

## Preface

# Preface to “Lithium isotope geochemistry”

The use of light stable isotopes to elucidate Earth processes dates to the pioneering work of Harold Urey, who was awarded the Nobel prize for chemistry in 1934 for his discovery of deuterium and determination of its fractionation from hydrogen as a function of temperature. Perhaps less well known, Urey was also one of the first to delve into lithium isotope geochemistry. Taylor and Urey (1938) used ion exchange chromatography to separate  ${}^6\text{Li}$  from  ${}^7\text{Li}$ , demonstrating the extreme isotopic fractionation achievable on a resin bed. The very large mass difference (~15%) between the two isotopes of lithium is responsible for both the potential utility and the difficulty in the application of lithium isotopes to geochemical problems. The utility stems from the very large mass fractionation that can occur due to natural processes; with the publication of this volume, up to 80‰ variation of  ${}^7\text{Li}/{}^6\text{Li}$  has now been documented in terrestrial samples. The difficulty stems from the fact that, as Taylor and Urey demonstrated long ago, these fractionations are not limited to nature, and successful quantitative measurement of lithium isotopic compositions requires extraction of 100% of the lithium present in a sample during laboratory processing. In addition to the intrinsically large fractionations observed for  ${}^7\text{Li}/{}^6\text{Li}$ , other properties, such as the single valence state, and the affinity of lithium for fluids, make it a potentially unique tracer for fluid–rock interaction in the Earth (see recent reviews by Elliott et al., 2004; Tomascak, 2004).

The properties that make lithium isotopes potentially powerful tracers in the Earth have also inhibited their widespread application in geosciences. As mentioned above, total sample dissolution and

complete lithium recovery during chromatographic separation are required for accurate isotope determinations. Moreover, because lithium has only two stable isotopes, quantitative measurements by thermal ionization mass spectrometry (TIMS) are non-trivial due to the need to quantify instrumentally induced mass fractionation (Moriguti and Nakamura, 1993). This has effectively limited TIMS measurements to still only a few laboratories. Nevertheless, these modern TIMS studies have revealed large variations of  $\delta^7\text{Li}$ <sup>1</sup> between the hydrosphere and oceanic basalts (Chan et al., 1992; Moriguti and Nakamura, 1998). The recent use of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to measure lithium isotopes (e.g., Tomascak et al., 1999a) has considerably broadened the lithium isotope field and increased the number of labs producing data. It is now well established that heavy lithium partitions preferentially into aqueous fluids over most silicate minerals (e.g., Chan et al., 1992; Zhang et al., 1998; Pistiner and Henderson, 2003), although the quantification of the fractionation factor,

<sup>1</sup> Like other stable isotope systems, variations in lithium isotopes are reported in terms of parts per thousand (permil) deviations from an international standard, in this case L-SVEC (Flesch et al., 1973), where

$$\delta^7\text{Li} = \left( \frac{\left( \frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{sample}} - \left( \frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{standard}}}{\left( \frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{standard}}} \right) \times 1000$$

Although both  $\delta^6\text{Li}$  and  $\delta^7\text{Li}$  notations appear in the literature, there is an emerging consensus to use  $\delta^7\text{Li}$  (Tomascak, 2004), so that, like other stable isotope systems, positive values of  $\delta^7\text{Li}$  reflect heavier isotopic ratios.

$\alpha$  (i.e.,  $(^7\text{Li}/^6\text{Li})_{\text{mineral}}/(^7\text{Li}/^6\text{Li})_{\text{fluid}}$ ), as a function of temperature remains an important outstanding goal. Thus, the fluid–mineral fractionation of lithium isotopes can be used to study interactions at the Earth’s surface, as well as tracing surface material that has been recycled into the Earth’s mantle.

In September of 2003, we convened a special symposium at the Kurashiki Goldschmidt meeting on lithium isotope geochemistry. The 11 papers in this volume stem from work presented in that symposium, as well as contributions from scientists who were unable to attend. The tremendous breadth of the application of lithium isotopes is reflected in the topics covered by these papers, which range from paleo-oceanography to mantle geochemistry.

With the goal of evaluating the use of lithium as a paleo-environmental indicator, Marriott et al. present laboratory measurements of  $\delta^7\text{Li}$  and Li/Ca ratios in calcite and aragonite as a function of salinity, as well as  $\delta^7\text{Li}$  and Li/Ca ratios in benthic foraminifera. They conclude that biological controls do not influence the means by which Li is incorporated into biogenic carbonates. They also find that  $\delta^7\text{Li}$  in carbonates may provide a faithful record of the lithium isotopic composition of seawater through time (provided post-depositional processes have not influenced  $\delta^7\text{Li}$ ).

Keeping to the oceans, but at higher temperatures, Foustoukos et al. present new  $\delta^7\text{Li}$  data for vent fluids from the Main Endeavour Field on the Juan de Fuca Ridge sampled shortly after a magmatic intrusion. They find that  $\delta^7\text{Li}$  is constant in all fluids, demonstrating that lithium isotopes are not fractionated by separation of a supercritical phase, and suggest that relative Li and B concentration may be a useful tracer of sub-seafloor magmatic activity.

The behavior of lithium isotopes during continental weathering is the topic of the next two papers (Kisakurek et al. and Rudnick et al.), which confirm the widely held belief that heavy lithium is leached from rocks as they weather at the Earth’s surface. However, interesting differences exist between these two studies, demonstrating that processes in addition to leaching affect the isotopic composition of continental regoliths. Kisakurek et al. show that a thick laterite developed on the Deccan traps contains a significant aeolian input of isotopically light lithium, presumably derived from weathering of crystalline basement. Rudnick et al. document that extreme

lithium isotopic fractionation ( $\delta^7\text{Li}$  down to  $-20\%$ ) during the development of saprolite in the Piedmont of South Carolina is accompanied by input of heavier, hydrospheric lithium from ground water.

In terms of solid Earth geochemistry, one of the great expectations for the fledgling field of lithium isotope geochemistry is that it might elucidate the complicated processes occurring during recycling of oceanic crust in subduction zones. Accordingly, three papers in this volume address this theme. Bouman et al. measured the lithium isotopic composition of material entering subduction zones: a comprehensive set of sea-floor sediments, as well as new data for altered oceanic basalts. They find that lithium concentration and  $\delta^7\text{Li}$  are both highly variable (ranging from 7 to 74 ppm and from  $-2\%$  to  $+14\%$ , respectively) and, on the average, are isotopically lighter than previously observed. Another interesting finding of their study is that old, altered oceanic crust is isotopically lighter than its younger counterpart, which may reflect exchange with overlying sediments or possibly a change in  $\delta^7\text{Li}$  of sea water over time. One way to evaluate the contribution of slab components to subduction zone lavas is to measure across-arc geochemical variations. In contrast to earlier work on the Izu arc, Moriguti et al. report that  $\delta^7\text{Li}$  does not change systematically across the NE Japan arc, where all lavas have mid-ocean ridge basalt (MORB)-like  $\delta^7\text{Li}$  values. They attribute the differences in lithium systematics between the two arc sections to differing thermal regimes in the down-going slab, with consequences for stability of accessory phases. In a similar study across a “hot” arc, Leeman et al. also find MORB-like  $\delta^7\text{Li}$  across the Cascades arc in southern Washington. They attribute the lack of an obvious slab contribution here to the high temperatures, which caused efficient dehydration in the forearc.

Assuming that isotopically fractionated lithium can make it past subduction zones, one might expect to see variable  $\delta^7\text{Li}$  in intraplate magmas that are suggested to sample ancient, recycled oceanic lithosphere. Ryan and Kyle show that intraplate basalts from Antarctica have MORB-like  $\delta^7\text{Li}$ , but that  $\delta^7\text{Li}$  changes during differentiation. Because lithium does not fractionate during crystal fractionation of basalts (Tomascak et al., 1999b), they suggest that the changing isotopic composition reflects assimilation

of lithospheric lithium. They also measured a variety of ocean island basalts (OIB), which, with two exceptions, also have MORB-like  $\delta^7\text{Li}$  values. The exceptions, Pribilof Island (back arc Aleutians) and St. Helena, both have slightly heavier  $\delta^7\text{Li}$  ( $\sim +7\%$ ), which may reflect input of recycled heavy lithium. In contrast to the rather constant  $\delta^7\text{Li}$  values seen in the whole rock data, Kobayashi et al. report widely varying  $\delta^7\text{Li}$  ( $-10$  to  $+8\%$ ) in glass inclusions in olivines from Hawaiian lavas. In the first study of its kind, these authors use an ion microprobe to measure  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$  and Pb isotopic ratios within single inclusions. They attribute the large Li, B and Pb isotopic variations found in these glasses to heterogeneities in the source of the Hawaiian lavas, which were likely introduced from recycled components. Collectively, both studies suggest that lithium isotopic heterogeneity may be much greater in the mantle source regions of intraplate basalts than is obvious from the basalts themselves.

Of course, the direct way to determine the lithium isotopic composition of the mantle is to measure peridotites, and two papers in this volume do just that. Seitz et al. studied mantle xenoliths from a variety of regions and find that  $\delta^7\text{Li}$  varies systematically between olivine, orthopyroxene and clinopyroxene, with whole rock  $\delta^7\text{Li}$  varying from  $+1\%$  to  $+4\%$  and correlating with the degree of metasomatism (the least metasomatized samples are heaviest). Importantly, they show that inter-mineral fractionation systematically decreases with increasing temperature, suggesting that lithium isotopes may fractionate at mantle temperatures ( $950$ – $1150$  °C). Brooker et al. report  $\delta^7\text{Li}$  in whole-rock peridotites and pyroxenites from Zabragad Island, Red Sea. Whereas most peridotites have  $\delta^7\text{Li}$  values overlapping with that seen in MORB, they find heavy  $\delta^7\text{Li}$  in a strongly metasomatized peridotite and in pyroxenite (up to  $+10\%$ ), which they attribute to influx of slab-derived lithium during pan-Africa subduction.

As the papers in this volume illustrate, the field of lithium isotope geochemistry is evolving at a rapid pace. These and previous studies provide a wealth of empirical results that shed new light on fluid–mineral interaction from the Earth's surface to the mantle. Yet, the field is far from mature, and important, first-order questions remain (e.g., Can lithium isotopes fractionate in igneous systems?). Robust interpreta-

tions of lithium isotope data await better quantification of partition coefficients (crystal–melt, crystal–fluid) and isotopic fractionation factors as a function of temperature.

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