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Review of the Lithium Isotope System as a Geochemical Tracer

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Abstract

Lithium isotopes have many advantageous characteristics as geochemical tracers for a wide range of geological processes, covering fluid/melt-mineral interactions from the Earth's surface to the mantle. The latest developments in Li isotope geochemistry, in terms of measuring techniques, major geochemical reservoirs, the contrasting behaviors during near-surface weathering, and crust/mantle cycling of materials in subduction zones, as well as the signature of convective mantle, and controlling factors in Li isotopic fractionation are briefly reviewed in this article. With better quantification of partition coefficients (mineral-melt/fluid) and fractionation factors (such as temperature and diffusion coefficients), the Li isotope system will become a powerful geochemical tracer in future studies.

Introduction

LITHIUM ISOTOPE GEOCHEMISTRY is a burgeoning research field, and has developed rapidly in recent years with the advance of mass spectrometric techniques that have overcome intrinsic difficulties in isotopic measurement of this light element. It was first used effectively following the development of a borate technique for measurement by thermal ionization mass spectrometry (TIMS) (Chan, 1987), and further enhanced by the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Tomascak et al., 1999a). There is a growing interest in Li isotope geochemistry as the nature of its potential to reveal important information covering a wide range of geochemical processes, such as continental weathering (Huh et al., 1998, 2001), alteration of the oceanic crust (Chan et al., 1994, 2002a; Seyfried et al., 1998), and crust-mantle cycling of materials (Moriguti and Nakamura, 1998a; Tomascak et al., 1999b, 2002; Zack et al., 2003; Elliott et al., 2004; Woodland et al., 2004).

Lithium has many favorable characteristics as a potential geochemical tracer. For example, the radius of Li^+ is similar to that of Mg^{2+}, so it can substitute for magnesium in olivine, enstatite, and diopside (Seitz and Woodland, 2000). This behavior contrasts with that of the large alkali ions (K, Rb, and Cs) and means that Li behaves like a moderately incompatible element during partial melting of mantle rocks. Li can be highly soluble in H_2O-rich fluids, but has $D_{solid/melt}$ values between 0.1 and 1.0 for most mantle minerals (Ryan and Langmuir, 1987; Brenan et al., 1998a, 1998b; Seitz and Woodland, 2000; Seitz et al., 2004). The large mass differences (~15%) between its two stable isotopes, ^6Li and ^7Li (their abundances are 7.5% and 92.5%, respectively) produce large isotopic fractionation in terrestrial systems, from –20 to +40‰ (Hoefs and Sywall, 1997; Rudnick et al., 2004), up to 80‰ variation of $^7Li/^6Li$ (Rudnick and Nakamura, 2004). Li isotopes appear to be strongly fractionated in low-temperature systems and highly variable in altered oceanic crust, hydrated mantle rocks, and eclogitic slabs (Chan and Edmond, 1988; Chan et al., 1994; Decitre et al., 2002; Pistiner and Henderson, 2003; Zack et al., 2003; Moriguti et al., 2004; Rudnick and Nakamura, 2004). With more people becoming interested in Li isotope geochemistry, it is important to have a comprehensive review of the current research state in this area. The purpose of this paper is to briefly summarize recent developments in Li isotope geochemistry, and to better understand its potential to serve as a geochemical tracer in crust/mantle recycling, mantle metasomatism, and near-surface processes.

Measurements and Compositions of Li Isotopes

Measurement of Li isotopic ratios

Like other stable isotope systems, variations in Li isotopes are reported in terms of parts per mil deviations from an international standard and expressed in a delta notation:

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$$\delta^7\text{Li}\ (‰) = [(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000.$$

The standard is conventionally the U.S. National Institute of Standards and Technology (NIST) high-purified Li_2CO_3 reference material NIST L-SVEC, which has $^7Li/^6Li = 12.02 \pm 0.03$ (Flesch et al., 1973). In early literature, both δ^7Li and δ^6Li have been used, but increasingly the δ^7Li has become standard. In this case, positive values of δ^7Li reflect heavier isotopic ratios, in keeping with other stable isotope systems. Measurements reported as δ^6Li can be readily converted to δ^7Li, yielding a value that generally closely approximates the corresponding δ^7Li.

Mass spectrometric techniques for Li isotopic measurement in geological materials have been well reported by Chan (2004). The first precise measurements of Li isotopic ratios were performed using TIMS (Chan, 1987; Moriguti and Nakamura, 1998b; James and Palmer, 2000a). However, the TIMS technique is time consuming and suffers from a complicated ion exchange procedure to obtain pure Li solutions (Moriguti and Nakamura, 1998b). Although Li is efficiently ionized by solid source mass spectrometers, highly reproducible isotopic ratios are more difficult to obtain by this technique than for the gas-source machines used to measure oxygen isotopes. The reproducibility of Li isotope measurements has thus lagged behind oxygen isotope measurements, typically ~0.5–1‰ compared to ~0.05‰ (2σ standard deviations). This has hampered application of Li isotopes to studying mantle processes, where variations in Li isotopic ratios are only a few per mil, but it has been sufficiently precise for documenting the larger isotopic variations in the near-surface environment. Despite an unstable instrumental fractionation, TIMS can yield very stable isotopic data during a run, and requires no external standard with a proper loading form. As a result, a large fraction of high quality data has been generated by TIMS (e.g., Huh et al., 1998; Moriguti and Nakamura, 1998a, 1998b; James et al., 1999; James and Palmer, 2000a; Huh et al., 2001; Chan, 2004).

The advent of multiple-collector ICPMS offers the opportunity for small concentrations of Li to be analyzed to high precision (Tomascak et al., 1999a; Nishio and Nakai, 2002; Bouman et al., 2004; Magna et al., 2004), which is highly significant for documenting Li isotopic variations in the mantle. The precisions of TIMS and ICP-MS for natural samples are comparable and the 2σ uncertainty of ICP-MS is close to 0.5‰ (Tomascak, 2004). In contrast with TIMS, ICP-MS produces a large fractionation and required correction using bracketing standards.

Other techniques for the measurement of Li isotopes include secondary ionization mass spectrometry (Chaussidon and Robert, 1998) and laser-excited atomic fluorescence spectroscopy (Smith et al., 1998). Although these methods have relatively low precision (1σ standard deviations ~3‰), their in situ spatial analytical ability is unique, and have been used to study minerals from mantle xenoliths (Bell et al., 2004; Hervig et al., 2004; Ottolini et al., 2004; Woodland et al., 2004), pyroxenes from meterorites (Beck et al., 2004; Barrat et al., 2005), synthetic minerals from experimental studies (Richter et al., 2003; Lundstrom et al., 2005) and glass inclusions in basalts (Kobayashi et al., 2004).

Li isotopic compositions of major reservoirs

A number of studies, starting with the pioneering work of Chan et al. (1987), have established that large fractionations of Li isotopes occur in the rock-H_2O system. The rapidly accumulating data support some general constraints on the Li isotopic character of the major geochemical reservoirs, as summarized in Tomascak (2004), which thus far is the most comprehensive review of Li isotope geochemistry, including data from both published literature and meeting abstracts. The ranges of Li isotopic ratios in major reservoirs are compiled in Figure 1.

The mantle, as represented by fresh basalt (i.e., MORB, and Hawaiian basalt, the later being representative of OIB), appears to have average δ^7Li values of about +3 to +5‰ (Fig. 1). The upper mantle is inferred to have a δ^7Li equal to that of average MORB, ~ +4 ± 2‰ (Chan et al., 1992, 2002b; Tomascak and Langmuir, 1999), because Li isotopes do not fractionate significantly at the high temperatures of mantle melting, >1000°C (Tomascak et al., 1999b). However, the mantle is not homogeneous. It has been shown by Nishio et al. (2004) that some mantle-derived peridotites have extremely light δ^7Li values down to –17‰. *In situ* Li isotopic analysis of glass inclusions in olivine phenocrysts from Hawaiian lavas also shows extremely large δ^7Li ranges, from –11 to +5‰ (Beck et al., 2004). Two oceanic island basalts reported by Ryan and Kyle (2004) have heavy δ^7Li values (8‰ and 10‰). These observations indicate the high heterogeneity of the mantle.

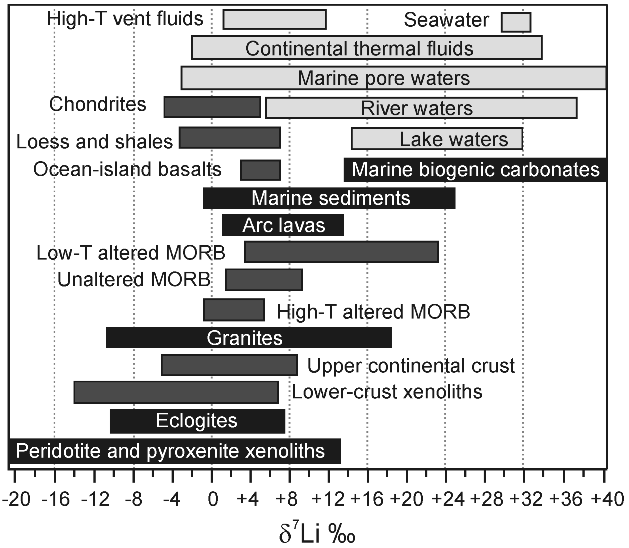

FIG. 1. Li isotopic composition of various reservoirs. Data sources: seawater (Chan and Edmond, 1988; You and Chan, 1996; Moriguti and Nakamura, 1998b; Tomascak et al., 1999b; James and Palmer, 2000a; Rudnick et al., 2004); river water (Huh et al., 1998, 2001); high-temperature vent fluids (Chan et al., 1993; Foustoukos et al., 2004; Kisakurek et al., 2004); arc lavas (Moriguti and Nakamura, 1998a; Tomascak et al., 2000, 2002; Chan et al., 2002b); oceanic island basalts (Tomascak et al., 1999b; Chan and Fery, 2003); fresh MORB (Chan et al., 1992, 2002b; Moriguti and Nakamura, 1998a; Tomascak and Langmuir, 1999); altered MORB (Chan et al., 1992, 2002a); marine sediments (Chan et al., 1994; Zhang et al., 1998; James et al., 1999; Chan and Kastner, 2000; Bouman et al., 2004); loess, shales, and upper continental crust (Teng et al., 2004); eclogite data (Zack et al., 2003); peridotite and pyroxenite xenoliths (Tang et al., unpubl. data; Tomascak, 2004); other reservoirs (Tomascak, 2004).

Despite a range beyond cited analytical uncertainties (δ^7Li ~ +29.3 to 33.3‰) (Rudnick et al., 2004, and references therein), seawater has a relatively homogenous Li isotopic composition, consistent with the relatively long residence time of Li in the oceans (Li, 1982), and is isotopically quite heavy, with an average of δ^7Li ~ +32‰ (Chan and Edmond, 1988; You and Chan, 1996; Tomascak et al., 1999a; James and Palmer, 2000a). Similarly, marine sediments have a wide range of δ^7Li (–1.6 to +25‰) (Chan et al., 1994; Zhang et al., 1998; James et al., 1999; Chan and Kastner, 2000; Bouman et al., 2004), whereas most altered basalts and marine sediments have δ^7Li values that are generally intermediate between that of the mantle and seawater, due to the uptake of heavier seawater Li.

Compared to the mantle, the upper continental crust has an even lighter δ^7Li of 0 ± 2‰ (Teng et al., 2004), obtained by dissolved and suspended river loads (Huh et al., 2001), shales, loess, and granites. This isotopically light composition is inferred to reflect the influence of weathering, with heavy Li partitioned into surface waters, leaving lighter Li in the weathered residua, which is supported by the isotopically heavy compositions of groundwater (Hogan and Blum, 2003), the isotopic fractionation between dissolved and suspended loads of rivers (Huh et al., 2001) and experimental data (Pistiner and Henderson, 2003). Orogenic eclogites (in the deep crust) have δ^7Li values lighter than the upper crust, which reflect loss of heavy Li during metamorphic dehydration of subducting slab (Zack et al., 2003). Rivers show a large range in δ^7Li, encompassing mantle and seawater values. The important processes affecting river-dissolved Li isotopic compositions are fractionation between solution and secondary minerals, and thus the intensity of weathering (Huh et al., 1998).

Li Isotopes as Geochemical Tracers

Li isotopes are significantly fractionated near the Earth's surface (Huh et al., 2001, 2004; Pistiner and Henderson, 2003; Kisakürek et al., 2004; Rudnick et al., 2004). The legacy of this process provides a robust tracer of surface material that is returned (recycled) to the mantle (Weaver et al., 1986; Brenan et al., 1998b; Moriguti and Nakamura, 1998a; Zack et al., 2003; Bouman et al., 2004). Thus, a comprehensive understanding of Li isotope fractionation during weathering is necessary for using Li isotopes to trace chemical cycles and igneous processes. In this section, the behaviors of Li isotopes in the near-surface environment are outlined in order to understand controls on Li isotope fractionation, and to present geochemical applications addressing current geologic problems.

Tracing weathering processes

Li has several advantages as an isotope tracer of weathering. Being a fluid-mobile trace element, Li tends to be widely distributed in the Earth's crust; Li is present only in the +1 valence state, so its isotopic composition is not influenced by redox reaction.

During weathering, the lighter isotope ^{6}Li is preferentially retained in the solid phase whilst ^{7}Li goes into solution (Huh et al., 1998, 2001, 2004; Pistiner and Henderson, 2003; Kisakürek et al., 2004)—i.e., heavy Li is leached from rocks due to weathering at the Earth's surface. Thus river waters have heavy Li isotopic compositions compared to the original bedrock and associated suspended load (Huh et al., 2001). Moreover, fractionation seems to be only slight in stable and warm climates where weathering is slow, but it may become large in tectonically active regions where weathering is rapid (Huh et al., 2001, 2004). Fractionation of Li isotopes can also occur during sorption onto mineral surfaces (James and Palmer, 2000b; Pistiner and Henderson, 2003). Different minerals have different ^{7}Li/^{6}Li ratios, so incongruent weathering can produce significant isotope shifts (Pistiner and Henderson, 2003; Huh et al., 2004).

The behavior of Li isotopes during continental weathering demonstrates that processes affect the isotopic composition of regoliths. For example, Kisakürek et al. (2004) showed that a thick laterite developed on the basaltic flows contains a significant aeolian input of isotopically light Li, presumably derived from the weathering of crystalline basement. Rudnick et al. (2004) reported that extreme isotopic fractionation (δ^7Li down to –20‰) during the development of saprolite is accompanied by input of heavier Li from ground water.

The Li isotopic composition of river water is not highly sensitive to that of the bedrock, in contrast to radiogenic isotopic ratios used to monitor chemical weathering (Huh et al., 1998). There is thus promise in using the evolution of the Li isotope ratio of seawater to assess past changes in the intensity of continental weathering (Raymo et al., 1988). In other words, it might be anticipated that a change to lighter Li isotopic compositions in ancient oceans would reflect lower weathering rates in the past. Whereas the general process of Li isotopic fractionation at the surface is clear, a more detailed understanding of their behavior during weathering, transport, and incorporation into the geological record is required before Li isotopic ratios can be used as weathering proxy (Henderson, 2002). An exciting prospect for the future is attracting an increasing number of groups to investigate this potential (Hoefs and Sywall, 1997; Kosler et al., 2001; Pistiner and Henderson, 2003; Marriott et al., 2004a). For evaluating their use as a paleo-environmental indicator, Marriott et al. (2004b) measured the δ^7Li and Li/Ca ratios in calcite and aragonite as a function of salinity, and concluded that biological controls did not influence the incorporation of Li into biogenic carbonates. Thus δ^7Li in carbonates might provide a faithful record of Li isotopic composition of seawater through time (provided post-depositional processes have not influenced δ^7Li).

Partitioning of Li between water and clays can produce major isotopic fractionation in the marine system (Chan et al., 1992; Seyfried et al., 1998; Zhang et al., 1998). Unlike radiogenic isotope systems (e.g., ^{87}Sr/^{86}Sr), where seawater represents an intermediate mix of hydrothermal input (mantle-dominated signature) and river water (continental signature), seawater has an Li isotope ratio heavier than its inputs (Fig. 2). This paradox can be explained by the low-temperature alteration of the oceanic crust to hydrous minerals (such as smectite). These alteration products are important sinks for oceanic Li and also preferentially uptake ^{6}Li from seawater during this process (Chan et al., 1992, 2002a). Enhanced removal of ^{6}Li from the oceans results in a heavy seawater composition of δ^7Li ~ +32‰ (James and Palmer, 2000a), heavier than its average input. Although the Li gained by the alteration materials is lighter than mean river water, δ^7Li < +23‰ (Huh et al., 1998), it is nevertheless heavier than fresh oceanic basalts, δ^7Li ~ +3‰ (Chan et al., 1992; Moriguti and Nakamura, 1998a).

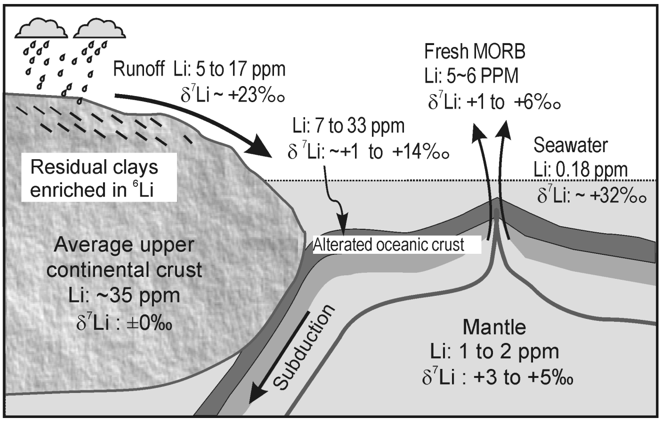

FIG. 2. Schematic illustration of Li isotope systematics in the hydrological cycle, modified from Elliott et al. (2004). Data sources are the same as those identified in Figure 1.

As summarized in Elliott et al. (2004), weathering of continental rocks results in the heavy Li isotopic compositions of river water that feeds the oceans. Low-temperature alteration of oceanic crust then makes seawater heavier than river water (Fig. 2). The process of increasing the δ^7Li of altered oceanic crust, as part of the low-temperature Li cycle, showing a distinctive signature to the oceanic plate that can be used to trace it. On the other hand, seawater Li concentrations and δ^7Li show potential as proxies for global silicate weathering processes, inasmuch as rivers presently contribute ~50% of the Li input to the oceans (Kisakürek et al., 2005).

Tracing crust/mantle recycling

In terms of solid Earth geochemistry, one of the great expectations for the fledging field of Li isotope geochemistry is to elucidate the complicated process of recycling of oceanic crust in subduction zones. Lithium isotopes have great potential to trace crust/mantle recycling in virtue of unique physicochemical characteristics: (1) Li can be concentrated in crust materials compared to mantle materials reflecting its moderate incompatibility during partial melting and fractional crystallization (Ryan and Langmuir, 1987; Brenan et al., 1998a). (2) It is expected that Li is strongly enriched by seawater weathering and alteration, and then released in the subduction zone due to its strong mobility in fluid-related processes, such as weathering and alteration on the sea floor, during metamorphism in the subduction zone (Seyfried et al., 1984; You et al., 1996; Brenan et al., 1998b), and attending partial fusion and magmatic crystallization (Richter et al., 2003). (3) Large mass differences between its two isotopes lead to large isotopic fractionations in terrestrial systems (Hoefs and Sywall, 1997; Rudnick and Nakamura, 2004), which develop during low-temperature alteration associated with water at the Earth's surface. In contrast, Li isotopic fractionation is extremely small when the temperature exceeds 350°C (Chan et al., 1994; Tomascak et al., 1999b), and thus is insignificant in magmatic processes, which suggests that Li isotopic composition in mantle-derived magmas may directly indicate the composition of source materials except for later modification. Hence, the Li isotopic variations in igneous rocks, especially those derived from the mantle, may indicate the involvement of surface material subducted into the source regions, preserving the variable Li isotopic compositions imprinted by water/rock interactions under near-surface conditions.

In contrast to earlier work on the Izu arc (Moriguti and Nakamura, 1998a), Moriguti et al. (2004) reported that d^{7}Li did not change systematically across the Northeast Japan arc, where all lavas had MORB-like δ^7Li values. They attributed the differences in Li systematics between the Northeast Japan arc and the Izu arc to differing extents of Li isotopic fractionation due to differing physical characteristics in the subduction zone, such as the thermal structure of the subducting slab and subduction angle. In a similar study, Leeman et al. (2004) also found MORB-like δ^7Li across the Cascades arc in southern Washington. They attrib-

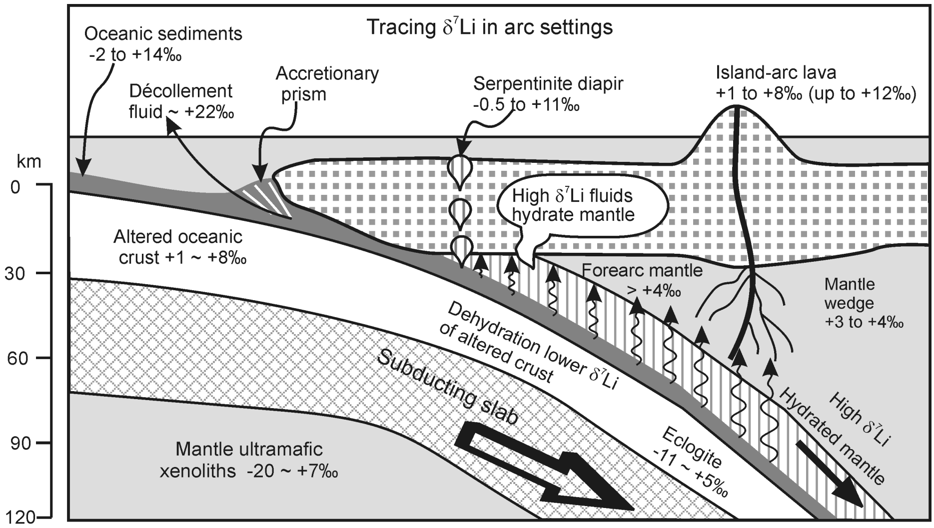

FIG. 3. Schematic illustration of Li isotope systematics in a subduction-zone setting, modified from Zack et al. (2003). Heavy Li in fluids from the décollement zone and serpentinite diapers reflect Li isotopic fractionation during the dehydration of altered oceanic crust. The high δ^7Li of fluids escaping the slab at low temperatures likely enrich the forearc mantle wedge and hydrate the adjacent mantle in ^{7}Li, which may be the sources of arc lavas. Thus, high δ^7Li values in arc lavas (up to +12‰) might be explained by incorporation of the forearc mantle. Data sources are the same as those identified in Figure 1.

uted the lack of obvious slab contribution to the high temperatures, causing efficient dehydration in the forearc. Evaluating the contribution of slab components to subduction-zone lavas indicates that not only chemical characteristics of the subducted slab but also the physical, as well as chemical characteristics of the subduction zone could affect the Li isotopic compositions of the slabs, producing heterogeneity of the mantle.

Assuming that isotopically fractionated Li can traverse the subduction zone, one might see variable δ^7Li in intraplate magmas that are suggested to sample ancient, recycled oceanic lithosphere. Ryan and Kyle (2004) found intraplate basalts with MORB-like δ^7Li in Antarctica, but δ^7Li changed during differentiation. Because Li does not fractionate during crystal fractionation (Tomascak et al., 1999b), they suggested that the changing isotopic composition reflects assimilation of lithospheric Li (Ryan and Kyle, 2004). In contrast to the rather constant δ^7Li values seen in the whole-rock data, widely varying δ^7Li (–10 to +8‰) in glass inclusions in olivines from Hawaiian lavas was reported (Kobayashi et al., 2004). The large isotopic variations were attributed to heterogeneities in the source of the lavas, which were likely introduced from recycled components.

Up to now, the use of Li isotopes in studying island-arc processes is a very new tool in geochemistry. Most studies have focused on the volcanic output of Li at subduction zones (Moriguti and Nakamura, 1998a; Chan et al., 2002b; Tomascak et al., 2002), and several articles on the slab input of Li—i.e., marine sediments and the altered downgoing oceanic crust (Bouman et al., 2004; Elliott et al., 2004).

Altered oceanic crust has a heavy Li isotopic composition. Heterogeneous distribution of subducted, altered oceanic crust in the mantle will result in the heterogeneity of Li isotopic ratios. The accumulating Li isotope dataset of mantle-derived materials indicates a significant range in Li isotopic ratios, which provides powerful evidence for the widespread distribution of recycled material in the convecting mantle. However, the passage of Li from surface to depth is not simple and is strongly affected by the subducting processes (Fig. 3). Water is successively released during subduction, first by porosity reduction during compaction and then through a series of prograde dehydration reactions as the descending slab becomes hotter (Kerrick and Connolly, 2001a, 2001b). As in the near-surface environment, the partitioning of Li between residual solid and liquid will result in isotopic fractionation (Chan and Kastner, 2000). Although isotopic fractionation diminishes with increasing temperature, there is still significant inferred (Chan et al., 1993; Huh et al., 1998) and measured (Seyfried et al., 1998) Li isotopic fractionation between minerals and water during hydrothermal circulation at ~350°C. Fluids, which are expelled during subduction and so-called décollement, are isotopically heavier than the associated sediments (Chan and Kastner, 2000). Analyses of serpentinites show a wide range of δ^7Li (Ryan et al., 2001), which clearly indicates that heavy subducted Li shifts to the oceans and shallow mantle wedge, but the amount of Li shifted from the slab in the early dehydration processes is estimated to be a minor fraction of the total Li subducted (Chan and Kastner, 2000). The forearc mantle wedge may form a sink for the high δ^7Li released from the subducted oceanic crust (Tomascak et al., 2002; Zack et al., 2003), which may be the source for serpentinites with high δ^7Li.

A few arc lavas have Li isotopic ratios heavier than MORB (Tomascak et al., 2002) (Fig. 1), which implies that little of the budget of heavy Li in the subduction zone is lost to the surface. This can be related to the relative affinity of Li for mantle phases. Due to its similar ionic radius to Mg, Li can occupy the abundant Mg lattice sites available in the mantle, although experiments show that Li is moderately incompatible in melt/fluid (Brenan et al., 1998a, 1998b). Thus heavy Li, initially carried from the slab in aqueous fluids, isotopically reequilibrates with the mantle (Tomascak et al., 2002). The heavy Li isotopic signature from the slab is effectively transferred to the cold portion of mantle lying above the slab (Fig. 3).

The extremely light Li isotopic ratios in Alpine eclogites provide evidence for the loss of heavy Li from the subducted oceanic crust during dehydration (Fig. 3). Zack et al. (2003) argued that the low δ^7Li values were likely produced by isotopic fractionation through Rayleigh distillation during dehydration of clays or chlorite at early stages of metamorphism. The Alpine eclogites thus represent the light complement of the heavy isotopic signature that left the slab to reside in the overlying mantle. These suggestions are consistent with isotopically heavy Li being released into the forearc mantle wedge, whereas an isotopically light component is subducted deeply and may form a distinct mantle reservoir that could be sampled by plume-related magmas.

The signatures of Li isotopic compositions in the subduction zone can be used to trace mantle convection. Deep-subducted altered oceanic crust becomes isotopically light, while the mantle adjacent to the slab becomes heavy (Fig. 3). Consequently, there are two influxes to the mantle because of the subduction, which have isotopic signatures different from the mantle itself. Inasmuch as Li isotopes are stable, these signatures of Li isotopic compositions can be associated with low-temperature processes near the surface of the Earth. As a result, Li isotopes can provide an important approach to trace geochemical processes in the subduction zone and corresponding mantle convection.

Recent research showed that old, altered oceanic crust is isotopically lighter than its younger counterpart, which may reflect exchange with overlying sediments, or possibly a change in δ^7Li of sea water over time (Bouman et al., 2004). Chan et al. (2002a) presented Li concentrations and isotopic profiles through the upper 2 km of the oceanic crust (Fig. 4); those profiles record alteration conditions and the Li exchange processes as a function of depth. In the upper part of the section, interaction with seawater at low temperature leads to enrichment of Li and heavier isotopic composition due to incorporation of Li into secondary phases. The rocks from the lower portion fall in the domain of unaltered MORB due to restricted fluid flow and rock-dominated conditions. The transition zone is enriched in Li but has a light isotopic composition resulting from precipitation from mixtures of seawater and Li-rich hydrothermal fluids. Sheeted dikes exhibit decreasing Li concentrations with depth. Interaction of seawater-derived hydrothermal fluids at high temperatures and low water/rock ratios results in depletion of Li and light isotopic compositions in greenschist- and sub-amphibolite–facies rocks. The range of δ^7Li may be explained by varying fluid compositions, temperature-dependent isotopic fractionations, and water/rock ratios. Crustal rocks of different alteration zones thus exhibit distinct characteristics in Li abundances and isotopic compositions, making Li a sensitive indicator of the conditions and history of alteration.

Signature of the convective mantle

Understanding material cycles in the Earth provide a better opportunity to study the nature and

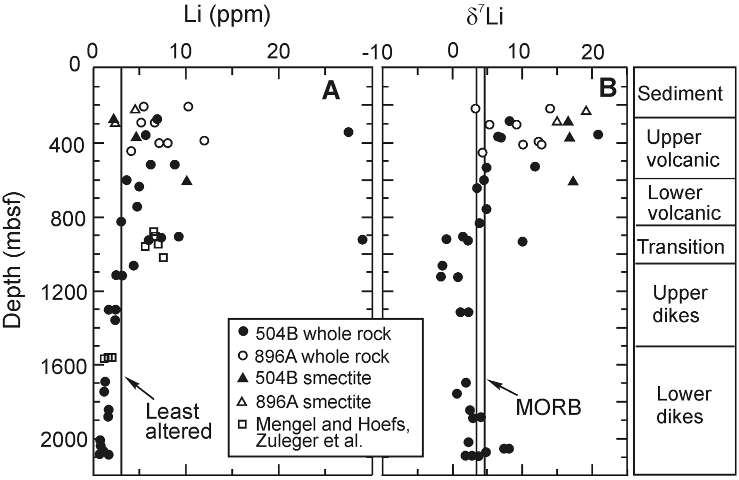

FIG. 4. Variation of Li concentration (A) and isotopic ratios (B) with depth for whole rocks and smectites from DSDP/ODP Sites 504B and 896A, shown with lithologic sections from Chan et al. (2002a). Also shown are concentration data for the transition zone from Mengel and Hoefs (1990) and at 1570 mbsf from Zuleger et al. (1996).

origin of the chemical heterogeneity of the mantle shown in Figure 5. Materials at the Earth's surface undergo various physicochemical processes, such as water/rock interaction underneath the ocean floor and subsequent dehydration/partial melting during subduction (Moriguti and Nakamura, 1998a; Seyfried et al., 1998; Chan et al., 2002a; Zack et al., 2003). Water-soluble elements (such as Li) during dehydration processes are preferentially released to metasomatize the overlying mantle wedge, which is the source region for island-arc magma (Ishikawa and Nakamura, 1994; Ryan et al., 1995). The slab is finally introduced into the mantle and may form a chemical anomaly, which could eventually become the source region for mantle plumes expressed at the Earth's surface as ocean island basalts (Hofmann and White, 1982). Unlike radiogenic isotopic ratios, the Li isotopic ratio is not affected by time or parent/daughter fractionation. Therefore, it is expected that Li isotopic compositions provide complementary information to familiar radiogenic isotopes.

The Li isotopic signatures of minerals in mantle-derived xenoliths have provided direct information on the evolution of lithosphere. Values of δ^7Li vary systematically between minerals; olivine has the heaviest δ^7Li (+1.4‰ to +4.5‰), followed by orthopyroxene (–1.0‰ to +3.9‰), and clinopyroxene has the lightest (–2.4‰ to +3.0‰), whereas whole-rock δ^7Li, from +1‰ to +4‰, correlates negatively with the degree of metasomatism of mantle xenoliths (Seitz et al., 2004). The degree of intramineral fractionation ($\delta^7\mathrm{Li}_{\mathrm{Ol\text{-}Cpx}}$) also negatively correlates with equilibration temperature, suggesting that Li isotope fractionation may occur at high magmatic temperatures (950–1150° C). Another study infers that an anhydrous EM1-like metasomatic agent may have an extremely low δ^7Li value, whereas a hydrous EM2-like agent may have a positive d7Li (Nishio et al., 2004) (Fig. 6). Due to the loss of heavier Li from the subducted slab during low-temperature dehydration, the δ^7Li value of subducted, highly altered MORB would be extremely low compared to that of fresh MORB. Thus, the metasomatic agent with extremely low δ^7Li is derived from subducted, highly altered basalt (Fig. 6). The enrichment of isotopically light Li may be a feature of the EM1 mantle reservoir. Because of apparent sensitivity of the Li isotopic composition to the alteration profile of subducted MORB, it may provide complementary information to Sr, Nd, and Pb isotopic compositions regarding the mantle source.

MORB and OIB represent primary samples of the mantle (Hofmann, 1997). MORB are derived from shallow (dominantly less than 60 km) decompression melting of the mantle, whereas OIB can be generated by upwelling, mostly related to mantle plumes, which have originated from a deeper mantle than that of MORB. Generally, a deep mantle layer is fed by subducted slabs and ultimately forms the source for OIB (Tackley, 2000). Based on the behavior

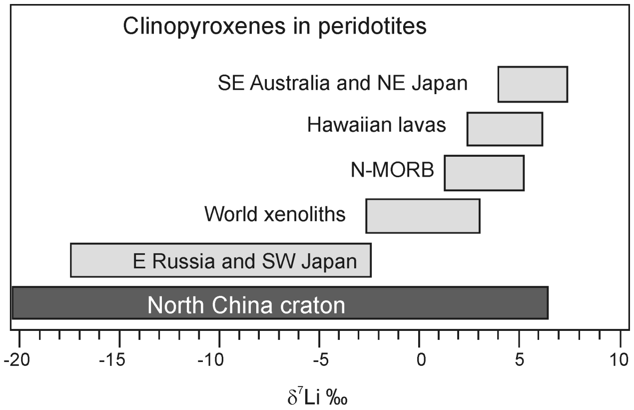

FIG. 5. Volumes of δ^7Li for clinopyroxenes from different world localities compared with published MORB and Hawaiian data. Data sources: Hawaiian lavas (Tomascak et al., 1999b; James and Palmer, 2000a; Chan and Fery, 2003; Pistiner and Henderson, 2003); N-MORB (the published MORB data are N-MORB–depleted compositions) (Chan et al., 1992; Moriguti and Nakamura, 1998a); clinopyroxenes in world xenoliths (Seitz et al., 2004); clinopyroxenes from the North China craton (Tang et al., 2006; unpubl. data); other data (Nishio et al., 2004).

of Li in the subduction zone, the lower mantle would possibly evolve toward a lighter Li isotopic composition than the upper mantle. Thus OIB should theoretically have a lighter Li isotope ratio than MORB. Therefore, the spread of δ^7Li in MORB data (Fig. 5) requires recycled materials, with lighter Li isotopic compositions, to be mixed with the upper mantle. This has long been proposed as a logical corollary of plate tectonics (Allégre and Turcotte, 1986), and has been recently corroborated by the subtle variations in oxygen isotopic ratios (Eiler et al., 2000). Based on the behavior of Li isotopes in the subduction zone, the idea of recycled material is strongly supported as well.

Li isotope analysis of OIB from Hawaiian lavas (Tomascak et al., 1999b; James and Palmer, 2000a; Chan and Fery, 2003; Pistiner and Henderson, 2003) has demonstrated that they are slightly heavier than N-MORB, although there is large overlap between the δ^7Li values (Fig. 5). New data for clinopyroxenes from xenoliths (Nishio et al., 2004; Seitz et al., 2004) provide an important supplement to the dataset of mantle-derived lavas. Despite some samples possessing δ^7Li values that overlap those of OIB, the clinopyroxenes from East Russia and Southwest Japan display δ^7Li as low as –17‰. These extremely light Li isotopic ratios implicate the involvement of subducted oceanic crust in the subcontinental mantle lithosphere represented by these xenoliths (Nishio et al., 2004).

It is obvious that further work is required to build on the above observations. From the primary understanding of the mantle based on the current data, the sources of OIB and enriched MORB (heavy in δ^7Li) should have a common origin in the down-dragged mantle adjacent to the subducting slab (Fig. 3). Fluids released from the downgoing plate will be heavy, but variable in composition, depending on the prior history of dehydration. This process could account for the large variability in δ^7Li not clearly related to other chemical tracers (Tomascak et al., 2002). Material from the slab has to pass into a hot portion of the mantle wedge before it triggers large-scale melting. The colder mantle layer overlying the slab will acquire a recycled signature, such as heavy δ^7Li, from the passage of slab-derived fluids through it (Fig. 3). Similarly, the mantle layer may also acquire a sedimentary signature. This overlying mantle will be viscously coupled to the slab, and so carried down beyond the subduction zone. As the slab descends and warms, the overlying enriched layer will cease to be viscously coupled. Depending on the thermal and dynamic history of the plate, the heavy δ^7Li layer of mantle may be carried to variable depths to contribute to both MORB and OIB sources. This scenario of recycling is highly speculative. What is clear, however, from our current understanding of the behavior of Li isotopes, is that there is ample evidence for the role of recycled material in some OIB and MORB sources.

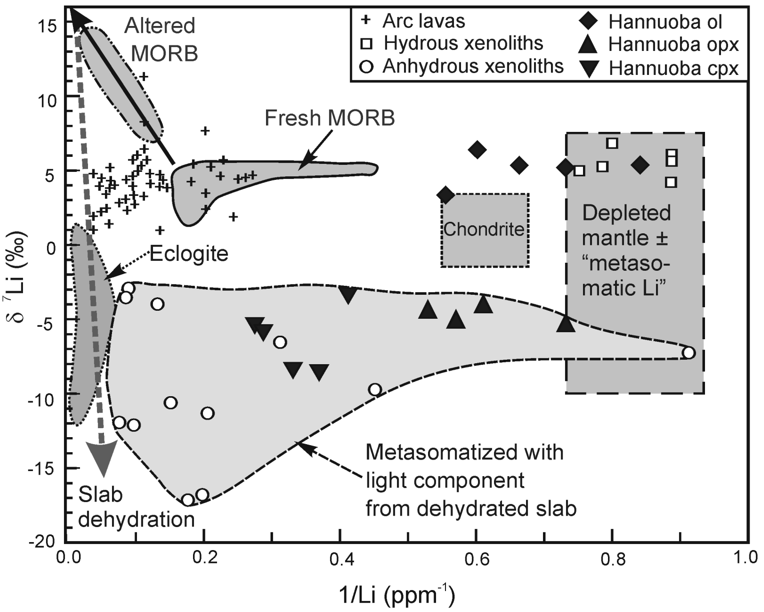

FIG. 6. Variation of Li concentrations vs. Li isotopic ratios. The black arrow shows the trend for alteration of oceanic crust, and the grey arrow depicts the dehydration trend of subducted oceanic crust. Data sources: fresh MORB (Moriguti and Nakamura, 1998a; Chan et al., 2002a, 2002b); altered MORB (Chan et al., 1992); dehydrated slab (i.e., eclogite) (Zack et al., 2003); arc lavas (Moriguti and Nakamura, 1998a; Tomascak et al., 2000, 2002; Chan et al., 2002a, 2002b); chondrite range (McDonough et al., 2003; Tomascak, 2004); minerals in peridotitic xenoliths from Hannuoba, North China craton (Tang et al., 2006); clinopyroxenes in hydrous and anhydrous xenoliths (Nishio et al., 2004).

Controlling Factors in Li Isotopic Fractionation

Temperature may be a key factor of Li isotopic fractionation (Seyfried et al., 1998; Tomascak et al., 1999b; Coogan et al., 2005). According to experiments involving Li isotopic fractionation between clinopyroxene and Cl- and OH-bearing aqueous fluids between 500 and 900°C at 2.0 GPa (Wunder et al., 2005), ^{7}Li is always preferentially partitioned into the fluid, and the isotopic fractionation of Li is temperature-dependent and approximated by the equation $\delta^7\mathrm{Li}_{\mathrm{Cpx\text{-}fluid}} = -4.61 \times (1000/T\ [\mathrm{K}]) + 2.48$ ($R^2 = 0.86$). This equation may be roughly applicable for quantification of fluid-rock interaction where Li in minerals resides in octahedral coordination (such as, pyroxene, amphibole, mica, and chlorite) (Wunder et al., 2005).

As discussed above, heterogeneity of lithium isotopes during crust-mantle cycling is mainly produced by hydration-dehydration processes, which may be related to different mechanisms of isotopic fractionation, such as isotopic fractionation between seawater and oceanic crust, slab and fluid, and intramineral isotopic fractionations between mantle minerals probably generated by diffusion during mantle melting due to different partition coefficients of Li in crystal-melt/fluid systems (Brenan et al., 1998a). As a result, effective diffusion coefficients of Li in water, minerals, or rocks may constrain the isotopic fractionation of Li associated with diffusion (Barrat et al., 2005; Richter et al., 2006; Teng et al., 2006).

Teng et al. (2006) found Li isotopic fractionation accompanying Li diffusion from an Li-rich pegmatite into country rocks. They attributed extreme fractionations (~30‰) to the large differences in diffusion coefficients between ^{6}Li and ^{7}Li, and Li concentrations between the pegmatite and country rocks. Experimental results of kinetic isotopic fractionation during diffusion of ionic species in water (Richter et al., 2006) show that isotopic fractionation in water is much smaller than that in molten silicate liquids (Richter et al., 2003). They considered that the distinction between water and silicate liquids is that water surrounds dissolved ions with hydration shells, which likely play an important but still poorly understood role in limiting the isotopic fractionation associated with diffusion (Richter et al., 2006).

Recently, we obtained Li isotopic compositions of minerals in a suite of spinel peridotitic xenoliths from the Hannuoba Cenozoic basalts, North China craton. The data (Fig. 6) show that the olivine separates have positive δ^7Li values (+3.3 to +6.4‰). In contrast, the pyroxenes have low and negative δ^7Li (–3.3 to –8.2‰ for clinopyroxene, and –4.0 to –6.7‰ for orthopyroxene), which require a metasomatic agent with low δ^7Li values. Considering that the highly altered oceanic crust preserves δ^7Li as low as –11‰ (Zack et al., 2003), the low δ^7Li values of pyroxene separates from the Hannuoba xenoliths may result from the interaction of mantle peridotites with silicate melt, which was released from subducted altered oceanic crust (Fig. 6). The diffusion fractionation of ^{6}Li and ^{7}Li during peridotite-melt interaction could elucidate the observed disequilibrium of Li isotopes (Tang et al., 2006).

Conclusions

Investigations of Li isotope geochemistry are developing very rapidly; the field covers continental weathering to crust-mantle cycling of the Earth. Yet, the subject is far from mature, and important questions remain (e.g., can Li isotopes fractionate in igneous systems? How is Li enriched during metasomatism?). It is of great interest to see how Li isotope signatures of recycling compare to radiogenic isotope measurements. Although the latter have long been used to infer the distribution of recycled material, their variations can be interpreted in other ways, and are much more equivocal. Robust interpretations of Li isotope data await better quantification of partition coefficients (mineral-melt/fluid), isotopic fractionation factors as a function of temperature, and effective diffusion coefficients of Li in water, minerals, or rocks. As is true for other stable isotopes (such as, O, S, N, B, etc.), *in situ* Li analysis is a good direction worthy of further development. In any event, the Li isotope system is an efficient geochemical tracer for better understanding near-surface weathering, crust/mantle recycling, growth of continental crust, and especially the nature and origin of chemical heterogeneity in the mantle throughout Earth history. In sum, Li isotope geochemistry has a bright future and will become even more powerful when combined with radioactive isotopes such as Sr, Nd, Pb, Os, and Hf in future studies.

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