



# Multi-mode Li diffusion in natural zircons: Evidence for diffusion in the presence of step-function concentration boundaries



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## ABSTRACT

Micron- to submicron-scale observations of Li distribution and Li isotope composition profiles can be used to infer the mechanisms of Li diffusion in natural zircon. Extreme fractionation (20–30‰) within each single crystal studied here confirms that Li diffusion commonly occurs in zircon. Sharp Li concentration gradients frequently seen in zircons suggest that the effective diffusivity of Li is significantly slower than experimentally determined (Cherniak and Watson, 2010; Trail et al., 2016), otherwise the crystallization/metamorphic heating of these zircons would have to be unrealistically fast (years to tens of years). Charge coupling with REE and Y has been suggested as a mechanism that may considerably reduce Li diffusivity in zircon (Ushikubo et al., 2008; Bouvier et al., 2012). We show that Li diffused in the direction of decreasing Li/Y ratio and increasing Li concentration (uphill diffusion) in one of the zircons, demonstrating charge coupling with REE and Y. Quantitative modeling reveals that Li may diffuse in at least two modes in natural zircons: one being slow and possibly coupled with REE+Y, and the other one being fast and not coupled with REE+Y. The partitioning of Li between these two modes during its diffusion may depend on the pre-diffusion substitution mechanism of REE and Y in the zircon lattice. Based on our results, sharp Li concentration gradients are not indicative of limited diffusion, and can be preserved at temperatures >700 °C on geologic timescales. Finally, large  $\delta^7\text{Li}$  variations observed in the Hadean Jack Hills zircons may record kinetic fractionation, rather than a record of ancient intense weathering in the granite source materials.

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## 1. Introduction

Lithium and its isotopes ( $^6\text{Li}$  and  $^7\text{Li}$ ) have seen a wide range of applications in geoscience (Tomascak et al., 2016; Penniston-Dorland et al., 2017). On one hand, Li isotopes can be a powerful tracer of chemical weathering (Chan et al., 1992; Pistiner and Henderson, 2003; Rudnick et al., 2004; Liu et al., 2013; Dellinger et al., 2017). On the other hand, the rapid diffusivity of Li and the associated large kinetic isotopic fractionations make Li a promising geospeedometer for determining rates of rapid geologic processes that can be difficult to determine using other

geospeedometers (e.g., Richter et al., 2003; Jeffcoate et al., 2007). Resolving the roles of equilibrium vs. kinetic mechanisms in driving Li isotopic fractionation is critical when applied to Li isotopic studies and understanding the geologic processes recorded by these data.

The Li isotopic composition of Hadean zircons has been interpreted to reflect intense chemical weathering during the earliest portion of Earth history (Ushikubo et al., 2008). Ushikubo et al. (2008) and Bouvier et al. (2012) argued that Li atoms are charge coupled with slow-diffusing REE and Y atoms in the zircon lattice, thereby inhibiting Li diffusion under most geological P–T–X conditions (i.e., pressure, temperature and composition, including  $\text{H}_2\text{O}$  content), and, thus, that zircon can preserve initial magmatic Li isotopic signatures. This assumption was later challenged by ex-

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perimental studies (Cherniak and Watson, 2010), which showed that Li can diffuse rapidly in zircon under crustal P–T–X conditions. Rather than using Li in zircon to track magmatic sources, the work by Cherniak and Watson (2010) suggested the possibility of using Li in zircon as a magmatic and metamorphic geospeedometer, with the first attempt made by Trail et al. (2016). Lithium diffusion in zircon was also reported by Gao et al. (2015), who studied Li isotopes in several zircon standards. Despite the evidence supporting Li diffusion in zircon under crustal P–T–X conditions, the diffusion mechanism remains elusive.

Here, we report the results of micron- to submicron-scale SIMS studies on Li distribution and Li isotope profiles in natural zircons. Our work confirms that Li diffusion occurs in zircon in the crust, and, for the first time, reveals multiple diffusion modes for Li in zircon that may involve charge coupling with REE+Y.

## 2. Background

At Earth's surface Li isotopes readily undergo equilibrium fractionation because of the relatively large mass difference between  $^6\text{Li}$  and  $^7\text{Li}$  (17%). They can also fractionate at high temperatures due to Li diffusion. Li isotopic compositions are typically reported in delta notation ( $\delta^7\text{Li} = ((^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}) * 1000$ ), where L-SVEC is a Li isotope standard.

### 2.1. Diffusive fractionation of Li isotopes

Lithium isotopes can fractionate during diffusion because  $^6\text{Li}$  diffuses faster than  $^7\text{Li}$  and such an effect can be preserved if cooling is rapid. Richter et al. (2003) first documented diffusion-induced Li isotopic fractionation in an experimental study that measured a Li isotopic profile across the interface of two compositionally distinct end-member lithologies, molten basalt and rhyolite, and found that  $^6\text{Li}$  diffuses  $\sim 3\%$  faster than  $^7\text{Li}$ . Later, Lundstrom et al. (2005) reported diffusive fractionation of Li isotopes in the Trinity Ophiolite. Following this, a series of studies reported Li diffusion within the country rocks adjacent to Li-rich intrusions (Teng et al., 2006; Marks et al., 2007; Liu et al., 2013), finding large and systematic Li isotopic variation over tens of meters and extremely low  $\delta^7\text{Li}$  (down to  $-20\%$ ) values, which they interpreted to be the result of diffusion-driven fractionation of Li isotopes. Jeffcoate et al. (2007) and Parkinson et al. (2007) observed diffusive fractionation of Li isotopes on a grain scale in peridotites and phenocrysts in basalt. Many additional studies of natural rocks have uncovered evidence of Li diffusion and associated isotopic fractionation, as summarized in Penniston-Dorland et al. (2017). These studies demonstrate that tens of permil fractionation of Li isotopes can be achieved by diffusion over length scales varying from millimeters to tens of meters.

### 2.2. Li isotopes in zircons

Zircon, known for its refractory nature, is the oldest known terrestrial material accessible on Earth. If zircon faithfully records magmatic Li isotopic signatures, it may extend the Li isotope probe of weathering intensity to the Hadean, a time for which other crustal materials are absent. Ushikubo et al. (2008) reported large  $\delta^7\text{Li}$  variations ( $>30\%$ ) in the Hadean Jack Hills zircons. Some of the zircons analyzed showed extremely low  $\delta^7\text{Li}$  (down to  $-20\%$ ). These authors interpreted their data to reflect incorporation of an intensively weathered component into the source region of the granite from which the zircon crystallized. Large  $\delta^7\text{Li}$  variations in zircon were also observed by Bouvier et al. (2012), who concluded that it reflected the signatures of the magma source materials.

One of the assumptions underlying the above interpretations is that Li isotopes do not fractionate within zircon and between

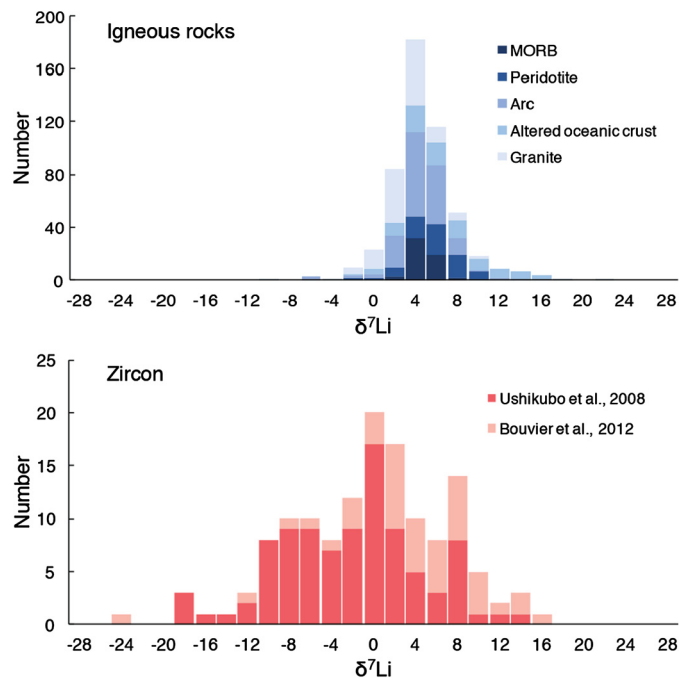


Fig. 1. Li isotopic compositions of igneous rocks and zircon. See Supplementary File 2 for a compilation of  $\delta^7\text{Li}$  in igneous rocks.

zircon and melt during and following magmatic crystallization. A number of studies have concluded that equilibrium fractionation of Li isotopes is limited during metamorphic dehydration, partial melting and fractional crystallization (Tomascak et al., 1999; Marschall et al., 2007; Teng et al., 2007, 2009; Qiu et al., 2009, 2011a, 2011b). However, it remains unclear whether or not Li diffuses, and thus creates kinetic isotope fractionation during zircon growth or metamorphic events. The range of  $\delta^7\text{Li}$  measured in zircons largely exceeds that of igneous rocks (Fig. 1), and the discrepancy mainly results from the extremely negative  $\delta^7\text{Li}$  values in the zircons. Such extreme  $\delta^7\text{Li}$  values have only been observed in highly weathered regoliths (Rudnick et al., 2004) and in rocks and minerals that experienced kinetic fractionation associated with Li diffusion (e.g., Teng et al., 2006; Jeffcoate et al., 2007).

Lithium isotopic compositions are spatially heterogeneous in reference zircons, with  $\delta^7\text{Li}$  ranging from  $8\%$  to  $20\%$  in these zircons: 91500, Plešovice, TEMORA 2 and BR266 (Li et al., 2011; Gao et al., 2015). These variations are significant given reported  $2\sigma$  analytical uncertainty is better than  $2\%$ . Li et al. (2011) and Gao et al. (2015) also documented that these reference zircons have heterogeneous Li concentrations. These observations stand in contrast to their homogeneous Hf and O isotopic compositions.

### 2.3. Experimental perspectives on Li diffusion in zircon

Lithium may substitute in a zircon lattice by coupling with trivalent REE and Y ions (Finch et al., 2001; Hanchar et al., 2001; Ushikubo et al., 2008; Bouvier et al., 2012), and in this case, Li diffuses together with REE and Y, which will slow Li diffusivity by orders of magnitude. However, this mechanism has not been observed by current experimental studies (Cherniak and Watson, 2010; Trail et al., 2016), both of which reported fast Li diffusion in zircon. Cherniak and Watson (2010) conducted “in” diffusion experiments using REE-depleted Mud Tank zircons, and thus their experiments are unlikely to have evaluated charge coupling effects. Using Lu- and P-doped synthetic zircons, Trail et al. (2016) carried out “in” diffusion and heating experiments, and their “in” diffusion experiments showed no discernable difference in Li diffusivity when compared to Cherniak and Watson’s results. These

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