 2003). This model was rapidly and widely accepted and boosted the interest of geochemists in applying Li isotopes to a range of high-temperature processes in the geosciences (Elliott et al. 2004).

LITHIUM FACTS BOX

Element: Lithium, Li (alkali metal)

- Atomic number: 3
- Molar mass: 6.94 g mol^{-1}

Two stable isotopes (natural abundances):

- ^{6}Li (7.4%–7.9%)
- ^{7}Li (92.1%–92.6%)

All radioisotopes of Li have half-lives <1 s

The delta notation for stable isotopes:

$$\delta^7\text{Li} = \frac{{}^7\text{Li}/{}^6\text{Li}_{\text{sample}}}{{}^7\text{Li}/{}^6\text{Li}_{\text{standard}}} - 1$$

This value is multiplied by 1,000 to express it in per mil (‰)

The standard for Li isotopes is NIST-RM8545, also called "L-SVEC", a Li_2CO_3 with ^{7}Li/^{6}Li = 12.019

δ^7Li values (in parts per mil) in the geologic framework:

- Continental crust: +1.7‰ ± 1.0‰
- Modern seawater: +31.2‰ ± 0.3‰
- Mantle (mid-ocean-ridge basalts): +3.5‰ ± 1.0‰
- Highest bulk sample (continental brine): +46.9‰
- Lowest bulk sample (eclogite): –21.9‰
- Natural variation among rocks and fluids: ~70‰

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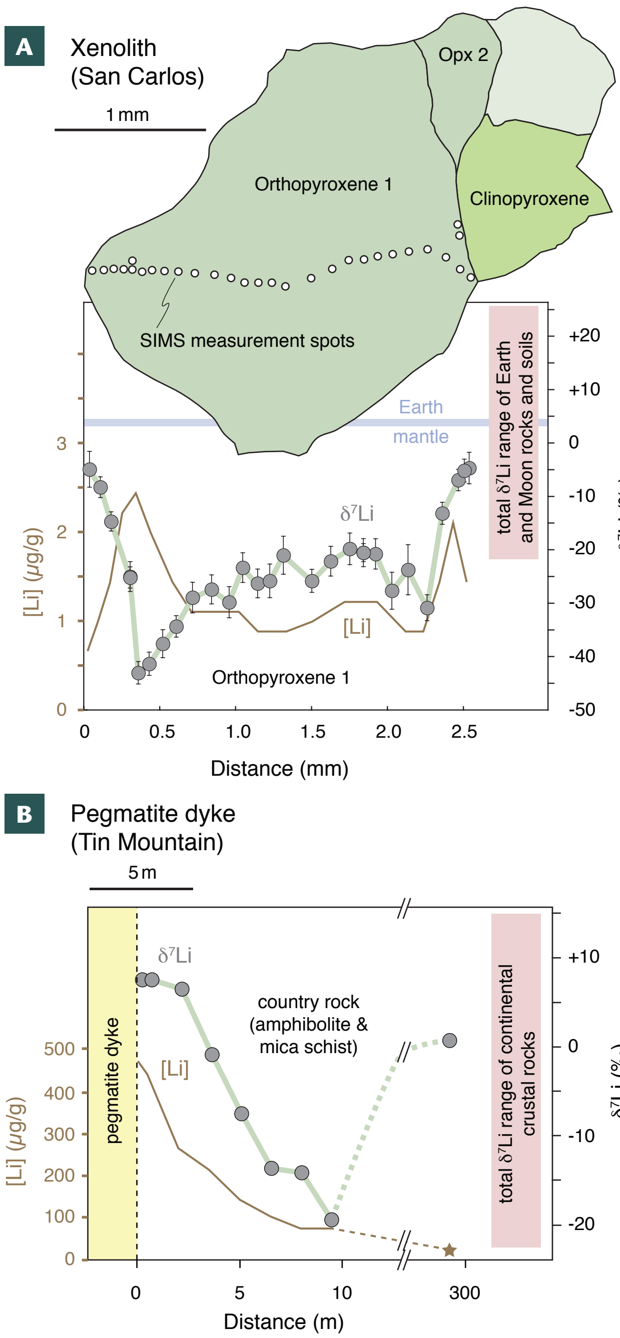

FIGURE 1 Two natural examples of very strong kinetic Li isotope fractionation on different length scales. (**A**) A millimeter-scale traverse through a mineral grain (orthopyroxene) in a mantle xenolith from San Carlos (Arizona, USA). This revealed a total range of 37‰ in δ^7Li within less than a millimeter, which is comparable to the total range of all bulk rock, sediment, and soil values from Earth and the Moon reported to date (rectangle at left). The mineral analysis spot map (orthopyroxene 1) shows the locations of the measurement spots. Opx = orthopyroxene. AFTER JEFFCOATE ET AL. (2007). (**B**) Diffusion processes on the meter-scale of an outcrop produced a range of 27.5‰ in δ^7Li (circles) within a distance of 10 m from the Tin Mountain pegmatite dike (South Dakota, USA) into its surrounding country rocks. [Li] = Li concentration (brown curve). Starred symbol represents a distant sample of country rock. δ^7Li = see Lithium Facts Box. AFTER TENG ET AL. (2006).

However, the notion that this novel geochemical tracer could be used to study deep-mantle recycling was dealt a blow when the world of geochemistry became aware of the fact that Li diffuses very rapidly at temperatures that are typical of magmatic and high-grade metamorphic processes and that Li isotopes are kinetically fractionated during diffusion (e.g., Richter et al. 2003; Teng et al. 2006; Parkinson et al. 2007). This mechanism of isotope fractionation had been well established in other disciplines (e.g., Arnikar 1959), but it took a number of detailed studies of rocks, minerals, and high-temperature experiments to convince the geochemical community that kinetic fractionation of Li isotopes was a mechanism that really operated in magmatic, metamorphic, and hydrothermal systems. Geochemists started to realize that the Li isotopic excursions produced via diffusion could, in many cases, far exceed the effects of equilibrium fractionation. For example, Teng et al. (2006) found a range of 27.5‰ in δ^7Li produced by diffusive isotope fractionation in the country rock of a pegmatite dike within a distance of approximately 10 m—a range in δ^7Li that nearly encapsulates all continental crustal and eclogite bulk rocks analyzed to date (FIG. 1). In another example, Jeffcoate et al. (2007) found an even larger range of 37‰ in the space of less than a millimeter within a single mineral grain in a mantle xenolith (FIG. 1).

The lithium isotope systematics of subducting slabs and their likely effect on mantle heterogeneity was revisited in the light of this understanding. It was concluded that dehydration does not change the Li isotopic composition of the slab to a large degree (Marschall et al. 2007). The subducting slab after (near) complete dehydration would, thus, carry a mix of isotopically heavy Li in eclogites and isotopically lighter Li in metasediments and would on average be very similar in δ^7Li to the ambient mantle (Marschall et al. 2007). Very low δ^7Li values observed in eclogites, accompanied in many cases by high Li abundances, have been reinterpreted as the result of diffusive influx of Li from surrounding rocks; in this case, they are the consequence of local diffusive redistribution of Li on the scale of minerals, hand-specimens, and outcrops and are not representative of the bulk chemical flux between crust and mantle (Marschall et al. 2007).

The realization that Li isotopes could, therefore, no longer be employed unambiguously as tracers of recycled surface materials in the deep mantle disappointed many a geochemist. Any sample of igneous or metamorphic rock could be suspected of having had diffusive Li exchange with other solids or fluids it might have encountered in its environment. Therefore, a sample's Li isotopic composition can only be interpreted in terms of larger-scale geodynamic processes after all possible diffusive effects have been positively excluded—a condition that is rarely fulfilled.

IS IT TIME FOR LITHIUM?

Prof. Jerry Wasserburg, the eminent geochemist, cosmochemist, and winner of the Crafoord Prize, once claimed, when referring to novel geochemical tools, that "sometimes science advances because of a new shovel and the urge to dig a hole somewhere" (Wasserburg 2000). It seems that, in the field of high-temperature geochemistry, we have been using Li isotopes to dig entirely in the wrong place. Our Li shovel was blunt and unsuited to tracing recycled materials in the mantle. But, if we use lithium's unique combination of fast diffusion and kinetic isotope fractionation we could develop a powerful geochronometer to use in a range of geologic settings. Over the past decade, studies have demonstrated a range of applications where Li isotopes can be employed successfully to constrain rates and durations of processes on and in the Earth or other solar system bodies. Time may be the variable that Li isotopes are best suited to dig into, begging the question in the title, "Is it time for Li isotopes?"

Much progress has been made over the past decades in reconstructing the geologic processes that shape the Earth's crust, but there remain large uncertainties concerning the timescales of many of these processes. This hampers the establishment of a meaningful connection between the physical conditions derived from the rock record and the models of events that may have formed them. For example, burial and exhumation rates, reaction rates in rocks under metamorphic conditions, and timescales of melting, magma transport, and storage are all cases where uncertainties in rates may span several orders of magnitude. Absolute dating using radioactive decay schemes has helped to place some constraints on the durations of the relatively slow processes that unfold over many times the precision of the radioisotope dates. Yet, in many cases, these constraints can set only upper limits on durations of processes, leaving large uncertainties for all timescales that are below the resolution of radiometric dating. Once the timeframe and rates of a rock-forming process are constrained, the number of possible scenarios for this process is reduced; these scenarios then guide us in the interpretation of dating results and in deriving time-resolved information on the thermal evolution of the lithosphere. Hence, there is a strong feedback between geochronology, geochronometry, and geodynamic models.

In isotope geochronology, an absolute age of a sample is determined by analyzing the amount of a radioisotope and its decay products in a sample. The clock is started at the time when a mineral grain crystallized or cooled below a certain temperature such that the decay products are trapped and cannot escape from the mineral or rock in question. Geochronology, thus, determines the time that elapsed between the start of the clock and the time of analysis. It provides an absolute age of a sample. Geochronometry, in contrast, determines the time that elapsed between two events in the past. It provides information about the duration of an event without necessarily telling us when the event took place. Geochronometry may be compared to a stopwatch that displays the duration a runner took to complete a race, but it does not tell us when the race happened.

A STOPWATCH FOR RAPID GEOLOGIC PROCESSES

A unique geochronometer that can be employed to retrieve durations of geological processes from the rock record is to document the length scales and shapes of chemical diffusion profiles that form when solids and/or fluids encounter one another out of equilibrium but are "quenched" by cooling before diffusion can act to equilibrate them. Such arrested diffusion profiles uniquely record information on the durations or timescales of geologic processes (e.g., Chakraborty 2008).

Diffusion geochronometry relies on sequences of events that start and stop the stopwatch through well-defined geological events. Initially, a mineral or rock should be chemically equilibrated, showing a homogeneous Li concentration and isotopic composition. For example, this could be a magma chamber in which phenocrysts are in equilibrium with the melt from which they grow (Fig. 2A). The system is then suddenly disturbed, for example by the influx of new melt of a different composition, leading to a different level of equilibrium Li concentration in the phenocrysts that may be recorded in a new Li-rich zone at the grain margin (Fig. 2B). This is the moment that triggers the stopwatch, as the new Li-rich zone is in contact with the low-Li cores of the grains. The high temperatures prevailing in the magma chamber lead to diffusion of Li from the high-Li to the low-Li zone that proceeds at a well-constrained pace, which depends dominantly on temperature and the type of phenocryst (Fig. 2C). This diffusion process will proceed as long as the magma remains at high temperatures, but ceases in the case of eruption, which leads to a temperature drop and quenches the diffusion process (Fig. 2D). The crystals can then be retrieved from the lava at any point in the future, and the arrested diffusion profiles can be analyzed. The time that elapsed between replenishment of the magma chamber and eruption can then be determined. The use of an element as a diffusion geochronometer requires tight constraints on the boundary conditions under which diffusion operated, such as temperature and the initial distribution of the element and isotopes of interest; it also requires quantitative knowledge of their diffusion coefficients in the material of interest (e.g., minerals, rocks, fluids) as a function of temperature and other parameters (e.g., Chakraborty 2008). These diffusion coefficients are typically determined experimentally.

Owing to its unique combination of small ionic radius and low ionic charge, Li diffuses significantly faster than most other elements. This makes Li an ideal geochronometer to constrain the timescales of the fast geological processes that operate at elevated temperatures and that are otherwise unresolvable. For example, John et al. (2012) determined a total duration for which dehydration channels in subducting slabs are active was ~200 years (subsequently updated to 760 years by Taetz et al. 2018). They employed arrested Li diffusion profiles in fossil fluid veins that had been active at eclogite facies and interpreted these data using diffusion models and previously published data on mineral–fluid Li partitioning. The diffusion clock was started when the fluid entered the rock and stopped when the flux ceased; in the absence of fluid, diffusion in the dry rock is too slow to further move Li on the scale of centimeters at the temperatures of interest (510 °C). Building on this approach, Taetz et al. (2018) quantified the duration of dehydration pulses in a subducting slab by studying Li isotope profiles in exhumed high-pressure rocks in New Caledonia. They found that dehydration reactions may be active over hundreds of thousands of years as the slab descends, but individual portions of fluid were apparently expelled in relatively brief events lasting only several months. The authors suggest that these pulses are linked to the build-up of fluid pressure at the slab–mantle interface, which leads to seismic slip events along the slab's surface.

A third example of Li geochronometry on the outcrop scale was presented by Beinlich et al. (2020). These authors investigated a fossil hydrothermal system that had once been active in serpentinites in an ophiolite near its metamorphic sole. The serpentinite was transformed into soapstone (i.e., a talc–magnesite rock) in the presence of fluids (transporting silica and CO_2) derived from the underlying metasediments. This led to a reaction front that progressively advanced via an interplay between chemical reaction, fluid advection, and diffusion. Beinlich et al. (2020) argue that reaction led to a transient increase in porosity, accelerating the advance of the reaction front to a pace comparable to the velocity of plate motion (~10 cm/y) and that fluid-driven reaction could be similarly fast in other contexts, such as carbon sequestration and the formation of hydrothermal ore deposits. The estimate of reaction front velocity was again based on arrested Li isotope profiles across the lithologic contact.

Lithium geochronometry based on arrested diffusion profiles is also increasingly being applied in single mineral grains. The diffusivities of Li in a range of common rock-forming minerals, as well as zircon, have been determined experimentally. Modern in-situ analytical techniques, such as laser ablation inductively coupled plasma mass

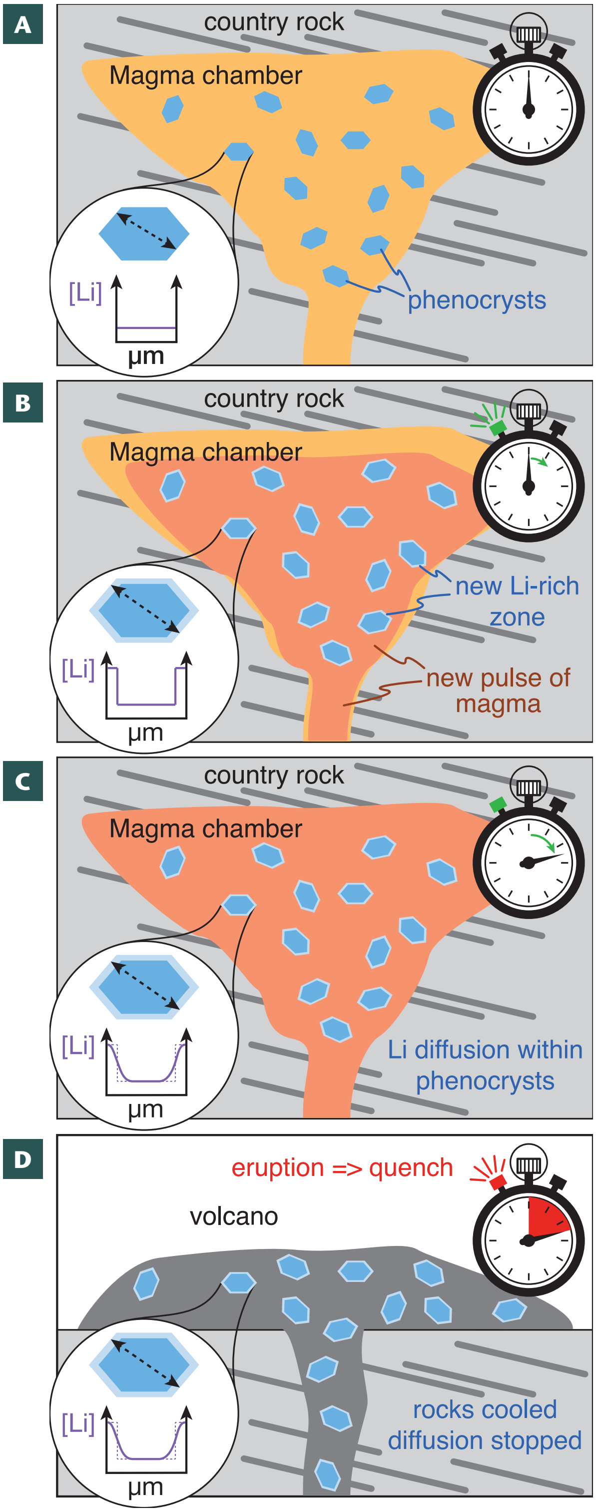

FIGURE 2 The principle of a diffusion geochronometer using magma chamber replenishment and eruption as an example. (**A**) Conditions before the event of interest are well equilibrated. The chemical profiles are flat. The stopwatch rests at zero. (INSET) Theoretical Li concentration profile through a phenocryst; compare Li profiles in subsequent phenocryst insets. (**B**) The system is disturbed by a sudden event that leads to the formation of a compositional discontinuity at a defined surface, e.g., Li enrichment in the marginal zone of a phenocryst. This event triggers the stopwatch. (**C**) The compositional contrast continues to be smoothed by diffusion for as long as the system remains at elevated temperatures. The stopwatch continues running. (**D**) The system is quenched, for example due to rapid cooling in the course of an eruption. Diffusion ceases. The stopwatch is halted and now displays the time that has elapsed between magma replenishment and eruption.

spectrometry (LA-ICP-MS) and conventional secondary-ion mass spectrometry (SIMS), can resolve chemical and isotopic gradients on a scale of tens of micrometers. With such a spatial resolution, Li can be employed to unravel magmatic processes that happen over only minutes to hours or up to thousands of years, depending on the mineral investigated (FIG. 3). Higher spatial resolution at submicrometer scales are obtainable by NanoSIMS and time-of-flight SIMS techniques, which may extend the precision of the Li stopwatch to even shorter timescales. In addition, Li diffusion in minerals is characterized by lower activation energies compared to most other cations, which means that it will remain highly diffusive even down to lower temperatures. This makes Li a sensitive chronometer to resolve the timescales even of hydrothermal and low-grade metamorphic processes.

Analyses using SIMS were employed by Coogan et al. (2005) to constrain the cooling rate of basalts in the sheeted-dike complex of the oceanic crust from the East Pacific (ODP Hole 504B) as a function of intrusion depth. These authors used Li profiles in clinopyroxene crystals in combination with experimentally determined Li diffusion coefficients and intermineral partitioning, and found cooling rates of the oceanic crust in the upper part of the sheeted dike complex in excess of > 450 °C/h. In this case, the stopwatch was triggered and stopped at approximately 900 °C and 700 °C, respectively. These temperature boundaries are set by equilibrium partitioning, which starts to demand a redistribution of Li among the magmatic phenocrysts (clinopyroxene and plagioclase) and the ceasing of diffusive Li exchange between the phenocrysts.

Parkinson et al. (2007) applied Li chronometry to olivine and clinopyroxene phenocrysts from the Solomon Islands and obtained a crystal residence time on the order of 10–100 days in arc magmatic systems, i.e., the time between replenishment of the magma chamber with more primitive magma and the eruption that was supposedly triggered by this process. Rubin et al. (2017) proposed that silicic magma reservoirs at Kaharoa (New Zealand) are cooled rapidly and stored at near-solidus temperatures for thousands to hundreds of thousands of years, punctuated by pulses of heating that last only for some years to centuries based on

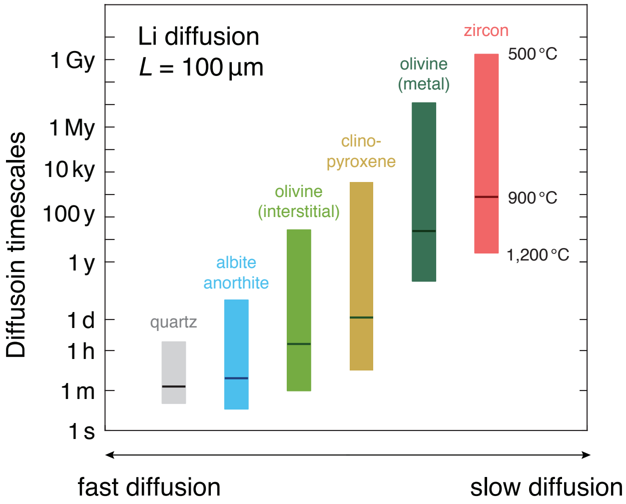

FIGURE 3 Calculated Li diffusion timescales over the temperature range 500 °C (upper end of bars) 900 °C (black line) to 1,200 °C (lower end of bars), assuming a characteristic diffusion length (*L*) of 100 µm, which is resolvable by laser ablation inductively coupled mass spectrometry and conventional secondary ion mass spectrometry. "Metal" in olivine refers to Li substitution into a crystallographic metal site. DATA FROM VERHOOGEN (1952); GILETTI AND SHANAHAN (1997); COOGAN ET AL. (2005); DOHMEN ET AL. (2010) AND CHERNIAK AND WATSON (2010).

U–Th dating in combination with the sharp Li zonation seen in zircons. Charlier et al. (2012) applied Li diffusion chronometry to plagioclase and quartz phenocrysts from the Oruanui supereruption of New Zealand's Taupo Volcano and determined magma decompression and ascent rates for the final 2 to 12 minutes of the magma before it reached the surface.

In some cases, the interpretation of Li concentration profiles is hampered by ill-constrained initial concentration profiles, and this is where Li isotopes come into play. Lithium isotope profiles can provide two pieces of information that cannot be obtained from Li concentration profiles alone: they help to distinguish diffusion from growth zoning, and they reveal the direction of Li diffusion. In silicates, for example, ^{6}Li diffuses approximately 3% faster than ^{7}Li, which in some cases leads to isotopic excursions of tens of per mil (e.g., Fig. 1A). Specifically, the δ^7Li values become characteristically low in the direction of diffusion, and the diffusion front is typically marked by a trough in δ^7Li profiles (Figs. 1, 4) (Teng et al. 2006; Parkinson et al. 2007; Dohmen et al. 2010). Equilibrium isotope fractionation is small at high temperatures, such that large Li isotopic excursions are generally diagnostic of diffusion processes.

MULTIMODE LITHIUM DIFFUSION

Lithium diffusion may generally be fast, but, in some cases, it is complicated by the fact that Li, like other cations, can occupy multiple sites within a crystal. Cations in different crystallographic sites typically have different diffusivities, and the measured concentration profiles may reflect the sum of multiple diffusion processes. For example, it has been experimentally shown that Li can diffuse simultaneously in metal vacancy sites and in interstitial sites in clinopyroxene and olivine, with Li strongly partitioning into the slow-diffusion metal sites (Fig. 4) (Dohmen et al. 2010; Richter et al. 2014, 2017).

Dohmen et al. (2010) developed a multimode model for Li diffusion in minerals that explains observed Li concentration and isotope profiles where simple diffusion models fail. In this scenario, Li occupies two different sites with one site showing faster diffusion than the other. In the case where Li strongly partitions into the fast-diffusing site, the diffusion process can be approximated by a single-mode diffusion model as given by the fast process; if, however, Li strongly partitions into the slow-diffusing site, the resultant diffusion profiles may display a number of (partly counterintuitive) characteristics (Dohmen et al. 2010). For example, sharp diffusion fronts do not relax, but persist with continuous diffusion, creating plateau-shaped diffusion profiles with step-function boundaries. In such a case, the δ^7Li trough is strongly asymmetric at the diffusion front, with δ^7Li abruptly rebounding to the unfractionated value. In some of these cases diffusion may be "up-hill" with Li diffusing from a low-concentration domain to a high-concentration domain (Fig. 4).

Zircon provides another excellent example of multimode Li diffusion in single crystals. Large, diffusion-induced Li isotopic excursions (20‰–30‰) and sharp [Li] gradients are observed in natural zircon (Tang et al. 2017). One zircon grain investigated by Tang et al. (2017) also shows "up-hill" Li diffusion, i.e., diffusion in the direction of increasing Li concentration (Fig. 4C). Tang et al. (2017) showed that these observations can be accounted for if a significant amount of Li charge couples with the slow diffusing rare earth elements (REEs) and Y in zircon. Multimode Li diffusion in zircon was, however, not captured in experiments (Cherniak and Watson 2010; Trail et al. 2016). This could possibly be due to a concentration dependence of the dominant diffusion mechanism (Dohmen et al. 2010). The experiments were conducted with Li concentrations in zircon that are 2–3 orders of magnitude higher than those in natural zircons. Such high Li concentrations probably saturated the REE and Y charge-coupling sites, forcing most of the Li to diffuse via the fast path. Recent experimental work by Sliwinski et al. (2018) confirms the strong charge-coupling relationship between Li and the REE + Y in natural zircons. These authors also identified an even faster diffusion mechanism for Li in zircon, which may be related to hydrogen degassing.

These different mechanisms add complexity to Li diffusion in zircon, but combined analyses of closely spaced Li concentration and Li isotopic compositions along across-grain profiles in zircon can reveal the (dominant) diffusion mode, as demonstrated by Richter et al. (2014, 2017) for clinopyroxene and olivine. This opens up a potentially

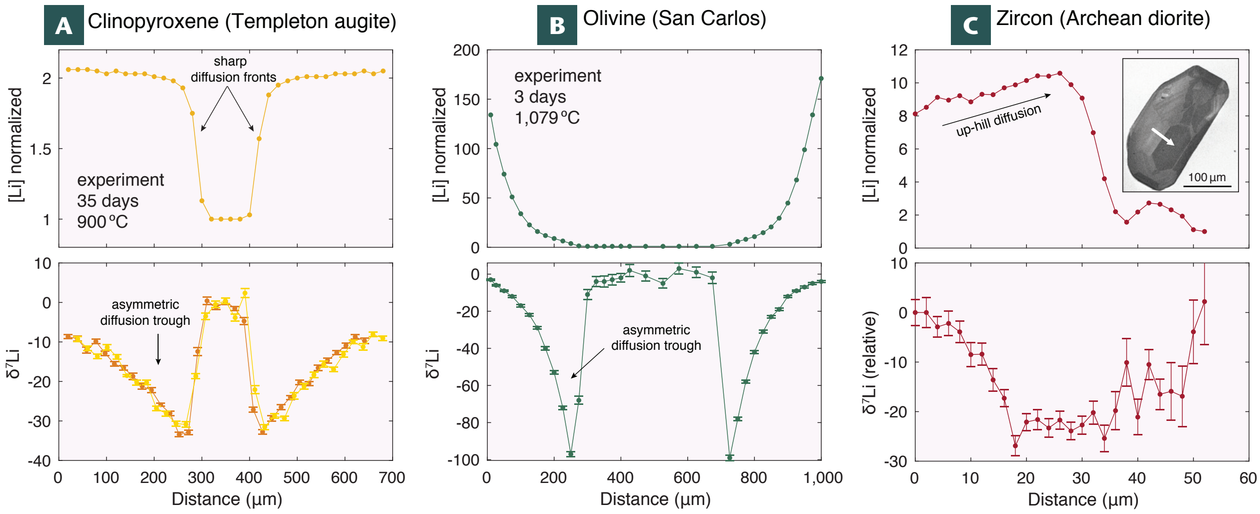

Figure 4 Examples of multimode Li diffusion in single crystals. Lithium concentrations, [Li], are shown in the top panels and the Li isotopic composition, δ^7Li, in the bottom panels. (**A**) Clinopyroxene from an experimental study using augite from Templeton, Quebec (Canada). (**B**) Olivine from an experimental study using San Carlos olivine (a forsterite-rich olivine from San Carlos, Arizona, USA, which is often employed as a standard). (**C**) A natural zircon from an Archean diorite from the Superior Province (Canada). After Richter et al. (2014, 2017); Tang et al. (2017).

wide application of the Li-in-zircon chronometer, which holds promises for timescales (years to millenia) that are otherwise not accessible.

The possibility of multiple Li diffusion mechanisms needs to be evaluated carefully for each mineral throughout the parameter space of interest (temperature, concentration, composition) and appropriate diffusion coefficients should be selected based on the dominant diffusion mechanisms. In particular, sharp [Li] gradients do not necessarily indicate limited diffusion and fast thermal events but may instead represent diffusion fronts produced by multimode diffusion in which Li is partitioned into the slow site. Paired Li concentration and isotope traverses through mineral grains can help to disentangle complex diffusion processes and constrain the timescales operating in magmatic and high-temperature metamorphic processes.

LESSONS FROM LITHIUM

Investigation of the high-temperature geochemistry of Li isotopes has been quite a rollercoaster in the past two decades, putting us through phases of excitement and high hopes, just to crush our beautiful models, leaving us to search for a new meaning in the next moment. Lithium isotopes essentially failed as a tracer of recycled surface material in the mantle. But they do offer significant hope as a unique geochronometer to probe process timescales that no other element can reach. The lesson learned from Li may also serve as a warning for other stable isotope systems (e.g., Mg, Fe, Ca) that may also be dominated by stronger diffusive fractionation than by equilibrium fractionation in magmatic and metamorphic systems.

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