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Developments in the Understanding and Application of Lithium Isotopes in the Earth and Planetary Sciences

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INTRODUCTION

The significant relative mass difference (c. 16%) between the two stable isotopes of Li (approximately ^{6}Li 7.5%, ^{7}Li 92.5%), coupled with broad elemental dispersion in Earth and planetary materials, makes this a system of considerable interest in fingerprinting geochemical processes, determining mass balances, and in thermometry. Natural mass fractionation in this system is responsible for c. 6% variation among materials examined to date (Fig. 1). Although the "modern era" of Li isotope quantification has begun, there are still many questions about the Li isotopic compositions of fundamental materials and the nature of fractionation by important mechanisms that are unanswered (e.g., Hoefs 1997).

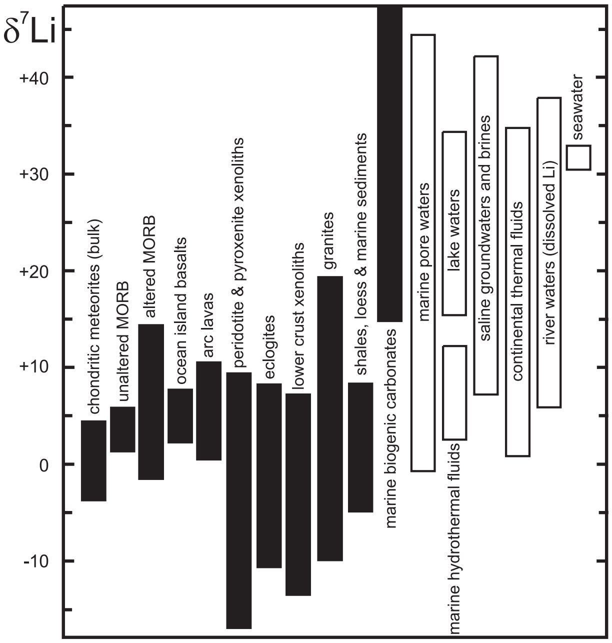

Figure 1. Summary of lithium isotopic compositions of Earth and planetary materials. Filled bars are solid samples, open bars are liquids. See text for references and details.

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The purpose of this chapter is to summarize the current understanding of Li isotopes in geo- and cosmochemical systems and to indicate (1) where Li isotopes have a high probability of adding new understanding of these systems; (2) where some of the more significant deficits in knowledge exist. The small but burgeoning Li isotope community has not yet compiled the volume of peer-reviewed literature needed to adequately assess even that which has been studied to date. As a result, significant portions of this chapter are based on data reported in abstracts, and as such are more than normally subject to revisions over time. This chapter is anticipated to serve as a starting point for those interested in research incorporating Li isotope geochemistry, or in understanding the state of extant research.

BACKGROUND: LITHIUM ISOTOPES IN THE SCIENCES

Experiments in Li isotope fractionation

Knowledge of significant Li isotopic fractionation during basic chemical processes is long-standing. The early experiments by Taylor and Urey (1938), in which Li isotopes were fractionated by incomplete extraction of an aqueous solution from a zeolite exchange column, demonstrated clearly that the degree of induced isotopic fractionation was considerable, with ^{6}Li preferentially retained by the exchange medium (Fig. 2). This indicated that natural chemical exchange processes, such as water-rock or water-soil interaction, had a strong potential to generate isotopically distinct reservoirs in the Earth. Nevertheless, a long interregnum followed this early discovery, leading up to the development of routine accurate and precise methods for Li isotope analysis nearly half a century later.

Lithium isotopes in fields outside geochemistry

Lithium is an important element in many industries (Bach 1985). Lithium is used medically as a treatment for bipolar disorders (Schou 1988). Lithium toxicity, especially to the renal system, is problematical. Estimating systemic elemental mass balance, especially for patients receiving oral Li dosing, is important, and is one area in which Li isotope ratios are

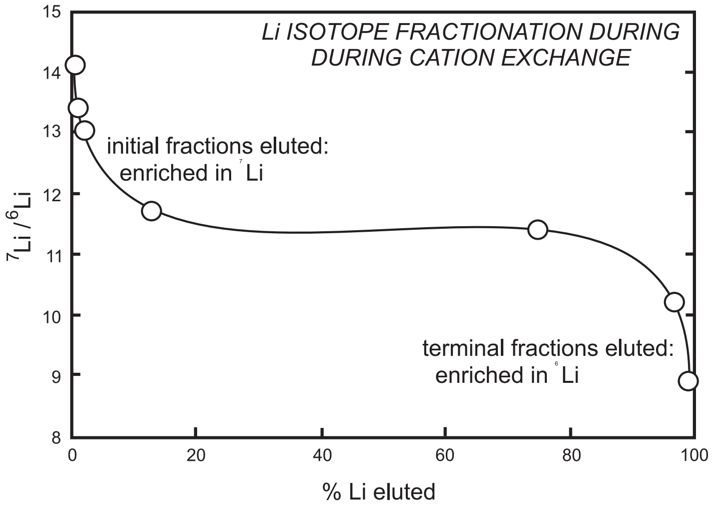

Figure 2. Lithium isotope separation effected during ion exchange with synthetic zeolite (Taylor and Urey 1938). As has been demonstrated repeatedly since that study, in both natural and synthetic experiments, ^{6}Li is fixed more effectively in the exchanger than ^{7}Li.

sought. Interest in the quantification of Li isotopes in biochemistry also stems from differential effects of ^{6}Li vs. ^{7}Li in kidney health (Stoll et al. 2001).

Lithium is an element of interest in astrophysics, owing to the marked variations in Li abundance and isotopic composition of materials emanating from different sources in the cosmos. The development of the "terrestrial" or "Solar system" Li isotopic compositions, which, to the limit of our current understanding, are quite different from values predicted for nucleosynthetic or interstellar Li, remains a puzzle for active astronomical research.

Large scale enrichment of lithium for thermonuclear uses took place at the Oak Ridge National Laboratory in the 1950's. The enrichment primarily employed ion exchange between aqueous/organic solutions and amalgam, commonly mercury-based (Palko et al. 1976). Electrochemical separation has also been employed for such operations (Umeda et al. 2001). These practices have not been taken up in academic laboratories in the intervening years, partly as they tend to be most effective only with relatively pure starting materials, partly because of the difference in scales involved. Enrichment factors of ^{6}Li of 1–7% are typical for these techniques (Symons 1985).

One interesting side-effect of the industrial isotopic enrichment of Li is the development of isotopically anomalous materials that make their way into other industries. For example, Qi et al. (1997a) found that commercial shelf standards for Li concentration had compositions that were over 300% enriched in ^{7}Li relative to known terrestrial materials (Fig. 3).

LITHIUM ISOTOPIC ANALYSIS

From early Li isotope measurement to the "modern era" of analysis

Shortly after the development of the early mass spectrometers, Li isotopes were identified by Francis Aston (1932). Although mass spectrometric techniques are those most commonly applied to the measurement of isotope ratios in geochemistry, attempts to quantify Li isotopes have been made using non-mass based emission methods (e.g., atomic absorption: Zaidel and Korennoi 1961; various nuclear methods: Kaplan and Wilzbach 1954; Brown et al. 1978;

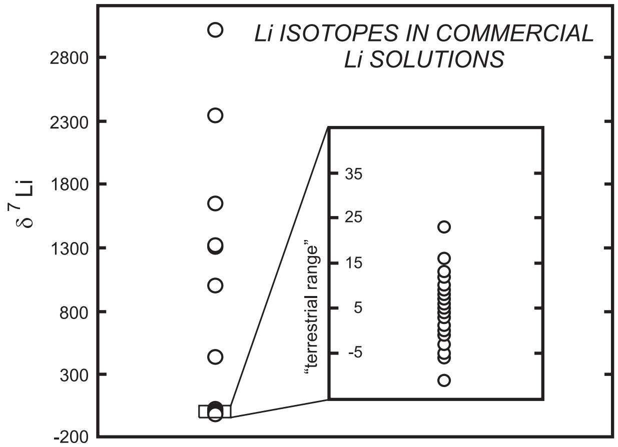

Figure 3. Lithium isotope data for a range of commercially-available synthetic concentration standards (Qi et al. 1997a). The inset expands the c. 60‰ range of reported natural samples. Although most anthropogenically-processed Li retains a broadly "terrestrial" value, nearly 20% of the samples examined show enormous isotopic enrichment in the heavy isotope.

Franklin et al. 1986). None of these techniques has enjoyed long term success. Measurement of Li isotopes by mass spectrometry faces the primary problem of controlling mass fractionation from the emitter. Ironically, the very property that makes Li geochemically interesting makes quantifying its isotopic composition with precision extraordinarily challenging. For this reason, mass spectrometric measurements of Li must be compared directly to a standard material. As long as all laboratories make use of the same standard material, its isotopic composition is academic, as the measured isotopic composition of the standard drops out of the arithmetic of normalization.

It is reasonable to assert that the "modern era" of Li isotope determination for geological materials began with the creation of an international standard for Li isotope measurement (NBS L-SVEC, now NIST SRM-8545; Flesch et al. 1973). The Li_2CO_3 standard was fabricated from "virgin" lithium ores (mainly spodumene) from near Kings Mountain, North Carolina. The homogeneity of the standard has been recently verified by analysis of aliquots used in four different laboratories (T Magna, written communication 2003). Since the manufacture of the L-SVEC standard, isotope ratios are presented in permil deviations (δ units) from the ratio measured for this material. The International Union for Pure and Applied Chemistry subsequently recommended the use of $^7Li/^6Li$ (Coplen et al. 1996), indicating that δ^7Li (= $[(^7Li/^6Li_{sample}/^7Li/^6Li_{L\text{-}SVEC}) - 1] \times 1000$) is the preferred normalized isotopic notation for lithium. Nevertheless, some authors continue to use the reverse notation (δ^6Li), following Chan (1987). At values within c. 7‰ of zero deviation from L-SVEC, a simple sign change is all that is required to switch between notations. At the extreme range of natural fractionation a value of $\delta^6Li = -38.5$ is equivalent to $\delta^7Li = +40.0$.

After the establishment of the L-SVEC standard, the development of accurate and precise quantification of Li isotope ratios was still more than a decade from being actualized. The initial publication of Chan (1987), using thermal ionization mass spectrometry (TIMS), was the first significant demonstration of routine precise determination of Li isotope ratios, although coeval work was ongoing in Belgium, at what would become the Institute for Reference Materials and Measurements (IRMM). The Li standard provided by the IRMM (IRMM-016; Michiels and DeBièvre 1983) has been assayed to have a Li isotopic composition indistinguishable from L-SVEC (Lamberty et al. 1987; Qi et al. 1997b).

In the late 1980's, methods for precise Li isotope determination (i.e., <2‰ long-term reproducibility) by a variety of TIMS methods became established. These techniques developed different strategies for dealing with the significant thermal mass fractionation of Li from the surface of a filament: from measurement of heavier ionic species (e.g., $Li_2BO_2^+$: Chan 1987, Sahoo and Masuda 1995; Li_2F^+: Green et al. 1988; $NaLiBO_2^+$: Chan et al. 1992) to evaporation of a Li molecule and subsequent ionization and measurement of Li as metal ions (Michiels and DeBièvre 1983; Xiao and Beary 1989; Moriguti and Nakamura 1993; Clausen 1995; You and Chan 1996; Sahoo and Masuda 1998).

Plasma-source mass spectrometry

Given considerations like availability and cost, isotope ratio measurement using single-collecting (quadrupole magnet) plasma source mass spectrometry (ICP-MS) has been an attractive pursuit, and Li isotopes have been measured using this equipment with improving success and precision over time (Sun et al. 1987; Koirtyohann 1994; Grégoire et al. 1996; Košler et al. 2001). Although the estimated precision is generally c. 2× poorer than mass analytical methods using sector-magnet deflection, quadrupole ICP-MS techniques are an attractive alternative, particularly in suites that show large isotopic fractionations and for surveying larger groups of samples.

The recent and meteoric development of plasma source mass spectrometers equipped with high stability sector-field magnets and multiple collectors (MC-ICP-MS) has lead to a colossal diversification in precise isotopic measurement, particularly with respect to the stable isotopes (Halliday et al. 1998). For Li isotope analysis, this instrumental advance has lead to the development of a set of techniques that have rapidly become widespread (Tomascak et al. 1999a; McDonough et al. 2001; Bouman et al. 2002; Magna et al. 2002; Nishio and Nakai 2002; Bryant et al. 2003a). These techniques have the common feature that Li isotope ratios are measured relative to bracketing standard analyses. Matrix effects, brought on by significant differences between the dissolved solid content of sample versus standard solution, perturb the essential smooth change in instrumental mass bias over time. The result of aspirating samples with unacceptable matrix loads into the plasma is erroneous sample/standard offsets. Unlike in TIMS analysis, however, the effect is obvious and suspect samples can be immediately culled.

Technical and theoretical aspects of MC-ICP-MS measurement were discussed in an earlier chapter of this volume (Albarède and Beard 2004). There are a few factors specific to Li isotope measurement by MC-ICP-MS that need to be assessed before analytical success can be achieved. Whereas measurement in the lightest part of the mass spectrum allows interference from molecular isobars to be avoided, both $^{12}C^{++}$ (on $^{6}Li^{+}$) and $^{14}N^{++}$ (on $^{7}Li^{+}$) interferences are possible, and need to be considered.

As the L-SVEC standard is ordinarily analyzed frequently among sample analyses by MC-ICP-MS, it is not useful to use this measurement uncertainty to estimate analytical precision (Tomascak et al. 1999a), but rather the reproducibility of independent measurements of samples in replicate or duplicate can be used. Parameters of accuracy and precision are discussed below.

Requirements in chemical separation

None of the bulk methods of Li isotope analysis permit high performance without isolation of Li from the sample matrix, although the degree to which other elements must be eliminated from an analyte solution differs among analytical methods. The techniques in common use for Li isolation involve chromatography with a variety of ion exchange media. The combined need for both good elemental purification and maximum Li yield has lead to the development of a plethora of techniques for Li separation chemistry in Earth materials (Chan 1987; Oi et al. 1997, 1999; Moriguti and Nakamura 1998a; Tomascak et al. 1999a).

Unlike exchange chemistry of, for example, long-lived radiogenic isotope systems (e.g., Sr, Nd, Pb), isolation chemistry for stable isotope quantification requires essentially 100% yield. Unless a multiple isotope spike is added, deviation from 100% yield introduces unquantifiable isotopic fractionation. Similarly, during digestion of solid samples, no residue can be tolerated, for the concern that Li in the residue will not be isotopically identical to that in the analyte solution. As shown by Oi et al. (1991), cationic solutions interacting with various types of commonly-used acidic exchange media show fractionation such that ^{6}Li has a higher apparent affinity for the stationery phase than ^{7}Li (analogous to the synthetic experiments of Taylor and Urey 1938; Fig. 2). Erroneously heavy compositions indicate a component of sample Li was left on the column, whereas erroneously light values can be manufactured by not collecting the elution from initial breakthrough of Li. A graphic demonstration of the potential for disaster in Li separation is given by Chan et al. (1999, 2002c), in which the Li elution from cation exchange resin was partly missed, resulting in measured $\delta^{7}Li$ up to 14‰ too low relative to later measurements with complete recovery during chemistry (Chan et al. 2002c). In many ion exchange procedures it is clear that the nature of the sample material added to a column has an effect on the specific volume needed to completely elute Li (e.g., Moriguti and Nakamura 1998a; Chan et al. 2002c; James and Palmer 2000a; Nishio et al. 2004), meaning that a single calibration of an exchange column may not be adequate for the entire range of materials a laboratory might process. This appears to be a particular problem for large samples with high Mg and Fe concentrations.

In situ analysis

Both for avoiding the rigors of chemical separation and for improving the spatial resolution of analysis, it has been desirable to perfect *in situ* isotope ratio measurement techniques. Although microsampling by laser ablation and introduction of sample material to a plasma source for ionization and mass analysis remains a "future direction" for the science, analysis by secondary ion mass spectrometry (SIMS) has been in practice for a number of years, with constant improvement (Chaussidon and Robert 1998; Hervig and Moore 2003; Layne 2003). Although this technique obviates the pitfalls of chemical removal of Li from samples, it is not without problems that historically limit its application in high precision isotope ratio measurement, in particular unpredictable shifts in mass fractionation caused by both instrumental and matrix effects.

A practical difficulty of SIMS Li isotope measurement is the paucity of appropriate mineral and rock standards with well characterized isotopic compositions. Although the estimated uncertainties are larger than for the more widespread TIMS and MC-ICP-MS techniques, the capacity to measure at very restricted spatial scales makes this a promising area of exploration, particularly for samples of restricted size and those with complex small-scale structure. The complimentary nature of *in situ* and bulk data in Li isotope studies shows promise for better understanding complex processes, e.g., fluid-rock interaction (Decitre et al. 2002).

Precision and accuracy

External precision is the ability to demonstrate analytical repeatability with multiple preparations and analyses of a material over a long period of time. The MC-ICP-MS techniques and the more widespread TIMS methods either demonstrate or claim external precisions in the range ±0.5 to 1.0‰ (2σ). The stated precision for most TIMS methods is estimated from the reproducibility of the L-SVEC standard. In many cases the analysis of individual samples prepared multiple times yields precisions poorer than this estimate. This is in part due to the heterogeneity of natural samples and in part due to effects introduced during preparation and analysis that are not experienced by the standard. Zhang et al. (1998) cite reproducibility of the L-SVEC standard of ± <1.0‰ (2σ), but their duplicate measurements of individual pore water samples vary from ±0.1‰ to ±6.1‰ (mean ±2.3‰; all 2σ). Later studies using refined TIMS procedures appear to achieve superior replicate precision (e.g., ±0.4‰ to ±1.1‰ for multiple replicates in Chan et al. 2002c).

Most MC-ICP-MS devices can demonstrate external precision in the range ±0.2 to 0.9‰ for synthetic standards (e.g., 10 month average of ±0.24 for 52 measurements of standard IRMM-016; Millot et al. 2004). However, natural samples, which require careful Li separation and purification from geological matrices, pose a significant and generally underestimated impediment to the achievement of long-term reproducibility much in excess of ±1.0‰. Nevertheless, given careful work, extremely high precision is now attainable (e.g., replicate reproducibility of 27 seawater aliquots of ±0.5‰; Millot et al. 2004).

As the achievable precision improves, more and more detailed geochemical problems can be realistically explored. That is, they may be explored if, at the new levels of precision, accurate measurement can be demonstrated. It is embarrassing to note the general absence of Li isotope analyses of international standard materials until fairly recently. It is only with the cross-reference of accepted standard compositions that comparisons of data among different laboratories can be accomplished. Table 1 lists the reported isotopic compositions of a variety of standard materials in the literature. Whereas the accumulated data for some materials agree quite well among laboratories (e.g., JR-2), others show poor agreement (e.g., JB-2, with a total range of 2.5‰). Lithium isotopic analysis of seawater is another means by which accuracy and precision have been estimated. This will be considered below under, "Lithium isotopic fractionation in the oceans."

Table 1. Reported Li isotopic compositions for international rock standards.

Name	*Producer**	*Material*	δ^7Li	*Source***
BHVO-1	USGS	basalt, Hawaii	+5.2 ± 0.5 (4)	1
BHVO-1			+5.1 ± 0.4 (2)	2
BHVO-1			+5.0 ± 1.9 (8)	3
BHVO-1			+5.8 ± 1.9 (3)	4
JB-2	GSJ	basalt, Japan	+6.8 ± 0.3 (3)	4
JB-2			+5.1 ± 1.1 (4)	5
JB-2			+4.3 ± 0.3 (5)	6
JB-2			+4.9 ± 0.7 (5)	7
JB-2			+5.1 ± 0.4 (3)	8
JB-3	GSJ	basalt, Japan	+3.9 ± 0.3 (3)	6
SRM-688	NIST	basalt, Nevada	+2.8 ± 1.1 (1)	5
JGb-1	GSJ	gabbro, Japan	+6.2 ± 2.5 (3)	4
DR-N	ANRT	diorite, France	+2.3 ± 1.1 (3)	4
JA-1	GSJ	andesite, Japan	+5.8 ± 0.7 (5)	6
G-2	USGS	granite, Rhode Island	−0.3 ± 0.4 (3)	2
G-2			−1.2 ± 0.6 (3)	4
JR-2	GSJ	rhyolite, Japan	+3.9 ± 0.4 (3)	1
JR-2			+3.9 ± 0.4 (1)	2
JR-2			+3.8 ± 1.0 (3)	4
JG-2	GSJ	granite, Japan	−0.7 ± 0.4 (2)	2
JG-2			+0.4 ± 1.0 (4)	3
JG-2			−0.4 ± 0.2 (3)	4
UB-N	ANRT	serpentine, France	−2.7 ± 1.1 (4)	4
UB-N			−2.6	9
SCo-1	USGS	shale, Wyoming	+5.3 ± 1.5 (3)	4

Note: uncertainties are those listed in the cited source or recalculated from data therein, 2σ population, where available; number in parentheses is number of analyses factored into this precision, where given

*Producers: USGS = United States Geological Survey; GSJ = Geological Survey of Japan; NIST = National Institute of Standards and Technology (USA); ANRT = Association Nationale de la Recherche Technique (France)

**Sources: 1 = Chan and Frey (2003); 2 = Pistiner and Henderson (2003); 3 = Bouman et al. (2002); 4 = James and Palmer (2000a); 5 = Tomascak et al. (1999a); 6 = Nishio and Nakai (2002); 7 = Moriguti and Nakamura (1998a); 8 = Chan et al. (2002c); 9 = Benton et al. (in review)

INTERNAL-PLANETARY SYSTEMS

Mass fractionation in igneous systems

At temperatures germane to melting and crystallizing mantle magmas, Li isotopes do not show permil-level mass fractionation (Fig. 4; Tomascak et al. 1999b). This has since been corroborated by examination of bulk rocks and olivine separates from basaltic lavas, which yield consonant isotopic values (Chan and Frey 2003). Also, whole rocks and omphacite mineral separates from alpine eclogite with metamorphic peak temperatures approximately 650°C (Zack et al. 2003) show no consistent Li isotopic difference.

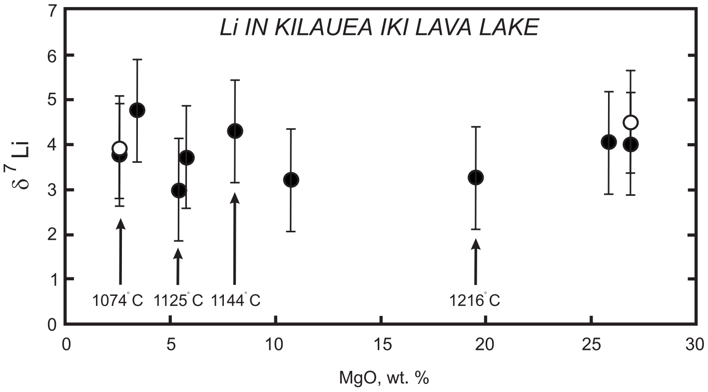

Figure 4. Plot of Li isotopic composition vs. MgO content for samples of the Kilauea Iki lava lake, Hawaii (Tomascak et al. 1999b). Cored basalt samples show a range of crystallization temperatures (estimated for four of the samples). The absence of permil-level variation in δ^7Li indicates that Li isotopes do not fractionate appreciably during crystallization in mantle systems. Open symbols (○) are replicate measurements.

However, evidence for mass fractionation at near-solidus temperatures in granitic systems exists. Early work on Li isotopes in crustal systems (Plyushin et al. 1979) suggested that significant isotopic effects could be seen in an evolving granitic system—effects that should be measurable using modern analytical methods. Similarly, permil-level variations in mineral isotopic compositions from different zones of the Tin Mountain pegmatite, South Dakota, have been interpreted to indicate the effects of crystallization of subsequent assemblages in the 500-600°C range (Tomascak et al. 1995c). Although these studies focus on mass fractionation introduced during crystallization processes, the potential for measurable isotopic fractionation during alkali diffusion has also been investigated (Lundstrom et al. 2001; Richter et al. 2003). These studies suggest that, because the greater diffusivity of ^{6}Li relative to ^{7}Li, contact zones where magmas flow through materials of contrasting concentration will show ^{6}Li enrichment. The magnitude of these effects in nature and their general importance in the interpretation of data from igneous systems awaits detailed study.

With the exception of these fractionation pathways, studies of igneous systems chiefly focus on the potential of Li isotopes as geochemical tracers: fingerprinting the cycling of Li derived from specific (low-temperature) sources through the solid Earth. The sections below deal with observations of Li isotopes in high-temperature systems, and the mechanisms for low-temperature fractionation processes are discussed after, under the heading, “Planetary surface systems.”

Mantle processes

The mantle, although Li-poor relative to the continents (5–6 ppm in normal MORB and c. 1 ppm in depleted peridotites; Ryan and Langmuir 1987; Eggins et al. 1998), is a significant reservoir due to its large volume (discussed below under, “Significance of lithium isotopes in the bulk Earth”).

Mantle reservoirs. The only quasi-systematic studies of igneous materials have centered on the mantle; in particular mid-ocean ridge basalts (MORB), ocean island basalts, and mantle peridotites. After reporting one MORB analysis in Chan and Edmond (1988), the first full study of MORB (Chan et al. 1992) reported three apparently unaltered Atlantic basalts and one from the East Pacific Rise, with a range in δ^7Li of +3.4 to +4.7 (Fig. 5). Subsequent studies have increased the global range of samples, the diversity of bulk compositions analyzed,

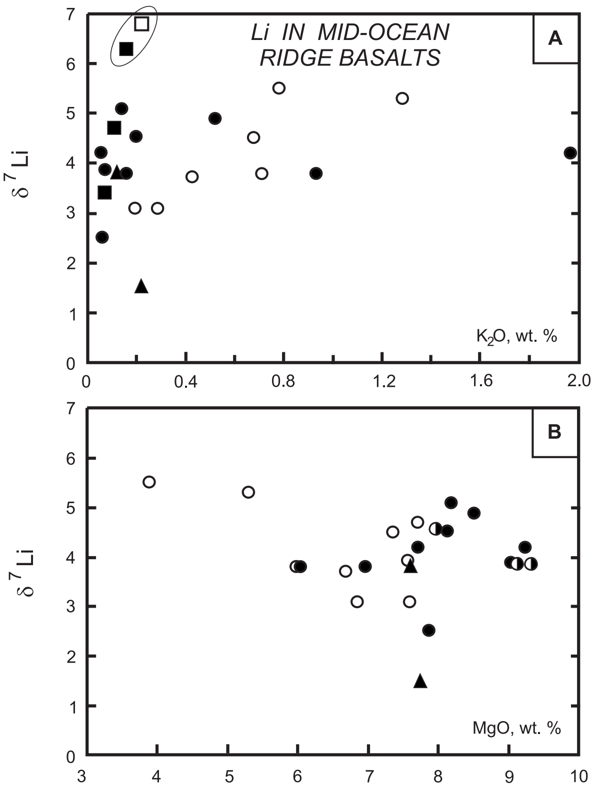

Figure 5. Plot of Li isotopic composition vs. (a) K_2O, (b) MgO for glassy mid-ocean ridge basalt (MORB) samples from various ridge segments. Symbols: square = Chan and Edmond (1988) and Chan et al. (1992); triangle = Moriguti and Nakamura (1998a); circle = Tomascak and Langmuir (1999). For all symbols, filled = Mid-Atlantic Ridge, open = East Pacific Rise, half-filled = Indian Ridge. The two encircled samples (δ^7Li > +6) were considered by Chan et al. (1992) to be altered, although this was not petrographically obvious. The lack of an indication of correlation between Li isotopes and major elements (as well as trace elements and radiogenic isotopes) in a global sample set cannot be explained by a simple contamination process with near-sea floor material, suggesting the isotopic variation may be intrinsic to the upper mantle.

and the isotopic range (δ^7Li = +1.5 to +5.6; Moriguti and Nakamura 1998b; Tomascak and Langmuir 1999; Nishio et al. 2002). Although relative to typical analytical uncertainties of c. ±1‰ this range is relatively restricted, the 5‰ range manifest in the current global data set indicates that this reservoir is not homogeneous with respect to Li isotopes.

The lack of correlation between Li isotopes and other geochemical attributes (e.g., major elements; Fig. 5) indicates this an area where more detailed studies employing superior precision would be useful. The global data set may, however, unfairly average away geochemical features of Li in the MORB mantle. Samples from portions of the East Pacific Rise showed correlated variations in δ^7Li (+2.7 to +6.0) and Sr isotopic composition (Elliott et al. 2003), which was interpreted as reflecting heterogeneity in mantle sources of these lavas. Similar slight enrichment in δ^7Li was seen in an enriched MORB sample from the Juan de Fuca ridge (+6.8; Benton et al. 1999). The implications for a singular pristine upper mantle Li isotopic composition are unknown without further research, but could be significant.

Given the difference in Li concentration between MORB and sea floor altered MORB (which are commonly >12 ppm; Stoffyn-Egli and Mackenzie 1984; Chan et al. 1992), small contributions of altered oceanic crust could have a substantial impact on the measured Li isotopic composition of sea floor lavas. Indeed, two basalts that were petrographically “fresh” were excluded from consideration as pristine MORB by Chan et al. (1992) by virtue of slightly higher K_2O contents (>0.13 wt. %; Fig. 5). Within the global MORB data set no correlation between K_2O and δ^7Li is observed, suggesting that the variations in Li isotopes in MORB are not controlled primarily by near-surface contamination.

Mantle composition can also be assessed through examination of lavas from other oceanic settings. In a study of well-characterized Hawaiian lavas, Chan and Frey (2003) found a total range in δ^7Li that overlaps the range for MORB, +2.5 to +5.7. Other data from Kilauea volcano substantiate this range (Tomascak et al. 1999b). The Hawaii data, when compared with other isotopic and elemental parameters, suggested incorporation of recycled altered oceanic crust into the source of the Hawaiian plume (Chan and Frey 2003).

Nishio et al. (2003) analyzed basaltic rocks from six south Pacific islands to assess potential Li isotope contributions to magma sources in rocks with pronounced radiogenic isotope anomalies relative to MORB (e.g., high ^{206}Pb/^{204}Pb, "HIMU" end member; Zindler and Hart 1986). Whereas all of the lavas they studied had slightly enriched Li contents (up to 11.6 ppm), only the samples from Mangaia (δ^7Li = +7.4) and Ua Pou (+6.1) were particularly different from MORB in terms of Li, and there was not a straightforward correlation between δ^7Li and ^{206}Pb/^{204}Pb. The data suggest incorporation of an isotopically heavy, ultimately surficially-processed component (perhaps altered oceanic crust) in the sources of HIMU magmas. Nonetheless more complete data are required to elucidate the full extent of mantle Li isotopic heterogeneity. The only other report of Li isotope data from ocean island lavas (Ryan and Kyle 2000) showed slight enrichment in heavy Li relative to MORB in a minority of samples (δ^7Li up to +7.0). In addition to hot-spot lavas, samples from back-arc basins have been examined. Pacific back-arc basin basalts with MORB-like trace element contents examined by Chan et al. (2002c) and Nishio et al. (2002) have δ^7Li = +2.3 to +4.8, in agreement with the observed range for normal MORB.

Unmetasomatized peridotite xenoliths are additional potential sources of information on Li isotopes in the upper mantle. To date, the xenolith data set is very sparse, owing largely to the analytical challenges of these low Li-abundance, Mg,Fe-enriched materials. Benton et al. (1999) reported a rather light isotopic composition in a sample of continental peridotite from San Carlos, Arizona (δ^7Li = +1.1). However, Chan et al. (2002c) determined that an unaltered peridotite from Zabargad Island had δ^7Li = +5.0, identical to the value reported by Brooker et al. (2000) for peridotites from the same area. Oceanic peridotite xenoliths from La Palma showed a range of values (δ^7Li = +4 to +7; Bouman et al. 2000), overlapping and slightly higher than the normal MORB range. Peridotite xenoliths that show less pristine upper mantle elemental and radiogenic isotope characteristics are discussed below.

Xenoliths from Siberian continental lithosphere, with Archean model ages, had δ^7Li as low as +0.5 (Bouman et al. 2000). If these values accurately represent the Archean mantle, they suggest the potential for Li isotopic evolution in the Earth, from lighter compositions in the ancient mantle to what is seen in present-day MORB. In spite of the analytical challenges presented by ultramafic rocks, more data from these materials are crucial to an understanding of Li in the mantle, and in resolving questions about the appropriateness of the accepted MORB mantle range.

Subduction zones and related rocks. Lithium isotope characteristics of subduction zones have been considered in multiple thorough studies. If Li is transferred from a subducting slab into the overlying mantle along with other fluid-mobile elements, and if the slab-derived fluid has δ^7Li dissimilar to the mantle, then Li isotopes should provide a means of assessing, and perhaps quantifying this mass transfer. Given the differences in fluid/mineral partitioning of Li and B ($D_{\text{fluid/clinopyroxene}}$(B) ~ 10 × $D_{\text{fluid/clinopyroxene}}$(Li); Brenan et al. 1998), studies combining the elemental and isotopic compositions of Li and B should be particularly powerful in this quantification (e.g., Moriguti and Nakamura 1998b).

The isotopic composition of Li in fluids that leave a subducting slab are constrained to some extent by the current data base. As discussed below, low temperature sea floor alteration tends to generate minerals enriched in heavy Li relative to those present in pristine MORB.

Although the role of isotopically light sediments cannot be disregarded (also discussed below), altered oceanic crust is likely to be a primary source of Li to most subduction zone fluids (Tatsumi et al. 1986). Thus, these fluids should be isotopically heavier than MORB. The residue from this dehydration process may, therefore, be enriched in light Li relative to MORB.

The first studies of Li isotopes in subduction zones concentrated on young convergent margin lavas. Moriguti and Nakamura (1998b) reported correlated Li isotope and fluid-mobile element (notably boron) concentration variations in the Izu arc, southeastern Japan (δ^7Li = +1.1 to +7.6), consistent with significant incorporation of Li from altered oceanic crust into arc lava sources (Fig. 6). A similar trend has been reported in samples of basalts and basaltic andesites from Mt. Shasta, California (δ^7Li = +2.5 to +6.5; Magna et al. 2003).

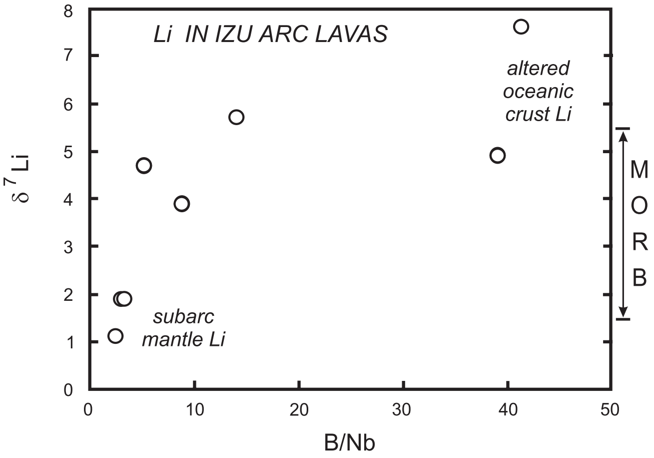

Figure 6. Plot of Li isotopic composition vs. B/Nb for a suite of samples from the Izu arc (Moriguti and Nakamura 1998b). The general correlation between high δ^7Li and elevated values of fluid mobile/immobile element ratios (as well as B and Pb isotopes) suggested incorporation of a Li component derived from the subducted slab, most likely from altered oceanic crust.

The majority of other studies on arcs, including true cross-arc evaluations, have not demonstrated strong correlations between Li isotopes and fluid mobile element contents of lavas or other geochemical parameters, although isotopic variations are apparent. Northeastern Japan arc lavas had compositions like MORB (δ^7Li = +1.5 to +5.5; Moriguti and Nakamura 2003). In the Marianas, the isotopically lightest sample (δ^7Li = +0.7) had elevated B/Nb and the isotopically heaviest sample (δ^7Li = +7.6) has somewhat lower B/Nb, but a systematic difference between Li isotopes and fluid mobile element enrichment is lacking (Benton and Tera 2000). Bouman and Elliott (1999) suggested that isotopic relations among a smaller set of Marianas samples could be satisfied by differences in inputs from isotopically light subducted sediments and isotopically heavier subducted altered oceanic crust. Chan et al. (2001; 2002b; 2002c) observed variability outside the MORB range in lavas from the South Sandwich Islands (δ^7Li = +3.4 to +7.4), part of the Aleutian chain (δ^7Li = +1.0 to +5.8) and regions within Central America (δ^7Li = +4.1 to +6.2), but the correlations relative to fluid mobile element enrichments were generally quite restricted (Fig. 7).

Tomascak et al. (2000, 2002) suggested that, for intra-oceanic arcs where such geochemical correlations were either restricted or non-existent, Li originating in the slab is likely removed from fluids/melts during mineral-fluid equilibration in the lower part of the subarc mantle. This reservoir of isotopically anomalous (heavy) slab-derived Li could be tapped in tectonically opportune situations, for instance in regions where young, warm crust is subducted (e.g., Panama: Tomascak et al. 2000; Cascades: Chan et al. 2001). Such processes

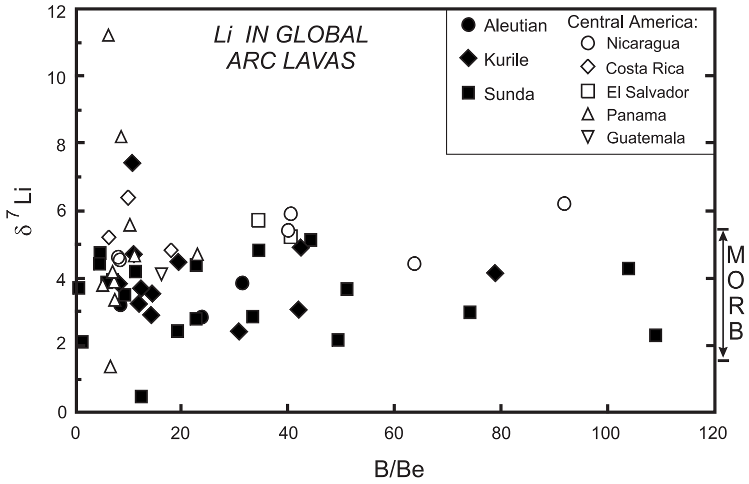

Figure 7. Plot of Li isotopic composition vs. B/Be for several suites of volcanic arc lavas. Filled symbols from Tomascak et al. (2002); open symbols circle from Tomascak et al. (2000) and Chan et al. (2002c). In these samples no simple strong correlation was seen between δ^7Li and indicators of slab-derived components. The lack of correlation and predominance of values around those seen in MORB suggested Li removal from slab derived fluids or melts in the subarc mantle prior to arc magma genesis (Tomascak et al. 2002).

would inevitably lead to the decoupling of Li isotopic systematics from fluid-mobile element contents (Tomascak et al. 2000). Slab Li incorporated into the subarc mantle might also persist there, perhaps later to be incorporated into the subcontinental lithosphere.

That dehydration of subducted oceanic crust leads to residues enriched in isotopically light Li is supported by a natural analog to the process. Alpine eclogites record, without significant later overprinting, the geochemistry of aborted subduction (Heinrich 1986). The eclogites of Trescolmen preserved δ^7Li as low as –11 (Zack et al. 2003) (Fig. 8). Calculation of the effect of distillation of altered oceanic crust during dehydration suggested that the more altered a basalt is prior to subduction, the lighter its isotopic composition after dehydration.

Eclogite xenoliths may yield complementary information to that gained from obducted eclogitic sections, while perhaps escaping some of the effects of pervasive retrograde re-equilibration. Eclogites with Archean Re-Os model ages from the Koidu kimberlite in Sierra Leone have δ^7Li that are both heavier and lighter than MORB (−2.3 to +8.0; Rudnick et al. 2003). This suggested that portions of subducted crust can retain geochemical records of both high and low temperature alteration histories on the ocean floor for geologically extensive durations.

Metasomatized mantle xenoliths, thought to derive ultimately from subduction-zone mantle that was affected by components (fluids and/or melts) discharged from the subducting lithosphere, are additional windows into mass transfer at convergent margins and into elemental cycling in the mantle. Pyroxenite veins from peridotites on Zabargad Island were dominantly isotopically heavier than their normal-mantle hosts (δ^7Li = +8.6 to +11.8), but also showed light values (−4.2) (Brooker et al. 2000). These signatures were interpreted to derive from metasomatism of subarc mantle by materials related to Pan-African subduction.

Metasomatized xenoliths studied by Nishio et al. (2004) show a diversity of Li isotopic compositions (δ^7Li = −17.1 to +6.8), some of these correlated with variations in radiogenic

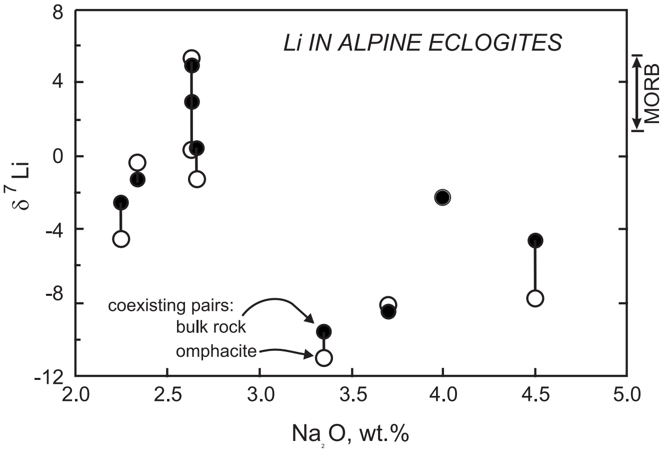

Figure 8. Plot of Li isotopic composition vs. Na_2O content of eclogites from Trescolmen, Swiss Alps (Zack et al. 2003). Data from pairs of bulk rock (●) and omphacite mineral separate (○) samples, indicating that bulk rocks generally preserve isotopic systematics of these rocks. Well-preserved, high pressure metamorphosed basaltic rocks were interpreted to retain much of their elemental character, and as such were good recorders of the residue remaining after subduction dehydration. The data indicated that originally isotopically heavy altered sea floor basalt could be transformed during subduction into some of the isotopically lightest materials in the Earth system.

isotopes. Lherzolite xenoliths from southeastern Australia retained essentially MORB-like Li isotopic compositions (δ^7Li = +5.0 to +6.0), but showed trends toward an end member composition with elevated δ^7Li and high ^{87}Sr/^{86}Sr (tentatively suggested to be EM2 of Zindler and Hart 1986; Fig. 9a,b). Xenoliths from three localities within the Sikhote-Alin district of eastern Russia possessed some of the lowest δ^7Li values measured. The data for these lherzolites defined arrays in Li isotope vs. ^{87}Sr/^{86}Sr and vs. ^{143}Nd/^{144}Nd space that suggested incorporation of a component with $\delta^7\text{Li} < -25$ (perhaps the EM1 end member of Zindler and Hart 1986; Fig. 9).

Regardless of the ultimate sources of these compositions, these results clearly show that strongly isotopically fractionated Li from crustal sources plays a role in the mantle. Processes active in subduction zones appear to be cardinal in the control of the Li isotopic composition of different parts of the mantle. The results to date imply that both isotopically enriched (δ^7Li > MORB) and depleted (δ^7Li < MORB) material are available for deep subduction, and that areas of the continental lithosphere may retain these records on long time scales.

Crustal processes

Crustal melting. No comprehensive study has yet to consider Li isotopes in igneous systems exclusive of purely mantle melting. Estimates of the Li isotopic composition of granitic rocks from various regions span a very wide range. Both Svec and Anderson (1965) and Isakov et al. (1969) showed large (percent-level) variability in Li isotopic compositions of minerals from granites and related deposits. As the analyses in these early works were not standardized, absolute values cannot be assessed and magnitudes may be questioned. Regardless of the vintage of these analyses, granitic systems (*sensu lato*) are likely to show substantial isotopic variability, the origins of which may prove to cement Li as an important tool in the study of petrogenesis or other processes.

Subsequent studies with improved analytical techniques include data from granitic rocks reveal values ranging from 15‰ lighter than MORB to 20‰ heavier. A number of granitic

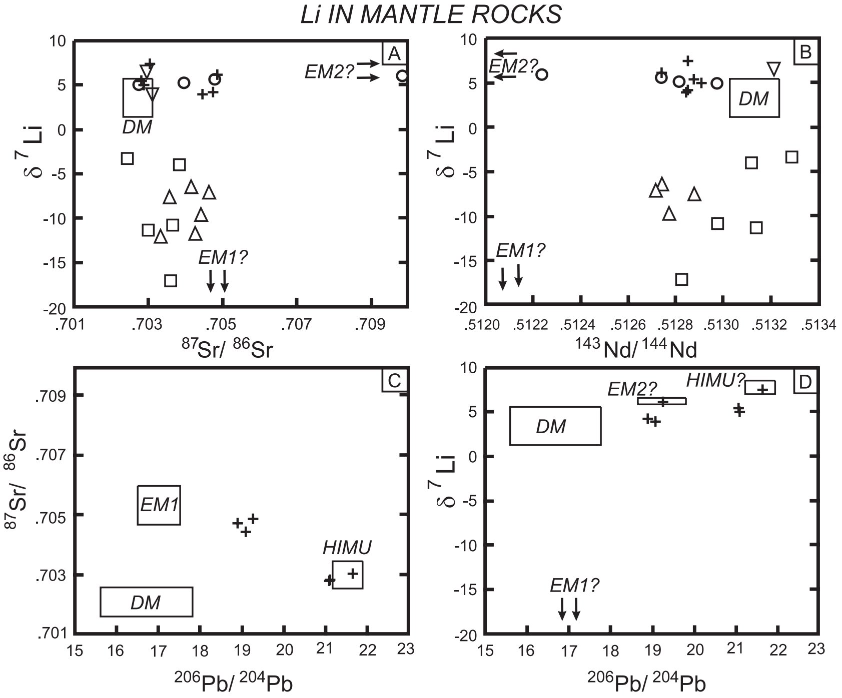

Figure 9. Plots of Li and radiogenic isotopes for mantle rocks. (a) δ^{7}Li vs. ^{87}Sr/^{86}Sr; (b) δ^{7}Li vs. ^{143}Nd/^{144}Nd; (c) ^{87}Sr/^{86}Sr vs. ^{206}Pb/^{204}Pb (d) δ^{7}Li vs. ^{206}Pb/^{204}Pb (Nishio et al. 2003, 2004). Symbols: + = south Pacific island basalts (six islands); ○ = lherzolite xenolith, Bullenmerri, Australia; □ = lherzolite xenolith, Sikhote-Alin, Russia (three localities); △ = dunite-peridotite-pyroxenite xenolith, Kyushu, Japan (two localities); ▽ = lherzolite xenolith, Ichinomegata, Japan. The ocean island data are from bulk rocks, the xenolith data are clinopyroxene separates. For explanations of the derivation of radiogenic isotope fields (DM, EM1, EM2, HIMU), see Zindler and Hart (1986). The estimate for Li isotopes in DM is based on MORB. The Li isotopic ranges for the other mantle reservoirs are based on Nishio et al. (2004) and Nishio et al. (2003), but these will require further examination (hence the use of question marks).

and rhyolitic rock standards have been analyzed, and they showed generally light but variable isotopic compositions: δ^{7}Li = −1.2 to +3.9 (Table 1; James and Palmer 2000a; Bouman et al. 2002; Chan and Frey 2003; Pistiner and Henderson 2003). The only large studies of granitic rocks to date examined rocks from eastern Australia, finding a range in δ^{7}Li of –1.4 to +8.0 (Bryant et al. 2003b; Teng et al. 2004). Of these, the granites derived from predominantly metasedimentary source rocks had lighter average compositions (S-type granites; δ^{7}Li = −1.4 to +2.1) than I-type granites (+1.9 to +8.0). Composite samples of granitic rocks from throughout China also had light isotopic compositions (δ^{7}Li = −3.4 to +3.0; Teng et al. 2004). Granites from the eastern Sierra Nevada, California, and Quaternary rhyolite from the Long Valley area had δ^{7}Li = 0.0 to +4.0 (Tomascak et al. 2003), overlapping values for least-hydrothermally altered rhyolite from the Yellowstone, Wyoming, area (+0.7; Sturchio and Chan 2003), and unaltered Liberty Hill granite, South Carolina (+2.3; Njo et al. 2003).

Individual samples of isotopically heavier granitic rocks have also been reported from the Canadian Shield (δ^{7}Li = +7.3 to +11.3; new and updated data from Bottomley et al. 2003) and from the Isle of Skye, Scotland (δ^{7}Li = +8.1; Pistiner and Henderson 2003). These are all rocks with long near-surface histories and modal chlorite or epidote, suggesting their isotopic compositions may not be pristine, igneous values (discussed below under, "Continental runoff and weathering processes").

Studies that have considered evolved granitic systems (associated with Li mineralization) have found both extremely isotopically light and highly variable isotopic compositions: Kings Mountain granite-pegmatite system, North Carolina: δ^7Li = −10 to +12 (Vocke et al. 1990); Harney Peak granite and related pegmatite, South Dakota: δ^7Li = 0 to +19 (Vocke et al. 1990; Tomascak et al. 1995c); Macusani high silica rhyolite, Peru: δ^7Li = −2.2 to −1.1 (Tomascak et al. 1999a). This dispersion of data may be an artifact of significant isotopic fractionation occurring at temperatures below the haplogranite granite solidus.

Metamorphism and ore formation. Variations in Li isotopes brought about regional metamorphism are essentially completely uncharacterized. Unattributed data in Huh et al. (1998) suggested values of δ^7Li > MORB for at least some regional metamorphic rocks, but a single analysis of a Precambrian schist yielded δ^7Li = +1.6 (Sturchio and Chan 2003). A variety of metamorphic rocks from the Canadian Shield had δ^7Li of +2.0 to +6.7, with a pegmatitic gneiss at +30.2 (Bottomley et al. 2003). Although Li isotope fractionation at granulite facies temperatures might be considered unimportant, highly fractionated compositions in lower continental crustal xenoliths, with δ^7Li as low as −13 (Teng et al. 2003), suggest that even at such conditions mass fractionation may take place, possibly governed by the presence (or composition) of a fluid phase, either as a part of lower crustal metamorphism or in the sources of these rocks.

Data on Li isotopic variations during local-scale metamorphism related to ore deposits are limited to analyses for which absolute values cannot be assessed. Morozova and Alferovskiy (1974) showed >1% variations in rocks/minerals of granite pluton contacts and amphibolite. Divis and Clark (1978) showed similar strong fractionation between granitic and volcanic rocks and their ore-related altered counterparts. The results of Divis and Clark (1978) suggest lighter isotopic compositions should be expected in higher-temperature ore zone rocks.

Differentiation of the highly geochemically evolved Tin Mountain pegmatite, South Dakota, led to fractionated isotope ratios in minerals during progressive crystallization, and suggested the possible viability of Li isotope thermometry (Tomascak et al. 1995c). In different internal zones of the lithium pegmatite, albite (δ^7Li = +7 to +11) was uniformly isotopically lighter than coexisting quartz and muscovite (δ^7Li = +16 to +19; Fig. 10). An increase of c. 2‰ in albite-quartz fractionation was observed from earlier- to later-crystallized assemblages which formed over an estimated temperature range from approximately 600°C to approximately 550°C, based on oxygen isotope data (Walker et al. 1986). This fractionation could be temperature-dependent equilibrium fractionation, where difference in magnitude of effect resulted from different available crystallographic sites in the crystallizing assemblage (considered in the next section). In light of the recent proposal of crystallization of this pegmatite at even lower temperatures (<400°C; Sirbescu and Nabelek 2003), the isotopic results should be considered cautiously.

Constraints on Li isotopic fractionation from equilibrium laboratory experiments in magmatic-hydrothermal systems have been examined in only one instance (Lynton 2003). This study examined Li in a quartz-muscovite-aqueous fluid system at conditions of formation of magmatic hydrothermal porphyry-type deposits (400–500°C, 100 MPa). In the presence of a fluid containing L-SVEC (δ^7Li = 0), quartz showed rapid shift from δ^7Li = +27 in the starting material to c. +10 at both run temperatures. Muscovite (initial δ^7Li = +9), shifted more sharply at 500°C (to c. +20) than at 400°C (to c. +13). Although the results are difficult to put directly into the context of a natural mineral deposit, they do indicate that over geologically relevant time scales, minerals in magmatic-hydrothermal systems should show appreciable Li isotopic fractionation, and that this may permit the composition and/or temperature of ore

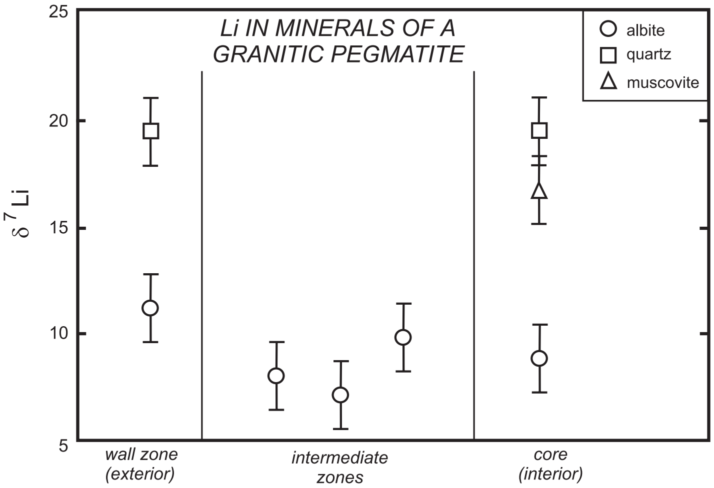

Figure 10. Lithium isotopic compositions of minerals from the Tin Mountain pegmatite, Black Hills, South Dakota (Tomascak et al. 1999c). Differences in the equilibrium quartz-feldspar oxygen isotopic compositions between the wall zone and intermediate zones suggested temperatures of 600 to 550°C (Walker et al. 1986). Despite poor precision of these data, they showed a consistent increase in the $\Delta^7\text{Li}_{\text{quartz-albite}}$ between the early-crystallizing wall zone and the later-crystallizing core.

fluids to be estimated. Despite the small number of data from natural and synthetic magmatic-hydrothermal systems, Li isotope research appears to offer the potential for new insights into the petrogenesis of magmatic and hydrothermal ore deposits.

PLANETARY SURFACE SYSTEMS

Mass fractionation in hydrologic cycle of Li

Most of the clearly identified isotopic fractionation in nature occurs close to the Earth's surface. The combination of low ionic charge, relatively small radius (approximately 0.068 nm; Shannon 1976), and high degree of covalency in its bonds affords Li potential for considerable adaptability in different geochemical environments. Lithium in aqueous solutions is highly hydrated relative to the other alkali metals, and ordinarily assumes tetrahedral hydrated coordination (Olsher et al. 1991). In most solids Li occupies either tetrahedrally- or octahedrally coordinated sites (Olsher et al. 1991; Wenger and Armbruster 1991). The occurrence of isotopic fractionation induced by recrystallization, in which an energetic advantage is gained by the incorporation of one isotope over another into a crystallographic site, is an important mechanism for near-surface isotopic fractionation (O'Neil 1986). Based on *ab initio* calculations, the isotopic effect of Li exchange into octahedral crystallographic sites from aqueous solution is preferential incorporation of ^{6}Li into the solid (Yamaji et al. 2001). This fractionation is borne out experimentally and in nature (examples summarized below), with a magnitude-dependent on reaction temperature and fluid/rock ratio.

The thermodynamic basis for considering Li isotopic fractionation during dissolution of primary minerals (equilibrium fractionation) takes into account small differences in bond energies of ions of different mass (O'Neil 1986). Breaking the higher energy bonds of ^{6}Li is energetically favorable, and so the equilibrium isotope effect would be to enrich the solution phase with the lighter isotope. However, Pistiner and Henderson (2003) suggested on the basis of laboratory dissolution experiments that incongruent mineral dissolution does not impart significant isotopic fractionation. It appears that this mechanism of isotopic fractionation is either not dominant in low temperature environments, or its effects are generally overprinted by later processes, as suggested by Huh et al. (2001) for continental weathering.

Fluid-particle interaction, in which aqueous ions are adsorbed by mineral surface sites, is another significant mechanism for the development of Li isotopic heterogeneity in the hydrosphere. Sorption of Li from aqueous solution by minerals at ambient temperatures has been demonstrated for a variety of materials (Taylor and Urey 1938; Anderson et al. 1989), despite the prediction that Li would tend to be the least sorbed of the alkalis, due to its high degree of hydration (Heier and Billings 1970). Sorption and retention of ions from solution depends largely on both mineral surface chemistry and the composition of the solution. Although it has been suggested experimentally that the magnitude of mass fractionation on desorption is equivalent to that on adsorption (Taylor and Urey 1938), natural and empirical data for both Li and Cs suggest that this fractionation is not reversible (Comans et al. 1991; James and Palmer 2000b). The irreversibility of this process is typically ascribed to incorporation of Li into crystallographic sites rather than surface ion exchange sites, suggesting that the magnitude of the effect will vary among minerals.

Zhang et al. (1998) examined the behavior of dissolved Li during sorption from seawater onto clay minerals and sediments. A similar degree of isotopic fractionation was observed for vermiculite, kaolinite and mixed Mississippi River suspended sediment ($\alpha \sim 0.978$; where $\alpha = {}^{7}\mathrm{Li}/{}^{6}\mathrm{Li}_{\mathrm{mineral}}/{}^{7}\mathrm{Li}/{}^{6}\mathrm{Li}_{\mathrm{solution}}$). Pistiner and Henderson (2003) conducted experiments on the isotopic effects of Li sorption on a variety of minerals. Their results suggested that sorption reactions in which Li was not structurally incorporated (physisorption) yielded no measurable isotopic fractionation. When the data indicated that Li was incorporated via stronger bonds (chemisorption), isotopic fractionation was observed, but was not homogeneous among minerals with different chemistry/structure, consistent with field studies (e.g., Anghel et al. 2002). The most significant effect was shown by gibbsite, with apparent $\alpha \sim 0.986$. It is clear that further experimental studies of isotopic fractionation effects of adsorption under geologically-relevant conditions are needed and will aid in understanding the hydrologic cycle of this element.

Transmission of solution through a semi-permeable membrane has been suggested as a means of inducing measurable stable isotope fractionation (Phillips and Bentley 1987); in principle, the concentration of ${}^{7}\mathrm{Li}$ would be depleted on the high-pressure side of the membrane (Fritz 1992; Fritz and Whitworth 1994). This experimentally-derived separation has yet to be documented in nature (Remenda 1994), although deep sedimentary basins with clay-rich strata, elevated pore pressures and low flow rates are a setting where such an effect might be geochemically important.

The importance of equilibrium versus kinetic effects has yet to be addressed in any coherent way by the limited laboratory experiments conducted for Li isotope study. It is clear from the study of other stable isotope systems that kinetic effects may dominate the fractionation pathways under many circumstances (e.g., Johnson and Bullen 2004), especially in laboratory simulations of low-temperature natural phenomena (Beard and Johnson 2004). The clarification of how kinetic effects on Li isotopic compositions are manifested remains a major area for future study in natural, synthetic and theoretical systems.

Primarily clastic sediments and sedimentary rocks

Lithium isotope studies of sediments and sedimentary rocks have thus far concentrated on marine clastic and carbonate material. No systematic description of the effects of diagenetic processes on sediments has been made. Clay rich sediments are important to Li budgets in near-surface systems, as they concentrate Li relative to marine carbonates, which are among the most Li-impoverished materials in the crust (Ronov et al. 1970). Lacustrine carbonates have higher Li concentrations than their marine counterparts, and minerals generated in evaporitic environments are commonly enriched in Li (Tardy et al. 1972; Calvo et al. 1995). Marine carbonates are discussed below, and evaporites are mentioned under "Deep and shallow crustal fluids."

The first modern publication of Li isotope data from sediments came from Chan et al. (1994a), who reported the isotopic compositions of unaltered turbidites from DSDP Hole 477 and 477A, from the Gulf of California. These samples have been reanalyzed (LH Chan, written communication 2003), yielding lighter values. Similarly, Chan and Frey (2003) suggested a range for marine clastic sediments (δ^7Li = −1 to +5.6) based on new data and re-analysis of samples previously considered to be isotopically heavy.

Contact metamorphosed, hydrothermally altered and greenschist facies metamorphosed equivalents of these sediments showed a wide range of generally lighter compositions (δ^7Li as low as −1.3), and all altered samples had lower Li contents by >1.4×, consistent with removal of Li during >300°C alteration. At ODP Site 918, in the Irminger Basin, southeast of Greenland, Zhang et al. (1998) found that quartz-rich silts tend to have heavier compositions (δ^7Li = +8.5 to +11.8) than underlying chalk-dominated sediments (δ^7Li = +3.2 to +8.8).

Sediments ranging from clay-rich to carbonate-rich from ODP Sites 1039 and 1040, outboard of Costa Rica, had variable isotopic compositions, unrelated to their bulk chemistry (δ^7Li = +9.5 to +23.3; Chan and Kastner 2000). Turbidites and underlying ash-rich mudstones at ODP Site 808, southwest of Japan, defined a similarly large range in isotopic compositions (δ^7Li = −1 to +8; You et al. 1995). James et al. (1999) reported δ^7Li for variably altered sandy to silty turbidites to hemipelagic muds from ODP Site 1038, off the coast of northern California (−0.5 to +5.6).

Data for shales range from δ^7Li = +4.5 to +8.0 for formations in the western U.S. (James and Palmer 2000a; Sturchio and Chan, 2003), to light values for the Shimanto shale, Japan (δ^7Li = −2.7 to −1.5; Moriguti and Nakamura 1998b). These ranges overlap measurements from the one large-scale study of sedimentary materials to date (Teng et al. 2004). This study reported data for from five loess localities (δ^7Li = −3.1 to +4.8) and for nine shales used in the compilation of the post-Archean average Australian shale composition of Nance and Taylor (1976) (δ^7Li = −3.2 to +3.9). Composite samples of well-characterized sedimentary rocks from throughout China give a similar range of values (δ^7Li = −5.2 to +1.2; Teng et al. 2004). The isotopically light values from these sedimentary rocks contrast with a measurement of Vicksburg, Mississippi loess (δ^7Li = approximately +15; Huh et al. 1998)

Lithium isotopic fractionation in the oceans

The oceans have a Li concentration of c. 180 ppb, or 26 μM (Morozov 1968). Lithium in the oceans is well mixed vertically and between basins, and has not varied over the past >40 Ma by more than a factor of 1.4 (Delaney and Boyle 1986). Dissolved oceanic Li has a residence time estimated between 1.5 and 3 Ma (Stoffyn-Egli and Mackenzie, 1984; Huh et al. 1998). As a demonstration of this, Chan and Edmond (1988; same data reported in Chan 1987) found indistinguishable isotopic compositions of Atlantic and Pacific samples from both shallow (~100 m) and deep (>3700 m) levels (δ^7Li ~ +33). Analyses of seawater since this publication have maintained the isotopically heavy and consistent character of this reservoir, although a range beyond cited analytical uncertainties is evident: δ^7Li = +29.3 (Nishio and Nakai 2002); +29.6 (Sahoo and Masuda 1998; Pistiner and Henderson 2003); +30.0 (Moriguti and Nakamura 1998a); +31.0 (Millot et al. 2004); +30.4 to +32.0 (Bryant et al. 2003a); +31.8 (Tomascak et al. 1999a); +32.2 (James et al. 1999); +32.4 (You and Chan 1996); +32.5 (James and Palmer 2000a) (Fig. 11). It is unlikely that modern seawater truly shows isotopic variability on the order of 4‰. The range in measured values spans a variety of analytical methods and

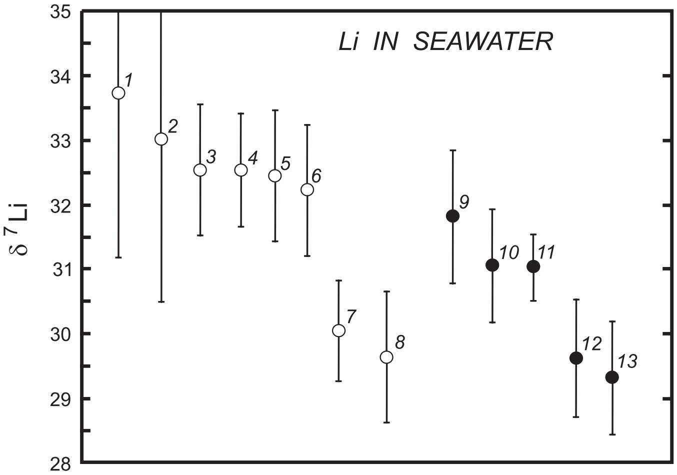

Figure 11. Reported Li isotopic compositions of seawater samples. ○ = analyses by TIMS, ● = analyses by MC-ICP-MS. Sources: 1 = Pacific average, Chan and Edmond (1988); 2 = Atlantic average, Chan and Edmond (1988); 3 = Gulf of Mexico, Zhang et al. (1998); 4 = location not given, James and Palmer (2000); 5 = Sargasso Sea, You and Chan (1996); 6 = Escanaba Trough, James et al. (1999); 7 = Mariana Trough, Moriguti and Nakamura (1998a); 8 = Japan Sea, Sahoo and Masuda (1998); 9 = central Pacific, Tomascak et al. (1999a); 10 = Great Barrier Reef, Bryant et al. (2003a); 11 = IRMM BCR-403, Millot et al. (in review); 12 = Pacific, off Hawaii, Pistiner and Henderson (2003); 13 = north Pacific, Nishio and Nakai (2002). Diagram uses conservative estimates of uncertainty (2σ) from the respective sources.

areas sampled in the oceans. Clearly analytical artifacts are present within this population and the true range for modern seawater remains to be conclusively determined.

The first substantive report of Li isotopes in any Earth materials (Chan and Edmond 1988) largely presaged what was to come in Li isotope research in the oceans. The interpretations therein, based on a handful of data from seawater, fresh and altered basalt, hydrothermal fluids and lake waters, laid out the foundation to what has come since, in terms of natural and laboratory-based studies of the marine geochemistry of Li isotopes.

As presently identified, only a few factors dominate the oceanic budget of Li and Li isotopes. Lithium is removed from the oceans via sea floor alteration reactions, high temperature sub-sea floor (hydrothermal) recrystallization, and adsorption on particle surfaces (discussed above). Lithium enters the oceans from rivers and from high and low temperature marine fluids. Crystallization of marine carbonates and biogenic silica are not important sinks (<5% total), given their low concentrations relative to their volumes (Chan et al. 1994b; Chan and Kastner 2000). Diffusion into and out of sediments are small components that roughly cancel one another (Stoffyn-Egli and Mackenzie 1984; Zhang et al. 1998; James and Palmer 2000b). The mass balance of oceanic Li has not yet been adequately resolved, due to the lack of a sink with sufficiently light Li isotopes. The components of the oceanic Li budget that have been examined in significant detail to date are summarized below.

Sea floor alteration. One of the most thoroughly studied settings in which Li isotope fractionation is observed is on the sea floor, during the alteration ("weathering" in many studies) of basalt (Chan 1987; Chan and Edmond 1988; Chan et al. 1992; Chan et al. 2002a) (Fig. 12). As oceanic basalt becomes altered, Li from seawater is taken up in the low temperature minerals that form (Stoffyn-Egli and Mackenzie 1984), most importantly clay minerals such as the smectites (Berger et al. 1988), such that the longer the exposure

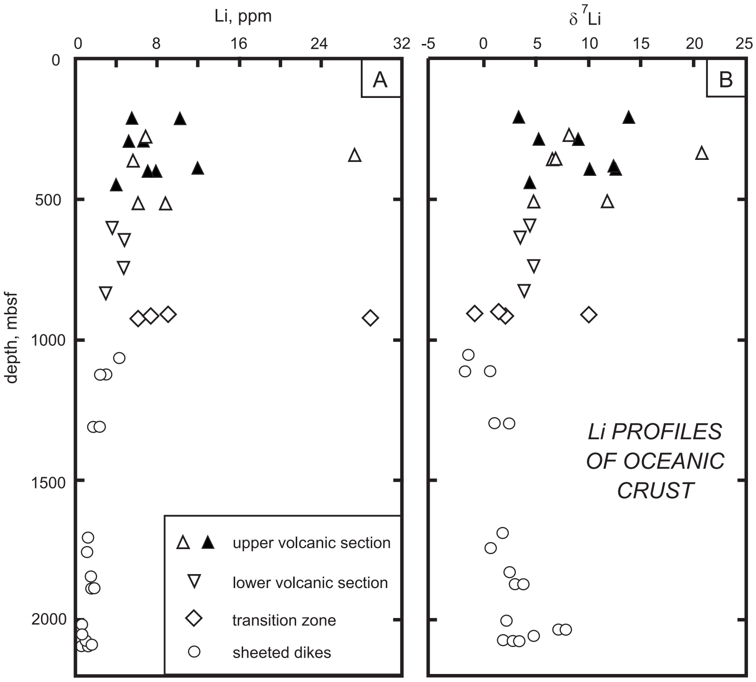

Figure 12. Depth profile of Li isotopic composition (a) and concentration (b) in drilled oceanic crust at ODP Sites 504B (open symbols) and 896A (filled symbols) off Costa Rica (Chan et al. 2002a). The transition zone exhibits mixing between hydrothermal fluids and seawater. Average oxygen isotopic (δ^{18}O) composition of bulk samples decreases with depth: upper volcanic zone = +7.8, lower volcanic zone = +6.4, transition zone = +5.4, sheeted dikes = +4.3. However, despite many sheeted dike samples having δ^7Li less than unaltered MORB, there is no simple relationship between concentration and Li isotopes.

on the sea floor, the higher the Li concentration of the altered rock (to an "end member" altered basalt with δ^7Li ~ +14 and >75 ppm Li; Chan et al. 1992) (Fig. 13). Summarily, the generation of secondary minerals during sea floor alteration provides a major control on the isotopic composition of Li in the oceans (Chan et al. 1992). It is clear from the data for altered sea floor basalts that the process is not simply mixing between a pristine and a totally altered composition. Seawater Li enters newly-formed minerals in altered basalts with an apparent fractionation factor $\alpha \sim 0.981$ at 2°C for dredged basalts from the Atlantic and Pacific (Chan et al. 1992; recalculated to maintain consistency in this text: $\alpha = {}^7\mathrm{Li}/{}^6\mathrm{Li}_{\mathrm{mineral}}/{}^7\mathrm{Li}/{}^6\mathrm{Li}_{\mathrm{solution}}$). Uniformity in this fractionation for exclusively sea floor temperature altered crust sampled in a variety of locations suggests that although individual minerals may have distinct α values, the process as a whole produces a fixed average fractionation.

Marine hydrothermal fluids and alteration. At divergent plate boundaries, thinning of oceanic crust brings mantle magma close to the sea floor and engenders hydrothermal circulation of seawater through crust and overlying sediments. The upwelling fluids are a significant source of Li to the oceans, although the magnitude of the hydrothermal flux is not precisely quantified (Elderfield and Schultz 1996).

Lithium is enriched in high temperature (c. 350°C) vent fluids by a factor of 20–50 relative to seawater (Edmond et al. 1979; Von Damm 1995). The Li isotopic compositions of marine hydrothermal vent fluids ranged from MORB-like to heavier compositions (see

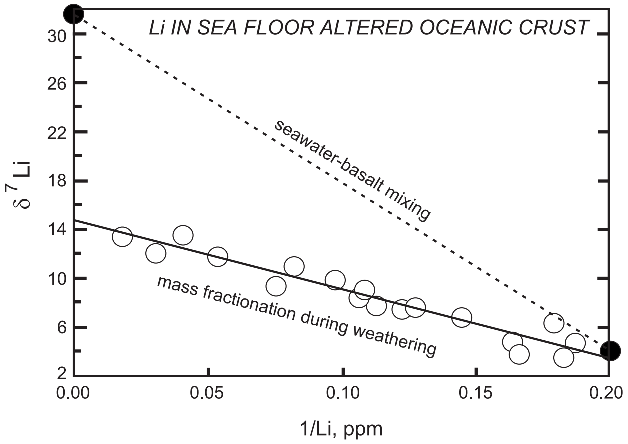

Figure 13. Plot of Li isotopic composition vs. inverse concentration for sea floor altered (weathered) mid-Atlantic ridge basalts (Chan et al. 1992). Solid line is the regression of the data ($R^2 = 0.927$), the dashed line shows the predicted relation of a pure mixture of seawater with unaltered basalt (Teng et al. 2004), underscoring that the altered basalts incorporated Li into secondary mineral with a fractionation factor $\alpha \sim 0.981$.

Figs. 14, 15). Fluids from vents in various settings showed a degree of isotopic variability, with values extending from the MORB range to several permil heavier (δ^7Li = +2.6 to +11.6; Chan and Edmond 1988; Chan et al. 1993, 1994a; Bray 2001; Foustoukos et al. 2003) (Fig. 14). In view of the absence of correlation between δ^7Li and spreading rate, Chan et al. (1993) suggested that circulating mid-ocean ridge hydrothermal fluids derived most of their Li from young, unaltered basaltic crust, and not from older, sea floor altered basalts. The altered basalts have higher Li concentrations and markedly heavier isotopic signatures compared to unaltered basalts. High temperature fluids from systems capped with thick sediment cover showed similar concentration and isotopic ranges as those from ridge areas that lack sediment cover, requiring the development of the isotopic signature by deeper processes that are not vitally affected by shallow materials that are enriched in Li available for hydrothermal leaching (Chan et al. 1994a).

Rocks that have been altered during interaction with these kinds of hydrothermal fluids and retain the Li isotope record of the process may be somewhat uncommon because of the prominence of re-equilibration with low temperature fluids. Based on the empirical and experimental evidence, hydrothermal alteration preferentially removes heavy Li from the rock; in the absence of retrograde mineral formation, this generates altered rock with lower Li concentration and lower δ^7Li than in the unaltered state. This was first recognized in dredged ocean floor greenschist-facies metabasalt (4.6 ppm Li and δ^7Li = −2.1; Chan et al. 1992). Subsequent reports of hydrothermally or greenschist facies metamorphosed sediments and basalt in the oceanic crust demonstrate reduction in Li concentrations and a general trend toward lighter isotopic compositions (Chan et al. 1994a; You et al. 1995; James et al. 1999), although this process may be complex when complete sections are examined (Fig. 12; Chan et al. 2002a).

In oceanic fracture zones as well as in actively-upwelling forearc mud volcanoes, seawater or other marine fluids interact directly with mantle rock (Bonatti 1976; Fryer 1985). Serpentinization of mantle rocks at temperatures broadly <350°C involves influx of water, as well as general increase in Li concentration in the newly-formed hydrous assemblage. Considering the low temperatures involved, Li isotope exchange during seawater-mantle

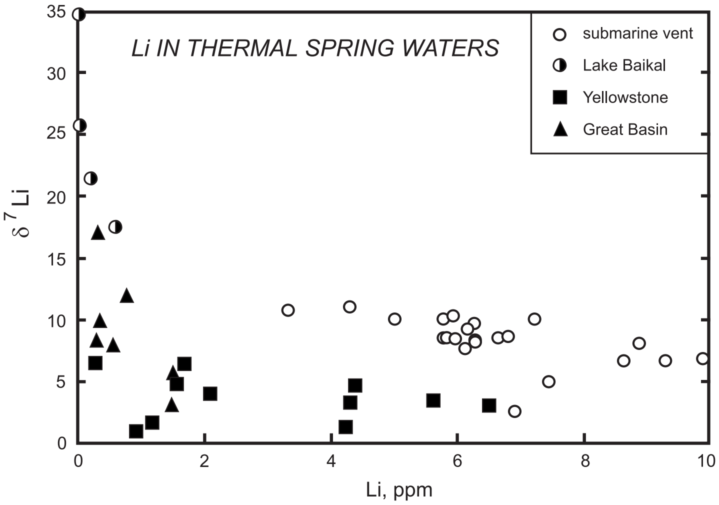

Figure 14. Plot of Li isotopic composition vs. concentration of thermal waters from the continents and the oceans (see text for references). Differences between the isotopic range of marine versus non-marine fluids emphasizes the variability in δ^7Li of continental rocks compared to oceanic basalt. The dilution of the continental fluids goes along with their lower temperatures; vent fluids are the only truly geothermal samples here, with temperatures in excess of 300°C.

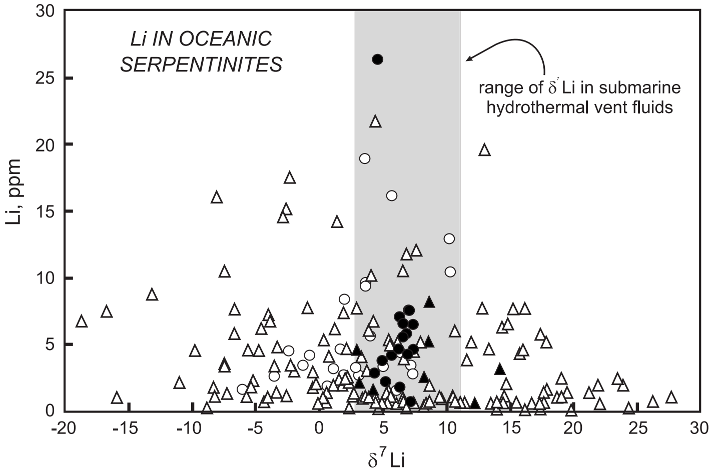

Figure 15. Plot of Li isotopic composition vs. concentration for serpentine and serpentinites samples (triangles = southwest Indian Ridge, Decitre et al. 2002; circles = Conical seamount, Marianas forearc, Benton et al. in review). For the Indian Ridge samples, open triangles represent *in situ* analyses (lower precision) of relict and alteration minerals, filled triangles are bulk samples. For the Conical seamount samples, open circles represent variably altered serpentinite clasts, filled circles are fine-grained homogenized serpentine muds that were the matrix to the clasts. The homogenized populations of these two geologically distinct settings display coherent systematics, with a mean value that overlaps the average for marine hydrothermal vent fluids (shaded region).

interaction can be expected. Results from dredged serpentinites (Decitre et al. 2002) and from forearc mud volcanoes (Savov et al. 2002; Benton et al. 1999) gave a consistent picture of fluid evolution during progressive interaction. Serpentinites in both studies were enriched in Li over unmetasomatized mantle rocks and were isotopically heterogeneous, ranging from much lighter than ordinary mantle rocks to slightly heavier (δ^7Li = −6.1 to +14.2 for bulk analyses, −19 to +28 for *in situ* analyses). Despite the differences in nature of formation of these two suites of serpentinites, the samples that showed the most coherent relations between elemental and isotopic data had a coincident mean δ^7Li = +7 ± 5‰, which was interestingly similar to the average composition of sea floor hydrothermal vent fluids (+8 ± 4‰) (Fig. 15).

Decitre et al. (2002) interpreted Li isotopic compositions of Indian Ocean serpentinites to represent internal recycling of Li from the basaltic crust into progressively-formed serpentinites, rather than Li extracted mainly from seawater. They envisioned the generation of the variable isotopic signatures in serpentinites (both lighter and heavier than the unaltered rocks) by interaction of mantle with a hydrothermal fluid that evolved, as it cooled and reacted with mantle rock along its flow path, toward heavier isotopic compositions. This model is consistent with the preponderance of compositions only slightly fractionated from MORB values, although better correlation between δ^7Li and Li concentration would be expected in the least complex scenario. The forearc serpentinites are considered to have been generated by infiltration of a fluid derived from the subducting Pacific plate (Benton et al. 1999), hence rather different in elemental contents than fluids expected to have interacted with fracture zone serpentinites.

Laboratory experiments have been carried out in order to gain insight on Li isotope behavior during interaction of high temperature fluids and various materials. Chan et al. (1994a) reacted Li-free aqueous fluid with a natural marine quartzofeldspathic mud (δ^7Li = +5.0) at an initial fluid/solid ~3. Fluids were sampled as temperatures were raised to 350°C over c. 600 h in the first experiment, and in a second run they were also sampled during cooling, after peak temperatures of approximately 350°C were reached (c. 540 h total). Both experiments demonstrated leaching of Li into solution, even at low temperatures, but more significantly as hydrothermal conditions are reached. The earliest fluids were isotopically heavy relative to the starting sediment, but under persistent hydrothermal conditions, fluid isotopic composition approached equilibrium with the starting solid. Fluids extracted in the second experiment during cooling also showed enrichment in heavy Li relative to the initial solid, and Li concentration in the fluid increased over the steady-state peak temperature value. The results are in general agreement with model predictions using empirical fractionation factors and assuming chlorite is the primary hydrothermal alteration mineral.

In the laboratory experiments of Seyfried et al. (1998), naturally altered sea floor basalt (δ^7Li = +7.4) was reacted with Li-free alkali-chloride aqueous fluid at 350°C for 890 hours (initial fluid/solid mass ratio ~2). Samples of the fluid were taken throughout the experiment, and showed initial rapid influx of isotopically heavy-enriched Li released by early-dissolving alteration minerals. However, with progressive reaction, isotopic composition of the fluid decreased and Li concentration reached apparent steady state. Although an equilibrium model applies best to the synthetic results, Rayleigh distillation was considered most likely to apply in hydrothermal reactions occurring in nature.

James et al. (2003) performed laboratory experiments in which aqueous fluids were reacted with natural samples of unaltered MORB (δ^7Li = +4.6) and a quartzofeldspathic mud/turbidite mixture (δ^7Li = +1.3). The starting fluids had elemental compositions generally intermediate between seawater and hydrothermal fluids, and were isotopically light (δ^7Li = −5.5). The initial fluid/solid was ~4. Fluid samples were extracted as the experiments were raised to 350°C over 400–500 h, and then during cooling (c. 740 h total). In both experiments Li was removed from solution at low temperatures, but the isotopic composition of the fluids rapidly shifted to heavier values. The Li isotopic composition of the fluid in the sediment experiment progressively changed toward that of the starting solid as the temperature reached 350°C, whereas that of the basalt changed more sluggishly, plausibly as result of coincident fractionation from secondary mineral formation at lower temperature (James et al. 2003).

All of the experimental evidence shows extraction of Li from basalt, altered basalt and sediments even at temperatures <100°C. Lithium was incorporated into clays at temperatures up to 150°C during basalt alteration (Seyfried et al. 1984; James et al. 2003), with affinity proportional to the fluid/rock ratio, such that Li was simultaneously added to and removed from fluids. Under high temperature, solid-dominated hydrothermal conditions (c. 350°C), Li was universally removed from materials and kept in solution, rather than in alteration minerals. The limited isotopic fractionation at these conditions has been estimated as $\alpha \sim 0.994$ (= $(^7\mathrm{Li}/^6\mathrm{Li}_{\text{secondary minerals}})/(^7\mathrm{Li}/^6\mathrm{Li}_{\text{solution}})$); Chan et al. 1993; Seyfried et al. 1998).

Marine pore fluid-mineral processes. During the diagenetic process (primarily compaction and mineral dehydration) fluids may be released from marine sediments, contributing waters of diverse chemical and isotopic compositions to the oceans. Pore fluids carry a record of fluid-sediment interaction. In the simplest case, fluids derived from seawater will possess lower concentrations of Li than seawater and $\delta^7\mathrm{Li} > +31$, as a result of fractionation during fluid-sediment interaction or crystallization of low temperature minerals. However, depending on local geology, pore fluids can embody much more complex evolutionary histories. In order to derive meaningful conclusions, studies of these fluids have to contend with the potentially overprinting effects of variable mineral reactions and fractionation factors from strata of differing mineralogy and changing temperature in the sedimentary stack, *in situ* diffusion of mobile elements through the permeability network, and the vertical and lateral mixing of fluids of variable compositions (e.g., You et al. 2004). Whether or not fluids reach steady state compositions (at any stage in their geochemical evolution) is another complicating factor in these studies.

You et al. (1995) studied bulk samples of fluids incorporated in sediments from ODP Site 808, in the Nankai Trough, southwest of Japan. Pore fluids have somewhat variable isotopic compositions ($\delta^7\mathrm{Li} = +10$ to $+21$), with a spike of light compositions near the basal decollement. These authors interpreted the decollement zone geochemical anomaly to represent influx of waters with Li derived from leaching of sediments at high temperatures.

Zhang et al. (1998) considered Li isotopes in pore fluids of marine sediments at ODP Sites 918 (Fig. 16a) and 919, southeast of Greenland. They found fluids with isotopic compositions reflecting a complex range of diagenetic processes and $\delta^7\mathrm{Li} = +24.5$ to $+43.7$. They identified the importance of $\mathrm{NH_4^+}$ concentrations in pore fluids as a counterion for Li exchange on sediments. The peak in $\mathrm{NH_4^+}$ concentration at Site 918 coincided with Li isotopic compositions lighter than seawater, suggesting that desorbed Li was isotopically lighter than its seawater starting composition. Zhang et al. (1989) estimated a fractionation factor for this process of $\alpha \sim 0.975$ (= $(^7\mathrm{Li}/^6\mathrm{Li}_{\text{mineral}})/(^7\mathrm{Li}/^6\mathrm{Li}_{\text{solution}})$). This provides an interesting biogeochemical slant to the interpretation of Li isotope data from some pore waters, since $\mathrm{NH_4^+}$ is a product of the biological degradation of organic matter. Lithium enrichment in deeper pore waters at Site 918 was interpreted to derive from influx of sediment-derived Li from lower horizons at higher temperatures (Zhang et al. 1998), a similar interpretation as has been applied since, where deep increases in pore water Li concentration have been observed.

James et al. (1999) reported findings from ODP Site 1038 (Fig. 16b), adjacent to the Gorda Ridge, an area of active hydrothermal venting through a thick sedimentary pile. Pore fluids there had a range in isotopic compositions ($\delta^7\mathrm{Li} = -0.6$ to $+27.5$) that were modeled in terms of initial hydrothermal removal of Li from sediments followed by down-temperature fluid fractionation during crystallization of secondary minerals, and ultimately dilution with

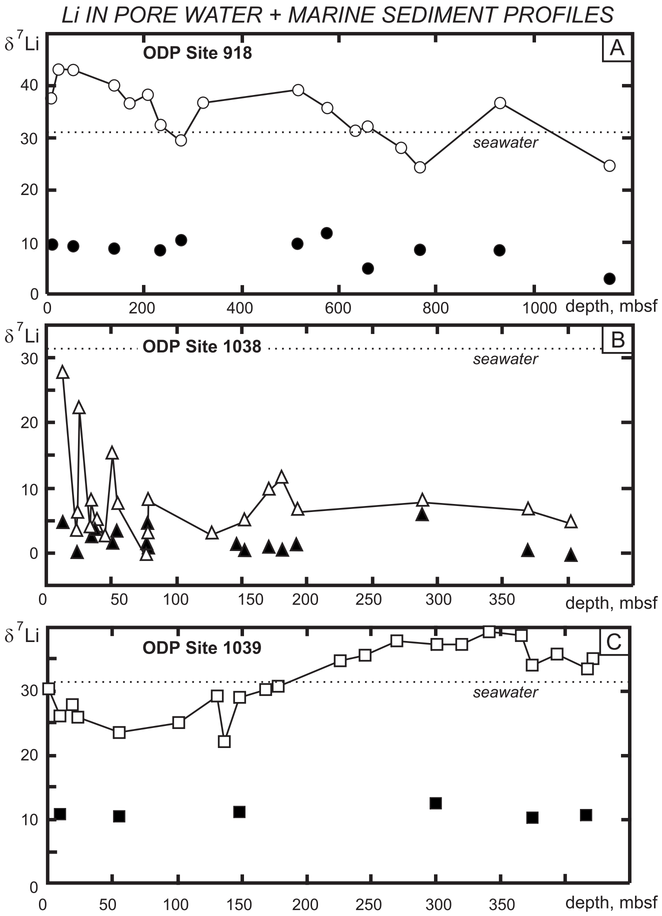

Figure 16. Depth profiles from three ODP Sites, showing Li isotopic composition variations in pore waters (open symbols) and associated sediments (filled symbols). (a) Site 918, Irminger Basin, north Atlantic (Zhang et al. 1998); (b) Site 1038, Escanaba Trough, northeastern Pacific (James et al. 1999); (c) site 1039, Middle American Trench off of Costa Rica (Chan and Kastner 2000). The average composition of seawater is noted on each profile with dashed line (note different scales). Whereas sediments have relatively monotonous compositions, pore waters have compositions reflecting different origins and processes in each site. Interpretations of the data are summarized in the text under, "Marine pore fluid-mineral processes."

seawater. This model fits the data more closely than simple mixing between hydrothermal fluid and sediment-derived Li, but fails to account for the isotopically lightest samples.

Chan and Kastner (2000) examined pore fluids from ODP Sites 1039 (Fig. 16c), 1040, and 1042, outboard of Costa Rica, with a total range in δ^7Li of +22.2 to +39.3. At Site 1039 they observed a pronounced correlation between Li concentration and Li isotopes, such that the pore waters with the highest concentrations (approximately equal to seawater) had the lowest δ^7Li. Variations in data from shallow depths at Site 1039 were interpreted to reflect superimposed effects of alteration of volcanic ash and ion exchange between Li^+ and NH_4^+ (Chan and Kastner 2000). The former consumes Li from fluids, the latter releases, but the isotopic fractionation upon desorption exceeds that of smectite formation (0.976 vs. 0.981), so the net process is a decrease in δ^7Li. Pore fluids deep at Site 1039 show increase in Li concentrations and decrease in δ^7Li, toward seawater values. This was interpreted as indicating mixing with a fluid derived from seawater infiltration, perhaps along the basement-cover boundary as a result of lithological control or non-uniform permeability structure (Chan and Kastner 2000). These are factors that should be common in deep sea sedimentary accumulations. The isotopically rather light pore fluids at Site 1040 have Li concentrations 10× greater than seawater and were interpreted to contain a component derived from mineral dehydration deeper in the sedimentary mass (at temperatures 100–150°C; Chan and Kastner 2000).

James and Palmer (2000b) analyzed pore fluids from a set of ODP locations in the Pacific northwest: Site 1037, adjacent to the Gorda Ridge, and Site 1034, in Saanich Inlet, BC, Canada. At the coastal Site 1034, pore fluids were more dilute than seawater with respect to Li and had δ^7Li less than seawater (+24.2 to +30.0). Moderate ammonium concentrations mimicked the Li concentration profile, suggesting that, particularly in the upper section of the Site, in spite of dilution by fresh water, some of the light isotopic signature came from isotopic fractionation during desorption. Pore fluids at Site 1037 showed a wide range of isotopic values (δ^7Li = +11.6 to +42.8). Controls on Li behavior were interpreted to be dominated by thermal alteration effects, perhaps up to c. 110°C. It was estimated that Li in pore fluids may have derived substantially (>65%) from Li initially adsorbed on particles in the water column (James and Palmer 2000b).

James et al. (2003) inferred, on the basis of comparison between experimental results and natural data, that upwelling rate is another parameter that is critical to interpretation of Li isotope signatures of pore fluids. At low temperatures (<100°C), Li may be lost to fluids by sediments (Chan et al. 1994a). However, enrichment in Li of pore fluids to concentrations greater than that of seawater near basement contacts may more prevalently reflect slow rate of upwelling, as fluid-sediment interaction is thereby favored. This interpretation is consistent with data from a variety of samples from ridge flanks (e.g., Elderfield et al. 1999; Wheat and Mottl 2000).

Marine biogenic and inorganic precipitates. Marine precipitates, ranging from biologically-secreted carbonate to the inorganic crystallization of ferromanganese minerals on the sea floor, have been of great interest in the quest for geochemical proxies of ocean chemistry and temperature. For Li isotopes, these studies have focused on either assessing temperature dependence in carbonate crystallization or on developing better tools for understanding weathering on the continents. Although but a few studies have thus far tantalized us with significant results, these will become more widespread as analytical barriers resultant from low concentrations (2 ppm average, with abundant biogenic carbonate shells possessing <1 ppm Li; Delaney et al. 1985; Hoefs and Sywall 1997; Huh et al. 1998) crumble. For example, studies dealing with small, single-species foraminiferal samples, for example, have recently become analytically feasible.

Pertinent laboratory experiments cast doubt on the viability of Li isotopes as paleotemperature tools (Marriott et al. 2004). This study showed no analytically resolvable isotopic difference among inorganic calcite precipitated from seawater composition over a range of 25°C (Fig. 17). The calcite was approximately 8.5‰ lighter than the solution from which it was precipitated, similar to the offset from natural *Acropora* coral. A sample of *Porites* coral was offset by approximately 11‰ from its seawater medium (Marriott et al. 2004), suggesting a difference in the metabolic effect in different species. Hence, use of Li isotopes as a seawater composition proxy in ancient corals, and perhaps other carbonate-secreting organisms, requires consideration of the specific creature being sampled, at least at the genus level. The only other examinations of dominantly inorganic carbonate precipitation were natural as opposed to synthetic studies, were less systematic, and arrived at different

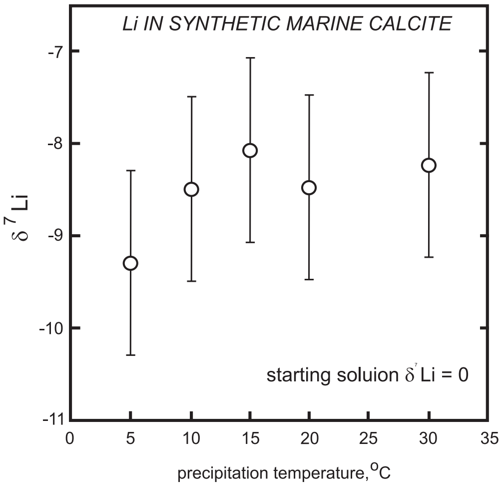

Figure 17. Plot of Li isotopic composition vs. temperature of growth for synthetic calcite crystallized from a solution containing Li from L-SVEC (Marriott et al. 2004). The results are most consistent with temperature not being a significant control on mass fractionation of Li during crystallization from aqueous solution, thus essentially eliminating Li isotopes as a paleotemperature proxy in marine carbonates.

conclusions. Chan (unpublished data, cited in Huh et al. 1998) indicated a 20‰ fractionation effect in the crystallization of Dead Sea aragonite, whereas Tomascak et al. (2003) observed no analytically-resolvable isotopic effect of crystallization of carbonate at Mono Lake, California. Clearly, additional laboratory studies, like that of Marriott et al. (2004), would be valuable in order to further map out the future of carbonate Li isotope proxies. The possible impact of crucial factors such as elemental composition of solution, carbonate ion content, and growth rate have yet to be revealed.

Foraminifera are also important in marine geochemistry studies, and Li isotopes have been measured in the shells of a variety of these organisms. The first report of this kind (You and Chan 1996) gave data for four Pleistocene samples of *P. obliquiloculata*: δ^7Li = +19.3 to +23.0 for two glacial period samples and +26.6 to +42.4 for two interglacial samples (data without blank correction). The species effect interpreted by Marriott et al. (2004) in corals has also been suggested for forams. In the study of Košler et al. (2001), core-top (i.e., Holocene) *P. obliquiloculata* samples yielded isotopic compositions close to modern seawater (δ^7Li = +27.8 to +31.1), whereas samples of *G. tumida* from the same samples had values of up to +50.5.

Samples of mixed foram species reported by Hoefs and Sywall (1997) showed a large isotopic range in samples as old as 57 Ma (δ^7Li = +3 to +41; recalculated assuming seawater with δ^7Li = +31.5). These data should be viewed skeptically, however, due to the large sample sizes and cleaning methods employed, which are not consistent with standard practices. Lithium isotope data for modern foraminifera show no such large variability. Forams of different genera (*Neogloboquadrina* and *Globorotalia*) from core tops at a single Indian Ocean site gave identical isotopic compositions of δ^7Li ~ +30 (Bruns and Elliott 1999).

Lithium isotope data from carbonate shells of other marine invertebrates have been reported. Hoefs and Sywall (1997) determined isotopic compositions of seven different species of modern bivalves from the North Sea coast. These samples had a relatively small range in δ^7Li (+15 to +21), which corresponds well to the seawater-carbonate offset from inorganic calcite and modern corals (Marriott et al. 2004).

Bulk carbonate samples have been analyzed in several studies. You and Chan (1996) determined the compositions of a pair of carbonate-rich sediment samples from ODP Site 851. The near-surface sample had δ^7Li = +6.2, whereas a sample from 196 m below the sea floor was +32.0. Carbonate-rich oozes from Hoefs and Sywall (1997) from the time period 81–9

Ma showed a large range in δ^7Li (−11 to +25). Although this study showed elemental data consistent with minimal incorporation of clays, the large sample size in this study makes the potential of contamination by small amounts of Li-rich clays a strong possibility, to say nothing of multi-species effects. The average δ^7Li of the oozes was considerably lower than of bulk foram samples over a similar time range (+8 for oozes vs. +23 for forams) and lower than oozes, marine chalk and oolites (+12.2 to +27.7) from Huh et al. (1998)—these are all consistent with the oozes incorporating variable proportions of isotopically light-enriched clays. Bulk Devonian to Cretaceous limestone samples from German localities had δ^7Li = −2 to +20 (Hoefs and Sywall 1997). Although low Li concentrations suggest a general lack of pervasive diagenetic alteration, this needs to be carefully assessed, particularly in bulk samples.

Non-carbonate marine precipitates are also used for the study of changes in ocean geochemistry over time. You and Chan (1996) reported data for three "hydrothermal" ferromanganese crusts with Li concentrations ranging from 9 to 30 ppm. The samples had δ^7Li = +25.7 to +36.6. Henderson and Burton (1999) reported a Li concentration of 4.62 ppm in a slow-accumulating Fe-Mn crust from the northwestern Atlantic and suggested that the low concentration, coupled with slow growth rate, indicates Li diffusion will be too rapid for a valid chemostratigraphy to be preserved.

Lithium isotopic fractionation on the continents

Although the processes that lead to Li isotope signatures of materials on the continents are somewhat similar to processes in the marine realm, Li isotopes in the latter are far more comprehensively studied at this point. The "starting materials" in the continents are more complex in terms of elemental and isotopic composition and history, so necessarily studies that consider materials on the continents have to compete with a larger initial level of complexity. Nonetheless, inroads have been made into understanding Li isotopes on the surfaces of the continents, particularly in quantifying the weathering process, and this remains among the most fertile areas for future study.

Continental runoff and weathering processes. Surface waters are generally dilute with respect to Li compared to groundwaters and other sub-surface fluids. Estimates of the global average Li concentration in river water range from 1.5 to 3 ppb for filtered samples (Morozov 1969; Edmond et al. 1979; Huh et al. 1998). Reported lithium contents of atmospheric precipitation range widely, and apparently depend somewhat on access to marine aerosols. Hence Li in Antarctic snow varies from approximately 0.05 ppb near the coast to <0.01 ppb inland (Ikegawa et al. 1999). Alpine snows have a lower range of reported concentrations (0.005–0.007 ppb; Bensimon et al. 2000). Limited data for Li contents of rainwater also show considerable variability. Filtered rainfall from Hawaii had 0.075 ppb Li compared to 1.01 ppb in unfiltered precipitation from the same area (Pistiner and Henderson 2003). By comparison, rainfall from eastern Maryland contained c. 0.1 ppb (Schwab et al. 1995). Such concentrations make precipitation an important consideration in the hydrologic budget of Li principally where rainfall is intensive and unweathered source rocks have low Li concentrations.

Two large studies on the geochemistry of rivers have been carried out in which Li isotope data are reported: an examination of rivers that make up c. 30% of total world discharge (Huh et al. 1998), and a detailed study of the Orinoco Basin (Huh et al. 2001). River data have been included in several other works (Chan et al. 1992; Falkner et al. 1997; Bottomley et al. 1999; Tomascak et al. 2003; Pistiner and Henderson 2003), and all are consistent with the larger, more comprehensive studies. Several important points about Li in continental runoff were manifest from these works. The global influx of Li to the oceans (δ^7Li = +6.0 to +37.5, with a flow-weighted average of +23.5) is isotopically lighter than seawater. Also, the suspended loads of rivers carry a substantial amount of the element, universally isotopically lighter than the associated dissolved loads.

How do these studies address the materials and processes that control the isotopic composition of Li in surface waters? From the works of Huh et al. (1998, 2001) a few details are clear. On a gross scale, the isotopic compositions of dissolved Li in world rivers showed no correlation with the lithology of the dominant exposed rocks of each basin. The Orinoco Basin data showed differences in the isotopic compositions of dissolved loads of tributaries draining the young Andes mountains (δ^7Li = +31.0 to +37.5) versus the ancient, low-relief craton (δ^7Li = +13.5 to +22.8) (Fig. 18). The elegant explanation from Huh et al. (2001) linked Li isotope signatures of dissolved loads not to lithology, but to fundamentally different weathering character: reaction-limited in the juvenile, high-relief Andes, transport limited in the stable craton. In the cratonic regions, weathering reactions were able to go closer to completion, and thus mean isotopic compositions were lighter. This hypothesis did not explain the isotopically heavy composition of water from the mouth of the Orinoco (δ^7Li = +33.3), however.

Similarly, rivers in Iceland (Vigier et al. 2002) showed a strong fractionation from the presumed-invariant isotopic composition of their solute sources (δ^7Li = +17.1 to +23.9, compared to approximately +4 for pristine basalts). Rivers draining terranes with the oldest exposed lavas yield low δ^7Li; a positive correlation exists between dissolved Li concentration and δ^7Li in Icelandic rivers. These observations are consistent with the data of Pistiner and Henderson (2003) for naturally weathered, historically-erupted Icelandic basalt. The outermost 4 mm of the basalt erupted in 1783 was shown to have δ^7Li 2‰ lighter than the interior of the sample, suggesting weathering over 200 yr, even in the arctic climate, lead to appreciable release of isotopically heavy Li to surface waters.

Soils are complex systems that require thorough examination in order to place data in a meaningful framework. For instance, Hawaiian soils from areas with essentially identical young basaltic bedrock and similar annual rainfall have been examined (Huh et al. 2002; Pistiner and Henderson 2003), but results are strikingly different. Huh et al. (2002) reported finding a 2× to 6× increase in Li concentration relative to unweathered basalt and variations in δ^7Li between +3 and +10 from lower to upper soil horizons. Pistiner and Henderson (2003) examined nine successive layers of volcanic soil that showed restricted variability in both

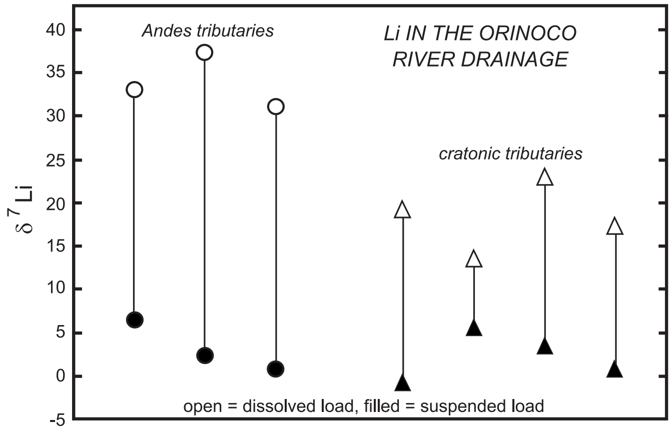

Figure 18. Orinoco River tributary Li isotope data (Huh et al. 2001). Tie lines connect samples pairs of dissolved (open symbol) and suspended load (filled symbol) for tributaries draining the Andes (circle) and those draining cratonic area (triangle). Isotopic compositions of suspended loads were similar in both cases, but the dissolved loads of Andes drainages were uniformly isotopically heavier. This difference was attributed not to lithology in the headwaters, but to transport- versus reaction-limited weathering conditions.

elemental content and isotopic composition relative to unweathered material. They suggested that heavy Li lost during weathering reactions was largely compensated for by the isotopic composition of rainfall (δ^7Li = +10.2 and +14.3, filtered and unfiltered, respectively). Both Hawaiian soil studies concurred that the influence of atmospheric Li (transporting both continental dust and seawater aerosols) was probably important to the Li isotope budget of weathered material in this environment. Also, the sequence examined by Huh et al. (2002) was considerably older than that in Pistiner and Henderson (2003) (400 ka versus 400 y).

Njo et al. (2003) presented results of a weathering study in a temperate, humid saprolite sequence in South Carolina. The unweathered metamorphosed basalt bedrock (δ^7Li = −4) showed correlated decrease in δ^7Li with higher degrees of cation leaching, to extremely light compositions (to δ^7Li = −20 in the most aluminous saprolite). Similarly, granite-bedrock saprolites in the same area exhibited strong isotopic fractionation in the same sense (from δ^7Li = +2.3 in granite to −6.8 in most weathered soil). These results suggest that soil sequences such as these may be an important missing link in understanding the continental weathering budget of Li, as they balance the heavy-Li-dominated dissolved loads in rivers, a role analogous to that played by isotopically light river suspended loads.

Pistiner and Henderson (2003) conducted laboratory experiments to examine Li isotope behavior during mineral dissolution. In the experiments, rocks were reacted with stronger acid than in natural weathering so as to minimize the potential for re-precipitation of secondary minerals. Solution recovered from partial dissolution of basalt in 0.8 M HNO_3 at 22°C and 45°C revealed no isotopic change from the initial rock. The same experimental process conducted with a Scottish granite (including chlorite, epidote, and calcite, suggesting it contained a non-igneous component from sub-magmatic alteration) reproducibly showed a removal of isotopically light Li to the solution (δ^7Li = +9.0 in starting granite, +1.6 in solution after reaction). Despite the acidity of the reacting solution, this may indicate that the precipitation of secondary minerals controlled the Li isotopic composition of the fluid.

The first report of the Li isotope geochemistry of lakes revealed the somewhat surprising result that some of the world's largest lakes had δ^7Li very similar to modern seawater (+32.1 to +34.4 in Lake Tanganyika, the Dead Sea and Caspian Sea; Chan and Edmond 1988) (Fig. 19). Later analyses of Lake Baikal found general agreement with these initial findings (δ^7Li = +28.7 to +33.4; Falkner et al. 1997), with the bulk of Baikal inputs having isotopic compositions similar to the lake itself. This is probably not generally the case: like the oceans, these lakes most commonly have inputs of Li that are isotopically lighter than their steady-state compositions. This suggests that the same processes that control the Li isotopic composition of the oceans may similarly govern the systematics of Li in these large lakes.

Hydrographically closed lakes are much more dynamic geochemical systems than the more persistent lakes, owing to the influences of climate and hydrology over short time scales. Compared to the lakes outlined above, closed lakes of the western U.S. Great Basin show highly variable modern Li isotopic compositions (δ^7Li = +16.7 to +23.7 for 5 lakes; Tomascak et al. 2003) (Fig. 19). In a detailed study of Mono Lake, California, Tomascak et al. (2003) constructed a general mass balance between fresh surface water inputs and saline spring inputs of both ambient temperature (tending toward heavy isotopic compositions) and elevated temperature (with light isotopic compositions). The data suggested the isotopic composition of the lake could be variable on short time scales as the balance between spring inputs changed. This hypothesis was tested in a set of samples from the Great Salt Lake, Utah (Tomascak et al. 2001). The lake waters, in which ^{87}Sr/^{86}Sr change correlated with decadal drought fluctuation, showed restricted Li isotope variability, weakly anticorrelated with radiogenic Sr. The study suffered from a lack of quantification of the isotopic compositions of solute source end members. Taken as a whole the lake data suggest a potential for Li isotopes to track hydrologic (and hence climatic) changes over lake histories.

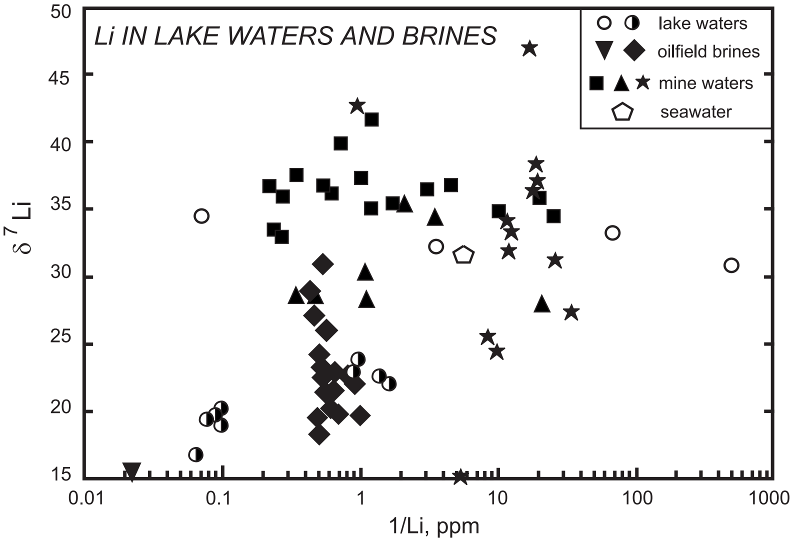

Figure 19. Plot of Li isotopic composition vs. inverse Li concentration for lakes and basinal/oilfield brines. Lakes: open circle = major global lakes (Chan and Edmond 1988; Falkner et al. 1997); semi-open circle = western U.S. closed basin lakes (Tomascak et al. 2003). Oilfield brines: inverted triangle = Williston basin, Saskatchewan (Bottomley et al. 2003); diamond = Israeli oilfields (Chan et al. 2002d). Mine waters (Canadian Shield basinal brines): square = Yellowknife, NWT (Bottomley et al. 1999); triangle = Sudbury, Ontario, area (Bottomley et al. 2003); star = Thompson, Manitoba, area (Bottomley et al. 2003). Average composition of seawater is included for reference.

Deep and shallow crustal fluids. Although comprehensive studies have yet to be undertaken, "ordinary" groundwater—ambient temperature water withdrawn from near-surface wells—exhibits a wide range in Li isotopic compositions, from extremely light (δ^7Li < -10; Gellenbeck and Bullen 1991) to similar to continental sedimentary rocks ($-10 < \delta^7$Li $< +20$; Tomascak et al. 1995a, 1999b; Tomascak and Banner 1998) to very heavy (δ^7Li $> +20$; Hogan and Blum 2003; Tomascak et al. 2003). This range no doubt reflects the variety of solute sources and fractionation processes that take place within aquifers. Saline groundwaters (0.01 to 16 ppm Li) are common in many arid to semi-arid regions. Where these have been examined, they exhibit relatively heavy Li isotopic compositions, evidently evolving from low temperature fluid-particle interactions (δ^7Li = +7.0 to +30.6; Vocke et al. 1990; Tomascak and Banner 1998; Tomascak et al. 2003).

Considering the sizeable contrast in Li isotopic characteristics between continental sediments and seawater, this system has been applied to geochemical problems related to the origins of solutes in deep sedimentary fluids, like basement and oilfield brines, or "formation waters." Bottomley et al. (1999) used Li isotopes to study Ca-chloride brines in the Miramar Con gold mine in Yellowknife, Northwest Territories, Canada. Shallow brines (c. 700 m below surface) had dissolved Li contents like saline groundwaters (39 to 99 ppb), whereas deep brines (>1000 m below surface) were considerably more saline and Li-rich (up to 4.3 ppm). The brines were isotopically fairly homogeneous, especially considering the range in Li concentration, with values equivalent to or heavier than modern seawater (δ^7Li = +33.2 to +41.8) (Fig. 19). Tritium concentrations indicate that all but the deepest mine fluids were in contact with the atmosphere within the last 40 years, but the light composition of local surface water (δ^7Li = +23.5) suggested it is not important to the process of brine formation. Combination of Li and Sr isotope and major ion concentrations suggested seawater, perhaps incorporated during the Devonian, was the ultimate source of solutes in these brines. The potential difference between Devonian and modern seawater δ^7Li was not considered.

In terms of Li content and isotopic signature, the Yellowknife mine waters are similar to waters from Sudbury (Ontario) area mines (0.05 to 2.9 ppm Li and δ^7Li = +27.9 to +42.6; Bottomley et al. 2003). Compositions of the Sudbury brines are consistent with predominance of preserved marine Li. These waters contrast with samples from mines in central Manitoba, which are dilute (Li concentration ≤ seawater) and show a wide range of δ^7Li (+15.0 to +46.9; Bottomley et al. 2003). These waters are plausibly mixtures of isotopically heavy brine (developed through fluid-rock interaction in fracture zones) and waters that had interacted with isotopically light country rocks.

Oilfield brines have been suggested as a natural resource for Li owing to their very high concentrations (Collins 1976). Chan et al. (2002d) investigated Li isotopes in oilfield brines from Israel. The Ca-chloride brines from the Heletz-Kokhav oilfield were Li-rich (1.0 to 2.3 ppm) and showed a range in Li isotopic composition lighter than modern seawater, unlike the Yellowknife basement brines (δ^7Li = +18.2 to +30.8) (Fig. 19). Evolution of these brines from seawater through a process of mineral reactions, evaporation and dilution was interpreted from the Li isotope and elemental data. The studies of Bottomley et al. (1999) and Chan et al. (2002d) succinctly illustrated the variable nature of Li in even broadly similar environments: in one case Li was taken up in secondary minerals, leaving a solution that was isotopically heavier than modern seawater; in the other case Li was interpreted to have been removed from sediments, leaving a solution isotopically lighter than seawater.

Continental hot spring waters, where essentially undiluted, have high Li concentrations (most in the range 0.1 to 10 ppm; Brondi et al. 1973; White et al. 1976; Shaw and Sturchio 1992). Although they showed a large range in Li isotopic composition (δ^7Li = +1.0 to +34.8; Bullen and Kharaka 1992; Falkner et al. 1997; Sturchio and Chan 2003; Tomascak et al. 2003), the majority of these fluids were fairly similar to marine hydrothermal vent fluids in terms of Li concentration and isotopic composition (average δ^7Li = +5.1 vs. +8.1 in vent fluids) (Fig. 14). As seen in a previous section, extensive hydrothermal alteration (that is not later overprinted by lower-temperature mineral reactions) will yield fluids with isotopic compositions that approach those of the materials from which Li is originally leached. Extant evidence from the eastern Sierra Nevada and Long Valley, California, and Yellowstone, Wyoming, are consistent with local geology having Li isotope characteristics congruent with the thermal fluids emanating from springs in these areas. The isotopically light sources of thermal waters at Yellowstone, lighter than any of the potential source materials of the area, would be satisfied by the high temperature dissolution of pre-existing alteration minerals in altered volcanic rocks, analogous to the laboratory results of granite dissolution by Pistiner and Henderson (2003).

Combinations of mineral reactions at lower temperatures and mixing with more dilute fluids are likely to result in the variations in concentration and isotopic composition in many of the continental thermal spring waters but not seen in their marine relatives. The extreme manifestation of this difference may have been generated in the dilute hot spring waters from around Lake Baikal, whose heavy isotopic compositions required extensive re-equilibration at temperatures 100–150°C (Falkner et al. 1997).

Minerals derived from evaporation of saline solutions have not been extensively examined. Evaporitic salts from the western U.S. Great Basin concentrated ^{7}Li (δ^7Li = +31.8 to +32.6; Tomascak et al. 2003). Evaporation of thermal waters from Yellowstone yielded travertine with extremely low δ^7Li (−4.8; Sturchio and Chan 2003), offset from its coexisting fluid by −11.1‰. Such evaporites, where preserved in the sedimentary record, could afford an opportunity to examine variations in spring water compositions and hence information on hydrothermal processes over time.

Environmental tracers. Given the interest in the hydrological community in developing new geochemical tracers of near-surface water flow, it is perhaps unexpected that Li isotopes have seen such little exploitation in this field (Bullen and Kendall 1998), especially given the widespread use of Li as a conservative solute tracer (e.g., Bencala et al. 1990). The studies that have used Li isotopes in environmental capacities have demonstrated significant spread in composition between end-members, indicating that the system is well-suited for discerning solute sources in areas of geological and hydrological complexity. Also, as noted above, the strong anthropogenic signature of "processed" Li (Qi et al. 1997a) that is likely to be widespread among sources of industrial waste, suggests that Li isotopes could be well-suited in tracing point-source pollution (Bullen and Senior 1992; Hogan and Blum 2003).

Gellenbeck and Bullen (1991) showed that possible groundwater pollutants in an Arizona field site showed isotopic contrast of c. 40‰ (ground water with δ^7Li ~ −21; cow manure leachate δ^7Li ~ +19). In a study of groundwater flow, Bullen and McMahon (1992) used Li isotopes to gain insight into the nature of chemical reaction along a flow path. They noted variations in δ^7Li that were interpreted to result from dissolution of marine-derived minerals in one part of the aquifer (providing isotopically heavy Li relative to recharge), and from ion exchange in more distal parts of the aquifer (imparting isotopically light-enriched Li). Similarly, Tomascak et al. (1995a, b) examined variations in stream water Li isotopic composition from before, during and after a rain storm in eastern Maryland. The flushing of a pulse of isotopically heavy-enriched water on the increasing limb of the storm hydrograph indicated that easily-extracted Li, possibly anthropogenic in origin, was rapidly removed from adjacent agricultural fields at the onset of overland flow generation.

In a study of groundwater in and around the Fresh Kills landfill, New York, Hogan and Blum (2003) used Li isotopes to define mixtures of seawater and isotopically lighter fresh water. Waters extracted from wells in the landfill had variable δ^7Li (+22.0 to +53.9). Mass fractionation of diluted seawater-source groundwaters, presumably during fluid-particle interaction in unconsolidated sediments, was interpreted to have produced samples with isotope/concentration systematics that did not follow simple mixing of fresh water and seawater. Thus, in areas that have an initial isotopic difference between end-member compositions—and these many be commonplace—Li has the potential of demonstrating both solute sources and pathways of chemical evolution of groundwaters.

SIGNIFICANCE OF LITHIUM ISOTOPES IN THE BULK EARTH

Among the most glaring deficits in our present compilation of fundamental Li isotope data is in meteorites. To an extent this deficit results from the low Li concentrations of most stony meteorites (commonly <2 ppm; Heier and Billings 1972; Anders and Grevesse 1989), and hence the need to process large samples for bulk analysis. The lack of comprehensive studies of Li isotopes in meteorites is particularly striking in view of the progress made in understanding galactic Li through observational astronomy over the last two decades. Lithium isotopic fractionation during astration is considered to have produced the background heavy Li of the Sun and solar wind (^{7}Li/^{6}Li > 30; Boesgaard and Steigman 1985; Ritzenhoff et al. 1997; Chaussidon and Robert 1999). Certain observations of Li in interstellar space indicate a very light isotopic composition (^{7}Li/^{6}Li ~ 2; Knauth et al. 2000), consistent with the composition predicted from collisions between atoms in space and high energy galactic cosmic rays (Reeves et al. 1970). Meteorites and terrestrial materials appear to have intermediate Li isotopic compositions (^{7}Li/^{6}Li ~ 12; Krankowsky and Müller 1967; Chaussidon and Robert 1998). How this value developed is unclear, so more detailed Li isotopic studies of meteorites and their inclusions might be able to resolve key details about early Solar system evolution.

There have been many studies on Li isotopes in meteorites, but few since the development of high precision techniques. Of the earlier studies, most agree that meteorites do not show gross isotopic variations, but there are exceptions, especially in some studies of refractory inclusions (Klossa et al. 1981; Schirmeyer et al. 1997). The total extent in Li isotopic data from bulk meteorite samples falls within the range determined by Chaussidon and Robert (1998) for *in situ* analyses of three chondrules from the LL3 chondrite Semarkona (δ^7Li = +10 ± 20; recalculated assuming ^{7}Li/^{6}Li of L-SVEC = 12.175). James and Palmer (2000a) analyzed Li in the CI1 chondrite Orgeuil (δ^7Li = +3.9). McDonough et al. (2003) reported Li isotopic compositions for a range of petrologic types of chondrites. Petrologic type 1 – 2 carbonaceous chondrites (highly hydrated bodies) have δ^7Li in the terrestrial MORB range (+1 to +4), whereas type 3 – 4 carbonaceous and ordinary chondrites show a range of compositions (δ^7Li = −3.6 to +3) (Fig. 20). These data permit the interpretation that chondrites carry Li isotopic records of parent body processes involving fluid-solid interaction, generating isotopically heavy low temperature minerals, but they could equally be interpreted to reflect heterogeneity of source materials in the early Solar system. Using both bulk and spatially resolved analytical techniques it appears that Li isotope studies of meteorites may yield important information about early solar system and planetary processes.

As demonstrated by Teng et al. (2004), the mantle Li isotopic composition governs the bulk Earth composition, and hence an accurate quantification of the mantle is essential. Published estimates of Li isotopes in the bulk Earth have used values consistent with modern ocean floor basalts (δ^7Li ~ +6: Chaussidon and Robert 1998; δ^7Li ~ +4: Teng et al. 2004). However, the present day mantle isotopic composition is still rather murky, as described above. Basically, it is not clear if one small range exists to describe this reservoir. Although the MORB range may be as small as 5‰, it has been suggested that the actual uncontaminated MORB value has δ^7Li closer to +1.5, and that the range to higher values indicates subtle alteration (Moriguti and Nakamura 1998b). This would be consistent with the findings of

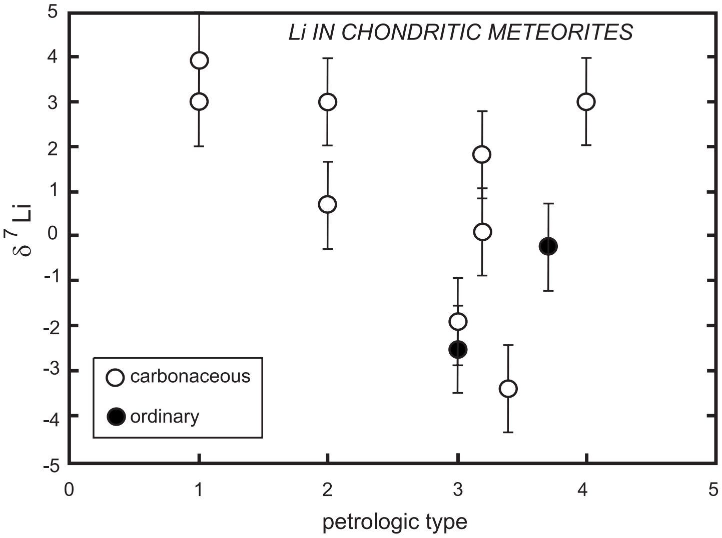

Figure 20. Lithium isotopic compositions of chondritic meteorites relative to their petrologic type (James and Palmer 2000a; McDonough et al. 2003). The extant data indicate lighter and more variable isotopic compositions in higher petrologic types of meteorites, those with the least record of hydrous parent body alteration.

Elliott et al. (2003). The data set for unmetasomatized peridotite xenoliths is too sparse to aid much in this controversy at present. As measurement reproducibility betters the ± 0.5‰ barrier, it is just a matter of analyzing the most appropriate samples before such questions can be answered and an accurate estimate can be made of the Li isotopic composition of the mantle, and hence of the bulk Earth.

CONCLUSIONS AND FUTURE DIRECTIONS

Although Li isotope study is still in its childhood in terms of mapping out the possibilities of the system, it is clear that many areas should benefit from further research. Based on the data generated to date, several general conclusions can be drawn and specific directions can be suggested:

1. There is no consensus on the specific mantle Li isotopic composition. Currently reported values for normal MORB suggest a range (δ^7Li = +1.5 to +5.6), but no single study has shed light on whether this range is an intrinsic feature of the upper mantle, to what extent cryptic contamination plays a role, or if bulk samples can only define an average for a reservoir with broad heterogeneity.
2. Given the fractionation of Li isotopes by processes near the Earth's surface, fractionated materials should be returned to the mantle throughout geologic time. There is apparent correlation between mantle heterogeneity in radiogenic isotopes and Li. Thus far the incorporation of material with δ^7Li < MORB, as predicted based on studies of subduction zone lavas and eclogites, is not evident in oceanic lavas. An initial attempt to track this recycling process over Earth history with peridotite xenoliths suggested an increase in δ^7Li by approximately 4‰ since the mid-Archean.
3. The extent to which isotopic fractionation occurs at sub-1000°C temperatures in magmatic and regional metamorphic systems is unstudied in detail, but limited natural and experimental data in granitic systems suggest that measurable fractionation may occur under these conditions. This fractionation might be applied in studies of magmatic and ore evolution, either for thermometry or mineral deposit exploration.
4. Clastic sediments are reservoirs of information about weathering processes, but are sufficiently complex that no study has yet to realize their potential. Despite a number of initial reports of relatively isotopically heavy samples, the majority of data for clastic sedimentary rocks have an average δ^7Li ~ 0, equivalent to the estimated average isotopic composition of the continental crust.
5. Although ocean water is well mixed with respect to Li, and many laboratories measure Li isotopes in seawater, the range in values reported in the literature (δ^7Li = +29.3 to +33) cast some uncertainty on this reservoir. As precision of analytical methods improves, a check of the viability of the "seawater standard" should be carried out.
6. Initial experiments on the viability of marine (as well as lacustrine) carbonates as geochemical proxies have produced encouraging results toward the goal of tracing temporal changes in the Li isotopic composition of the Earth's surface. Inorganic and biogene carbonate precipitation appears to favorably incorporate light Li, but this fractionation is not temperature sensitive. A better understanding of metabolic effects of invertebrate species will be necessary. More laboratory experiments and controlled natural studies should address the prospective of Li isotopes in assessing

compositional changes in waters over time. Modern analytical techniques, permitting precise analysis of small (≤1 ng Li) samples, will permit the examination of detailed populations of these low concentration materials.

7. Weathering releases isotopically heavy Li to the near-surface environment, regardless of the intensity of chemical weathering. Much of this Li goes to stream flow, contributing to the riverine average δ^7Li ~ +24. The detailed histories of weathering products on the continents--sediments and soils--can be complex, but studies of simple systems suggest retention of isotopically light material, and hence an evolution of the continents toward lower δ^7Li over Earth history.
8. Consensus should be reached on the interpretation of Li isotope data for chondritic meteorites. Can bulk planetary Li isotopic compositions be accurately estimated from meteorites, or do these objects preserve only parent body near-surface or metamorphic histories? Are either of these possibilities viable? Detailed, high precision studies should permit this assessment.

This is an exciting time for the study of Li isotopes, given the rapidly diminishing sample size boundary with a consequent increase in precision, allowing heretofore unachievable inroads into areas where isotopic variations are small. The capacity to make routine, high precision measurements is now possible by a number of techniques at a large number of laboratories. Although the community needs still be constantly vigilant that chemical preparation of samples imparts no laboratory fractionation effects, these problems are acknowledged and actively scrutinized by all engaged in the work. To continue to expand the analytical frontier, emphasis should be placed on the reproducibility of data for replicates (that is, complete reprocessing and reanalysis of a sample material) and on cross-checking and collaborating between laboratories and among different instrumental techniques.

Although certain areas still benefit from even modest-precision Li isotope analysis (i.e., where end-member compositions are sufficiently disparate), assessing small variations in Li isotopic composition will be important to a variety of future studies. Studies of xenoliths have the prospect of shedding light on: the nature and origin of chemical heterogeneity in the mantle over the course of Earth history, the process by which material is transferred from slab to mantle during subduction, and how the continental crust has grown. Analysis of marine carbonate samples (e.g., small single-species foram populations) has the potential of further defining the chemical evolution of the oceans and highlighting the style of continental contributions to the oceans, ultimately linked to climate change. Minerals generated during weathering on the continents (and by experimental simulations of these processes) will define in clearer detail the prospects for Li isotopes as tools in studying near-surface geochemical processes and fingerprinting these in the geological record.

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