LITHIUM ISOTOPES IN THE EARTH AND TERRESTRIAL PLANETS

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH
for the degree of
Doctor of Natural Sciences

presented by

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Zürich 2006
Frontcover: A view of the Apollo 11 lunar module "Eagle" as it returned from the surface of the Moon to dock with the command module "Columbia". A smooth mare area is visible on the Moon below and a half-illuminated Earth hangs over the horizon. The picture was taken by command module pilot Michael Collins just before docking on 21 July 1969. Credit: NASA (http://www.nasa.gov)
Acknowledgement

This work would not be possible without an extreme effort of two prominent personalities to whom I am more than grateful for their support, enthusiasm and criticism. Alex Halliday was always well disposed and full of ideas and possible directions of the PhD project. I also wish to thank him for giving me the opportunity to enter the great team of geoscientists housed at ETH. Uwe Wiechert was the best choice I could ever get for a supervisor. He pushed me further in my work and forced me to think about every single piece of what I was doing, saying or writing. He always had time to talk, discuss and even spend his time together with me in the lab during many long evenings; I really appreciate that. This I found of much use for the future and I am indebted to Uwe for such an approach in supervising my PhD. I hope he did not get mad after correcting first drafts of individual chapters of the Thesis. In this place it is also appropriate to acknowledge Chris Ballentine who fortunately for me, failed in trying to change my mind to noble gases.

In this place it is worth to thank Christoph Heinrich for overtaking the responsibility after Alex Halliday which in turn lead to finishing the Thesis. Tim Elliott and Tim Grove are acknowledged for taking a part as co-referees and also for their help and advice that I was often asking for at various stages of my work. I also thank Fin Stuart for his effort and invaluable input during the work on Iceland and Jan Mayen manuscript. I am grateful to Torsten Vennemann for language corrections of “Kurzfassung” and Francois Bussy, Denise Bussien, Mike Cosca, Othmar Müntener and Torsten Vennemann for comments on first versions of my presentation.

From the beginning to the end of my stay at ETH, Britt Meyer was helping me in various things not always necessarily related to the academic and without her help I could hardly live as easy as I used to. Also, Valentina Müller-Weckerle often provided help during my stay at ETH.

I am indebted to Felix Oberli for introduction into the multi-collector mass spectrometry and thorough and detailed explanations of every single aspect of the large Nu1700 mass spectrometer and for always a proper troubleshooting (including weekends). Martin Meier provided much help in the lab with acid purification and material support. I am grateful to Heiri Baur for time that he dedicated me on various occasions while explaining me different
and always complex things (primarily in noble gas lab but subsequently in other aspects too). Machinery and electronics unit (Urs Menet, Andreas Süssli, Bruno Rütsche and Donat Niederer) is a well-coordinated team that provided much help by manufacturing and/or repairing plenty of necessary things. My lab work was in part possible due to effort of Marie-Theres Bär, Irene Ivanov-Bucher and Ramon Aubert who provided invaluable help in making columns, preparing samples and introducing me into the mineral separations, respectively.

While many people appeared on various occasions in my vicinity during the period of my doctoral study at ETH, it would be a heroic effort to provide all names. Hence, I will pick up individual people from this endless list. Darrell Harrison was a superb guy all the time and helped me many times with variety of things and problems, easy or complicated (complicated in most cases, of course). Rainer Wieler was paying attention to my frequent questions and always tried to find a solution. He also introduced me into complex problematic of lunar research. Special thanks go to Bettina Zimmermann for helping me with many things. Martin Frank, Marcus Gutjahr and Uwe Wiechert shared the lab with me and as such, they provided a lot of help or suggestions. The early ETH days in the noble gas lab were smoother due to assistance of Veronika Heber and Nadia Vogel (and again, of course, Heiri Baur). The productive team of PhD students and post-docs in IGMR was a fantastic group and I thank all of them for sharing their time, contacts, ideas and other things without which it would not be such a joy and pleasure to do a doctorate study at ETH Zürich.

Last, but not least and definitely the most important for me was the patience and everlasting support of my family. In particular, the last time was variegated by the birth of my daughter Eliška in May 2005, the light of my life and sense of my being. This Thesis belongs to Jiřina and my family in a great part.
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Abstract

Lithium isotopes display very large relative mass difference between the two naturally occurring isotopes, $^6$Li and $^7$Li, which reaches ~17%. It is the largest difference among non-gaseous elements. Due to this, lithium is prone to extensive isotope fractionation in nature. Special attention has been paid to surface processes and those in the hydrosphere, e.g. weathering and seawater alteration, where this fractionation may reach values as large as 30%. Pristine mantle rocks have been studied only very recently with the development of improved analytical procedures and plasma source mass spectrometry techniques. However, the mantle represents the largest portion of the Earth and thus, it should have a well-defined Li isotope composition. This dissertation was aimed at partly filling the gap resulting from a lack of Li isotope data for mantle rocks together with volcanic rocks from subduction zones and ocean island basalts. Additional new data were obtained for a variety of meteorites and lunar rocks.

A new rapid method of chemical isolation and purification of Li has been developed in this dissertation for precise and accurate determination of Li isotopes. This newly developed separation technique was combined with measurements of Li isotopes on a large-sector MC-ICPMS. Mass spectrometry measurements involved sample bracketing with standards to correct for instrumental mass bias. Long-term reproducibility of isotope measurements ($\pm 0.3\%$, 2σ) has been significantly improved by a factor of 2-3 compared to the classical TIMS methods. Li isotope homogeneity of the international Li standard material has been verified. A number of international reference rocks have been characterised in terms of Li isotopes that could further improve an inter-laboratory comparison.

Primitive olivine tholeiites and basaltic andesites from the southern Cascadia subduction zone show a range of $\delta^7$Li values that correlate inversely with distance from the arc trench. Olivine tholeiites provide evidence for heterogeneous mantle beneath Mt. Shasta and Medicine Lake. On the contrary, basaltic andesites and primitive magnesian andesites show remarkably diverse Li isotope patterns below the two studied volcanoes. This has been attributed to distinct values of $\delta^7$Li of the fluids involved in the generation of basaltic andesites, with fluids depleted in $^7$Li interacting with Medicine Lake lavas. This likely
reflects continuous Li isotope fractionation during dehydration of the subducted slab with preferential removal of $^7\text{Li}$ into the fluid phase at shallow depths.

Suites of picritic basalts from Hengill, Iceland, and ankaramitic basalts from Jan Mayen support the view of a homogeneous upper mantle ($\delta^7\text{Li} \sim +4\%$), irrespective of the degree of trace element enrichment. Inverse and linear co-variation of Li and He isotopes in Icelandic lavas is not reflected in other trace element or isotope ratios. It is suggested that three mantle components provide an explanation for the observed trends, contrary to previously proposed implementation of altered Icelandic crust. At least one of these components carries a recycled component as evidenced by positive Eu anomaly and super-chondritic Sr/Nd. Jan Mayen lavas seem to accommodate a signature of enriched mantle (EM2).

Samples from terrestrial planetary bodies (chondrites, eucrites, Martian meteorites, lunar basalts and terrestrial mantle peridotites) have significant variations in $\delta^7\text{Li}$ values with predominantly light Li in chondrites. All other planetary objects display nearly identical Li isotope compositions indistinguishable from the assumed terrestrial upper mantle at $\delta^7\text{Li}$ of about $+4\%$. Lunar rocks span a substantial range of $6\%$ with extremely high $\delta^7\text{Li}$ for the lunar crust which is likely caused by equilibrium isotope fractionation during plagioclase segregation from the early lunar magma ocean. Variations of $\delta^7\text{Li}$ among lunar basalts and glasses can be explained by melting of early- and late-stage cumulates with variable amounts of major minerals with isotopically different Li. Lack of Li isotope fractionation among inner solar system planetary bodies relative to lighter Li in chondrites could provide evidence for small but significant isotope fractionation during planetary formation processes.
Kurzfassung


Eine neue und schnelle Methode für die chemische Trennung und Aufbereitung des Lithiums ist als Teil dieser Dissertation entwickelt worden, um eine genauere und präzisere Bestimmung der Li-Isotopie als bisher zu ermöglichen. Nach der neuen Aufbereitungsmethode wurden die Messungen der Li-Isotopie an einem MC-ICPMS mit hoher Auflösung mittels einem gezielten Standard-Probe-Standard Messverfahren analysiert, um den instrumentalen Massenbias deutlich zu verringern. Die langfristige Reproduzierbarkeit der Isotopenmessungen ($\pm 0.3\%$, $2\sigma$) ist zwei- bis dreifach verbessert worden, im vergleich zu den klassischen TIMS Methoden. Isotopenhomogenität des internationalen Lithiumstandards ist nachgewiesen worden. Eine Reihe von internationalen Referenzgesteinen wurde ebenfalls bezüglich der Lithiumisotopen charakterisiert, was einen Vergleich der Daten zwischen verschiedenen Labors vereinfachen soll.

Olivin-führende Tholeiite und Basalt-Andesite aus der Süd-Cascadia Subduktionszone zeigen grosse Variationen von $\delta^7$Li, die negativ mit dem Abstand vom Graben korrelieren. Die Olivin-Tholeiite weisen auf einen heterogenen Mantel unter Mt. Shasta und Medicine Lake. Im Kontrast dazu, haben die Basalt-Andesite und Magnesium-Andesite
bemerkenswerterweise sehr unterschiedliche Profile der Lithiumisotopen unter den zwei Vulkanen. Diese Unterschiede können verschiedenen $\delta^7\text{Li}$ Werten der Fluide die sich an der Generation der Basalt-Andesite beteiligt haben, zugerechnet werden. Vorwiegend leichte Lithiumisotopie der Fluide wurden für Proben von Medicine Lake gemessen. Vermutlich reflektiert das eine kontinuierliche Lithiumisotopenfraktionierung während Dehydration der subduzierten Platte zusammen mit bevorzugter Abgabe von $^7\text{Li}$ in die fluide Phase bei niedrigen Subduktionstiefen.


Die Meteoritproben (Chondrite, Eukrite, von Mars stammende Meteorite, Mond-Basalte und terrestrische Mantelperidotite) zeigen massgebliche Variationen in $\delta^7\text{Li}$ Werten, wobei die Chondrite vorwiegend leichte Lithiumisotopenverhältnisse haben. Alle anderen Proben zeigen fast identische Lithiumisotopenverhältnisse, identisch mit denen die für den terrestrischen oberen Mantel angenommen werden ($\delta^7\text{Li} \sim +4\%$). Mond-Gesteine erstrecken sich wesentlich über 6% mit extrem schweren Werten für die Kruste des Mondes, die voraussichtlich durch Gleichgewichtsisotopenfraktionierung während einer Trennung des Plagioklas vom frühen Magmaocean des Mondes verursacht ist. Unterschiede zwischen Mond-Basalten und Gläsern sind wahrscheinlich auf Schmelzprozesse mit unterschiedlichen Mengen von Früh- und Spätstadiumkumulaten der Hauptminerale zurück zu führen, wobei diese Minerale unterschiedliche Lithiumisotopenverhältnisse haben. Abwesenheit einer Isotopenfraktionierung von Lithium zwischen den inneren Planeten im Vergleich zu einem geringen Unterschied dieser zu den Chondriten, deutet auf geringe aber doch messbare Isotopenfraktionierung während der Bildung der Planeten.
Chapter 1

Introduction
1.1 Lithium isotopes in the global geochemical cycle

This PhD thesis is dedicated to the investigation of lithium (Li) isotopes in volcanic arcs, ocean islands, mantle rocks and samples from the moon and other planetary bodies. The large mass difference of ~16% between $^6$Li and $^7$Li causes large isotope fractionation in global geochemical cycles and makes Li isotopes an interesting geochemical tracer (e.g. ELLIOTT et al., 2004; TOMASCAK, 2004). The total variation of $\delta^7$Li among terrestrial materials is as large as 70%o (see Fig. 1.1). Rivers carry heavy Li to the oceans (HUH et al., 1998, 2001; VIGIER et al., 2002; PISTINER and HENDERSON, 2003; POGGE VON STRANDMANN et al., 2006) and residual weathered products may develop extremely light $\delta^7$Li (RUDNICK et al., 2004). The upper continental crust tends to have low $\delta^7$Li compared to mantle and averages at about $\delta^7$Li $\approx$ 0%o (TENG et al., 2004) although our current knowledge of Li in the continental crust is based on only two systematic studies (BRYANT et al., 2004; TENG et al., 2004) and sparse measurements of single granitic rocks (JAMES and PALMER, 2000; TOMASCAK et al., 2003; RUDNICK et al., 2004). Considerable diversity in the Li isotope compositions of marine sediments has been illustrated recently (CHAN et al., 2006). The $\delta^7$Li of global marine sediments varies widely (-4 to +15%) and reflects lithology, provenance and diagenetic processes. There is no relation between distribution of Li isotopes and arc-trench location. Marine sediments yield a range of $\delta^7$Li (CHAN et al., 2006) that closely resembles that reported for altered oceanic crust (CHAN et al., 1992, 2002a; BOUMAN et al., 2004). This complicates a direct fingerprinting of the slab components in arc volcanics.

The most puzzling Li isotope results to date are perhaps related to subduction zone volcanism. It has been shown that Li abundances correlate with fluid signatures (e.g. DORENDORF et al., 2000) but Li isotope ratios are not correlated (Chapter 3). At least in two volcanic arcs Li isotopes change systematically with increasing distance from the arc trench (see Chapter 3 and MORIGUTI and NAKAMURA, 1998b). This is clear evidence that Li isotopes fractionate during subduction of oceanic lithosphere into the mantle. Experimental studies provide evidence that Li may be efficiently retained in the slab by several mineral species, e.g. staurolite, serpentine, phengite or Ti-clinohumite (WOODLAND et al., 2002; ZACK et al., 2003; SCAMBELLURI et al., 2004; WUNDER et al., 2006) but the exact mechanism and response of Li isotopes to progressively changing pressures and temperatures, i.e. mineralogy, is poorly constrained (MARSCHALL et al., 2006, 2007). It is further unclear whether dehydration and metamorphism of subducted oceanic lithosphere generates distinct mantle
reservoirs because eclogite samples seem to preferentially carry isotopically light Li to the lower mantle. Lithium isotope compositions from ferropericlase inclusions are light compared to oceanic basalts and upper mantle rocks (SEITZ et al., 2006a). This suggests that isotopically light Li is recycled into the deep mantle mainly by eclogites and/or dehydrated serpentinites. This is, however, not supported by data from ocean island basalts, which are predominantly composed of isotopically heavy Li.

1.2 Physiochemical properties of lithium

Lithium has its origin in the Greek name for stone: λίθος (lithos). It was discovered by J.A. Arfvedson in 1817 (ten years after potassium and sodium were isolated by Sir Humphry Davy) and isolated as a metal using electrolysis one year later by Sir Humphry Davy. Lithium is the lightest metal of the alkali group and the lightest of all solids of the periodic table with a density of just 0.543 g cm\(^{-3}\). Its atomic weight is 6.941 ± 0.002. In metallic form Li forms a cubic lattice. It has the highest melting and boiling temperature (180.5 and 1342°C, respectively) of all alkali metals. The first ionisation energy of Li (5.39 eV) is also higher compared with other elements of this group. Some chemical and physical properties of Li are caused by the small ionic radius of the Li\(^+\) ion (~76 pm) which is similar to that of Mg\(^{2+}\) (72 pm) allowing Li to substitute for Mg. The two naturally existing isotopes of lithium, \(^{6}\)Li and \(^{7}\)Li, were unambiguously distinguished in the early '20s (DEMPSTER, 1921) and further investigated by ASTON (1927, 1932) who refined the abundances and atomic weight of Li.

Lithium is a lithophile element. Although in the mantle Li is only slightly incompatible (RYAN and LANGMUIR, 1987), in granitic rocks it can accumulate during the late stages of magmatic differentiation. Pegmatites have generally high Li abundances in percent levels (e.g. FABRE et al., 2002; TENG et al., 2006b) in which Li often forms its own minerals like spodumene or petalite.

1.3 Artificially isotopically enriched lithium

Lithium is an element of interest also in fields outside geochemistry, e.g. medical sciences (SCHOU, 1988), astrophysics and astronomy or the nuclear industry (OLIVE and
Chapter 1 Introduction

Light grey vertical line represents reference material (L-SVEC; SRM8545), dark grey vertical line represents Li isotope composition of pristine, non-metasomatic upper mantle ($\delta^7\text{Li} = 4.1 \pm 0.4\%$; see Chapter 5).

The nuclear industry has been using $^6\text{Li}$ as a moderator because of the large thermal neutron cross-section. The nuclear industry, therefore, processed large quantities of natural Li to produce $^6\text{Li}$-enriched lithium. The residual Li is extremely enriched in $^7\text{Li}$. These $^7\text{Li}$-rich materials are commercially distributed and eventually re-occur in e.g. reference solutions and/or as impurities in some chemical reagents (Qi et al., 1997). This can lead to severe analytical problems for concentration measurements, e.g. when mass spectrometry is used for trace element studies. Another problem arises from metallurgic use of Li$_2$B$_4$O$_7$ to decrease melting temperatures of substances, e.g. for XRF analysis of geological samples. When these reagents are made from industrially processed Li, even minute quantities of Li$_2$B$_4$O$_7$, e.g. contamination by dust particles, may dramatically alter Li isotope ratios of natural samples. This is illustrated in Fig. 1.2 for several Cameroon Line basalts presumably contaminated by Li$_2$B$_4$O$_7$ powder and discussed next in more detail.

Fig. 1.1: Lithium isotope compositions of various terrestrial materials and chondrites (after Tomascak, 2004).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta^7\text{Li}$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>-20</td>
</tr>
<tr>
<td>Lakes</td>
<td>-10</td>
</tr>
<tr>
<td>Marine biogenic carbonates</td>
<td>0</td>
</tr>
<tr>
<td>Shales &amp; loess</td>
<td>10</td>
</tr>
<tr>
<td>Granites</td>
<td>20</td>
</tr>
<tr>
<td>Peridotite &amp; pyroxenites</td>
<td>30</td>
</tr>
<tr>
<td>Arc lavas</td>
<td>40</td>
</tr>
<tr>
<td>OIB</td>
<td>50</td>
</tr>
<tr>
<td>Altered MORB</td>
<td>40</td>
</tr>
<tr>
<td>Fresh MORB</td>
<td>30</td>
</tr>
<tr>
<td>Chondrites</td>
<td>20</td>
</tr>
</tbody>
</table>

Schramm, 1992; Ritzenhoff et al., 1997; Suzuki et al., 2000; Montalban and Rebojo, 2002.)
Common terrestrial basaltic rocks have $\delta^7\text{Li}$ values between $\sim +1\%o$ and $\sim +6\%o$. These comprise fresh mid-ocean ridge basalts (MORBs), ocean island basalts (OIBs) and island arc basalts (IABs). Deviations are ascribed to secondary processes, e.g. weathering or interactions with seawater. However, these changes do not exceed a few percent; the maximum $\delta^7\text{Li}$ reaches $\sim +44\%o$ as recorded in pore fluids of marine sediments (ZHANG et al., 1998).

Moreover, seafloor alteration at $\sim 2^\circ\text{C}$ with an apparent fractionation factor $\alpha \approx 0.981$ (CHAN et al., 1992) generates altered basalts with $\delta^7\text{Li}$ of about $+14\%o$ which cannot explain the observed $^7\text{Li}$ enrichment in some of the Cameroon Line basalts. One possibility of producing the extremely light Li isotope compositions could be a fractionation on ion-exchange columns (MORIGUTI and NAKAMURA, 1998a; KOŚLER et al., 2001) but the recovery of Li in Cameroon Line basalts reached 100% within error. Therefore, analytical artifacts related to column chemistry are not a viable explanation for high $\delta^7\text{Li}$ values for some Cameroon Line basalts. More likely it is caused by contamination with artificially $^7\text{Li}$-enriched material picked up at Edinburgh University where the samples were prepared for XRF analysis.
1.4 Objectives of this study

A major objective of this study was to establish a new rapid technique to separate Li from silicate matrices for precise Li isotope measurements using MC-ICPMS. The analytical method, mass spectrometry and data evaluation are described in Chapter 2. Another step became necessary to separate Cr from Li when clinopyroxenes or fertile mantle xenoliths were studied (see Chapter 5). This latter step of analytical treatment has been applied to samples from Jan Mayen (Chapter 4) and to lunar rocks and meteorites (Chapter 5).

The following investigations were performed in this study:

a) Lithium isotope measurements of a suite of high-alumina olivine tholeiites and basaltic andesites from Mt. Shasta and Medicine Lake volcanoes (northern California Cascades) have been performed to study the geochemical behaviour of Li in subduction zones. Similar studies were performed at other arc locations. However, the southern Cascades are distinct as they consist mainly of basaltic lavas. We provide evidence for isotope fractionation of Li during subduction. (Chapter 3).

b) Lithium isotopes have been used to identify recycled components in the source of Icelandic lavas from Hengill and Jan Mayen Island lavas. For Hengill lavas a trend between Li and He isotopes has been found which most likely reflects a minimum of three distinct components in the plume head and adjacent mantle. Jan Mayen ankaramitic basalts have a homogeneous isotope composition of $\delta^{7}\text{Li} = 4.2 \pm 0.6\%$ within error identical with that of the bulk silicate earth (Chapter 4).

c) Mineral separates from primitive unmetasomatised peridotites were investigated to constrain the Li isotope composition of the terrestrial upper mantle. Data for lunar rocks have revealed systematic Li isotope variations related to the crystallisation of the lunar magma ocean. The Li isotope compositions of other terrestrial planetary bodies of the inner solar system have been constrained (Chapter 5).
Chapter 2 *

Low-blank isotope ratio measurement of small samples of lithium using multiple-collector ICPMS

2.1 Abstract

A new method is presented for separation of lithium from silicate rocks and high precision MC-ICPMS analysis. A relatively small (3.57 meq) resin volume is able to separate lithium from all silicate rocks in a single step using only 16 ml of nitric acid mixed with methanol. Some advantages of the method are high sample throughput, low blanks and elution parameters that are insensitive to lithology. Elution schemes are presented for a range of igneous rocks and minerals. δ7Li values for standards from the U.S. Geological Survey (USGS) for BCR-1, BHVO-2 and AGV-2 are 2.4‰, 4.6‰ and 7.9‰, respectively. Reference materials from the Geological Survey of Japan (GSJ) JB-2 and JR-2 give δ7Li values of 4.7‰ and 3.8‰, respectively. The data for most reference rocks reproduce to within better than 0.5‰. This column method can also be used for the direct separation of high-field-strength elements (Ti, Zr, Hf, Nb, Ta) from silicate rocks.

2.2 Introduction

Lithium (Li) isotope geochemistry has developed rapidly in recent years. It was first used effectively following the development of a borate technique for measurement by thermal ionization mass spectrometry (TIMS; CHAN, 1987). However, it has been further enhanced by the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS; TOMASCAK et al., 1999a). The ionic radius of Li+ (~ 0.59Å) is similar to that of Mg²⁺ (~ 0.57Å). Therefore, lithium can substitute for magnesium in olivine, enstatite and diopside (SHITZ and WOODLAND, 2000). This substitution behaviour 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. In aqueous solutions lithium is strongly hydrated. These chemical properties make Li and its isotopes interesting for the study of hydrothermal processes (CHAN et al., 1992), continental weathering rates (ZHANG et al., 1998; HUH et al., 2001), and as a tracer of subducted oceanic crust in the mantle (MORIGUTI and NAKAMURA, 1998b; TOMASCAK et al., 1999b).

Lithium has two stable isotopes, ⁶Li and ⁷Li, with a large relative mass difference of ~17%. Mass-dependent lithium isotope fractionation has been known since TAYLOR and UREY (1938) observed isotope fractionation of 25% as they percolated a lithium solution through a zeolite column. Early attempts to measure the isotope composition of lithium in
geological materials were inconclusive and not precise enough to resolve any isotope variations (Smales and Webster, 1958). The first accurate and precise measurements of lithium isotopes were performed using TIMS (Chan et al., 1993; 2002a; Sahoo and Masuda, 1995; You and Chan, 1996; Moriguti and Nakamura, 1998b; Chan and Kastner, 2000; James and Palmer, 2000; Chan and Frey, 2003). However the TIMS technique suffers from a highly unstable instrumental fractionation and requires Li that is virtually free of matrix (You and Chan, 1996; Bickle et al., 2000). Therefore, complicated ion exchange procedures have to be applied to obtain very pure Li solutions (Moriguti and Nakamura, 1998a). Quadrupole ICPMS is able to measure isotope ratios on very small amounts of lithium but is limited to lower precision compared with MC-ICPMS (Kosler et al., 2001; 2003). Other techniques that have been used for the measurement of lithium isotopes include atomic absorption spectrometry (Chapman and Dale, 1976; Meier, 1982), secondary ionization mass spectrometry (Chaussidon and Robert, 1998) and laser-excited atomic fluorescence spectroscopy (Smith et al., 1998). The advent of multiple-collector ICPMS offers the opportunity for small amounts of lithium to be analysed to high precision (Tomascak and Tera, 1997; Tomascak et al., 1999a; Nishio and Nakai, 2002).

Most recently the procedures that have been developed to separate lithium from silicate rocks use large eluant volumes (Tomascak et al., 1999a; Nishio and Nakai, 2002; Jeffcoate et al., 2004) and, therefore, are limited to relatively large sample amounts and are sensitive to (Mg, Fe)-rich rock matrices (Chan et al., 1999, 2002b). Here we describe a rapid and matrix-independent method for separation of lithium from very small silicate rock samples. The capability of measuring Li isotopes using MC-ICPMS, with a high degree of accuracy and precision is demonstrated with data for international reference rock standards.

2.3 Experimental

The natural abundances of $^6$Li and $^7$Li are 7.5% and 92.5%, respectively. That the heavier isotope $^7$Li is more abundant than the lighter $^6$Li, has led some authors to write $\delta$-values as $\delta^6$Li. In this way positive $\delta$-values are isotopically light and negative $\delta$-values are isotopically heavy. This is the opposite of how $\delta$-notation is used for stable isotopes of carbon, nitrogen, oxygen, sulphur and many other new isotope systems. We feel therefore it is advisable to report data in the standard $\delta^7$Li-notation in agreement with the recommendations (Coplen et al., 2002):
The lithium isotope composition is given in per mil relative to NIST SRM 8545 or L-SVEC ($^{7}\text{Li}/^{6}\text{Li}=12.02 \pm 0.03$; Flesch et al., 1973). Other standards are utilized sometimes, e.g. seawater (Hohs and Sywall, 1997; Millot et al., 2004) or IRM-016 (Olt et al., 1997). One advantage of seawater as a standard for the lithium isotope scale is that seawater is a large homogeneous reservoir. However, using seawater as a reference requires an additional calibration step. Therefore, it is a potential source of errors and might cause additional problems when data from different laboratories are compared.

2.3.1 L-SVEC preparation

Approximately 100 mg of L-SVEC powder ($\text{Li}_2\text{CO}_3$) from USGS was dissolved gently in 2 ml of concentrated HNO$_3$, then evaporated to dryness and taken up in 500 ml of 2% HNO$_3$. This produces a 40-ppm stock solution that can be further diluted to Li concentrations suitable for high sensitive mass spectrometer analyses.

Galy et al. (2003) have reported isotopic heterogeneity in the magnesium international reference material SRM 980. Therefore, comparisons between aliquots were made to confirm isotopic homogeneity of L-SVEC standard material. For this purpose 50-ppb solutions of L-SVEC aliquots were prepared from three international labs.

2.3.2 Sample preparation

All acids were twice distilled to reduce Li, Na and B blanks, methanol was distilled once; this removes sodium from the acids and methanol which may have concentrations high enough to cause matrix effects, i.e. shifts in isotopic ratios of samples relative to L-SVEC. Indeed, the Li blank is also particularly crucial. Olt et al. (1997) reported highly anomalous lithium isotope compositions ($> 1000\%\text{e}$) in some chemical reagents.

Approximately 100 mg of each rock powder was digested in Savillex® screw-top beakers with 3 ml concentrated HF and 0.5 ml concentrated HNO$_3$ for 24 hours on a hot plate at ~130°C. After evaporation of the solution, the residue was re-dissolved and dried down three times in concentrated HNO$_3$ to remove fluorides completely. Finally, the sample was dissolved and stored in 8 ml 6M HCl. An aliquot (¼th of the solution, equivalent to ~12.5 mg of the original sample powder) from the 6M HCl solution was then evaporated and dissolved.
in 0.5 ml of 0.67M HNO₃ in methanol. This is made from a 30% v/v solution of methanol, which dilutes concentrated HNO₃ to the desired concentration and is hereafter referred to as 0.67M HNO₃/methanol. The final concentration of methanol in the solution is ~27%. This aliquot was used for Li separation by ion exchange chromatography.

2.3.3 Chromatography

The separation of lithium from other elements using mixtures of mineral acids and organic media is based on the previous work of Šulcěk and co-workers (ŠULCEK et al., 1965; ŠULCEK and RUBEŠKA, 1969). They established the technique employing a mixture of HCl and methanol for separation of lithium from silicate rock matrices. The advantage of an HCl-methanol mixture compared to pure HCl is the better separation of lithium from sodium, i.e. methanol increases the difference of the partition coefficients between lithium and the other alkali metals on cation resins. The extraction of lithium was further improved by using HNO₃; HCl may create Fe(III)-complexes that are not retained by cation resins and may therefore elute Fe together with lithium (STRELOW et al., 1974). Moreover, HNO₃ increases the distribution coefficient of Na but the behaviour of lithium is unchanged, i.e. Na is even more strongly bound to the resin than with HCl. Such a methanol-nitric acid mixture has previously been used by a number of research groups. For MC-ICPMS it was first used by TOMASCAK et al. (1999a). KÖSLER et al. (2001) optimised the method for separation of small amounts of lithium from carbonate rocks and shells of planktonic foraminifera. However, successful separation of lithium from silicate rocks has been hampered by high eluant volumes and matrix effects. The former may potentially cause high blanks that limited early studies of lithium isotopes to samples with relatively high Li concentrations (e.g. basalts). Only in a more recent study have these problems been overcome successfully (JEFFCOATE et al., 2004) although still large eluant volumes are used.

For this study Teflon columns with a volume of 2.1 ml were packed with BioRad® AG 50W-X8 (200-400 mesh) cation exchange resin. The columns are conical in shape with 6-mm upper and 5-mm lower internal diameter. The resin is cleaned before the first use by repeated rinsing with 6M HCl and de-ionized water, then with 3M HCl and de-ionized water. When the columns are not used, they are stored in weakly acidified de-ionized water. Prior to loading of a sample, the column is rinsed with 4 ml HCl and 4 ml de-ionized water and preconditioned with 2 ml 0.67M HNO₃/methanol. The sample is loaded onto the resin in 0.5 ml.
of 0.67M HNO$_3$/methanol. Subsequently cations are eluted with 1M HNO$_3$ in methanol. This is made from an 80% v/v solution of methanol, which dilutes concentrated HNO$_3$ to the desired concentration and is hereafter referred to as 1M HNO$_3$/methanol. The final concentration of methanol is ~75%. The eluate is then evaporated to dryness. Finally, samples are dissolved in 2% HNO$_3$ for analysis on the mass spectrometer. The time for passing 1 ml through the columns is approximately 15 min. The procedural blank is usually less than 20 pg Li.

The total capacity of the resin in 2.1-ml column is 3.57 meq (1.7 meq/ml). For 12.5 mg of BHVO-2 the total capacity of major elements (total iron as Fe$^{3+}$) is 0.283 meq. Silicon is not included because it is fumed out by decomposition of the sample. Thus, the capacity of the elements represents less than 10% of the total exchange capacity of the resin, which is in the range for optimal separation of cations on this type of resin.

### 2.3.4 Mass spectrometry

Lithium isotope ratios were measured on Nu1700 (Nu Instruments), a new large-geometry high-resolution MC-ICPMS (Halliday et al., 2002). The Nu1700 is equipped with 3 electron multipliers and 16 Faraday cups with the outermost Faraday detectors L7 and H8 covering a mass dispersion of approximately 14% by neutral quadrupole setting conditions. All Faraday cups are equipped with $10^{11}$Ω resistors. We utilized the two outermost movable Faraday cups L7 and H8 for the $^6$Li and $^7$Li beam, respectively. Sample solutions were introduced through either desolvating spray nebulizer DSN-100 (Nu Instruments) or Aridus.

<table>
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<th>Instrumental settings and conditions</th>
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<td>RF power (W)</td>
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<td>Accelerator voltage (kV)</td>
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<tr>
<td>Resolution</td>
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<td>Analyzer pressure (mbar)</td>
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Conditions for DSN-100, only argon is used
* 1 psi = 0.06895 kg/cm$^2$
(Cetac) desolvator and ionized in argon plasma at 1400W. The other instrument parameters are listed in Table 2.1.

For lithium measurements a "wide-angle" (WA) skimmer cone was used because this increases sensitivity, compared with a standard cone, by a factor of 2 - 3. With this configuration total ion beam intensities of \(10 \times 10^9\) amps per ppm of Li in solution were obtained at an uptake of about 80 \(\mu\)l/min. Samples were run at a mass resolution of 700-800 \(m/\Delta m\); \(\Delta m\) is defined at 5% peak height. This is sufficient to resolve doubly charged \(^{12}\)C and \(^{14}\)N on masses \(^6\)Li (required resolution 400) and \(^7\)Li (required resolution 490), respectively. We scanned for \(^6\)LiH\(^+\) on mass \(^7\)Li at a resolution of ~1400 (required resolution 1010) but no hydrides have been detected. Each measurement consists of 40 to 60 cycles of 10 seconds of integration resulting in a total integration time of 400 to 600 seconds. Our standard procedure uses between 30 - 50 ng Li per analysis. However, a useful measurement can still be obtained with ca. 5 ng Li at lower precision.

Concentration measurements of Li were performed on a quadrupole ICPMS (VG Elemental PlasmaQuad 2+). All samples were diluted by 1000 to 3000 times and measured relative to a L-SVEC standard solution. High dilution factors were chosen to keep the lithium memory low. Matrix effects were corrected for using beryllium as an internal standard. The least square regression coefficient of the calibration line was always between 0.98 and 1. The reproducibility of the concentration measurements is ± 10% (2SD) based on multiple standard analyses.

### 2.4 Results and discussion

#### 2.4.1 Separation of lithium

The first 8 ml of 1M HNO\(_3\)/methanol removes Ti, Zr, Hf, Nb and Ta from the resin. From 9 to 16 ml lithium is eluted. Sodium, the next element to elute after lithium, is not present in the first 20 ml, i.e. an excellent separation of lithium and sodium is achieved. The earliest breakthrough of Li is \(^7\)Li-enriched whereas the tail is enriched in \(^6\)Li (Moriguti and Nakamura, 1998a; Köbler et al., 2001). This means that \(^6\)Li is preferentially taken up by AG 50W-X8 resin. This is because of a difference in the zero point energy and vibrational frequencies of the two isotopes (Bigeleisen, 1965). The process must be essentially an equilibrium fractionation between AG 50W-X8 resin and 1M HNO\(_3\)/methanol rather than
diffusion, since the lighter isotope would elute first in a kinetic process. However, fractionation of lithium on AG 50W-X8 can be as high as 100% for small-sized columns (see Fig. 4 in Köhler et al., 2001). Thus complete recovery of lithium is essential to avoid chromatographic fractionation effects. The quantitative recovery of lithium is monitored by concentration measurements prior to separation and thereafter. Samples for which less than 100% lithium (within analytical errors) was recovered have not been taken for isotope analysis.

Chan et al. (2002b) reported a significant change of the elution behaviour of lithium related to high magnesium and iron concentrations in volcanic rocks. In order to test whether different rock matrices influence the elution parameters of our analytical procedure we have analysed a series of samples with a range of MgO and SiO$_2$ content: OK-1 eclogite from Oberkotzau, Germany (51% SiO$_2$ and >10% MgO; Schramm, 1993); the rock standards JB-2, a basalt (53.3% SiO$_2$ and 4.6% MgO), AGV-2, an andesite (59.3% SiO$_2$ and 1.8% MgO).
and JR-2, a rhyolite (76% SiO₂ and 0.04% MgO). Results of the column calibration are shown in Fig. 2.1. In all these cases, lithium was quantitatively recovered between 9 and 16 ml.

Two mineral separates with completely different composition were also tested - an olivine from Iherzolite 8520-9 (WIECHERT et al., 1997) and a spodumene from a zoned pegmatite (Tin Mountain mine, Harney Peak, USA; SIRBESCU and NABELEK, 2003). Lithium is a trace element in olivine (SEITZ and WOODLAND, 2000; PAQUIN and LUTHERR, 2002; PAQUIN et al., 2004). On the other hand, lithium in spodumene (nominally LiAlSi₂O₆) is a major element, thus, matrix is absent because Li itself is the major element. This makes such minerals useful for testing whether the separation is suitable for these extreme compositions. The results (Fig. 2.2) show that even such different compositions were not able to disturb the separation scheme. Lithium is eluted from olivine within exactly the same span as from all rocks mentioned above, starting with 9 ml and ending by 16 ml without concomitant elution of magnesium. The only problem follows from the huge amount of Li in spodumene. Thus, the elution window for Li has to be broadened until 19 ml is eluted because the Li tail is still

![Graph 1: Elution of lithium from olivine from Iherzolite 8520-9.](image1)

![Graph 2: Elution of lithium from spodumene from Harney Peak (USA).](image2)

*Fig. 2.2: Elution of lithium for mineral separates. a) olivine from Iherzolite 8520-9 and b) spodumene from Harney Peak (USA). Note that elution of lithium is within exactly the same volume as for rocks. Opening the window for spodumene is caused by large amount of lithium present in the sample.*
high. This test also shows that an excellent separation of large abundances of lithium from other elements is achieved. Therefore, only unusual and dramatically high lithium concentration in rocks or minerals may change lithium elution parameters, i.e. the method is matrix independent for most silicate materials.

2.4.2 Instrumental mass fractionation

Nu 1700 can accommodate the mass dispersion of ~15% suitable for simultaneous detection of both lithium isotopes. However, all plasma source mass spectrometers suffer from a mass bias effect (Freedman, 2002) that increases towards lighter masses. It depends on cones, extraction lenses and many other parameters. To detect natural stable isotope variations it is necessary to distinguish between instrumental and natural fractionation. For stable isotopes in the lower mass range this is only possible by comparing samples with a standard by using the so-called “sample-standard bracketing” technique (Tomascak et al., 1999a). During this study 40-60 individual isotope ratios for each sample and standard run were measured. The isotope ratio of the sample was calculated relative to the average of two bracketing standards (Fig. 2.3). Typically three to four L-SVEC-normalized isotope ratios for one sample were measured in one analytical session. The mass spectrometer extraction and focusing potentials were tuned daily to yield the best signal stability. No tuning was performed during the measurements because any changes of the instrumental setting would change the mass bias. The precision of a single run varied between 0.06-0.15‰ (2SE) whereas errors calculated from averages of at least 4 sample runs give ≤ 0.5‰ (2SD).

To ensure that the Nu1700 was functioning correctly, a lithium solution prepared from LiNO₃ (Merck) was measured before each analytical session. With the LiNO₃ the accuracy and precision of the mass spectrometer can be monitored, excluding any effects from column chemistry. The isotope composition of the LiNO₃, measured over the past 12 months, is 0.91 ± 0.15‰ (2SD, n=15) relative to L-SVEC. This error also states our best possible long-term reproducibility because this solution is not treated with the column chemistry procedure.

In order to evaluate possible background contributions to the analytical uncertainty of the measurements, we tested a DSN-100 (Nu Instruments) and Aridus (Cetac) desolvating nebulizer in standard mode and time-resolved analysis (TRA) mode. A key difference of the two analysis routines lies in how the zero correction is carried out. The standard mode measures zeros by deflecting the ion beams whereas in TRA mode zeros are measured with
Fig. 2.3: Standard-sample-standard bracketing technique. $^{7}\text{Li}/^{6}\text{Li}$ ratios of 4 single sample measurements (squares) bracketed by 5 L-SVEC analyses (diamonds) are shown. Each symbol represents 40-60 single measurements. The slight increase of the sample $^{7}\text{Li}/^{6}\text{Li}$ ratios is corrected by a similar increase of the ratio for bracketing standard.

ion beams on cups, i.e. for the zero measurement a clean zero or blank solution is applied. Typically zero measurements on mass 7 were in the range of several mV whereas 40 ppb Li in solution gave between 5 and 7 volts (uptake rate 80 ìL min$^{-1}$). The $^{7}\text{Li}/^{6}\text{Li}$ ratio of the background has been detected at ~12.6, while measured ratios of L-SVEC varied between 13.8 and 14.4 depending on cones, gas flow conditions and lens settings. To find the best analysis procedure for lithium isotope measurements, L-SVEC solutions with concentrations ranging from 10 to 45 ppb are compared with a 50-ppb L-SVEC standard solution. The measured isotope ratios for these L-SVEC solutions vary by ~3.5% for the 10 ppb solution relative to the 50-ppb solution for the DSN-100 when measured in standard mode (see Fig. 2.4). When the standard mode is employed together with the Aridus, lithium isotope ratios are altered by ~2.0% (see Fig. 2.4). When the TRA mode is applied, isotope ratios are independent of sample concentrations (see Fig. 2.4).

We conclude that the mass bias effect on lithium isotopes is, within error, concentration independent. It is likely that insufficient time elapses to wash out lithium between standard and sample analysis. Between samples and standards it has been washed with 2% HNO$_3$ for 120 seconds. Methods measuring zeros by deflecting ion beams cannot correct for any
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Fig. 2.4: Lithium isotope ratio measurements of L-SVEC solutions with different concentrations using an Aridus (Cetac) and DSN-100 (Nu Instrument) desolvating nebulizer for sample introduction. Plotted are isotope ratios versus concentration of the sample solution relative to 50-ppb L-SVEC solution as total beam intensity (I) ratios (I-SA/I-50ppb). Both Aridus and DSN-100 show a “concentration” effect when zero values are obtained by ion beam deflection with the electrostatic analyser (ESA). In contrast, isotope ratios obtained by time-resolved analysis do not show a concentration dependence of Li isotope ratio measurements (see text for discussion). Symbols represent average values of at least 4 single measurements. Errors are 2SD.

lithium memory independent from the used desolvator. Better results are achieved by measuring zeros using blank solution in TRA mode. Alternatively concentrations of sample and standard solutions could be balanced within ±10%. Then memory effects become negligible independent of which method is used (Fig. 2.4).

Any matrix element in the sample solution may change the instrumental fractionation (mass bias) and alter the isotope ratio of samples in a different way to the standard (e.g. Zhu et al., 2002). Therefore, all solutions have been monitored for Na, Mg, Ca, Al and Fe. These elements have been selected because of distribution coefficients similar to lithium in analytical procedure or because they are major elements. In no case did we observe significant amounts of Na, Mg or any other of these elements in the Li aliquots. In the worst case the total fraction might make up 20% of the lithium. Such amounts would not have any
detectable effect on lithium isotope ratios. Despite not observing any significant amounts of alkalis beside lithium, the effect of large concentrations of alkali elements in the final eluate was tested. Pure L-SVEC solutions were individually doped with Na, Mg, Al, and a multi-element matrix consisting of Na, Mg, Al, Ca, K and Fe. Solutions with Na/Li, Mg/Li, and Al/Li ratios of 1:1 and 5:1 and multi-element/Li solution with equal concentrations of all elements were prepared and the isotope ratio of lithium was compared with pure L-SVEC standard solution (Fig. 2.5). Sodium has no effect on lithium isotope ratio in either Na/Li proportions. Magnesium causes slightly higher lithium isotope ratios but only at higher concentrations (Mg/Li 5:1). Low magnesium concentrations (Mg/Li 1:1) have no detectable effect. Aluminium shifts the Li isotope ratio toward lighter isotope ratios already at low Al/Li (1:1). However, the effect is not concentration dependent because higher Al/Li (5:1) fractionate lithium isotopes by exactly the same extent. The multi-element solution (Na+Mg+Al+K+Ca+Fe/Li 1:1) shows no effect when compared with pure L-SVEC. This suggests lithium isotope measurements on the Nu-1700 can be affected by matrix elements at

![Fig. 2.5: The effects of matrix elements. L-SVEC solutions doped with Na (diamonds), Mg (circles), Al (squares), and a multi-element (Na, Mg, Al, Ca, K and Fe) matrix (triangle) are compared with pure L-SVEC solutions. Each symbol represents the average of 4 single measurements. The grey field gives the reproducibility of lithium isotope ratios for pure L-SVEC solutions. Open symbols represent element/lithium ratios of 1:1, closed symbols 5:1. Error bars are 2SD.](image)
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only high concentrations (see also BRYANT et al., 2003b). However, for the data reported here, matrix elements did not make up more than 20% of the lithium, and this precludes any alteration of the isotope ratios by the matrix effects discussed above.

2.4.3 L-SVEC measurements

The international reference material for Li isotope analysis, L-SVEC, was prepared from several kilograms of high-purity carbonate and its Li isotope composition measured. This yielded an absolute ratio of $^{7}\text{Li}^{6}\text{Li} = 12.02 \pm 0.03$ (FLESCH et al., 1973). However, such a large error is greatly in excess of that needed for geological problems because lithium isotope variations in nature are never larger than several tens of per mil (see TOMASCAK (2004) and references therein). GALY et al. (2003) have shown that Mg international reference material SRM 980 suffers from large amounts of heterogeneity in $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{26}\text{Mg}/^{24}\text{Mg}$. Therefore, we tested the homogeneity of Li L-SVEC. We measured three aliquots of L-SVEC from three international labs (Univ. Maryland, USA; Open Univ., UK; Charles Univ. in Prague, Czech Rep.) together with our own aliquot that has been used as a bracketing solution. The results are shown in Fig. 2.6. All three aliquots were identical to our own within

![Fig. 2.6: Comparison of several selected L-SVEC aliquots. It is clear that this reference material is homogeneous in terms of lithium isotope composition. Open symbols represent individual runs; closed symbols are the averages of the respective runs with 2SE error bars (diamonds – P. Tomascak, $\delta Li = 0.01 \pm 0.05\%$; circles – J. Koller, $\delta Li = 0.04 \pm 0.05\%$; squares – R.H. James, $\delta Li = 0.01 \pm 0.07\%$; solid line is the average of our L-SVEC aliquot with dashed lines as 2SE error bars, $\delta Li = 0.003 \pm 0.099\%$).](image-url)
± 0.03‰. Thus, this standard would appear to be homogeneous and very suitable for high precision isotope ratio mass spectrometry.

### 2.4.4 International reference rocks

The data for international reference rocks from this study are presented in Table 2.2. The error of all averages is given as 2SD. Outliers are excluded from the calculations of averages using 3σ-confidence limits. There is no systematic correlation between measured concentrations and isotope ratios of individual samples.

We chose a broad variety of reference rocks from basic to acidic compositions to test whether our column chemistry is sensitive to different igneous rock types and to determine precision and accuracy of the new lithium separation scheme on the 2.1ml columns and using MC-ICPMS. Different volcanic rocks ranging from high MgO, low SiO₂ concentrations to high SiO₂, low MgO chemistry were selected (see also section 2.3.1).

The δ⁷Li value of 4.7 ± 0.3‰ (2SD) for JB-2 from this study (10 separate digestions of JB-2) is in good agreement with previously published values 5.1 ± 1.1‰ (2SD; TOMASCAK et al., 1999a) and 4.9 ± 0.7‰ (2SD; MORIGUTI and NAKAMURA, 1998a) and within analytical error of 4.3 ± 0.3‰ (2SD; NISHIO and NAKAI, 2002). However, this value is significantly different from a δ⁷Li of 6.8 ± 0.2‰ (2SD) reported by JAMES and PALMER (2000). A compilation of available data for JB-2 is given in Fig. 2.7.

For BHVO-2 a total of 9 averages gives a δ⁷Li of 4.55 ± 0.3‰ (2SD). This is in excellent agreement with δ⁷Li of 4.5 ± 1.0‰ (2SD) reported by ZACK et al. (2003). A δ⁷Li value of 5.3 ± 0.2‰ (2SE) has been obtained for BHVO-1 which is in the middle of the range of published δ⁷Li values from 5.0 to 5.8‰ (JAMES and PALMER, 2000; BOUMAN et al., 2002; CHAN and FREY, 2003). Although both BHVO-1 and BHVO-2 come from the same lava flow, they are distinct by about 0.8‰ in δ⁷Li and do not overlap within analytical error in our study. This may be explicable by some small-scale heterogeneity. Heterogeneity for lead isotopes has been reported for BHVO-2 (WOODHEAD and HERGT, 2000).

For JR-2 a δ⁷Li of 3.8 ± 0.2‰ (2SE) has been measured which is within analytical error the same as reported by JAMES and PALMER (2000; δ⁷Li = 3.9 ± 0.8‰; 2SD) and 3.9 ± 0.4‰ (2SD) reported by CHAN and FREY (2003) using TIMS techniques. It is interesting to note that this rhyolite still has a δ⁷Li similar to that for pristine mantle rocks (CHAN, 2003) consistent
with no isotope fractionation during magmatic differentiation as reported by Tomascak et al. (1999b) for a sub-alkalic to alkalic basaltic rock suite.

<table>
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<th>Li (ppm)</th>
<th>Li (ppm)</th>
<th>δ²⁷Li (%)</th>
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<th>n²</th>
<th>Average (2SD)</th>
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</tbody>
</table>

recomm. – recommended

a number of individual measurements

b Bouman et al. (2002)

c James and Palmer (2000)


e Zack et al. (2003)

f Tomascak et al. (1999a)

g Moriguti and Nakamura (1998a)

h Nishio and Nakai (2002)
A $\delta^7$Li of $7.9 \pm 0.6\%$ (2SD) measured for AGV-2 is clearly above the $\delta^7$Li range of fresh MORB mantle rocks (Zack et al., 2003). The Li in AGV-1 and AGV-2 is slightly different. The $\delta^7$Li value of AGV-1 ($6.7 \pm 0.2\%$, 2SE) is substantially lower.

2.4.5 Other reference materials and rocks

Lithium abundances and isotope compositions of several other materials are summarized in Table 2.3. The lithium isotope composition of NIST SRM 612, the nominally 50-ppm multi-element glass standard used for laser-ICPMS, is close to seawater ($\delta^7$Li = $35.3 \pm 0.8\%o$, 2SD). The Li content of ~33 ppm measured during this study is lower when compared to the nominal value which reflects heterogeneity of this reference material as shown also by other elements (see Pearce et al. (1997) and references therein). This may also be the source of the poorer reproducibility of this reference material.
A $\delta^{7}\text{Li} = -8.3 \pm 0.2\%$ (2SD) for the eclogite OK-1 is consistent with a MORB protolith (Schrömm, 1993) and fractionation of lithium isotopes related to subduction and dehydration as proposed by Zack et al. (2003) for eclogitic rocks from Trescolmen, Switzerland. Recently, even more negative $\delta^{7}\text{Li}$ values were reported for peridotitic rocks from far-east Russia that have been metasomatised by an eclogitic melt (Nishio et al., 2004).

### Table 2.3: $\delta^{7}\text{Li}$ values for other rocks and standard materials

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<tr>
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<th>Li (ppm) measured</th>
<th>Li (ppm) recomm.</th>
<th>$\delta^{7}\text{Li}$ (%)</th>
<th>2 S.D.</th>
<th>$n^a$</th>
<th>Average</th>
<th>2 S.D.</th>
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<td>(Münchberg, Germany)</td>
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<td>Li nitrate</td>
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recomm. = recommended  

$^a$ number of individual measurements  

$^b$ Concentration matched to 40ppb of L-SVEC  

$^c$ Pearce et al. (1997)

The olivine fraction of peridotite 8520-09 has a low Li concentration of 1.4 ppm, which is consistent with previous findings for garnet peridotites from Alpe Arami (Central Alps, Switzerland; Paquin and Altherr, 2002) and for mineral separates of peridotitic rocks from Kenya, France, Australia, Italy and Germany (Shitz and Woodland, 2000). Isotope analysis...
of this olivine yielded $\delta^7\text{Li} = 3.6 \pm 0.4\%_e$ (2SE). This is consistent with the conclusions, that $\delta^7\text{Li}$ of unmetasomatized mantle is $4.2 \pm 0.8\%_e$ (Chan, 2003) similar to values for peridotites reported by Chan et al. (2002b) and Brookfield et al. (2000). Spodumene from Tin Mountain, Harney Peak, has $\delta^7\text{Li} = 7.2 \pm 0.2\%_e$ (2SE). This is similar to lithium isotopes measured for I-type granites from Australia (Bryant et al., 2003a). However, granites from the Harney Peak region are considered S-type, which are expected to have low $\delta^7\text{Li}$ values. Therefore, the Li-isotope composition of this pegmatite is unlikely a magmatic source signature. It may be related to late stage fractionation and/or alteration process occurring in that region (Sirbescu and Nabelek, 2003). Further studies are required to solve this paradox.

2.5 Conclusions

We have presented lithium isotope data for 7 international reference rocks and some other rocks and materials that comprise a wide range of silicate rocks. The results obtained in this study are in good agreement with published data showing that our method for Li separation is suitable for the basalt-to-rhyolite span of silicate rocks. The technique is also suitable for other materials (Li minerals) that can be treated in exactly the same way as whole rock samples without any influence on the isotope ratios. A precision of $\leq 0.5\%_e$ (2SD) obtained over 12 months is comparable to or better than that reported for larger columns. We conclude that much smaller acid volumes and therefore low blanks allow us to analyse ~5 ng lithium to high precision. This opens up the field for new studies on sample-size-restricted objects and/or materials with low lithium concentration.

Acknowledgement – We thank J. Košler (Charles University, Prague, Czech Republic) for useful suggestions about the column chemistry and comments on earlier versions of the manuscript and M. Vobecký (Academy of Sciences, Prague, Czech Republic) for fruitful debates on resin problems. Mona Sirbescu (Central Michigan University, Michigan, USA) provided sample of spodumene. J. Košler, P. Tomascak (Univ. Maryland, USA) and R.H. James (Open Univ., Milton Keynes, UK) kindly provided aliquots of L-SVEC. This work was supported by ETH and Swiss Nationalfonds.
Chapter 3 *

Lithium isotope fractionation in the southern Cascadia subduction zone

3.1 Abstract

We present lithium (Li) abundances and isotope compositions for a suite of anhydrous olivine tholeiites (HAOTs) and hydrous basalt-andesitic (BA) lavas from the Mt. Shasta and Medicine Lake regions, California. The values of $\delta^{7}$Li vary from $+0.9\%$ to $+6.4\%$ and correlate inversely with distance from the trench. These data are consistent with continuous isotope fractionation of Li during dehydration of the subducted oceanic lithosphere, an interpretation corroborated by uniformly high pre-eruptive H$_2$O contents in basaltic andesites accompanied by high Li, Rb, Sr, Ba and Pb abundances. The subduction-derived component that was added to these hydrous magmas is shown to be very similar beneath both Mt. Shasta and Medicine Lake volcanoes despite characteristically distinct Li isotope compositions in the magmas themselves. More evolved andesites and dacites from Mt. Shasta have $\delta^{7}$Li from $+2.8$ to $+6.9\%$ which is identical with the range obtained for HAOTs and BA lavas from Mt. Shasta. Therefore, Li isotopes do not provide evidence for any other crustal component admixed to Mt. Shasta andesites or dacites during magmatic differentiation and magma mixing in the crust.

3.2 Introduction

At convergent plate boundaries cold and brittle oceanic lithosphere descends into the more ductile asthenospheric mantle resulting in explosive volcanism, high-magnitude earthquakes and fast morphological evolution of the overriding plate. Several processes may ultimately lead to melt production: (i) percolation of aqueous slab fluids into the mantle wedge (Tatsumi and Maruyama, 1989; Grove et al., 2002), (ii) partial melting of the slab (Kelemen, 1995), (iii) reaction of slab melts generated by partial melting of the subducted slab with the overlying mantle (Kay, 1978; Youdinski et al., 1995), or (iv) more complicated two-step processes such as hydrous metasomatism of cold lithosphere and subsequent melting of “wet” mantle segments related to back-arc rifting (Dorendorf et al., 2000).

Lithium isotope fractionation is mainly related to low temperature processes at the surface and provides a geochemical tracer of recycled crust in volcanic rocks. Volcanism in the Cascadian arc in California is dominated by basalts with subordinate andesitic to dacitic lavas (Gill, 1981; Grove and Kinzler, 1986). These evolved lavas are multi-component
mixtures of mantle melts and andesite, dacite and rhyodacite magmas produced by fractional crystallization. The high-alumina olivine tholeiites (HAOTs) and basalt-andesitic (BA) lavas of this study do not show a strong overprint of fractional crystallization, crustal contamination and/or magma mixing, making them excellent samples for studying processes in subduction zones (GROVE et al., 2002).

Lithium exhibits large isotope fractionation in the subduction zone environment (MORIGUTI and NAKAMURA, 1998b; CHAN et al., 2002b; ZACK et al., 2003). Generally, it is believed that heavy isotope inputs are provided into the subduction zone by serpentinitized peridotites that may have $\delta^7$Li values as heavy as +20‰ (DECITRE et al., 2002; BENTON et al., 2004) and altered oceanic basalts (CHAN et al., 1992, 2002a; JAMES et al., 2003). Altered seafloor is substantially enriched in Li over fresh ridge basalts to as much as ~80 ppm accompanied by distinctly heavy isotope compositions ~+14‰ (CHAN et al., 1992, 2002a; SEYFRIED et al., 1998). However, the concept that heavy Li is transferred into the subduction zone environment has been recently questioned because of the light or “mantle-like” $\delta^7$Li values (mainly between -1 and +5‰) found in pelagic clays, oozes, muds and claystones (BOUMAN et al., 2004) combined with the observation that arc lavas have predominantly MORB-like Li isotope ratios (TOMASCAK et al., 2002). Progressive shifts toward very negative $\delta^7$Li had been already recognized and were related to preferential loss of $^7$Li into the fluid phase leaving the residue isotopically light (ZACK et al., 2003). Indeed, the extent of depletion in $^7$Li is greater with larger degrees of seafloor alteration. However, the behaviour of Li in subduction zones still remains largely unexplored and rather ambiguous Li cross-arc trends (i.e. linked or not linked to the fluid expulsion from subducted slab) were revealed in various subduction zones and volcanic arcs, e.g. Japan (MORIGUTI and NAKAMURA, 1998b; MORIGUTI et al., 2004), northern Cascades (LEEMAN et al., 2004), Mariana arc (BENTON et al., 2004), Kurile, Aleutian and Sunda arcs (TOMASCAK et al., 2002), Central American Volcanic Arc – CAVA (CHAN et al., 1999, 2002b) or Panama arc (TOMASCAK et al., 2000). It is thought that the initiation of slab melting may produce extremely light Li isotope compositions (NISHIO et al., 2004).

In this paper Li abundances and isotope data are presented for HAOTs and primitive BA lavas from Mt. Shasta and the Medicine Lake regions, northern California. These data are used to place new constraints on the Li isotope geochemistry of convergent plate margins and the inputs of Li to the source of arc volcanics.
3.3 Geology of the region

Mt. Shasta lies near the southern end of the Cascades chain and is flanked to the west by pre-Tertiary rocks of the Klamath Mountains province. In the northeast and east Mt. Shasta is bordered by Tertiary and Quaternary volcanics of the High Cascades. Medicine Lake lies about 60 km to the east. This back-arc shield volcano has erupted large amounts of basaltic to rhyolitic volcanics. The Lassen Volcanic Field is ~130 km to the south. Tertiary sandstones, shales, and andesitic volcanics, Mesozoic granitic rocks of the Trinity ophiolite and Mesozoic and Palaeozoic meta-sedimentary rocks are present in the Mt. Shasta region and have been inferred to be present beneath the volcano (Fuis et al., 1987).

Subduction zone volcanism in northern California is related to the Juan de Fuca plate, which is being subducted at a half spreading rate of 40 mm per year (Wilson, 1988). The location of the subducted slab can be estimated at ~110 km depth below Mt. Shasta and has been inferred to be at ~200 km depth below the Medicine Lake region (Zucca et al., 1986; Harris et al., 1991; Benz et al., 1992). The age of the oceanic plate beneath Mt. Shasta is inferred to be 12–14 million years (Green and Harry, 1999). Four major eruptive phases comprise the volcano, Sargents Ridge (<250–130 ky), Misery Hill (80–10 ky), Shastina (10–9.4 ky) and Hotlum (6–2 ky; Christiansen et al., 1977). Previous geochemical and petrologic studies of Mt. Shasta include those of, for example, Anderson (1974).

Some of the samples from this study have been characterized by Grove et al. (2002, 2003, 2005), Baker et al. (1994), Kinzler et al. (2000), Wagner et al. (1995) and Elkins Tanton et al. (2001). The reader is directed to these authors for further petrologic and geochemical descriptions. The suite of samples comprises two Mt. Shasta and six Medicine Lake primitive high-alumina olivine tholeiites (HAOTs), four basaltic andesites (BA) and one primitive magnesian andesite (PMA) from Mt. Shasta and two basaltic andesites and two samples of the Lake Basalt (Wagner et al., 1995) from Medicine Lake. Additionally, we have analysed six andesites and eight dacites from the Mt. Shasta stratocone.

3.4 Analytical techniques

Samples were digested in a mixture of doubly distilled concentrated HF and HNO₃ (6:1 by volume), evaporated to dryness and treated three times with concentrated HNO₃. Subsequently the samples were dissolved in 6M HCl and loaded on columns. A single step of
ion exchange chromatography (BioRad AG50W-X8, 200-400 mesh) was used to separate Li from matrix elements, using 1M HNO₃ made up in 80%-methanol as elution media. A detailed description of the method is given in MAGNA et al. (2004b). The purified Li solutions were measured on the large-geometry high-resolution multiple-collector ICPMS Nu1700 (Nu Instruments) at m/Δm ~700. An in-house standard has been measured before measuring unknown samples to monitor the quality of the mass spectrometric measurements. International reference rock standards such as JB-2 from the Geological Survey of Japan (GSJ) were prepared with unknown samples to check for possible lithium isotope fractionation on the ion exchange columns and/or blank effects. Samples were measured with a standard-sample bracketing method using L-SVEC as a reference (FLESCH et al., 1973). Lithium isotope ratios are calculated as $\delta^7\text{Li} (\text{‰}) = \left( \frac{^{7}\text{Li}^{6}\text{Li}}{^{7}\text{Li}^{6}\text{Li}_{\text{standard}}} \right) \times 1000$. The in-run precision of single measurements varied typically between 0.05 and 0.10‰ (2σ). Three to five individual runs were performed for each sample from which the mean and 2σ analytical uncertainty were calculated. The long-term reproducibility and precision of our in-house Li standard is $\delta^7\text{Li} = 0.94 \pm 0.14$‰ (2σ, n=28). Analyses of JB-2 prepared together with Mt. Shasta volcanic rocks averaged $\delta^7\text{Li} = 4.79 \pm 0.29$‰ (2σ, n=4) in four analytical sessions. This is in excellent agreement with published data (MORIGUTI and NAKAMURA, 1998a; TOMASCCK et al., 1999a; CHAN and FREY, 2003; JEFFCOATE et al., 2004; MAGNA et al., 2004b).

Concentration measurements were performed on a quadrupole ICPMS VG Elemental PQ2 prior to separation and thereafter using beryllium as an internal standard for matrix element correction. The Li concentrations so determined were used to calculate yields and to reject samples with <95% recovery. We also used the PQ2 to monitor each sample for the presence of matrix elements (Na, Mg, Al, Ca, Fe) after ion-exchange chromatography. Samples with a total matrix content that exceeded 20% of the Li abundance were not used for isotope analysis. Trace element concentrations, with the exception of Li, were determined on the PQ2 using rhodium as an internal standard. The accuracy and precision of trace element analyses were checked against analysis of JB-2 (GSJ), BHVO-2 and AGV-2 (USGS). Barium contents were higher by about 10-15% relative to reference values. Accordingly, Ba abundances for tholeiites, basaltic and magnesian andesites were corrected down by 15% and for andesites and dacites down by 10%. The 2σ errors on concentration measurements were better than 5% for most elements, with some scatter for Cs (<10%).

41
Strontium (Sr) and neodymium (Nd) were separated following procedures of Horwitz et al. (1992) and Cohen et al. (1988), respectively. Strontium and Nd isotope compositions were measured on a Nu Plasma MC-ICPMS (Nu Instruments). Masses 83 and 85 were used to correct for Kr and Rb interferences, respectively, that were <1% of the respective Sr isotope beam. The instrumental mass bias was corrected using an exponential fractionation law. The $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios were corrected for mass bias using $^{88}\text{Sr} / ^{86}\text{Sr} = 8.3752$ and $^{143}\text{Nd} / ^{144}\text{Nd}$ was corrected using a $^{146}\text{Nd} / ^{144}\text{Nd}$ of 0.7219. All $^{143}\text{Nd} / ^{144}\text{Nd}$ ratios were normalized to the JMC-Nd standard using $^{143}\text{Nd} / ^{144}\text{Nd} = 0.511833$ (cross-calibrated to a ratio of 0.511858 for La Jolla standard). $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios were normalized to the accepted ratio of 0.710245 for the NIST SRM 987. These new Sr data are within ±0.01% (1σ unit) of previous Sr isotope data for Medicine Lake olivine tholeiite 82-72a (Baker et al., 1991) and basaltic andesite 79-24E (Kinzler et al., 2000).

### 3.5 Results

Lithium abundances and isotope data for Mt. Shasta and Medicine Lake lavas are presented with other radiogenic isotope data in Tables 3.1 and 3.2 (see Grove et al. (2002) for Sr, Nd and Pb isotope data for Mt. Shasta lavas). Lithium contents of olivine tholeiites and basaltic andesites are within the range reported for arc volcanics from southern Washington Cascades (Leeeman et al., 2004) and Central America (Chan et al., 2002b) but are about half of those of subduction-related calc-alkaline lavas of the Panama arc (Tomascak et al., 2000). The Li abundances range from 3.2 to 7.8 ppm in HAOTs, are between 5.0 and 11.4 ppm in BA and Lake Basalt lavas, and yield a value of 10.2 ppm for PMA sample 85-41b. Most andesites and dacites have Li concentrations ranging from 6 to 11 ppm. The $\delta^7\text{Li}$ values of HAOTs, BA lavas and PMA vary between +0.9‰ and +6.4‰ relative to L-SVEC with only slight overlap between Mt. Shasta and Medicine Lake volcanics (Fig. 3.1). A subset of two andesites and two dacites exhibits high Li abundances (up to 35 ppm) compared to other evolved lavas; this is paralleled by high Rb, Cs, Ba, Pb, Th and U concentrations and slightly elevated $^{87}\text{Sr} / ^{86}\text{Sr}$. All andesites and dacites from Mt. Shasta have $\delta^7\text{Li}$ values between +2.8‰ and +6.9‰ which is within the range of BA lavas and HAOTs.
Table 3.1: Lithium concentrations and isotope compositions in Mt. Shasta and Medicine Lake lavas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Li</th>
<th>δ²⁷Li</th>
<th>2σ</th>
<th>n</th>
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<tbody>
<tr>
<td><strong>Mt. Shasta</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85-38*</td>
<td>HAOT</td>
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<td>3.04</td>
<td>0.24</td>
<td>1</td>
</tr>
<tr>
<td>85-51*</td>
<td>HAOT</td>
<td>6.3</td>
<td>3.02</td>
<td>0.02</td>
<td>3</td>
</tr>
<tr>
<td>82-94a²</td>
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<tr>
<td>85-44*</td>
<td>BA</td>
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<td>4.04</td>
<td>1.23</td>
<td>2</td>
</tr>
<tr>
<td>95-15*</td>
<td>BA</td>
<td>6.8</td>
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<td>0.49</td>
<td>2</td>
</tr>
<tr>
<td>95-17*</td>
<td>BA</td>
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<td>5.14</td>
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<td>3</td>
</tr>
<tr>
<td>85-41b³</td>
<td>PMA</td>
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<td>4.74</td>
<td>0.58</td>
<td>2</td>
</tr>
<tr>
<td>82-94d⁴</td>
<td>A</td>
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<td>6.27</td>
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<tr>
<td>85-55*</td>
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<td>11.2</td>
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<tr>
<td>85-48b³</td>
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<td>6.44</td>
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<tr>
<td>85-59*</td>
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<td>0.15</td>
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<tr>
<td>82-85*</td>
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<tr>
<td>82-92a⁵</td>
<td>D</td>
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<td>0.40</td>
<td>3</td>
</tr>
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<td>82-95*</td>
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<td>5.97</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>83-58*</td>
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<td>D</td>
<td>9.1</td>
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<td>0.07</td>
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</tr>
<tr>
<td><strong>Medicine Lake</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>82-72a</td>
<td>HAOT</td>
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<td>2.42</td>
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<td>HAOT</td>
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<td>1.22</td>
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<td>1</td>
</tr>
<tr>
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<td>2.33</td>
<td>0.16</td>
<td>1</td>
</tr>
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<td>95-5*</td>
<td>HAOT</td>
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<td>1.19</td>
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<td>1</td>
</tr>
<tr>
<td>95-6*</td>
<td>HAOT</td>
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<td>0.09</td>
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<td>5.02</td>
<td>0.29</td>
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<tr>
<td>1665m</td>
<td>LB</td>
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<td>3.28</td>
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</tr>
<tr>
<td>1672m</td>
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<td>1.95</td>
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</tr>
<tr>
<td>1399m</td>
<td>BA</td>
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<td>2.36</td>
<td>0.14</td>
<td>1</td>
</tr>
<tr>
<td>79-24E</td>
<td>BA</td>
<td>11.4</td>
<td>0.93</td>
<td>0.30</td>
<td>2</td>
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<td><strong>Reference standards</strong></td>
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<td>BHVO-2</td>
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<td>8.14</td>
<td>0.66</td>
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<td>2</td>
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</table>

Li concentrations are given in ppm. Li isotope compositions expressed in per mil relative to L-SVEC standard. HAOT – high-alumina olivine tholeiite, BA – basaltic andesite, PMA – primitive magnesian andesite, A – andesite, D – dacite, LB – Lake Basalt

* see Grove et al. (2005) for Sr, Nd and Pb isotopes and trace element geochemistry; ³ see Baker et al. (1991); ² see Elkins Tanton et al. (2001); ⁴ see Wagner et al. (1995); ⁵ see Kinzler et al. (2000); ⁶ **number of full replicate measurements including sample dissolutions**
Selected trace element concentrations are presented in Tables 3.3 and 3.4, respectively, and are within 5% of the abundances previously reported for these elements (BAKER et al., 1991, 1994; WAGNER et al., 1995; KINZLER et al., 2000; GROVE et al., 2002). MORB-normalized patterns are remarkably similar with only subtle differences in Nb (Ta) depletion and REE pattern of HAOTs (Fig. 3.2). HAOT and BA lavas from Mt. Shasta and Medicine Lake cannot be resolved from each other in their normalized patterns.

Fig. 3.1: Histogram of $\delta^{7}\text{Li}$ values in tholeiites, andesites and dacites from Mt. Shasta and Medicine Lake. High-alumina olivine tholeiites are in black, basaltic andesites in dark grey, primitive magnesian andesite with pattern, andesites are in light grey and dacites are in white. Progressive enrichment in $^{7}\text{Li}$ is found in Mt. Shasta BA lavas, whereas BA lavas from Medicine Lake have light $\delta^{7}\text{Li}$ values, probably as a result of Li isotope fractionation during subduction.
Chapter 3 Southern Cascades

3.6 Discussion

3.6.1 High-alumina olivine tholeiites

High pressure experiments (BARTELS et al., 1991) show that HAOTs from the Medicine Lake area originate from near-anhydrous melting of spinel peridotite consistent with low water contents of melt inclusions in olivine (SISSON and LAYNE, 1993). Anhydrous melting has also been assumed for HAOTs from Mt. Shasta on the basis of very similar major element chemistry (GROVE et al., 2002) and low pre-eruptive water contents in HAOTs from northern California Cascades (SISSON and LAYNE, 1993). Analysis of primitive HAOTs from the Cascades region has shown that the magmas underwent fractional crystallization of olivine + plagioclase and the depth of their generation increases eastwards parallel to modeled corner flow lines rather than dip of subduction (ELKINS TANTON et al., 2001). The Li isotope compositions of HAOTs from Mt. Shasta give an identical $\delta^7\text{Li} = +3.0\%o$ whereas HAOTs from the Medicine Lake region range from $+1.2$ to $+5.0\%o$. There is no indication from existing data that Li isotopes fractionate during partial melting or magmatic differentiation on Earth (TOMASCAM et al., 1999b). An exception might be the extensive magmatic differentiation during crystallisation of the lunar magma ocean which produced a range of cumulate sources with distinct Li isotope signatures (MAGNA et al., 2006b). Nevertheless, Li isotope variations observed in HAOTs in this study most likely reflect heterogeneity of the mantle below the Mt. Shasta and Medicine Lake regions. Such chemical variability of the mantle sources has been drawn from trace element models in primitive HAOTs and BA lavas from adjacent Lassen region (CLYNNE and BORG, 1997). There is no evidence for assimilation of granitic crust and/or contamination of HAOTs by Trinity harzburgites, inferred beneath Mt. Shasta (BAKER et al., 1994). Therefore, relative fertility of mantle wedge segments beneath Mt. Shasta and Medicine Lake (BORG et al., 1997) may account for the observed several per mil scatter in HAOTs.

HAOTs are relatively enriched in fluid mobile elements such as Pb, Sr and Li compared to MORB (Fig. 3.2). The enrichment of highly fluid mobile elements provides evidence for a subduction-related component in HAOTs (see also HART, 1985). This is consistent with metasomatic enrichment of this mantle segment before melt extraction. Therefore, HAOTs contain variable proportions of mantle and slab-derived Li. It has been argued that these trace element patterns provide evidence for a connection with the recent subduction volcanism in the Cascades (DONNELLY-NOLAN et al., 1991; BAKER et al., 1994; BACON et al., 1997). In
contrast, Hart (1985) noted that radiogenic Sr isotope ratios continue to the east of the arc and seems not related to modern subduction zone volcanism. The latter is consistent with radiogenic strontium of $^{87}$Sr/$^{86}$Sr = 0.70434 for Mt. Shasta HAOTs whereas Medicine Lake HAOTs range from 0.7032 to 0.70345. At least some HAOTs seem to contain a component with high time-integrated Rb/Sr that is related to metasomatism by slab-derived fluids some time in the past. Although the timing of the enrichment in fluid mobile elements is unclear the anhydrous lavas provide evidence for an isotopically heterogeneous mantle wedge with predominant isotopically light Li beneath Medicine Lake.

Fig. 3.2: Trace element patterns for HAOT and BA lavas from Mt. Shasta and Medicine Lake (not separated). The dark grey field is that of HAOTs. The most depleted HAOT lava 82-72a is plotted separately as black squares and shows a pattern that is similar to that of other samples 82-72a1 (Donnelly-Nolan et al., 1991) and 82-72f (Bacon et al., 1997) studied previously. The HAOTs from Mt. Shasta and Medicine Lake are identical in their trace element patterns. The light grey field represents BA lavas; PMA lava 85-41b is plotted separately (white diamonds). Two BA lavas and two Lake Basalt lavas from Medicine Lake cannot be resolved from Mt. Shasta BA lavas based on their trace element patterns. All lavas exhibit similar trace elements pattern with enriched Cs, Ba, Pb, Sr and Li and Nb, Ta depletion. For normalization N-MORB data from Sun and McDonough (1989) are used.
3.6.2 Basaltic andesites and primitive magnesian andesites

The pre-eruptive H2O contents of these lavas provide constraints on the composition of the slab component and the process of melt formation. The BA lavas have high Mg#s providing evidence for equilibration with spinel peridotite (GROVE et al., 2002). Olivines with a forsterite content of ~93.6 have been reported for the primitive Mg-andesites (PMA). Experiments show that both BA lavas (85-44; BAKER et al., 1994) and PMA (85-41b; PARMAN, 2001), are saturated with olivine and orthopyroxene at ~1.0 GPa and 1200°C. The olivine crystals in the PMA are igneous and crystallized from a magma that was derived from an extremely depleted mantle source (BAKER et al., 1994). The experiments provide evidence that the major-element chemistry of BA lavas and PMA from Mt. Shasta are in equilibrium, or nearly so, with peridotites at the base of the crust (GROVE et al., 2002).

Geochemical variations in primitive BA lavas from the southern Cascades have been accounted for by reactions of fluid phases with mantle wedge peridotites (BORG et al., 1997, 2000). However, boron (B) abundance and isotope data place ambiguous constraints on the nature of the fluid phase in the primitive Mt. Shasta BA lavas and do not distinguish a B-depleted hydrous fluid from a H2O-rich slab melt (ROSE et al., 2001). The major element chemistry of BA lavas and PMA is in equilibrium, or nearly so, with peridotite. However, up to 99% of the fluid-mobile trace elements such as Rb, Sr or Ba may come from the subducted oceanic lithosphere. Lithium is easily mobilized from altered basalts or sediments during shallow-depth reaction with hydrothermal fluids (SEYFRIED et al., 1998) or in accretionary

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>87Sr/86Sr</th>
<th>143Nd/144Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>82-72a</td>
<td>HAOT</td>
<td>0.703402 (11)</td>
<td>0.513010 (8)</td>
</tr>
<tr>
<td>95-3</td>
<td>HAOT</td>
<td>0.703457 (14)</td>
<td>0.512952 (8)</td>
</tr>
<tr>
<td>95-4</td>
<td>HAOT</td>
<td>0.703554 (11)</td>
<td>0.512917 (6)</td>
</tr>
<tr>
<td>95-5</td>
<td>HAOT</td>
<td>0.703556 (16)</td>
<td>0.512930 (7)</td>
</tr>
<tr>
<td>95-6</td>
<td>HAOT</td>
<td>0.703579 (13)</td>
<td>0.512933 (6)</td>
</tr>
<tr>
<td>95-9</td>
<td>HAOT</td>
<td>0.703480 (10)</td>
<td>0.512986 (9)</td>
</tr>
<tr>
<td>1665m</td>
<td>LB</td>
<td>0.703762 (13)</td>
<td>0.512860 (6)</td>
</tr>
<tr>
<td>1672m</td>
<td>LB</td>
<td>0.703626 (13)</td>
<td>0.512921 (5)</td>
</tr>
<tr>
<td>1399m</td>
<td>BA</td>
<td>0.703646 (12)</td>
<td>0.512891 (6)</td>
</tr>
<tr>
<td>79-24E</td>
<td>BA</td>
<td>0.703780 (11)</td>
<td>0.512845 (7)</td>
</tr>
</tbody>
</table>

Numbers in parentheses are 2σ errors and refer to the last two digits for Sr and the last digit for Nd.

HAOT – high-alumina olivine tholeiite, LB – Lake Basalt, BA – basaltic andesite
prisms (You et al., 1995). However, during continuing subduction and change in P-T conditions, the remaining Li is more strongly bound in the slab, presumably in mineral phases such as omphacite, Ti-clinohumite and olivine (Zack et al., 2003; Scambelluri et al., 2004), with relatively high Li abundances, generally exceeding 10 ppm. Recently, variable δ^7Li values have been reported for a suite of Mariana forearc serpentinites, the data scattering between −6.1‰ and +10.3‰ (Benton et al., 2004). This complicates estimates of the exact Li isotope composition of slab-derived fluids.

Strontium, Nd and Pb isotope compositions provide evidence that at least two fluid-rich geochemical reservoirs were involved in the generation of Mt. Shasta lavas, one with MORB-like ⁸⁷Sr/⁸⁶Sr (−0.7028) and εNd and a second with high ⁸⁷Sr/⁸⁶Sr (−0.7037) and low εNd (Grove et al., 2002). The δ^7Li of basaltic andesites from Mt. Shasta varies between +4.0‰ and +6.4‰. Both fluid-rich reservoirs exhibit high δ^7Li. This is consistent with an origin from variably altered mid-ocean ridge basalts (Tomascak, 2004) which are ^7Li-enriched and may show Sr isotope variation. The high-⁸⁷Sr/⁸⁶Sr fluid reservoir is unlikely to reflect detrital sediments while the upper continental crustal materials seem to be isotopically light, averaging δ^7Li of ~0‰ (Teng et al., 2004). A different fluid source with δ^7Li < 0.9‰ is indicated by BA lavas and Lake Basalt lavas from the Medicine Lake region. However, all BA lavas and PMA have low Rb/Nb (<3.7) and intermediate Sr/Y (16-73) and are enriched in Li over similarly compatible elements like Y or Ho (Fig. 3.2).

Lithium isotopes provide a tracer of near surface fractionated materials. Therefore, the most obvious explanation of the difference between Mt. Shasta and Medicine Lake lavas is distinct mantle components above the Cascadia subduction zone. However, there are several lines of evidence that this model is incorrect or at least greatly simplified.

First, the BA lavas and Lake Basalt lavas from the Medicine Lake region have ⁸⁷Sr/⁸⁶Sr = 0.7036 and 0.7038 respectively, and cannot be distinguished from Mt. Shasta BA lavas with the “sediment signature” (⁸⁷Sr/⁸⁶Sr = 0.7037 to 0.7039; Table 3.2 and Grove et al., 2002). The latter indicates that the hydrous Mt. Shasta and Medicine Lake lavas were derived from similar sources despite distinct Li isotope compositions. Second, if δ^7Li is behaving like a radiogenic tracer for crustal material in the Cascadia subduction zone, then correlations with other fluid mobile elements or element ratios, e.g. Rb, Ba or Sr isotopes, would be expected. However, Li isotopes do not correlate with any of these (Fig. 3.3).

A likely explanation for the difference between Mt. Shasta and Medicine Lake lavas is that Li isotopic effects are dominated by fractionation during subduction of the oceanic
lithosphere. Dehydration of a subducting plate extracts heavy Li into the fluid and leaves residues that are depleted in $^7$Li. Lithium isotope fractionation during dehydration of oceanic crust is evident from fluids of the Costa Rica decollement zone (Chan and Kastner, 2000) and serpentine diapirs, both with $\delta^7$Li of about +20‰. $\delta^7$Li values of dehydration residues change during prograde metamorphism with increasing degree of dehydration. Eclogites from Trescolmen (Zack et al., 2003) and an eclogite sample from Oberkotzau, Germany (Magna et al., 2004b) have negative $\delta^7$Li values. Both provide evidence for a $^7$Li-depleted eclogitic residue in subduction zones. The pathways of Li depletion and isotope fractionation

![Graph](image_url)

**Fig. 3.3:** Trace element ratios vs. $\delta^7$Li values in Mt. Shasta lavas. An apparent scatter of data with no systematic behavior among diverse lava types reflects Li isotope fractionation decoupled from release of a fluid phase during dehydration. Closed diamonds – high-alumina olivine tholeiites; grey diamonds – basaltic andesites; open diamond – primitive magnesian andesite; closed triangles – andesites; reversed open triangles – dacites.
Table 3.3: Trace element concentrations in Mt. Shasta and Medicine Lake lavas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Rb</th>
<th>Cs</th>
<th>Sr</th>
<th>Ba</th>
<th>Sc</th>
<th>Y</th>
<th>Zr</th>
<th>Hf</th>
<th>Nb</th>
<th>Ni</th>
<th>Co</th>
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</thead>
<tbody>
<tr>
<td>85-38</td>
<td>HAOT</td>
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<td>0.10</td>
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<td>117*</td>
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<td>57</td>
<td>1.3</td>
<td>0.77</td>
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<td>85-51</td>
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<td>60</td>
<td>1.4</td>
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<td>14</td>
<td>3.8</td>
<td>1.7</td>
<td>0.51</td>
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</tbody>
</table>

**Mt. Shasta**

**Medicine Lake**

82-72a  | HAOT | 1.0| 0.017| 164| 24* | 26 | 17.1| 41 | 1.5| 1.4| 494| 75 | 0.36| 0.21| 0.08 |

85-3     | HAOT | 11.1| 0.450| 473| 389* | 31 | 28.1| 137| 2.9| 6.3| 456| 43 | 3.7 | 1.6  | 0.50 |

85-4     | HAOT | 4.4 | 0.190| 358| 240* | 27 | 20.3| 95 | 2.1| 6.9| 98 | 39 | 2.9 | 1.3  | 0.42 |

85-5     | HAOT | 2.2 | 0.065| 390| 94*  | 32 | 21.9| 82 | 1.6| 6.7| 123| 47 | 6.0 | 0.37 | 0.08 |

85-6     | HAOT | 3.1 | 0.043| 370| 127* | 25 | 22.6| 110| 2.2| 10.7| 133| 45 | 0.97 | 0.53 | 0.17 |

85-9     | HAOT | 1.3 | 0.034| 287| 98*  | 25 | 21.1| 61 | 1.4| 2.3| 187| 52 | 0.85| 0.32 | 0.09 |

1665m    | LB   | 5.5 | 0.297| 538| 242* | 20 | 14.3| 69 | 1.6| 2.8| 60 | 28 | 3.0 | 1.3  | 0.35 |

1672m    | LB   | 6.0 | 0.350| 585| 241* | 23 | 17.2| 77 | 1.7| 5.0| 41 | 30 | 2.2 | 0.79 | 0.25 |

1399m    | BA   | 9.0 | 0.395| 357| 194* | 26 | 21.7| 97 | 2.1| 4.3| 77 | 37 | 2.7 | 1.1  | 0.37 |

79-24E   | BA   | 16.3| 0.810| 445| 241* | 23 | 16.8| 88 | 1.9| 4.4| 108| 35 | 5.0 | 1.6  | 0.51 |

**Reference standards**

JB-2     | 6.1 | 0.67| 199| 235* | 49 | 23.0| 47 | 1.3| 0.67| 19.7| 38 | 5.3 | 0.31 | 0.17 |

BHVO-2   | 7.7 | 0.09| 407| 138* | 30 | 24.8| 165| 4.1| 19.7| 126| 46 | 1.5 | 1.34 | 0.44 |

AGV-2    | 71  | 1.31| 712| 1142*| 14 | 19.0| 225| 4.5| 15.5| 20 | 16 | 13  | 6.7  | 1.76 |

All trace element concentrations are given in ppm.


LB – Lake Basalt

* corrected down for 15%

b corrected down for 10%
### Table 3.4: Rare earth element concentrations in Mt. Shasta and Medicine Lake lavas

<table>
<thead>
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<th>Sample Type</th>
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<th>Medicine Lake</th>
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</tr>
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<td>85-51 HAOT</td>
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<td>4.60</td>
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<td>82-94a BA</td>
<td>Pr 1.68</td>
<td>1.24</td>
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<td>85-44 BA</td>
<td>Nd 8.20</td>
<td>2.77</td>
</tr>
<tr>
<td>95-15 BA</td>
<td>Sm 2.60</td>
<td>2.77</td>
</tr>
<tr>
<td>95-17 BA</td>
<td>Eu 0.57</td>
<td>0.57</td>
</tr>
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<td>85-41b PMA</td>
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<td>0.82</td>
</tr>
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<td>85-55 A</td>
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</tr>
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<td>85-48b A</td>
<td>Er 2.37</td>
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<td>Tm 0.37</td>
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<tr>
<td>82-85 A</td>
<td>Yb 0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>82-92a D</td>
<td>Lu 0.37</td>
<td>0.37</td>
</tr>
</tbody>
</table>

**Reference standards**

- JB-2: 2.35, 6.88, 12.4, 6.4, 2.4, 0.97, 3.12, 0.61, 3.95, 0.88, 2.60, 0.41, 2.55, 0.39
- BHVO-2: 15.5, 38.6, 5.56, 24.9, 6.23, 2.29, 6.4, 1.08, 5.54, 1.06, 2.64, 0.42, 2.12, 0.38
- AGV-2: 39.4, 71.7, 8.6, 31.3, 5.8, 2.04, 5.6, 0.69, 3.6, 0.71, 1.95, 0.26, 1.69, 0.27

All rare earth element concentrations are given in ppm.

HAOT – high-alumina olivine tholeiite, BA – basaltic andesite, PMA – primitive magnesian andesite, A – andesite, D – dacite, LB – Lake Basalt
are not expected to be constant at all pressure and temperature conditions in subduction zones. However, dehydration at low temperatures will fractionate $^7\text{Li}$ into the fluids and produce a $^6\text{Li}$-enriched residue. Therefore, fluids that derived from the slab below $\sim$75 km are expected to be isotopically lighter than unaltered MORB as also recently experimentally verified (Wunder et al., 2006).

3.6.3 Andesites and dacites

Andesites (A) and dacites (D) from Mt. Shasta have been modeled as products of multiple recharge of magmatic reservoirs by parental H$_2$O-rich PMA magmas (e.g. 85-41) accompanied by fractional crystallization of olivine + pyroxenes + amphibole + plagioclase throughout (or within) the continental crust. Possibly some BA lavas were also introduced into the system (Grove et al., 2005) and served as parent magmas. Experimental work provides evidence for high pre-eruptive H$_2$O contents (up to 10 wt.%) in some evolved magmas (Grove et al., 2003). Similar water contents have been observed in northern Cascadia (Blundy and Cashman, 2001). Although crustal rocks are present in the area (Zucca et al., 1986), Sr and Nd isotope data do not indicate contamination by continental crust. This is also endorsed by U-Th-Ra disequilibria for young volcanic rocks (Volpe, 1992). Andesites and dacites are therefore derived from a H$_2$O-rich PMA-magma by fractional crystallization and mixing with related, but more evolved magmas (Grove et al., 2005). This mode of origin differs from that proposed for the generation of andesitic, dacitic and rhyodacitic lavas in the High Cascades where melting of amphibolitic and granulitic rocks at various crustal levels without significant mafic contributions has been suggested (Conrey et al., 2001). Average continental crust and Trinity peridotite as contaminants have been excluded based on major and trace elements (Grove et al., 2005). Continental crust has been advocated formerly (Newman et al., 1986). The likely contaminant has been identified as highly evolved differentiated residual liquids from long-lived magmatic systems that underwent fractional crystallization, recharge of magma and mixing (Grove et al., 2005). Andesites and dacites show a similar range of trace element characteristics with, for example, depletion in Nb and Ta, accompanied by enrichment in Ba, Pb, Sr and Li (Fig. 3.4). The $\delta^7\text{Li}$ range measured for andesites and dacites is identical to the Li isotope composition of tholeiites and basaltic andesites. This precludes a voluminous contamination of andesites and dacites by old or upper crustal material and restricts its volume to less than 5% (andesites: Li = 10 ppm, $\delta^7\text{Li} = 7\%$, Sr = 1200 ppm, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7028$, continental crust: $\delta^7\text{Li} = 0\%$, Li =
35 ppm (Teng et al., 2004), \( ^{87}\text{Sr}^{86}\text{Sr} = 0.740 \), Sr = 276 ppm, CC2 composition in Table 5 from Hart, 1985). Although the upper continental crust appears to have \( \delta^7\text{Li} \sim 0\% \) (Teng et al., 2004), the Sr and Nd isotope compositions will have evolved in a manner that is distinct from those of the mantle and basaltic systems. Evolved calc-alkaline lavas of Panama arc show a considerable range in \( \delta^7\text{Li} \) from +3.9\% to +11.2\% (Old Group in Tomascak et al., 2000). This has been ascribed to release of isotopically heavy Li from previously subduction-fertilized mantle in an environment where ridge subduction was being initiated. In contrast, adakitic lavas from the Panama arc exhibit a much more limited range in \( \delta^7\text{Li} \) from +1.4\% to +4.2\% and may represent slab melts. Such an interpretation is broadly consistent with the model presented in this study.

![Figure 3.4](image)

*Fig. 3.4: Trace element patterns for andesites and dacites from Mt. Shasta. Andesites (light grey) and dacites (white) display nearly identical patterns with only subtle differences. Andesites are more homogeneous than dacites with less variable trace element ratios, e.g. (La/Sm)\text{N} or Sr/Y, however are they generally indistinguishable from dacites in N-MORB-normalized patterns.*

A subset of four Li-rich samples (85-59, 82-85, 82-92a, 82-95) shows distinct \( ^{87}\text{Sr}^{86}\text{Sr} \) ratios compared to the rest of andesites-dacites group. These samples carry a Sr isotope signature of a sediment-derived fluid-rich component (Grove et al., 2005). Lithium
abundances between 18 and 35 ppm also provide evidence for varying degrees of contamination by rhyolitic rocks. However, their $\delta^7\text{Li}$ values scatter substantially and this may reflect heterogeneity in the rhyolitic contaminant. It is possible that variability in the $\delta^7\text{Li}$ is a characteristic of this rhyolitic residuum (Grove et al., 2005).

We suggest that the mineralogy of the subducted slab does not have a large effect on the Li isotope composition of andesites and dacites, as these are products of multiple mixing of parental $\text{H}_2\text{O}$-rich magmas with fractionally crystallized lavas at crustal depths (Grove et al., 2003, 2005).

### 3.7 Li isotope fractionation in the southern Cascadia zone

The high temperatures of melting in the spinel peridotite source regions beneath Mt. Shasta and Medicine Lake (1300-1450°C; Elkins Tanton et al., 2001) rule out isotope fractionation of Li isotope compositions from the parental peridotite. Fluids added to the source region of HAOTs from Mt. Shasta are probably responsible for the variations in $\delta^7\text{Li}$ and represent a source material that is different from that provided by the subduction-derived fluid-rich components that were added when the hydrous basalts and basaltic andesites from Mt. Shasta and Medicine Lake formed. The BA, PMA and Lake Basalt lavas display a decrease in $\delta^7\text{Li}$ away from the arc trench (Fig. 3.5). This may reflect heterogeneity of the mantle wedge and continuous Li isotope fractionation as fluids are released from the slab at progressively greater depths (Zack et al., 2003).

It is a reasonable generally accepted scenario that fluids with heavy Li are injected from the subducted slab into the viscously coupled overlying mantle at shallow depth (Fig. 3.6). This hydrous mantle segment (probably serpentinite) is dragged down by the subducting plate (Elliott et al., 2004) and metamorphosed. Just below Mt. Shasta the mantle segment begins to dehydrate as a consequence of the breakdown of serpentinite and / or chlorite at temperatures >600°C (Ulmer and Trommsdorff, 1995). The high temperatures of these dehydration reactions would be expected to lead to only a small fractionation of Li isotopes between the source serpentinite and the fluid. It is therefore unlikely that this mantle segment after losing its Li has very low $\delta^7\text{Li}$. The low $\delta^7\text{Li}$ values for Mt. Shasta lavas probably were added during the subsequent vapor-saturated melting that occurred as the fluids ascended and encountered higher temperatures in the mantle wedge, i.e. the low-$\delta^7\text{Li}$ lavas from Mt. Shasta included a mantle wedge component with relatively “normal” Li. That is, the Li is diluted.
Fig. 3.5: Distance from the arc trench vs. $\delta^7$Li values (panel A) and pre-eruptive water contents (panel B), respectively. Distinct Li isotope signatures are found dependent on distance from trench. A general trend of decreasing $\delta^7$Li with increasing distance from the trench (and conversely, depth of Wadati-Benioff zone) is similar to that observed for the Izu arc (Moriguti and Nakamura, 1998b) and has not been found in the northern Cascadia arc (Leeman et al., 2004) or Kurile and Sunda arcs (Tomascak et al., 2002). This has been interpreted in terms of a lack of Li isotope fractionation because Li is relatively strongly retained in subducted slab (Tomascak et al., 2002; Leeman et al., 2004). Similar conclusions were drawn by Moriguti et al. (2004) for northeastern Japan. Diamonds – Mt. Shasta lavas (closed – HAOTs; grey – BAS; open – PMA); squares – Medicine Lake lavas (closed – HAOTs; grey – BAS; open – Lake Basalts). The mantle composition shown as a bar is defined as $\delta^7$Li = 4.1 ± 0.5%$^*$ as inferred from analyses of spinel lherzolites and their olivines (Magna et al., 2006b). In panel B, pre-eruptive water contents can be seen to decrease in “flux-melted” magmas as a function of distance from the trench. Significant water contents are recognized in basaltic andesites and Lake Basalt lavas from Medicine Lake.
Fig. 3.6: Schematic figure of evolution of Li isotopes in the southern Cascadia subduction zone. Altered oceanic crust (AOC) provides source of heavy Li isotope input into the subduction zone due to $^7$Li being preferentially adsorbed in secondary clay minerals. This Li is easily released during low-T events just after passing the arc trench. Overlying serpentinite diapirs become isotopically heavy. Progressive $^7$Li depletion in successive steps of slab dehydration and/or slab melting is reflected in lighter Li isotope composition of BA lavas further away from the trench. HAOTs from both Mt. Shasta (with a source located just beneath the base of the continental crust, depicted as a vertically lined oval) and Medicine Lake (horizontally patterned oval indicating a deeper source of these HAOTs) represent near-anhydrous melting of spinel peridotites. Slightly different $\delta^7$Li values mirror heterogeneity of the mantle segments beneath the two volcanoes.

with a mantle component with $\delta^7$Li $\sim$ 4‰. Therefore, $\delta^7$Li variation observed in Mt. Shasta lavas reflects both: different proportions of Li derived from the slab and Li isotope heterogeneity in the mantle wedge. Further evidence of a heterogeneous mantle wedge is provided by anhydrous volcanics from the Mt. Shasta–Medicine Lake region that exhibit a large range of $\delta^7$Li values. The complexity of this heterogeneous mixing process may explain why $\delta^7$Li does not correlate with fluid mobile trace elements and strontium isotopes.

The H$_2$O-rich lavas from Medicine Lake (which also have a large contribution from the slab in their incompatible element abundances) are uniformly low in $\delta^7$Li. These lavas are likely generated by vapor-saturated melting in the mantle wedge as the slab-derived fluids ascend. That the metamorphosed subducted slab contains reasonable amounts of Li has been recently shown (SCAMBELLURI et al., 2004). In particular mineral phases such as staurolite
(DUTROW et al., 1986), serpentine, phengite, chlorite and Ti-clinohumite can hold high Li abundances. The breakdown of those minerals that are H2O-rich such as lawsonite or phengite may occur in subducted metamorphosed oceanic crust just beneath Medicine Lake. In addition, breakdown of serpentine in the subducted oceanic slab can be an effective source of Li at Medicine Lake. Such fluids will be isotopically light because heavy Li is lost at shallow depths causing metasomatic overprinting of the overlying mantle wedge with predominantly heavy Li. Thus, progressive dehydration reactions with the accompanying higher temperatures deeper in the downgoing slab causes the distinct $\delta^7$Li observed in Mt. Shasta and Medicine Lake basaltic andesites.

Studies of eclogites from Trescolmen, Switzerland (Zack et al., 2003) and Oberkotzau, Germany (Magna et al., 2004b) have revealed negative $\delta^7$Li values. Fluids derived from such an eclogitic source are Li rich and expected to be light (Zack et al., 2003) because the fractionation between rock and fluid is small at high temperatures. Therefore, the data are consistent with the Wadati-Benioff zone being at greater depth and higher temperature below Medicine Lake than Mt. Shasta. The isotope fractionation in subduction zones would explain why Li isotopes do not correlate with fluid mobile trace elements and strontium isotopes. Such a decoupling has also been described for oceanic arcs (Tomascak et al., 2002; Chan et al., 2002b) and seems to be a characteristic of most arc magmas.

3.8 Comparison with other arcs

Lithium isotopes have been studied in several arcs. However, only the Izu arc (Moriguti and Nakamura, 1998b) and the southern Cascades (this study) show a decrease in $\delta^7$Li values with increasing distances from the trench (or depth of the slab). These two arcs deviate from the other localities by abundant proportions of basalts (Fig. 3.7). For the Izu arc a mixing model has been proposed in which mantle wedge Li mixes with slab-derived Li (Moriguti and Nakamura, 1998b). The fluids have a signature mainly of altered oceanic crust. Such a mixing model is consistent with a study on trace elements and radiogenic isotopes by Hochstaedter et al. (2001). However, the model (Moriguti and Nakamura, 1998b) relies on a mantle end member that has $\delta^7$Li $\approx 0$ to $+2\%$, which is inconsistent with the vast majority of oceanic basalts and unmetasomatised peridotite xenoliths. Therefore, continuous Li isotope fractionation in the slab during subduction and an interpretation of the light end member being a slab signature seems to provide a more satisfactory explanation of
Fig 3.7: Comparison of Li isotope profiles of various arcs. Lithium isotopes fractionate strongly with increasing distances (or increasing depth of Wadati-Benioff zone) from the arc trench in northern California Cascades (A) and in Izu arc (C) with predominantly basaltic volcanism (Gill, 1981). On the other hand, arcs with prevalent basalt andesitic and andesitic lavas show across-arc patterns of $\delta^7$Li values that are similar among these latter settings, i.e. restricted invariant range of $\delta^7$Li values. A - Li isotope data from Mt. Shasta (this study), B - southern Washington Cascades (see Leeman et al. (2004) for distinctions between Group I and Group II), C -Izu arc (Moriguti and Nakamura, 1998b), D - northeastern Japan arc (Moriguti et al., 2004), E - Kurile arc (Tomascak et al., 2002), F - Sunda arc (Tomascak et al., 2002). Symbols are plotted irrespective of the petrologic evaluation and major element chemistry of corresponding samples. Insets: basalts are in black, basaltic and acid andesites are in dark grey and dacites are in white. Inset 7C: basaltic andesites are in dark grey and acid andesites are in light grey. Note the variations of relative proportions of major magma types in the insets (Gill, 1981). WBZ - depth of Wadati-Benioff zone.
For andesitic lavas from northeastern Japan a slightly smaller range of $\delta^7\text{Li}$ values from +2.0 to +4.4‰ is reported but no systematic variation across the arc has been detected (Moriguti et al., 2004). The subducted slab in northeastern Japan sinks with a dip angle of ~30° into the mantle whereas the dip angle for the Izu arc is ~50°. The different geometry and a higher temperature at the top of subducting slab in the northeastern Japan (Moriguti et al., 2004) may result in a dehydration of the slab at very shallow, crustal levels which are not sampled by the volcanism. It may be that in northern Japan only Li from a $^7\text{Li}$-depleted slab is incorporated in subduction zone lavas. Therefore, very heavy Li isotope ratios of up to 7‰ are missing. Indeed, Li-Pb isotope modeling shows that $\delta^7\text{Li}$ of slab-derived fluid and mantle wedge end members are potentially very similar resulting in lack of Li isotope fractionation during continuous subduction. A convex-upward trend of Li/Y was observed across the northeastern Japan arc and was explained by the possible influence of lawsonite breakdown (Moriguti et al., 2004). This could be a consequence of shallower subduction and thus, different P-T conditions for northeastern Japan compared to Izu arc. Whether this could influence the $\delta^7\text{Li}$ path across the arc is presently unclear. A concave-upward profile of $\delta^{11}\text{B}$ across the northeastern Japan arc has been explained by involving tourmaline as a minor mineral phase that carries a substantial portion of the boron in the subducted slab (Moriguti et al., 2004).

Across the southern Washington Cascadia $\delta^7\text{Li}$ values of tholeiites to basaltic andesites range from +2.5 to +4.2‰ and are randomly distributed across the arc (Leeman et al., 2004) which is distinct from the Li isotope patterns observed in lavas from this study. The fluid-mobile element abundances decrease from the forearc lavas towards the backarc. A corresponding effect on Li isotopes is not observed but B isotopes change systematically across the arc. It has been suggested that this is because Li is retained in the subducted slab more efficiently than B. Such an inference is in good agreement with previous observations made for other arc settings (Tomascak et al., 2002; Moriguti et al., 2004). Hence, the Li isotope signatures in these lavas may represent the composition of the mantle wedge because there has been only a small input of isotopically distinct fluids from the slab (Leeman et al., 2004).

Lithium isotope compositions of basaltic andesites and andesites in the Kurile arc range from +2.4 to +4.9‰ and are randomly distributed across the arc (Tomascak et al., 2002). In contrast, B isotope ratios vary systematically with the distance to the trench (Ishikawa and
TERA, 1997). It has been suggested that this is either due to very low Li contents in fluids or Li has been removed from fluids by interaction with minerals in the mantle wedge (TOMASCAK et al., 2002). Apart from one sample, tholeiites and high-K alkali lavas of the Sunda arc display a narrow range of $\delta^7$Li values from +2.1 to +5.1‰ (TOMASCAK et al., 2002). This range is as observed in lavas from southern Washington Cascades, Kurile and northeastern Japan arc. Mixing of isotopically heterogeneous mantle Li and a homogeneous slab-derived Li in fluids or melts is proposed for the observed B/Be and Sr-Nd-Pb isotope systematics in Sunda arc (EDWARDS et al., 1993). Possible explanations for the distinct Li isotope patterns in arcs involve either Li-poor slab fluids or removal of Li from the fluids by interaction in the mantle wedge (TOMASCAK et al., 2002). In the first case, Li would be retained in the slab. Indeed, some evidence is found for such behaviour of Li during subduction (see sections 3.6.2 and 3.7, respectively). This Li would not contribute significantly to the Li isotope budget of arc volcanics (TOMASCAK et al., 2002). In the latter case, Li is sequestered in rims of minerals in the mantle wedge. Decoupling of Li and B isotope patterns indicates a chromatographic separation of Li isotopes as fluids percolate through the mantle wedge. This may erase the slab signature of a moderately incompatible element like Li (TOMASCAK et al., 2002) but not that of highly incompatible element like B.

In conclusion, the dip angle and the temperatures in subduction zones will affect the extent of dehydration in the subducting slab. Most $^7$Li may be lost into the crust where subduction is shallow. In only two locations do Li isotopes show an inverse correlation with depth of Wadati-Benioff zone (or distance from trench). In these arcs, basalts are the dominant lava type. As discussed above, arcs dominated by basalts provide evidence that Li isotopes continuously fractionate in the slab during subduction. In contrast, Pb isotopes and other radiogenic tracers provide evidence that ascending fluids or melts interact and mix with distinct components in the mantle wedge.

3.9 Conclusions

1) High-alumina olivine tholeiites are near-anhydrous melts of spinel peridotites. Lithium isotopes are not fractionated during melting and most likely reflect Li isotope composition of the uppermost mantle beneath Mt. Shasta.
2) Lithium in the hydrous BA lavas in the Mt. Shasta region is heavy whereas BAs and basalts from Medicine Lake have isotopically light Li providing evidence for isotope fractionation during subduction of the lithospheric slab.

3) Basaltic andesites exhibit the same $\delta^7$Li range as andesites and dacites from Mt. Shasta reflecting the composition of the mantle source. Thus, our data provide further evidence that solely magmatic differentiation processes are not fractionating Li isotopes.

*Acknowledgement* – We are indebted to Irene Ivanov-Bucher for her help with the sample preparation, Darrell Harrison for his careful reading of early versions of the manuscript, Felix Oberli for technical assistance on Nu1700 and Marcus Gutjahr for his help with Sr and Nd isotope analysis. Lui-Heung Chan, James Gill, Bill Leeman and Paul Tomascak are acknowledged for their valuable information. We are grateful to Paul Tomascak for detailed and insightful review, Tim Elliott for offline comments to the manuscript and David Price for editorial handling. ETH and Swiss Nationalfonds (SNF) supported this study.
Supplementary figure

Supplementary figure SI: Schematic map of sample locations of Mt. Shasta and Medicine Lake lavas analyzed for lithium concentrations and isotope compositions. Solid lines with numbers represent roads, dashed lines represent contour lines with elevation in feet.
Combined Li and He isotopes in Iceland and Jan Mayen lavas and the nature of the North Atlantic mantle

* to be submitted for publication in *Geochimica et Cosmochimica Acta* as Magna T., Halliday A.N., Wiechert U., Stuart F.M. and Harrison D.: Combined Li and He isotopes in Iceland and Jan Mayen lavas and the nature of the North Atlantic mantle
4.1 Abstract

We present lithium (Li) isotope data as well as supporting isotope and trace element compositions for two suites of basaltic volcanic rocks from Iceland and Jan Mayen. Basaltic glasses from the Hengill fissure system are depleted in $^{18}$O, U, Th and Li, enriched in Ba, Nb and Eu and have variable Sr/Nd. They can be divided into enriched ($La_N/Sm_N > 1.1$) and depleted ($La_N/Sm_N < 0.52$) lavas. The latter have superchondritic Sr/Nd and are anomalously depleted in Pb. The two groups define a collinear trend when $\delta^7$Li (+3.8 to +6.9‰) is plotted against $^{3}$He/$^4$He (12 to 20 Ra). There is no well-defined correlation between the Li or He isotope compositions and other isotope or trace element parameters. The isotope variability in the Iceland suite contrasts strongly with the homogeneous Li ($\delta^7$Li = +3.9 to +4.7‰) and He ($^{3}$He/$^4$He = 5 – 7 Ra) isotope compositions of basalts from Jan Mayen. These lavas show large degrees of enrichment in incompatible trace elements ($La_N/Sm_N > 3.2$) with patterns similar to those of the Hengill Enriched Group, the only striking difference being a large positive Pb anomaly.

The linear relationship between Li and He isotope systematics in Hengill would indicate that the end members had similar Li/He. The highest $^{3}$He/$^4$He of 20 Ra is associated with “normal” mantle $\delta^7$Li of +3.8‰. There is no reason why this should be the case unless it represents an end member composition. Therefore, despite the light oxygen isotope compositions and Eu and Nb anomalies, the high-$^{3}$He/$^4$He end member carries no Li isotope trace of being the product of recycling of altered slab or wedge material. Neither does it appear to reflect a high-$^{3}$He/$^4$He volatile-rich lower mantle reservoir else the correlation with Li isotopes would be non-linear. The Jan Mayen basalts provide evidence of a third source characterised by EM2-like trace element enrichments and $^{3}$He/$^4$He that is lower than in MORB accompanied by the same normal $\delta^7$Li as the high-$^{3}$He/$^4$He Hengill basalts. Therefore, MORB and OIB can display a dramatic range in He isotope compositions from 5 to 20 Ra and large variations in trace element compositions associated with recycled components whilst exhibiting no sign of surface altered slab or wedge material in the Li isotope composition. Furthermore, there is no sign of a high-$^{3}$He/$^4$He reservoir selectively dominating the variability in He isotope composition. One possible explanation for these data is that the He isotope compositions reflect small variations in (U+Th)/He in ancient low-$^{18}$O lower oceanic crust and upper mantle material. The high $\delta^7$Li (+6.9‰) component with $^{3}$He/$^4$He = 12 Ra includes samples that tend to have higher Nb/U, Sr/Nd and Eu anomalies providing
evidence of a cumulate enriched source that may also be part of an ancient altered ocean floor slab.

4.2 Introduction

The role of recycled material in the formation of ocean island basalts (OIB) has been the focus of considerable debate (Hofmann and White, 1982; Halliday et al., 1995; Hofmann, 1997; Niu and O'Hara, 2003). Lithium (Li) isotope fractionation in nature is mainly the result of low-temperature processes near the Earth’s surface (Chan et al., 1992, 2002a). Fractionation of Li isotopes accompanying aqueous alteration of oceanic crust, and its subsequent dehydration during subduction has the potential to be used to trace subducted material in the convecting mantle (Elliott et al., 2004; Magna et al., 2006a). Dehydration leads to an enrichment of $^7$Li in the overlying mantle wedge with substantial loss of Li from the subducted slab into the fluid phase (Zack et al., 2003). However, a significant proportion of the Li inventory is still retained in the residual slab even after large-degree dehydration (Scambelluri et al., 2004). Lithium tends to be depleted and isotopically heavy in gabbros relative to unaltered seafloor basalts (Chan et al. (2002a) and T. Magna, unpublished data). Less altered portions of recycled crust show $\delta^7$Li that is elevated over unaltered basalts (up to +7.4‰; Nishio et al., 2005) whereas highly altered oceanic crust (up to +14‰; Chan et al., 1992) is thought to leave a residue that has extremely negative $\delta^7$Li, as low as −11‰, after dehydration (Zack et al., 2003). Therefore, the exact estimate of the Li isotope compositions of the sources feeding ocean island basalts is problematic due to variable $\delta^7$Li within the oceanic crust pile and the ill-defined nature of what portion contributes to the recycled signature of OIBs.

Unaltered mid-ocean ridge basalts (MORB) show a relatively large range of $\delta^7$Li (+1.5 to +5.6‰; Tomascak et al., in press; Chan et al., 1992; Moriguti and Nakamura, 1998b; Elliott et al., 2004, 2006) with only subtle differences between N-, T- and E-MORB lavas from different ridge systems. This range is similar to that observed in ocean island basalts, e.g. Hawaii (+2.5 to +5.7‰; Tomascak et al., 1999b; Chan and Frey, 2003; Kobayashi et al., 2004) and indistinguishable from previously published data for Icelandic basalts (+3.1 to +4.0‰; Ryan and Kyle, 2004). HIMU-OIB lavas from Polynesia yield slightly elevated $\delta^7$Li >5.0‰ which has been explained as a result of being derived from recycled altered oceanic crust that underlies the recycled uppermost crust (Nishio et al., 2005). The range of Li
isotope compositions in HIMU and other OIB types (EM1 and EM2) remains obscure (Tomascak, 2004).

Lithium is isotopically heavy in seawater ($\delta^7\text{Li} \sim +31\%$) and in meteoric water (see comprehensive review by Tomascak, 2004). Lithium is strongly fractionated in the ocean floor and during subduction and has the potential to be used for tracing the source components in ocean island basalts. However, extremely light Li isotope ratios are not observed in any OIBs (Elliott et al., 2004). Here we report new Li isotope data for basalts from the Western Rift Zone of Iceland and from Jan Mayen in order to characterise the source of recycled components in the mantle beneath the North Atlantic Ocean and improve our understanding of how Li isotopes fractionate during subduction and recycling of oceanic crust.

4.3 Samples and geologic background

Icelandic volcanism has long been attributed to the presence of a mantle plume, a hypothesis supported by seismic imaging of low-velocity material extending to ~700 km depth (Wolfe et al., 1997). The presence of recycled oceanic crust in the Iceland plume has been proposed on the basis of incompatible trace elements (Chauvel and Hémond, 2000), Pb isotopes (Thirlwall et al., 2004) and $^{18}$O-depleted crustal components (Skovgaard et al., 2001). Support for this is provided by trace elements and He-O isotopes in basalts from central Iceland that display a large range of $^3$He/$^4$He (1.6-34.3 Ra) and low $\delta^{18}$O values (<4.8%; Macpherson et al., 2005). Several origins for the recycled component have been proposed:

(i) heterogeneous basaltic oceanic crust (Thirlwall et al., 2004),

(ii) a mixture of recycled basaltic oceanic crust and low-$\delta^{18}$O Icelandic mantle (Thirlwall et al., 2006),

(iii) both gabbroic and basaltic part of the oceanic crust (Chauvel and Hémond, 2000; Skovgaard et al., 2001),

(iv) lower oceanic crustal gabbros (Breddam, 2002).

Model (i) has been proposed based on detailed mapping of coupled Pb-Sr-Nd isotopes in Iceland and on adjacent ridges. The Pb isotope systematics are believed to reflect preferential hydrothermal addition of U to the Palaeozoic oceanic crust and contemporaneous depletion of lead during dehydration of the subducted slab (Thirlwall et al., 2004). Model
(ii) is predicated on several lines of evidence (Thirlwall et al., 2006). The uniquely low $\delta^{18}O$ of Icelandic basalts could be considered to reflect a contribution of recycled Ordovician crust with oxygen isotope compositions that are vastly different from modern oceanic crust. Alternatively, host mantle may be the carrier phase of low $\delta^{18}O$ (and, simultaneously, high $^3$He/$^4$He) signature whereas other geochemical features of enriched Icelandic mantle would be dominated by incompatible element enriched recycled crust (Thirlwall et al., 2006). The idea that low $\delta^{18}O$ is generated by oxygen isotope fractionation in the D" layer was discussed and dismissed by Thirlwall et al. (2006). In model (iii) variable but low volumes of ~3 Gyr gabbros and basalts are required to account for the mixing relationship observed in e.g. Theistareykir lavas as modelled for combined O-Os isotopes (Skovgaard et al., 2001). The source of depleted lavas is thought to involve the gabbroic part of the oceanic crust because of excess Sr, Ba and Eu, positive (Sr/Nd)$_N$ and deficiencies in Hf (and Zr) relative to the REE. These characteristics closely resemble plagioclase-clinopyroxene-rich gabbros (Chauvel and Hémond, 2000). It has been proposed that some enriched Icelandic basalts have a HIMU-affinity (Stracke et al., 2003) and could be sourced in Palaeozoic oceanic crust (Thirlwall et al., 2004). This is inconsistent with other evidence for more ancient recycled oceanic crust the isotope fingerprint for which develops through long-term storage in the mantle (Chauvel and Hémond, 2000; Skovgaard et al., 2001). Model (iv) has been proposed as the explanation for the compositions of depleted Icelandic lavas representative of high-degree melts (Breddam, 2002). It is supported by the presence of excess strontium [(Sr/Nd)$_N$>1] and a positive correlation between (Sr/Nd)$_N$ and $^{143}$Nd/$^{144}$Nd that discriminates between enriched and depleted plume components.

The Icelandic basalts studied here are olivine phenocryst- and Cr-diopside megacryst-bearing olivine tholeiites and picritic glasses from the 15 km long Máelifell-Miðfél fissure system (MMF), Hengill, approximately 45 km east of Reykjavik (Harrison et al., 1999). The lavas erupted rapidly without significant crystallisation within the crust (Tronnnes, 1990; Hansteen, 1991). Oxygen isotope compositions of glasses from MMF show remarkably low $\delta^{18}O$ (Gurenko and Chaussidon, 2002; Burnard and Harrison, 2005) that may reflect either alteration by low-$^{18}O$ aqueous fluids or recycling of an old recycled oceanic lithosphere. That MMF glasses escaped significant contamination by Icelandic crust has been shown by broadly uniform and light boron isotope compositions in glass inclusions entrapped in olivine with an average $\delta^{11}B$ of -11‰ (Gurenko and Chaussidon, 1997) matching that
of "primitive mantle". The magmas have been explained in terms of <20% fractional melting at depths of between 75 and 30 km (Gurenko and Chausson, 1997).

The basalts have depleted trace element patterns (Hemond et al., 1993; Chauvel and Hemond, 2000) and lithophile radiogenic isotopes provide evidence of several mantle components that contribute to the observed variability of Icelandic basalts (e.g. Hemond et al., 1993; Kempton et al., 2000; Fitton et al., 2003). The $^{3}$He/$^{4}$He ratio increases from 12.7 to 20.2 RA in SW-NE direction along the fissure system. Samples with the highest $^{3}$He/$^{4}$He also show the most extensive degassing. However, the degassing does not exceed 30% (Harrison et al., 1999, 2003). An inverse correlation between $^{3}$He/$^{4}$He and CaO/Al$_2$O$_3$ has been interpreted as reflecting variable clinopyroxene assimilation (Burnard and Harrison, 2005). Correlations between the isotope compositions of argon and oxygen are consistent with low $\delta^{18}$O (~4.6‰) in the source regions of these magmas (Burnard and Harrison, 2005).

Jan Mayen (71°N, 8°30'W) is situated south of the NW-SE trending Western Jan Mayen Fracture Zone (WJMFZ) which separates the Kolbeinsey Ridge and the Mohns Ridge. The island is composed of several cycles of potassic trachybasalts erupted by the Beerenberg stratovolcano (2227 m above sea level). Volcanism is dominated by primitive alkali basalts that evolve from the volumetrically dominant ankaramites through alkali olivine basalts to trachytes (Maaløe et al., 1986). Partial melting of a spinel lherzolitic source at > 1400°C and ~ 20 kbar followed by late-stage gravitational settling of alkali basalt magmas at low pressure has been proposed as a way of generating the variability of Jan Mayen basalts and trachytes (Maaløe et al., 1986). The Sr-Nd-Pb-Hf isotopes and incompatible trace element systematics of Jan Mayen and the adjacent platform differ markedly from the nearby Kolbeinsey and Mohns Ridges (Schilling et al., 1999; Trønnes et al., 1999; Mertz et al., 2004; Blichert-Toft et al., 2005) in that they represent low-degree partial melts of enriched mantle reservoir (Trønnes et al., 1999). Lead isotope signatures of Jan Mayen basalts provide support for a HIMU-like source (Trønnes et al., 1999) whereas the absence of a strongly radiogenic Pb isotope signature ($^{206}$Pb/$^{204}$Pb ~ 18.6) reflects a short isolation time (approximately 500 Myr) for the subducted material, consistent with conclusions from Icelandic basalts (Thirlwall, 1997). On the basis of Pb isotope composition of basalts dredged from the Jan Mayen platform, Blichert-Toft et al. (2005) describe its source as a mixture of depleted mantle (DM), component "C" (as defined by Hanan and Graham (1996) based on Pb-Hf-Nd isotope systematics) and an enriched mantle end member (EM2).
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We have analysed clinopyroxene and olivine phenocryst-bearing basalts (strictly ankaramites) from Jan Mayen that show minimal post-eruption alteration and have MgO > 8% to avoid the effects of wall-rock assimilation. The $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{3}\text{He}/^{4}\text{He}$ variation is limited (0.7034-0.7035, 0.51289-0.51291 and 5-7 RA, respectively; STUART et al., submitted manuscript), but these samples represent some of the most enriched basalts in the North Atlantic Ocean mantle (STUART et al., submitted manuscript). Lead isotopes (STUART et al., submitted manuscript) are consistent with the young HIMU-like source proposed previously (TRONNES et al., 1999). The narrow range of $^{3}\text{He}/^{4}\text{He}$ (5-7 RA) is typical of basalts with a strong HIMU affinity, however similar values are recorded for the OIBs with enriched mantle (EM) affinities (GRAHAM, 2003).

4.4 Analytical techniques

Lithium was separated using an HNO$_3$-methanol mixture with 2.1-ml cation-exchange resin BioRad AG50W-X8 (mesh 200-400). The second step of cleaning was applied to Jan Mayen samples using 0.6-ml cation-exchange resin BioRad AG50W-X12 (mesh 200-400) for additional purification as described elsewhere (MAGNA et al., 2006b). Lithium isotope measurements were performed on Nu1700 (Nu Instruments, Wrexham, UK) multiple-collector inductively coupled plasma mass spectrometer (MC-ICPMS) using simultaneous collection of $^{6}\text{Li}$ (low-mass Faraday cup L7) and $^{7}\text{Li}$ (high-mass Faraday cup H8). Samples were measured relative to the L-SVEC international reference standard (FLESCH et al., 1973) and reported as $\delta^{7}\text{Li}$ (‰) = [(7Li/6Li)$_{\text{sample}}$/7Li/6Li$_{\text{standard}}$]-1×1000. A detailed description of the method is given in MAGNA et al. (2004b). Two reference materials were measured together with samples to assess reliability of the analytical method. JB-2 (Geol. Survey of Japan) and BHVO-2 (US Geol. Survey) yielded $\delta^{7}\text{Li} = 4.84 \pm 0.15$‰ (2σ) and $4.58 \pm 0.32$‰ (2σ), respectively. This is in excellent agreement with previously published values (MORIGUTI and NAKAMURA, 1998a; TOMASCAK et al., 1999a; JEFFCOATE et al., 2004; MAGNA et al., 2004b).

Lithium concentrations were measured on a quadrupole ICP-MS PlasmaQuad 2 (VG Elemental) using beryllium as internal standard. For other trace element concentrations rhodium was used as an internal standard. The precision for most trace element measurements was better than 5% (2σ), for Cs, Ta, Pb, Th and U better than 10% (2σ). Accuracy of the data
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was monitored with BHVO-2 (US Geological Survey) and JB-2 (GSJ), which were analysed together with samples.

Strontium (Sr) and neodymium (Nd) were separated from the Icelandic basalts using the procedures of Horwitz et al. (1992) and Cohen et al. (1988), respectively. Strontium and Nd isotope compositions were measured on a Nu Plasma MC-ICPMS. Masses 83 and 85 were used to correct for Kr and Rb interferences, respectively. The instrumental mass bias was corrected using an exponential fractionation law. Measured \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios were corrected for mass bias using \(^{88}\text{Sr}/^{86}\text{Sr} = 8.3752\) while \(^{143}\text{Nd}/^{144}\text{Nd}\) were corrected using \(^{146}\text{Nd}/^{144}\text{Nd} = 0.7219\). The \(^{144}\text{Nd}/^{144}\text{Nd}\) ratios were further normalised to the JMC-Nd standard using a \(^{143}\text{Nd}/^{144}\text{Nd} = 0.511833\) (cross-calibrated to La Jolla standard value 0.511858) and \(^{87}\text{Sr}/^{86}\text{Sr}\) were normalised to the ratio of 0.710245 for the NIST SRM 987.

4.5 Results

Lithium concentrations and isotope compositions from the Iceland and Jan Mayen basalts are presented in Table 4.1 along with other pertinent radiogenic isotope data. Trace element data for Iceland and Jan Mayen lavas are presented in Tables 4.2 and 4.3, respectively. The trace elements define two distinct patterns (Fig. 4.1). The “Enriched Group” samples show elevated \(\text{La}/\text{Sm}_N > 1.1\), while the “Depleted Group” is characterised by \(\text{La}/\text{Sm}_N < 0.6\). The Depleted Group has pronounced Zr and Hf depletions relative to similarly incompatible REEs (Fig. 4.1). The samples display a narrow range of \(^{87}\text{Sr}/^{86}\text{Sr} = 0.7030-0.7032\) and \(^{143}\text{Nd}/^{144}\text{Nd} = 0.51302-0.51312\) (Table 4.1).

The Li isotope compositions scatter substantially in Icelandic picritic glasses. The \(^{7}\text{Li}\) values of the Enriched Group range between +3.9 and +5.8‰ whereas the Depleted Group shows slightly larger variation in \(^{7}\text{Li}\) (+3.8 to +6.9‰). There is a striking linear and negative correlation between \(^{7}\text{Li}\) and \(^{3}\text{He}/^{4}\text{He}\) (Fig. 4.2) in which low \(^{7}\text{Li}\) values, typical of MORB-like mantle, are associated with high \(^{3}\text{He}/^{4}\text{He}\) that are diagnostic of the Iceland plume. We explore the implications of this later.

Lithium concentrations of Jan Mayen ankaramitic basalts vary between 2.2 and 5.1 ppm but, in contrast to the Icelandic basalts, they show extremely homogeneous \(^{7}\text{Li} (+3.9 to +4.7‰); Table 4.1). This is consistent with the homogeneous trace element (Table 4.1) and Sr-Nd isotope compositions (Stuart et al., submitted manuscript) of these samples, and Jan Mayen basalts in general (Tronnes et al., 1999; Blichert-Toft et al., 2005). The rare earth
element patterns (La\textsubscript{N}/Sm\textsubscript{N} > 3.25) are steeper than in the Iceland lavas (Fig. 4.1) and imply a more enriched source. Unlike the Icelandic basalts, the Jan Mayen ankaramites show Pb enrichment relative to neighbouring elements (Fig. 4.1). The Jan Mayen basalts are enriched in Zr and Nb relative to MORB and possess strongly positive ΔNb (FITTON et al., 1997) values (0.42-0.49; Table 4.3). Subtle depletions in Sr, Zr and Hf relative to neighbouring elements of similar incompatibility are observed.

| Table 4.1: Li concentrations and Li, Sr and Nd isotope compositions of Iceland and Jan Mayen basalts |
|---------------------------------|---------|---------|---------|---------|
| Iceland                        | Li (ppm) | δ\textsuperscript{6}Li (%) \textsuperscript{a} | 2σ | 87\textsuperscript{Sr}/86\textsuperscript{Sr} \textsuperscript{b} | 143\textsuperscript{Nd}/144\textsuperscript{Nd} \textsuperscript{c} |
| DICE 5                         | 2.8      | 6.90    | 0.34 | 0.703040 (14) | 0.513115 (6) |
| DICE 7                         | 2.6      | 6.29    | 0.19 | 0.703015 (12) | 0.513115 (9) |
| DICE 8                         | 3.8      | 5.84    | 0.37 | 0.703104 (14) | 0.513066 (6) |
| DICE 9                         | 4.5      | 3.88    | 0.39 | 0.703141 (17) | 0.513027 (5) |
| DICE 10                        | 2.6      | 4.57    | 0.37 | 0.703089 (14) | 0.513081 (7) |
| DICE 11                        | 2.4      | 3.72    | 0.19 | 0.703095 (14) | 0.513083 (6) |
| DICE 13                        | 4.1      | 4.01    | 0.18 | 0.703209 (12) | 0.513023 (6) |
| DICE 15                        | 4.1      | 5.21    | 0.17 | 0.703120 (11) | 0.513038 (5) |
| DICE 43                        | 5.0      | 4.38    | 0.26 | 0.703194 (17) | 0.513019 (7) |
| MAE                            | 2.8      | 5.50    | 0.09 | 0.703007 (13) | 0.513101 (7) |
| Jan Mayen                      | JM 14    | 5.1     | 3.88   | 0.25 |
|                                | JM 44    | 4.8     | 3.92   | 0.41 |
|                                | JM 78    | 3.9     | 4.00   | 0.16 |
|                                | JM 207   | 4.3     | 3.86   | 0.20 |
|                                | JM 208   | 4.0     | 4.38   | 0.33 |
|                                | JM 16837 | 3.8     | 4.70   | 0.39 |
|                                | JM 16841 | 2.9     | 4.49   | 0.23 |
|                                | JM 16852 | 2.2     | 4.04   | 0.44 |

Sr and Nd isotope compositions of Jan Mayen ankaramitic lavas from this study are given elsewhere (STUART et al., submitted manuscript).

\textsuperscript{a} Li isotope compositions are expressed in per mil relative to Li reference standard L-SVEC (NIST SRM 8545).

\textsuperscript{b} Numbers in parentheses are 2σ errors and refer to the last two digits.

\textsuperscript{c} Numbers in parentheses are 2σ errors and refer to the last digit.
Table 4.2: Trace element concentrations of Iceland picritic lavas

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Trace element concentrations are given in ppm. Trace element ratios are normalised to primitive mantle (SUN and MCDONOUGH, 1989).

* EuN/Eu is calculated from the interpolated Eu* defined by the primitive mantle-normalised abundances of Sm and Gd.
### Table 4.3: Trace element concentrations of Jan Mayen ankaramitic lavas

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Trace element concentrations are given in ppm. Trace element ratios are normalised to primitive mantle (SUN and MCDONOUGH, 1989).

- Eu/Eu* is calculated from the interpolated Eu* defined by the primitive mantle-normalised abundances of Sm and Gd.

- ΔNb is calculated after FITTON et al. (1997) as $\DeltaNb = 1.74 + \log(Nb/Y) - 1.92\times\log(Zr/Y)$
Fig. 4.1: Primitive mantle-normalised trace elements from Iceland and Jan Mayen. Trace element patterns for basaltic glasses from MMF system can be divided into the Enriched Group (open) and Depleted Group (black). Both lava groups are depleted in Li and Pb and enriched in Ba, Nb and Ta compared to similarly compatible elements. Depleted Group is also enriched in Sr and Zr- and Hf-depleted relative to neighbouring elements. A similar trace element pattern has been observed independently of our study in the Hengill picrite HEN5 and ascribed to recycled oceanic crust as one constituent for Icelandic plume (Clauvel and Hémon, 2000). A small positive Eu anomaly has been detected for both lava groups; Li is depleted in both groups. Trace element pattern of Jan Mayen ankaramites is shown in grey colour. It closely resembles that of Jan Mayen lavas from Trönnes et al. (1999). Note Li depletion and Pb enrichment relative to neighbouring elements. Enriched character of the lavas is documented by steepness of the primitive mantle-normalised pattern with high La/SmN values >3.2. Normalisation values are taken from Sun and McDonough (1989).

4.6 Discussion

4.6.1 Lithium isotope composition of the North Atlantic mantle constrained from Icelandic basalts and Jan Mayen ankaramites

Surprisingly few data exist for Li isotope compositions of Icelandic basalts. Two studies reveal $\delta^{7}$Li values that are indistinguishable from the results in this paper (Pistiner and
HENDERSON, 2003; RYAN and KYLE, 2004). One basalt with major element compositions similar to the Depleted Group (AU389) gives $\delta^7$Li of +4.0‰ (RYAN and KYLE, 2004), consistent with the high-\(^3\)He/\(^4\)He DICE 10 and DICE 11 lavas. The interior part of the effectively unaltered Laki basalt shows slightly lighter Li isotope compositions ($\delta^7$Li = +3.2‰) with some scatter throughout the sample transect (±1.1‰; PISTINER and HENDERSON, 2003), a value in agreement with data from this study. A preliminary study of olivine tholeiites from Theistareykir and Krafla, two geographically distinct volcanic centres in Iceland, shows a large spread of $\delta^7$Li at both localities (+0.9 to +4.3‰; -0.8 to +6.3‰, respectively; HANSEN et al., 2005). Light Li isotope compositions of primitive high-MgO (>8%) post-glacial Theistareykir lavas do not reflect contamination by Icelandic crust but are believed to represent intrinsic features of the magmatic sources as also evidenced by radiogenic isotopes (e.g. ELLIOTT et al., 1991; STRACKE et al., 2003). On this basis the Icelandic plume may have $\delta^7$Li in a similar range to that found for Theistareykir lavas (HANSEN et al., 2005).

Data from this study show $\delta^7$Li values for high-\(^3\)He/\(^4\)He lavas that are similar to those of the above studies (see Table 4.1). Lavas with \(^3\)He/\(^4\)He higher than 17 RA have an average $\delta^7$Li of ~+4.3 ± 1.0‰. This is in excellent agreement with the inferred mantle $\delta^7$Li value at ~+4‰ based on data from pristine spinel lherzolites (MAGNA et al., 2006b). Recent $\delta^7$Li data of fresh MORBs seem to be inconsistent with any provinciality in distribution of Li isotopes among Mid-Atlantic Ridge, Southeast Indian Ridge and East Pacific Rise (TOMASCAK et al., in press). Furthermore, chemical variability ($K_2O/TiO_2 = 0.05-1.55$) is not mimicked in any way by large Li isotope variations in MORB. Three fertile peridotites from the study of JEFFCOATE et al. (2007) show an average $\delta^7$Li of +3.6‰ and are consistent with previous investigations of Li isotopes in pristine peridotites (SEITZ et al., 2004; MAGNA et al., 2006b). These peridotitic data further validate the recently postulated Li isotope composition of the upper mantle at +4.2 ± 0.8‰ (CHAN, 2003) as inferred from fresh MORBs and a single Hawaiian lava.

That intra-plate basaltic volcanism from Hawaii and Iceland have $\delta^7$Li close to +4‰ (TOMASCAK et al., 1999b; CHAN and FREY, 2003) implies a single value for the Li isotope composition of the terrestrial mantle which is constant and independent of trace element depletion/enrichment. This is corroborated by Jan Mayen data from this study that show an
overall homogeneity in $\delta^7$Li ($\pm 4.2 \pm 0.6\%$). Therefore, Li seems quite homogeneous, regardless of the fact that $^3$He/$^4$He $<$ MORB in these lavas (Stuart et al., submitted manuscript) and $^3$He/$^4$He $>$ MORB in the majority of MMF lavas (Burnard and Harrison, 2005). Both of these suites involve distinct components required to produce the observed trace elements and radiogenic isotopes.

The explanation for this could be that the Li isotope compositions are to some extent buffered by a dominant mantle component even after entrained material with different trace elements and isotope ratios was added. Deviations to either light or heavy $\delta^7$Li values would in turn provide evidence for incorporation of volumetrically significant pollutants with largely different Li isotope signatures (eclogites, seawater-altered crust, continental crust). However, lack of Li isotope data for other OIBs does not permit precise estimates of the $\delta^7$Li of such environments. Collectively, the data from this study suggest only limited variations in Li isotope compositions with a global mantle average $\delta^7$Li $\approx +4\%$.

4.6.2 Li-He isotope correlation in Icelandic basalts

The Icelandic basalts from this study display an inverse and linear correlation between $\delta^7$Li and $^3$He/$^4$He (Fig. 4.2) that is, however, not well reflected in other trace element and/or radiogenic isotope data. Eclogites lend to have very low, even negative $\delta^7$Li combined with radiogenic $^3$He/$^4$He as marked in inset of a by red and green line that, by keeping linear relationship, give an estimate of the minimum $\delta^7$Li required from the highest $^3$He/$^4$He in Iceland (red line; 37 $R_A$ and $-2\%$) and worldwide (green line; 50 $R_A$ $\sim -7\%$). Blue horizontal bar represents $\delta^7$Li of the Earth's mantle estimated from available pristine peridotitic data ($+3.6$ to $+4.2\%$). In b, He isotopes are plotted against Nb/U, which is generally homogeneous in MORB and OIB reservoirs (Hofmann, 1997). Hence, high Nb/U is most likely inherited from depletion in U and residual enrichment in Nb during alteration of ocean floor and subduction. The Jan Mayen lavas lie away from the Icelandic lavas because their Nb/U ratios fall close to average value of $\sim 50$ inferred for oceanic basalt suites (Hofmann, 1997). In c, broadly negative correlation of He and O isotopes may be observed, in particular obvious for Enriched group lavas (see text for discussion).
isotope ratios. The high $^3\text{He}/^4\text{He}$ of Iceland plume-derived basalts are thought to reflect the contribution from a deep mantle that is less degassed of primordial volatiles than upper asthenospheric mantle (STUART et al., 2003). Therefore, the simplest explanation for the observed He-Li isotope trend is that it represents a mixing between a primordial gas-rich deep mantle source and altered Icelandic crust. Altered crust represents a reservoir with enrichment in $^7\text{Li}$ and high Li abundances in tens of ppm. The mantle likely has $\delta^7\text{Li} \approx +4\%$ with minimal scatter. Parts of the deep mantle may carry high $^3\text{He}/^4\text{He} \approx 50$ Ra (STUART et al., 2003) whereas crustal materials have a large contribution of radiogenic $^4\text{He}$ tending to low $^3\text{He}/^4\text{He}$. However, four lines of evidence suggest that this model is too simplistic.

Firstly, the $\delta^{18}\text{O}$ of all samples (4.1 to 4.6%; BURNARD and HARRISON, 2005) is lower than most oceanic basalts. The depletion in $^{18}\text{O}$ transcends the trace element enrichment/depletion and is common to the whole sample suite. It has been suggested that Ar-O isotope systematics in these lavas could reflect surficial processes (e.g. assimilation of meteoric fluids or material altered by meteoric fluids; BURNARD and HARRISON, 2005). However, as pointed out above this is not considered to be a likely explanation for the ubiquitous low-$^{18}\text{O}$ Icelandic volcanism. It is very possible that large-scale hydrothermal alteration with meteoric fluids provided source rocks with low $\delta^{18}\text{O}$ (GAUTASON and MUEHLENBACHS, 1998) that were formed in the past, as in Palaeozoic ophiolites (MUEHLENBACHS et al., 2004) for example, and then recycled. A low-$\delta^{18}\text{O}$ mantle end-member is required that is depleted in incompatible trace elements and carries $^3\text{He}/^4\text{He} < 12$ Ra together with elevated $\delta^7\text{Li}$ values, Eu enrichment and superchondritic Sr/Nd. Incompatible-trace-element-enriched lavas could well represent a mixture of such a recycled low-$\delta^{18}\text{O}$ component with a less degassed mantle component having high $^3\text{He}/^4\text{He}$ (BURNARD and HARRISON, 2005) and normal mantle Sr/Nd. In this case, a negative correlation between $\delta^{18}\text{O}$ and $^3\text{He}/^4\text{He}$ would be observed (THIRLWALL et al., 2006). Indeed, such a tendency can be seen in the MMF lavas (Fig. 4.2).

Second, trace elements provide evidence of recycling and feldspar accumulation, even though none of the basalts analysed contain feldspar as a phenocryst phase. The Eu anomaly is always positive (Table 4.2) and correlates with Sr/Nd (Fig. 4.3), consistent with plagioclase accumulation. Recycled gabbroic cumulates that have been converted to eclogite or pyroxenite could carry the positive Eu anomalies and high Sr/Nd imparted from an earlier cumulate history, as has been proposed for Hawaii (HOFMANN and JOCHUM, 1996). The evidence for feldspar accumulation in the prehistory of these magma sources is striking. The
samples that characterise the low-$^3$He/$^4$He high-$^7$Li end-member (DICE 5, 7 and MAE) are rich in feldspathic cumulates. In principle, these could be either sub-Icelandic crust or recycled gabbroic lower oceanic crust. If these magmas reflected vastly different portions of a recycled component it would be hard to explain the restricted range of $^{87}$Sr/$^{86}$Sr = 0.7030-0.7032 and $^{143}$Nd/$^{144}$Nd = 0.51302-0.51312 (Table 4.1) and similar overall trace element patterns (Fig. 4.1).

Fig. 4.3: $\text{Eu}_N/\text{Eu}^*$ and $(\text{Ba}/\text{Th})_N$ vs. $(\text{Sr}/\text{Nd})_N$. The plot reveals that Enriched Group lavas have lower $\text{Sr}/\text{Nd}$ ratios than Depleted Group lavas. Within each group a steep positive trend can be seen. The largely distinct $\text{Sr}/\text{Nd}$ element ratios require different sources. $\text{Eu}_N/\text{Eu}^*$ is calculated from the interpolated $\text{Eu}^*$ defined by the chondrite-normalised abundances of Sm and Gd. $(\text{Ba}/\text{Rb})_N$ vs. $(\text{Sr}/\text{Nd})_N$ plot (not shown) has very similar pattern as $(\text{Ba}/\text{Th})_N$ vs. $(\text{Sr}/\text{Nd})_N$ plot. Jan Mayen lavas mostly lie on the intercept of mantle values for $(\text{Sr}/\text{Nd})_N$ and $\text{Eu}_N/\text{Eu}^*$ but two samples (16841, 16852) show remarkable Th depletion relative to other Jan Mayen lavas which results in their substantially higher $(\text{Ba}/\text{Th})_N$ ratios. The symbols are the same as in Fig. 4.2.
Third, high Nb/U and negative Pb and Li anomalies are a characteristic of most samples. High Nb/U in particular implicates U-loss during a prior subduction history. Niobium is effectively retained in the subducted residue (Rudnick et al., 2000) whereas U is removed into the mantle underlying arc and back-arc lavas (Kelley et al., 2005). Alteration of the upper oceanic crust elevates U abundances (Elliott et al., 1999) whereas the Nb budget remains largely undisturbed. The mobility of U was only augmented after the Archean as a result of dramatic increase in oxygen fugacity (Elliott et al., 1999). All but one sample has Nb/U higher than the upper range of the global average (47 ± 10) compiled by Hofmann (1997) and eight out of ten Icelandic lavas from this study have Nb/U > 70 (see Fig. 4.2). This superchondritic Nb/U must have evolved in an ancient subduction event and cannot reflect present-day processes.

Fourth, if the Li-He isotope correlation represents a mixing between altered Icelandic crust and deep mantle, the linearity of the data array requires that the [He]/[Li] of the end members are broadly similar. From the He-O isotope relationship, Burnard and Harrison (2005) inferred a mixing between depleted MORB mantle and hypothetical Iceland source region where [He]_DMM ≥ 10×[He]_ICE. Keeping this relationship would, accordingly, entail a ten-fold difference in Li abundances between the two respective end-members which is not a likely option for the mantle components because the bulk distribution coefficient for Li in mantle melting is probably not far from unity with Li abundances that differ by a factor of ∼2-3 at most between depleted MORB mantle and Iceland source region.

Hydrothermally altered rocks carry in general isotopically light Li (Chan et al., 2002a). However, at this time insufficient is known to evaluate whether this is a normal feature of 18O-depleted altered oceanic crust. Petrologic studies and major element chemistry that show that all these samples ascended through the Icelandic crust quickly because they contain numerous gabbroic xenoliths and both DICE 10 and DICE 11 contain partially resorbed olivines (Tronnes, 1990). Sparse analyses of gabbroic rocks show that they may have δ7Li > fresh MORB while maintaining low Li contents (Chan et al. (2002a) and T. Magna, unpubl. data) which could be a result of addition of late stage low-temperature alteration products (Chan et al., 2002a). The Icelandic silicic rocks carry Sr and Nd isotope compositions like those of the basalts (e.g. O’Nions and Grönvold, 1973; Sigmarsson et al., 1991, 1992; Gunnarsson et al., 1998; Martin and Sigmarsson, 2007). However, these evolved rocks are strongly depleted in Ba, Sr and Eu (Jónasson, 1994, 2007; Gunnarsson et al., 1998; Martin and Sigmarsson, 2007) and carry δ18O values heavier than those measured in DICE
lavas (Sigmarsson et al., 1991, 1992; Burnard and Harrison, 2005; Martin and Sigmarsson, 2007). These features combined with the major element compositions, render the silicic rocks an improbable contaminant.

By extrapolating the correlation to the highest $^3\text{He}/^4\text{He}$ measured in Iceland ($\approx 37$ R$_A$; Hilton et al., 1999; Ellam and Stuart, 2004) or globally ($\approx 50$ R$_A$; Stuart et al., 2003), the high-$^3\text{He}/^4\text{He}$ end-member would possess $\delta^7\text{Li} < \sim -2\%$ or $\sim 7\%$, respectively (see inset in Fig. 4.2). So far, the only rocks with negative Li isotope compositions are eclogites which have suffered dehydration during subduction (Zack et al., 2003). However, the loss of mantle He during subduction of oceanic crust, and the subsequent ingrowth of radiogenic He from U (and Th) decay will, in all likelihood, leave eclogites with extremely low $^3\text{He}/^4\text{He}$ making them unlikely candidates as the high-$^3\text{He}/^4\text{He}$ reservoir in the Earth. More importantly, the fact that the lowest $\delta^7\text{Li}$ found in the Iceland samples is the same as “normal” mantle renders as extremely unlikely the notion that this composition is a fortuitous mixture of the exactly correct mixture of light and heavy Li. Accepting this to be the case the “light” end member actually has $\delta^7\text{Li} \sim 4\%$ and $^3\text{He}/^4\text{He} = 20$ R$_A$.

Experimental partitioning data for noble gases (Heber et al., 2007) show that, like Li, they are less incompatible than K, U and Th in olivine and clinopyroxene, and tentatively also in orthopyroxene. Hence, recycling of previously melt-depleted ancient lithosphere with reasonably constant He/Li but depletions in K, U and Th may lead to variable $^3\text{He}/^4\text{He}$ while maintaining low total He abundances and lead to a linear functional relationship between Li and He isotope compositions. This would be consistent with the relationships between the Nd and Sr isotope compositions of the Iceland samples and their parent / daughter ratios (Sm/Nd and Rb/Sr, respectively; not shown) which are consistent with fractionation during the Phanerozoic.

Recent work has highlighted the relative importance of diffusion-driven Li isotope fractionation (Richter et al., 2003; Lundstrom et al., 2005) that may add to Li isotope variability in the limited scales of transects. Although it may prove important for local-scale sampling and for intra- and inter-mineral diffusive isotope fractionation as illustrated recently (e.g. Jeffcoate et al., 2007; Rudnick and Ionov, 2007), lavas from MMF system are dispersed along some $\sim 15$ km and are not directly related to each other. Also, any changes in $\delta^7\text{Li}$ due to diffusion vanish after some one hundred meters away from contact and Li abundances vary only within few meters of the contact (Teng et al., 2006a). Therefore, a direct assessment of diffusive Li isotope fractionation is irrelevant here. Diffusive
fractionation of He isotopes was advocated for a suite of samples from Siberia which was underlain by assuming faster diffusion of $^3$He and by positive correlation between $[^4\text{He}]$ and $^3\text{He}/^4\text{He}$ (Harrison et al., 2004). Also Burnard et al. (2004) have shown that some limited fractionation of He isotopes due to diffusion is plausible though not explaining total variation in $^3\text{He}/^4\text{He}$. There is, however, no similar correlation observed in MMF lavas from this study and we infer diffusion-driven isotope fractionation is an unlikely mechanism for the observed Li-He isotope correlation.

4.6.3 Implications for the origin of Jan Mayen basalts from Li isotopes

Further evidence that recycled components are important in the North Atlantic mantle despite normal Li isotopes comes from the Jan Mayen ankaramites. The incompatible trace element concentrations in Jan Mayen basalts (Table 4.3) are at least twice as high as those in basalts from adjacent Mohns and Kolbeinsey Ridge (Mertz et al., 1991; Haase et al., 1996; Schilling et al., 1999). Combined with highly radiogenic Sr and the least radiogenic Nd (Stuart et al., submitted manuscript) and Hf (Blichert-Toft et al., 2005) measured in the North Atlantic they provide evidence for a particularly enriched mantle beneath Jan Mayen that is exotic and largely dissimilar to other localities in the North Atlantic Ocean. The Jan Mayen basalts have trace element compositions that may indicate a contribution of HIMU-like mantle in the source region (Thirlwall, 1997; Trønnes et al., 1999). However, the Pb isotopes are not highly radiogenic (Stuart et al., submitted manuscript) and the $^7\text{Li}$ values (+3.9 to +4.7\%) appear to be markedly different from previous analysis of basalts with a HIMU affinity. Heavy $^7\text{Li}$ values ($^7\text{Li} > +5\%$) are recorded for the HIMU component in basalts from the Polynesian islands (Nishio et al., 2005). Ryan and Kyle (2004) have modelled the HIMU component in alkali basalts from St. Helena to have $^7\text{Li} = +8.5\%$. Although these basalts show clear signatures of weathering which might explain the high $^7\text{Li}$ (Ryan and Kyle, 2004), the lavas record no loss of alkali elements which in turn means they likely reflect the original magmatic signature. The simplest interpretation for the source of the heavy Li isotope component in HIMU basalts is that they are derived from melting of a partially-dehydrated deep oceanic crust (Nishio et al., 2005), a suggestion in agreement with input of heavy Li into the subduction zones (Bouman et al., 2004). This is consistent with the origin of HIMU in dense oceanic crust that has been hydrothermally depleted in lead, on the basis of Pb isotopes and trace elements (Hofmann, 1997; Willbold and Stracke, 2006).
Although the absence of heavy Li isotope component in the Jan Mayen basalts contrasts with HIMU basalts, similar $\delta^7\text{Li}$ values (+3 to +5%) have been measured in intra-plate Antarctic basaltic lavas with HIMU affinity (Ryan and Kyle, 2004). Their Li isotope compositions were explained as a mixture of a HIMU component with moderately elevated $\delta^7\text{Li}$ (~ +8.5%) and a depleted mantle source of MORB. Such heavy Li signatures ($\delta^7\text{Li}$ ~ +7.5%) have been observed in Polynesian HIMU lavas (Nishio et al., 2005) that have been explained by entrainment of a less altered basaltic part of oceanic crust in the source of these lavas. Hawaiian lavas with HIMU-like Pb isotope signatures possess $\delta^7\text{Li}$ values that are indistinguishable from MORB (Kobayashi et al., 2004). However, glass inclusions trapped in some of these lavas do carry extremely negative Li isotope compositions ($\delta^7\text{Li}$ ~ -10%) explained by recycled dehydrated oceanic crust in the source of Hawaiian mantle plume (Kobayashi et al., 2004). This is similar to a conclusion made for two anomalously light samples from Koolau volcano ($\delta^7\text{Li}$ ~ +2.6%; Chan and Frey, 2003).

The Jan Mayen ankaramites display large Pb enrichments and Th-U depletion relative to neighbouring elements which is inconsistent with HIMU. Such basalts in general show significant Pb depletion (Hofmann, 1997; Willbold and Stracke, 2006). In fact, the trace element pattern of Jan Mayen ankaramites (Fig. 4.1) and trace element ratios (e.g. Rb/Sr, Th/U, Ce/Pb, U/Pb, Ba/La, Rb/La) are more similar to those of the EM2 component (Workman et al., 2004; Willbold and Stracke, 2006). The Jan Mayen basalts may be a mix of normal depleted mantle with enriched component where the $\delta^7\text{Li}$ is dominated by Li contribution from the depleted mantle, following Ryan and Kyle (2004). This is supported by the presence of a similar chemistry in off-axis volcanism elsewhere in the North Atlantic Ocean (Haase and Devey, 1994; Trønnes et al., 1999).

Trønnes et al. (1999) have argued that Jan Mayen basalts are melts of laterally dispersed Iceland mantle plume. Although the $\delta^7\text{Li}$ values for the Enriched Group of MMF basalts (+3.9 to +5.9%) overlap the Jan Mayen ankaramites (+3.9 to +4.7%), several lines of evidence are inconsistent with Jan Mayen and Iceland having the same source. First, the projection of Icelandic mantle plume material to the north of Iceland is spatially restricted to several hundreds of kilometres northwards (Thirlwall et al., 2004). Second, radiogenic isotope trends in Iceland do not approach those measured in Jan Mayen (Mertz et al., 1991). This is observed in more radiogenic Sr and less radiogenic Nd isotope compositions for Jan Mayen ankaramites relative to MMF picritic glasses. Third, He isotopes show no sign of the high values typical of the Iceland plume and are well below MORB (R/Ra<7; Stuart et al., 83
submitted manuscript). Fourth, Jan Mayen basalts have been produced by larger degrees of enrichment in Nb-Zr than Icelandic basalts with resulting high ANb values (Table 4.3). This parameter cannot be simply changed by entraining or contamination of a Nb-Zr-rich component but largely reflects a source characteristic (Fitton et al., 1997, 2003).

It is obvious from trace element data (Table 4.3) that HIMU is not an ideal end-member for Jan Mayen. Indeed, global dispersion of HIMU is strictly limited to the southern hemisphere and is by no means conspicuous in the northern hemisphere. The trace element pattern more likely resembles that of other enriched mantle end-members (see Willbold and Stracke, 2006) and a similar prognosis has been made based on detailed Pb isotope studies of basalts dredged from the Jan Mayen platform (Blichert-Toft et al., 2005). EM1 seems to carry strongly negative δ7Li values (Nishio et al., 2004), as if originating from eclogitic melts whereas the EM2 end-member might be expected to be slightly heavier than MORB (Tomascak et al., in press; Nishio et al., 2004). The available Pb isotope data fall well into the field of North Atlantic MORB given by Blichert-Toft et al. (2005) who assume that Jan Mayen may reflect mixing of depleted mantle and EM2 component. A tentative estimate for EM2 end-member is given at δ7Li ~+6‰ (Nishio et al., 2004), much like the still heavier HIMU end-member (Nishio et al., 2005). Available Pb isotope data show rather limited variations for EM2 compositions (206Pb/204Pb between ~17.8 and ~19.2 as compiled by Hofmann (1997) and thus, do not exclude a spike of such material in the source of Jan Mayen lavas (Fig. 4.4). A metasomatic origin has recently been proposed for EM2 (Workman et al., 2004) in contrast to an involvement of discrete portions of the upper continental crust mixed with recycled oceanic lithosphere (Willbold and Stracke, 2006). However, the upper continental crust has rather narrow average of δ7Li (0 ± 2‰) and high Li abundances of ~35 ppm (Teng et al., 2004). This limits the maximum material from the upper crust to <5%.
### 4.7 Conclusions

We have presented Li isotope data for two suites of basaltic lavas from the North Atlantic. Lithium isotope compositions of lavas from Mælifell-Miðfél Fissure (MMF) system (Hengill area, Iceland) show a striking inverse and linear correlation with He isotopes. The high-$^3$He/$^4$He lavas show rather narrow range of $\delta^7$Li averaging $\sim +4.3\%$ whereas low-$^3$He/$^4$He lavas possess isotopically heavier Li. The simple interpretation of the observed relationship as being a mixture between mantle and surface altered crust is rendered improbable by trace element data. Instead, recycled gabbroic oceanic crust is required in the source of MMF lavas from coupled Li isotopes and trace element systematics. Although exact qualification of these end members is not straightforward, the observed ubiquitous Eu enrichment hints to an old recycled component, efficiently mixed into the source of Depleted...
DICE lavas. Data from this study do not support diffusive fractionation of both Li and He isotopes, nor do they provide evidence of contamination by silicic volcanic rocks. The Jan Mayen ankaramitic lavas are homogeneous in terms of Li isotopes and trace elements that show remarkable enrichments in LREE. A possible HIMU origin of the enriched component of Jan Mayen Island lavas is not easily reconciled with the data and we suggest these lavas may include an EM2-like component.

Lithium isotope compositions of lavas from this study support a view of relatively homogeneous mantle $\delta^7$Li value of $+4\%$ irrespective of their chemical enrichment / depletion and evidence of recycling. The fact that He isotopes vary greatly in North Atlantic lavas all displaying the same mantle-like Li isotope composition, $^{18}$O depletion and variable trace element enrichments reflecting recycled cumulates provides evidence that recycled lower oceanic crust with variable $(U+Th)/He$ was an important part of the source region. The fact that Li isotopes are correlated linearly with He isotopes in Iceland provides evidence of an additional recycled altered oceanic crustal component with different $(U+Th)/He$ ratio but the same He/Li. This is consistent with the fact that He and Li are both slightly but not highly incompatible. There is no evidence that the He isotope compositions have been affected by a high-$^3$He component from a relatively undegassed reservoir.

**Acknowledgement**  We thank Marie-Theres Bär for making the columns, Heiri Baur, Donat Niederer, Bruno Rütsche, Urs Menet and Andreas Süsli for the electronics and mechanical workshop services, Irene Ivanov-Bucher for help with sample preparation, Marcus Gutjahr and Martin Frank for assistance by Sr and Nd isotope analyses and, in particular, Felix Oberli for maintenance and troubleshooting of Nu 1700. We are grateful to Mark Rehkämper, Paul Tomascak and Helen Williams for comments on previous version of the manuscript and Francis Albarède, Janne Blichert-Toft, Karsten Haase and Kaj Hoernle for helpful suggestions and/or information. Kaj Hoernle kindly provided samples from Canary Islands. ETH and Swiss National Fonds (SNF) supported this work financially.
Chapter 5

New constraints on the lithium isotope compositions of the Moon and terrestrial planets

5.1 Abstract

High-precision lithium (Li) isotope data are reported for samples from the Earth, Moon, Mars and Vesta and provide evidence of broadly similar compositions that are slightly heavy relative to those of chondrites. Mare basalts exhibit a large range of Li isotope compositions ($\delta^{7}\text{Li} = +3.4 \text{ to } +6.4\%$) that correlate with indices of magmatic differentiation. Three samples (quartz-normative basalts and picritic orange glass) that are thought to have formed by melting of relatively primitive source regions yield a mean $\delta^{7}\text{Li} = +3.8 \pm 0.4\%$ taken as the best estimate for the average composition of the Moon. Other samples are isotopically heavier correlating with increases in Rb and Hf and probably reflecting transport of isotopically heavy Li that formed in specific high-Ti cumulate – melt layers during crystallisation of the magma ocean. The most extreme lunar $\delta^{7}\text{Li}$ is found in a ferroan anorthosite ($+8.9\%$). Terrestrial mantle olivines fall into a tight range between $+3.6\%$ and $+3.8\%$. If these olivines reflect the composition of the bulk Earth, the Li isotope compositions of Earth and Moon are identical. The Li isotope compositions of samples from the Moon, Earth, Mars and Vesta provide no evidence for differences between large inner solar system mantle reservoirs. This in turn provides evidence that core formation, volatile loss and the presence of a crust and hydrosphere have not significantly influenced the bulk Li isotope composition of the mantles of these objects. The fact that chondrites are isotopically light compared with differentiated planetary bodies of the inner solar system is consistent with a small but significant Li isotope fractionation within the accretionary disc or chondrite parent bodies, the origin of which is presently unclear.

5.2 Introduction

Theoretical models and isotope approaches for studying the origin of the solar system are becoming increasingly sophisticated and powerful (CAMP and AGNOR, 2000; HALLIDAY, 2003; CHAMBERS, 2004), but a major issue of current debate is the origin of the heterogeneous distribution of volatiles, which it is now thought may partly relate to accretion processes. It has been proposed on the basis of Sr isotopes that there were significant losses of moderately volatile elements during the late (>10 Myrs) accretionary history of the material that formed the Earth and Moon (HALLIDAY and PORCELLI, 2001). More recently it has also been argued that the slightly heavier Fe isotope composition of basalts from the Moon,
relative to those from Vesta and Mars, may reflect volatilisation of Fe during the Giant Impact (POITRASSON et al., 2004). Iron is only slightly volatile and the degree to which this effect reflects vaporisation of molten iron metal as opposed to silicate is unclear. If the effect is produced by volatilisation of silicate it should be present in other elements of similar half mass condensation temperature. Lithium is such a slightly volatile element. O’NEILL (1991) predicted complete or nearly complete condensation of Li while most Na is evaporated during formation of the Moon. Being very light, Li is expected to show sizeable isotope fractionations during partial volatile loss.

Lithium (Li) isotope abundances have already been reported from a few meteorites using high-precision multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS; MCDONOUGH et al., 2003; SEPHTON et al., 2004). However, most of these are chondrites. The few existing analyses suggest that different chondrite groups may have distinct Li isotope compositions. This variation could reflect aqueous alteration on parent bodies resulting in isotopically light Li in the residual highly metamorphosed chondrites and isotopically heavy Li related to chondrites with high alteration index (MCDONOUGH et al., 2003). CM chondrites show large internal Li isotope variation (SEPHTON et al., 2004) providing evidence of a complex history of evaporation and condensation of Ca- and Al-rich refractory inclusions and chondrules in the solar nebula. These two constituents of chondrites seem to have negative δ7Li values resulting partly from incorporation of spallogenic Li into chondritic matter in the early solar system (CHAUSSIDON et al., 2001; 2006).

The exact Li isotope composition of the bulk silicate Earth or primitive mantle has proven problematic because the variation in Li isotope compositions in mantle rocks is large (-17 to >+10‰; CHAN et al., 1992; 2002b; MORIGUTI and NAKAMURA, 1998b; TOMASCAK et al., 1999b; CHAN and FREY, 2003; ZACK et al., 2003; KOBAYASHI et al., 2004; NISHIO et al., 2004; SEITZ et al., 2004). Most estimates of the Li isotope composition of the terrestrial mantle are made on the basis of MORB and very limited data for Hawaii (δ7Li of 4.2 ± 0.8‰; CHAN, 2003). Available analyses of peridotitic rocks seem to be consistent with a δ7Li close to +4‰ for the Earth (BROOKER et al., 2004; SEITZ et al., 2004) although samples from the latter study may have been influenced by subduction zone processes with heavy Li. Isotope compositions of peridotites, calculated from mineral data, showed rather variable values (δ7Li from -1.1 to +4.1‰; SEITZ et al., 2004). Two fertile lherzolites from Vitim (Russia) and Dreiser Weiher (Germany) have calculated bulk δ7Li of +3.8 and +4.1‰, respectively (SEITZ
et al., 2004), consistent with the above mantle value. Also Elliott et al. (2004) stressed that the $\delta^{7}\text{Li}$ in N-MORB lavas displays a tight range of 3-4‰ with slightly higher values in OIB.

We have analysed a range of samples to assess whether there are systematic differences in Li isotope composition between planetary objects, in particular the Moon and to constrain a $\delta^{7}\text{Li}$ value for the bulk Earth. In addition to data for lunar basalts, eucrites, martian meteorites and chondrites, we present Li isotope ratios for a suite of olivines, clinopyroxenes and orthopyroxenes from spinel lherzolites in order to better estimate the $\delta^{7}\text{Li}$ of the Earth’s mantle.

### 5.3 Methods and samples

All samples have been dissolved in a mixture of HF and HNO$_3$ (6:1 v/v) and after complete decomposition evaporated and refluxed with HNO$_3$ several times to remove fluorides. We used small-volume (2.1 ml) ion exchange columns packed with BioRad AG50W-X8 (mesh 200-400) cation-exchange resin and employed 1M HNO$_3$ – 80% methanol (v/v) mixture as an elution media. Isotope measurements were performed on the large-geometry high-resolution multiple-collector ICPMS Nu1700 (Nu Instruments). Details of analytical and mass spectrometric procedures are given in Magna et al. (2004b).

Additional small columns (0.6 ml) packed with BioRad AG50W-X12 (mesh 200-400) were used for final cleaning and effective removal of large quantities of chromium that appeared in the Li fraction after the first step. This problem was notable for clinopyroxenes from spinel lherzolites which contain up to 1-2% Cr. The use of 0.5M HNO$_3$ eluted all Cr in 2 ml such that the subsequent Li fraction was completely “clean” (see Figure 5.1). Although this second step was precautionary and we did not quantify the influence of Cr on the accuracy of Li isotope measurements it appears to be important for the acquisition of high quality data.

Lithium abundances were measured using a PQ-2 quadrupole ICPMS (VG Elemental) with beryllium as an internal standard for matrix effect corrections. Other trace element data for lunar rocks, eucrites, Allende and martian meteorites were obtained using the PQ-2 quadrupole ICPMS (VG Elemental) with rhodium as an internal standard. Basaltic reference standards were measured prior to samples and 2σ errors (two standard deviations) were better than 5% for most elements. Uncertainties in U and Pb determinations were better than 10%
(2σ), Cs determinations were better than 20% (2σ). The Eu anomaly Eu/Eu* was calculated from the interpolated Eu* defined by the chondrite-normalised abundances of Sm and Gd.

Terrestrial samples comprise mineral separates of olivine, clinopyroxene and orthopyroxene extracted from spinel lherzolites from San Carlos and Kilbourne Hole (USA), Vitim (Russia), Atsagin-Dush and Tariat (Mongolia). Additionally, three lherzolites and one harzburgite from Atsagin-Dush were analysed for whole-rock δ7Li composition. San Carlos is a primitive spinel lherzolite from Arizona, USA, studied for its major and trace elements by Jagoutz et al. (1979). Vitim (Siberia, Russia) has been depicted as a fertile off-craton peridotite and in detail studied by Ionov et al. (2005). Samples from Atsagin-Dush, Mongolia, were previously described in detail by WIECHERT et al. (1997). 8520-09 is a spinel lherzolite for which Li concentration and isotope data for olivine and orthopyroxene were acquired. 8520-12, -19 and -20 are spinel lherzolites whereas 8520-30 is a harzburgite. Tariat spinel lherzolite is located in Tariat depression, Mongolia, and has been described in detail by PRESS et al. (1986). Kilbourne Hole (New Mexico, USA) is a spinel lherzolite, another aliquot of which has been studied by Jagoutz et al. (1979). Mineral separates from spinel lherzolites were ultrasonically cleaned in weak HCl for 20 minutes to remove surface contamination, subsequently rinsed with de-ionised water and ultrasonically washed for 30 minutes in de-ionised water. The lunar samples include the more important magmatic rock types collected during various Apollo missions: high-Ti mare basalts, picritic glasses, olivine-, ilmenite- and quartz-normative basalts as well as one ferroan anorthosite. In addition, 2 martian meteorites, 6 eucrites and 2 chondrites were analysed.

Lithium isotope compositions were calculated using the following formula: δ7Li (%) = [(7Li/6Li)sample/(7Li/6Li)standard-1]×1000. We used L-SVEC as a reference standard (Flesch et al., 1973). Accuracy and precision of the method has been monitored by multiple analyses (full replication including sample dissolution) of BHVO-2 and JB-2, two international reference rocks of the US and Japanese Geological Surveys, and OK-1 an in-house eclogite standard from Münchberg (Germany) with well-defined δ7Li = -8.27 ± 0.20‰ (Magna et al., 2004b). During this study δ7Li values of 4.52 ± 0.18‰ (2σ; n=10), 4.65 ± 0.39‰ (2σ; n=9) and -8.24 ± 0.33‰ (2σ; n=3) have been obtained for BHVO-2, JB-2 and OK-1, respectively. These values are in good agreement with previously published data and results reported by other groups (Moriguti and Nakamura, 1998a; Tomascak et al., 1999a; Jeffcoate et al., 2004).
5.4 Results

Lithium abundances and isotope compositions for non-terrestrial samples are given in Table 5.1. Trace element data for non-terrestrial samples are provided in Table 5.2. Two chondrites Allende (CV3) and Bruderheim (L6) contain 2.1 and 2.7 ppm Li, respectively. Nakhla, a martian clinopyroxene cumulate, and Zagami, a martian shergottitic basalt, contain 4.8 and 4.0 ppm Li, respectively. Eucrites show substantially higher Li abundances (8.3-13.1 ppm) as do lunar rocks and glasses (6.0-13.3 ppm). Two ferroan anorthosites have 0.8 ppm Li (62255) and 0.14 ppm Li (65315), respectively. Total repeat analyses of five samples including the full analytical procedure replicated very well (see Table 5.1).
Table 5.1: Lithium concentrations and isotope compositions of non-terrestrial samples

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n.a. – not analysed
### Table 5.2: Measured trace elements concentrations of non-terrestrial samples

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<th>Cachari</th>
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</table>

All trace element data are listed in parts per million (ppm). Precision of the concentration data for Le-rich anorthosite 62255 is lowered to 20-40% (2σ) due to very low concentrations of most trace elements.
The Li isotope compositions of the samples range from $+1.5$ to $+8.9\%_o \delta^7{\text{Li}}$ (Fig. 5.2). The chondrites are isotopically light relative to all the other samples, Bruderheim (L6) yielding $\delta^7{\text{Li}} = +1.5\%_o$, whereas two duplicate measurements of Allende (CV3) average $\delta^7{\text{Li}} = +3.1\%_o$. Although this is an inadequate characterisation of chondrites, the data are fully consistent with the recent and more comprehensive study of chondrites reported by McDonough et al. (2003), who also report compositions that are variable but light relative to the values for the various silicate samples reported in Table 5.1. The best estimate for average chondritic compositions is $\delta^7{\text{Li}} = +2.0 \pm 1.5\%_o$ (W. McDonough, personal communication to ANH, 2005). The martian meteorites Nakhla and Zagami yield $\delta^7{\text{Li}} = +5.0\%_o$ and $+3.9\%_o$, respectively. Eucrites span a narrow range from $+3.0\%_o$ to $+4.2\%_o$ excluding Cachari with a high $\delta^7{\text{Li}}$. The same aliquot of Cachari also has anomalously heavy oxygen (Wiechert et al., 2004). The range of $\delta^7{\text{Li}}$ values in lunar basalts and glasses (i.e. excluding the anorthosites) exceeds $3\%_o$ ($+3.4$ to $+6.4\%_o$) and appears to vary with lithology. Quartz-normative basalts have the lightest Li isotope compositions whereas high-Ti mare basalts are isotopically heavy. Picritic glasses, olivine- and ilmenite-normative basalts have intermediate $\delta^7{\text{Li}}$ values. An extreme $\delta^7{\text{Li}}$ value of $+8.9\%_o$ has been measured in a ferroan anorthosite (62255).

Lithium abundances and isotope compositions of terrestrial samples are given in Table 5.3. Terrestrial basalts, e.g. MORB and OIB, are variable in Li concentrations but most have 3-6 ppm Li consistent with the comprehensive study of Ryan and Langmuir (1987). Olivines from spinel lherzolites are notably homogeneous with 1.5-2.2 ppm Li. Pyroxenes are depleted in Li compared to olivines, and orthopyroxenes are more depleted than clinopyroxenes, consistent with findings of Seitz and Woodland (2000) for peridotitic lithologies. All olivines and bulk peridotites have $\delta^7{\text{Li}}$ values indistinguishable from the currently accepted mantle $\delta^7{\text{Li}}$ of $4.2 \pm 0.8\%_o$ (Chan, 2003). Olivine separates are particularly homogeneous with $\delta^7{\text{Li}}$ ranging from 3.6 to 3.8\%o. Whole-rock analyses of peridotites from Mongolia show constant Li abundances of 1.4-1.7 ppm Li and a remarkably narrow range of $\delta^7{\text{Li}} = 3.8-4.3\%_o$. The $\delta^7{\text{Li}}$ of the harzburgite is slightly lighter (by $\sim0.4\%_o$) than the values for spinel lherzolites.
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Fig. 5.2: Lithium isotope composition of terrestrial and extraterrestrial materials. MORB range is from TOMASCAK (2004) and ELLIOTT et al. (2004), Iceland range is from PISTINER and HENDERSON (2003), RYAN and KYLE (2004) and high-^3^He/^4^He samples from MAGNA et al. (2004a), Hawaii from CHAN and FREY (2003), ^8^Li range of chondrites is from MCDONOUGH et al. (2003) and JAMES and PALMER (2000). Olivines from spinel lherzolites are from this study. BHVO-2 and JB-2 are displayed as long-term reproducibility standards (see Chapter 2 and MAGNA et al., 2004b). Apparent variations of ^8^Li among lunar rocks cannot be related to possible surface exposure to isotopically heavy solar wind particles, even not in case of low-Li ferroan anorthosite 62255 due to its extremely short exposure history <2 Ma. Grey glass 74240 comes from the same location as orange glass 74220 and is very similar in chemical composition to this spatially related orange glass (apart from slightly elevated Na contents; RHODES et al., 1974; KOROTEV and KREMSEK, 1992). Large proportions of basaltic fragments and grey "ropy" glass spherules cause macroscopically grey colour; orange glass component represents only a very small portion of grey glass. Clinopyroxene is the most abundant mineral phase. It has been suggested that the grey glass is a product of a local large highland impact (HEIKEN and MCKAY, 1974).
In contrast to these uniform values, pyroxenes show a considerable range in $\delta^7$Li from 2.6 to 6.0‰ and two reference peridotites measured during the course of this study show completely distinct $\delta^7$Li values. JP-1 (GSJ) has $\delta^7$Li = 3.97 ± 0.41‰, consistent with the olivine and Mongolian bulk peridotite data, whereas PCC-1 (USGS) yields $\delta^7$Li = 8.85 ± 0.41‰ (see Table 5.3) which is indistinguishable from a value of 8.9‰ for this reference rock given by SIEITZ et al. (2004). However, PCC-1 is a partially serpentinised harzburgite, which can readily account for its heavier $\delta^7$Li value compared to the other peridotites. Bulk Li isotope compositions of peridotitic rocks must be considered with caution as they may be influenced by metasomatism and alteration at various possible stages.

| Table 5.3: Lithium concentrations and isotope compositions of terrestrial samples |
|----------------------------------|------------------|------------------|
| Peridotites – minerals           | Li (ppm)         | $\delta^7$Li (%) |
| San Carlos ol                    | 1.6              | 3.64             |
| San Carlos opx                   | 0.52             | 3.32             |
| Vitim 314-58 ol                  | 1.9              | 3.76             |
| Vitim 314-58 opx                 | 0.39             | 3.78             |
| Vitim 314-58 cpx                 | 1.4              | 5.21             |
| Atsagin-Dush 8520-09 ol          | 1.5              | 3.55             |
| Atsagin-Dush 8520-09 cpx         | 0.82             | 5.96             |
| Tariat MPH 79/1 ol               | 2.0              | 3.75             |
| Tariat MPH 79/1 cpx              | 1.4              | 2.57             |
| Kilbourne Hole 96-2 ol           | 1.7              | 3.56             |
| Peridotites – whole rocks        |                  |                  |
| Atsagin-Dush 8520-12 wr          | 1.6              | 4.11             |
| Atsagin-Dush 8520-19 wr          | 1.7              | 4.23             |
| Atsagin-Dush 8520-20 wr          | 1.6              | 4.27             |
| Atsagin-Dush 8520-30 wr          | 1.4              | 3.77             |
| Peridotites – standards          |                  |                  |
| PCC-1 (USGS)                     | 1.1              | 8.85             |
| JP-1 (GSJ)                       | 1.8              | 3.97             |

ol – olivine; opx – orthopyroxene; cpx – clinopyroxene; wr – whole rock

5.5 Discussion

5.5.1 Lunar Li and the isotope effects of exposure

Among the various analysed planetary bodies most Li isotope variation is found in lunar materials (Table 5.1). This could of course reflect the fact that we have analysed many more
lunar samples. The variability on the Moon is still surprising however. Oxygen isotopes provide evidence that the Earth and Moon formed from the same raw material (WIECHERT et al., 2001). Therefore, the Li isotope compositions for the total Earth and Moon should be identical, assuming Li isotopes have not been fractionated by the putative Moon-forming Giant Impact. Lithium isotope fractionation on Earth is dominated by the large effects associated with the hydrosphere. Therefore, Li isotope fractionation within the dry Moon is expected to be much smaller with basaltic compositions similar to the best estimate for the Earth’s mantle ($\delta^7\text{Li} \sim +4\%$). In fact lunar basalts might offer greater insights into the Li isotope composition of terrestrial planetary mantles because of the anticipated absence of large fractionations.

The overall range of Li isotope composition among lunar samples is, however, surprisingly broad. The most extreme composition found among the various lunar samples is for the lunar highlands anorthosite 62255 ($\delta^7\text{Li} = +8.9\%$). The issue arises as to whether this spread might be caused by secondary irradiation / implantation. Solar wind (SW) and galactic cosmic rays (GCR) may alter those rocks at the lunar surface not protected by a magnetic field. The bulk Sun has $^7\text{Li}/^6\text{Li} \sim 10^6$ (DELBORGO-SALVADOR et al., 1985) and solar wind has a $^7\text{Li}/^6\text{Li} \sim 31$ (CHAUSSIDON and ROBERT, 1999). $^7\text{Li}/^6\text{Li} \sim 2$ have been reported in galactic-cosmic-ray-induced spallation reactions (EUGSTER and BERNAS, 1971), and the interstellar medium $^7\text{Li}/^6\text{Li}$ has been estimated at $\sim 12$ (KNAUTH et al., 2003), and $\sim 2$ (KNAUTH et al., 2000).

Cosmogenic effects would produce roughly equal amounts of $^6\text{Li}$ and $^7\text{Li}$ by fission of heavy nuclides because spallation production $^7\text{Li}/^6\text{Li}$ ratio can be as low as $\sim 1.0$ (e.g. (LEMOINE et al., 1998). Rather higher values of $\sim 2$ were measured for low-energy galactic cosmic rays (RAMATY et al., 1996). Spallogenic Li has been detected in lunar soils yielding values of $^7\text{Li}/^6\text{Li} \sim 2$ (EUGSTER and BERNAS, 1971). Therefore, Li of purely spallogenic origin is extremely light $\delta^7\text{Li} \approx -850\%$ (CHAUSSIDON et al., 2001). This component has been detected in small quantities in refractory inclusions from several meteorites (CHAUSSIDON and ROBERT, 1996; CHAUVSSIDON et al., 2001) and in four lunar soils studied with depth profiling (CHAUSSIDON and ROBERT, 1999). It is impossible that spallogenic effects are responsible for $^7\text{Li}$ enrichment as detected in lunar samples.

An effect from exposure to heavy solar wind (CHAUSSIDON and ROBERT, 1999) would of course generate higher $^7\text{Li}/^6\text{Li}$. However, the depth of SW penetration into regolith particles is on the order of just tenths of microns (CHAUSSIDON and ROBERT, 1999).
Therefore, this effect is generally expected to be very small. More accurately and independently from grain size and solar flux one can calculate the proportion of solar-wind-derived Li using \( ^{36}\text{Ar} \) abundances. Elevated \( ^{36}\text{Ar} \) abundances are usually found in fine-grained fractions of lunar soils with up to 5-fold \( ^{36}\text{Ar} \) enrichment in the finest fractions relative to coarser-grained fractions (ASSONOV et al., 2002). An abundance of \( 0.32 \times 10^{16} \) atoms / gram was reported for the 25-42\,\mu m fraction of the lunar soil 67601 (WIELER and BAUR, 1995). By applying the enrichment factor of 5 to the <25\,\mu m fraction we obtain \( ^{36}\text{Ar} \) of \( 1.6 \times 10^{16} \) atoms / gram. The lunar soil 67601 <25\,\mu m fraction does in fact yield an \( ^{36}\text{Ar} \) concentration of \( 60000 \times 10^{-8} \) cc / g or \( 1.6 \times 10^{16} \) atoms / gram, in excellent agreement with this prediction (R. Wieler, personal communication to TM and UW, 2005). The solar abundances of \( ^{7}\text{Li} \) and \( ^{36}\text{Ar} \) normalized to \( 10^6 \) silicon atoms (ANDERS and GREVESSE, 1989) are 52.8 and 8.5 \times 10^4 respectively. From these a solar \( ^{7}\text{Li} / ^{36}\text{Ar} \) of \( 6.2 \times 10^{-4} \) can be calculated. Using the measured \( ^{36}\text{Ar} \) abundances and solar \( ^{7}\text{Li} / ^{36}\text{Ar} \) one obtains \( 9.9 \times 10^{12} \) of \( ^{7}\text{Li} \) atoms / gram derived from the solar wind in the <25\,\mu m fraction. This number has been multiplied by a factor of 3 in order to account for lower ionization energy of Li compared with argon (FIP factor). This gives \( 3 \times 10^{13} \) of \( ^{7}\text{Li} \) atoms per gram that is the expected portion implanted by the solar wind (fraction <25\,\mu m of sample 67601). An average of 5.2 ppm Li of the 3 coarse fractions of 67601 is used to calculate the number of lunar \( 2 \times 10^{16} \) Li atoms / gram in the <25\,\mu m grain size fraction. The solar wind portion of Li corresponds only to about 0.15% of the Li in fraction <25\,\mu m micron. On the basis of a solar wind composition of \( ^{7}\text{Li} / ^{6}\text{Li} = 31 \) and assuming no fractionation by the implantation process a \( \delta ^{7}\text{Li} = +7.6\% \) is calculated for the <25\,\mu m fraction based solely on measured \( ^{36}\text{Ar} \) abundances and the lunar lithium concentration. This calculation provides strong evidence that solar wind is detectable in grain size fractions <25\,\mu m of lunar soil using MC-ICPMS.

To test this theoretical approach we have conducted independent studies of the extent of the effects of solar wind implantation on lunar soils. The Li abundances and isotope compositions have been measured for size fractions from immature lunar soil 67601 (Table 5.4), which has an exposure age of \( \sim 55 \) Myrs, and in bulk soil 64421 with a higher exposure age of \( \sim 210 \) Myrs (KIRSTEN et al., 1973). We find clear \( ^{7}\text{Li} \) enrichment in soil 64421 (\( \delta ^{7}\text{Li} = 8.3\% \)) and in the finer-grained fractions of 67601 (Figure 5.3 and Table 5.4) but this effect diminishes rapidly with increasing grain size. The three coarser fractions (>42\,\mu m) of soil 67601 have uniform \( \delta ^{7}\text{Li} \sim +5\% \). The measured \( \delta ^{7}\text{Li} = 8.4 \% \) for the fraction <25\,\mu m is in
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good agreement with predicted value in the above calculations, given the range of uncertainties. This provides strong evidence for solar-wind-derived Li in lunar soils. The explanation for such trend toward heavy $\delta^7\text{Li}$ values could be a large proportion of abraded surface layers of soil particles that are enriched in $^7\text{Li}$. This effect is insignificant in coarse-grained fractions with volumetrically negligible quantities of such eroded material. Therefore, bulk rock samples of igneous material, even with long exposure age should show no significant effects and the two components (solar wind, spallogenic reactions) can be neglected when interpreting the data set of lunar rocks from this study.

Fig. 5.3: Size fractions vs. $\delta^7\text{Li}$ in Apollo 16 soil 67601. Apparent trend toward heavier $\delta^7\text{Li}$ values with finer fractions of the North Ray crater soil reflects most probably implantation of isotopically heavy solar wind (CHAUSSIDON and ROBERT, 1999). Dashed line is the average of three coarse-grained fractions with $\delta^7\text{Li} = 5.20 \pm 0.46\%\sigma$ (2σ; grey bar) that may reflect the starting isotope composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Split</th>
<th>Size Fraction (μm)</th>
<th>Li (ppm)</th>
<th>$\delta^7\text{Li}$ (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67601</td>
<td>7</td>
<td>&lt;25</td>
<td>5.4</td>
<td>8.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25-42</td>
<td>5.6</td>
<td>7.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42-90</td>
<td>5.2</td>
<td>5.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90-250</td>
<td>5.2</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;250</td>
<td>4.7</td>
<td>5.31</td>
</tr>
<tr>
<td>64421</td>
<td>5</td>
<td></td>
<td>7.4</td>
<td>8.26</td>
</tr>
</tbody>
</table>
This is confirmed by the observation that the Li isotope compositions of the bulk rocks studied here display no correlation with exposure age (Figure 5.4). In particular the very heavy $\delta^7\text{Li}$ measured in ferroan anorthosite 62255 is accompanied by an extremely short exposure on the lunar surface with Kr exposure age of <2 Myrs (Drozd et al., 1977). In some respects this is not surprising since neither implantation of solar wind nor spallogenic effects can account for the apparent relationships between Li isotope composition and rock type (Table 5.1). Similarly, it would be hard to explain the correlations with trace element indices of magmatic differentiation, discussed in the next section.

![Fig. 5.4: Exposure ages vs. $\delta^7\text{Li}$ for lunar samples. Closed diamonds – high-Ti mare basalts, triangles – volcanic glasses (open – orange glass 74220, dark grey – grey glass 74240, light grey – green glass 15426), polygon – olivine-normative basalt 15555, closed circles – quartz-normative basalts, open square – ferroan anorthosite 62255. No systematic trend is observed among the data. Exposure ages are taken from Drozd et al. (1977), Eugster et al. (1977), Hötz et al. (1975), Huneke et al. (1973), Stettler et al. (1973) and Yokoyama et al. (1974).]}

5.5.2 Lithium isotope composition of the Moon

A thorough model and review of geochemical and magmatic evolution of the lunar magmasphere has been given elsewhere (Taylor and Jakès, 1974; Shearer and Papike, 1999). Lithium isotope variation among lunar basalts most likely reflects heterogeneity in the source. The mare basalts analysed have primitive major element compositions and probably
segregated only relatively small amounts of olivine and/or pyroxene. This is unlikely to have caused a detectable change in $\delta^7\text{Li}$ (Tomascaš et al., 1999b). The mare basalts are the products of melting of cumulate sources that crystallised from the Lunar Magma Ocean (LMO) at distinct stages. All investigated mare basalts show a negative Eu anomaly (Figure 5.5) providing evidence that the cumulate sources were formed after significant crystallisation of plagioclase in the LMO. It is believed that floating plagioclase formed the early lunar crust (Taylor and Jakš, 1974). The $\text{Eu}_n/\text{Eu}^*$ value provides a monitor of how much plagioclase crystallised from the magma ocean. Early cumulates have REE patterns with virtually no Eu anomaly (Shearer and Papike, 1989). Later cumulates should develop a REE pattern with negative Eu anomalies and be systematically depleted in Ni and Co and enriched in incompatible elements. The inverse trend of $\text{Eu}_n/\text{Eu}^*$ vs. $\delta^7\text{Li}$ for lunar mare basalts (Figure 5.6) provides evidence of a relation between magmatic differentiation of the LMO and Li isotope fractionation. However, the trend is scattered and cannot be explained by feldspar fractionation alone. Because the Li content of an anorthosite mainly composed of calcic plagioclase is very low (see Table 5.1), the overall contribution of the lunar crust to the Li budget of the Moon is particularly limited. Therefore, plagioclase segregation is an unlikely mechanism for generating a significant Li isotope effect.

The sources of the low-Ti mare basalts were composed of early-formed ultramafic cumulates (predominantly olivine and low-Ca orthopyroxene). Flotation of plagioclase imposes a negative Eu anomaly on the crystallising mafic cumulates and produces a complementary positive Eu anomaly in the feldspathic lunar crust. Most of the models for the generation of primary high-Ti basalts require the melting of source rock types consisting of olivine, clinopyroxene, ilmenite ± plagioclase ± orthopyroxene (Snyder et al., 1990; Shearer and Papike, 1993). Accurate data of relevant mineral-melt fractionation factors ($\alpha_{\text{min-melt}}$) are currently unavailable for Li isotopes but the data on mantle minerals reported in this study provide evidence of $\sim2\%$ equilibrium fractionation between olivine and clinopyroxene at magmatic temperatures. The dominance of clinopyroxene in the source of high-Ti mare basalts and the ultramafic olivine-dominated cumulates of the low-Ti mare basalts could already account for most of the $\delta^7\text{Li}$ range detected in mare basalts. This is fully consistent with trends between $\delta^7\text{Li}$ and REE ratios or Zr/Hf (Figure 5.6) because clinopyroxene and to a lesser extent titanite are the major Zr/Hf-fractionating phases (David et al., 2000; Weyer et al., 2003).
Fig. 5.5: C1-normalised REE patterns of lunar rocks. Symbols are the same as in Figure 5.4. Grey squares – ilmenite-normative basalt 12045. Also REE pattern for Fe-anorthosite 65315 is plotted. Note apparent scatter in trace element data for both anorthosites caused by larger analytical uncertainties. Bottom pattern of Fe-anorthosite 65315 is approximative only due to analytical uncertainties for most elements exceeding 50% (2σ).

Strong correlations between Li isotopes and trace elements are found for indices that span a greater relative range of variability in basalts. For example Li/Yb and Ga/Hf vary widely in the basalts and clearly correlate inversely with δ7Li (Figure 5.6). Gallium and lithium are considered to be at most only slightly incompatible and no phase fractionates them strongly. This is endorsed by the basalts, which yield Ga and Li concentrations that vary by a factor of two at most (Tables 5.1 and 5.2). In contrast the REEs and high field strength elements (HFSEs) vary in concentration by more than a factor of four. Therefore, the variation in Ga/Hf and Li/Yb is actually dominated by a large degree of variability in HFSEs and REEs. The samples with lowest Ga/Hf and Li/Yb are the Apollo 17 glasses and high-Ti mare basalts. This is fully in line with a source consisting mainly of late clinopyroxene-rich cumulates. These samples are also more enriched in alkalis leading to a positive correlation between Rb concentration and δ7Li (Figure 5.6) and therefore, clearly more evolved than low-Ti basalts. On the basis of a study of a terrestrial volcanic rock sequence it has been stated earlier that magmatic differentiation has no effect on δ7Li (TOMASCAK et al., 1999b).
However, TOMASCAK et al. (1999b) explored only some ten percent segregation of olivine ± pyroxene ± plagioclase whereas the sources of high-Ti basalts are thought being formed after >95% of the LMO had been crystallised. That such extensive magmatic differentiation can fractionate stable isotopes has been shown with oxygen isotopes. For example, a significant shift has been produced by olivine segregation in highly evolved melts (MgO$_{melt}<$2%; EILER, 2001). Assuming a fractionation factor $\alpha_{\text{olivine-melt}} = 0.999$ between olivine and silicate melt (as inferred from olivine measurements in this study) a simple Rayleigh fractionation model produces significant Li isotope fractionation. If 95% of the LMO is crystallised, the $\delta^7$Li value of the residual melt increases by more than 2.5‰ compared with the starting composition. This may in addition contribute to the $\delta^7$Li range observed for the lunar basalts.

The lunar crust is about ~60km thick and consists mainly of anorthosite that is complementary to the source of mare basalts. This is also reflected in the REE pattern (Figure 3 in TAYLOR and JAKES, 1974). Lithium concentration of 0.8 ppm for the studied anorthosite implies a Li concentration of about 4 ppm for the magma ocean assuming an element partition coefficient for plagioclase and basaltic melt $D_{\text{plag-melt}}$ of ~0.2 (BINDEMAN et al., 1998). The $\delta^7$Li value of 8.9‰ for the lunar anorthosite is somewhat surprising. This gives a fractionation factor between plagioclase and basaltic melt $\alpha_{\text{plag-melt}}$ of 1.0049 (assuming a $\delta^7$Li value of 4.0‰ for the lunar magma ocean) and represents an extreme value for equilibrium fractionation at temperatures $\geq$1150°C. Whether the high $\delta^7$Li of the lunar crust reflects equilibrium fractionation by plagioclase crystallisation is unclear.

It is possible that the Li isotope composition of 62255 is not in equilibrium with the LMO. The Li concentration of 0.8 ppm measured for this sample is much higher than the 0.14 ppm obtained for a second Fe-anorthosite 65315 which is believed to be one of the most pristine lunar highland crust samples available as deduced also from low C1-normalised REE patterns (Figure 5.3 and EBIIHARA et al., 1992). Such low Li abundances as in 65315 would mean approximately 0.8 ppm Li for the LMO if $D_{\text{plag-melt}}$ ~0.2 but such a low Li content of the LMO is highly unlikely. The possibility that the high $\delta^7$Li value of 62255 reflects Li derived from late fluids or melts that percolated through the lunar crust cannot be excluded. Unfortunately, the amount of Li extracted from 65315 was too small for an isotope ratio measurement. However, the extremely low Li abundances are hard to reconcile with the conclusions of DREIBUS et al. (2003) who suggest preferential Li incorporation into a plagioclase crystallising very early from the LMO.
Fig. 5.6: Indices of magmatic fractionation vs. δ²⁷⁸Li in lunar basalts and glasses. Symbols are the same as in Figure 5.4. Ferroan anorthosite 62255 is not plotted. Variations in Rb abundances, Li/Yb, Eu/Eu'', Ga/Hf and Zr/Hf ratios are related to precipitation of clinopyroxene, ilmenite, armalcolite, spinel and titanite and possibly anorthite from the LMO. Excess Eu in 62255 (Eu/Eu'' > 25) relative to other rocks is caused by Eu substitution for Ca in anorthosite that is nearly pure anorthite (>97%). K abundance data are from PAPKE et al. (1974), RHODES and HUBBARD (1973), RHODES et al. (1974), ROSE et al. (1974; 1975) and TAYLOR et al. (1973).

The δ²⁷⁸Li value of the bulk Moon can be estimated from basaltic lavas thought to be derived early from the LMO crystallised cumulates. Among the first reservoirs that separated
from the LMO are the sources of two quartz-normative basalts (15058, 15475) and an orange
glass (74220) with $\text{Eu}_\text{N}/\text{Eu}^*$ as high as $-0.8$. These three samples have $\delta^7\text{Li}$ values of $3.7 \pm 0.1\%$, $3.4 \pm 0.3\%$, and $4.2 \pm 0.3\%$, respectively. One of the most primitive and little
fractionated material available from the Moon is often considered to be the green picritic
glass 15426 released from depths $>$700km (Longhi, 1992). However, relatively high Ti
content of this glass provides evidence for late stage mixing with magmas derived from
clinopyroxene- and ilmenite-rich cumulates. This is consistent with a slightly elevated $\delta^7\text{Li}$
($4.7 \pm 0.2\%$) compared with the former samples. Finally, olivine basalt 15555 is viewed by
some as being representative of the Nd and W isotope composition of pristine, unfractionated
lunar mantle (Nyquist et al., 1995; Kleine et al., 2003). But the large negative Eu anomaly
indicates equilibration with a more evolved lunar magma ocean and its Li isotope
composition ($\delta^7\text{Li} = 4.3 \pm 0.2\%$) may be slightly affected by magmatic segregation of
olivine. Therefore the mean of the two quartz-normative basalts and one orange glass sample,
taken as providing the most reliable estimate of the bulk composition of the Moon, is $\delta^7\text{Li} =
+3.8 \pm 0.4\%$ (1$\sigma$).

5.5.3 Lithium isotope composition of the terrestrial mantle

In order to constrain the Li isotope composition of the Earth’s mantle, we studied
mineral separates of spinel lherzolites and whole-rock peridotites. Spinel lherzolites probably
best represent the Li isotope composition of the upper mantle. Modal proportions of olivines
in spinel lherzolites from this study range from 47 to 62 modal% (San Carlos: 47.2% (Köhler and Brey, 1990), Vitim: 62.3% (Ionov, 2004), Atsagin-Dush: 60.6% (Wiechert et al., 1997), Tariat: 57.1% (Press et al., 1986), Kilbourne Hole: 57%). Therefore, olivine
contains between 80 and 90% of bulk sample Li and is a good approximation for the Li
isotope composition of peridotitic mantle rocks. The average $\delta^7\text{Li}$ of olivines from spinel
lherzolites is $3.65 \pm 0.20\%$. Whole-rock analyses of three spinel lherzolites (8520-12, 8520-
19, 8520-20) and one harzburgite (8520-30) are also consistent with a $\delta^7\text{Li}$ value of the
terrestrial mantle close to $+4\%$ (see Figure 5.7). These values are similar to the calculated
bulk $\delta^7\text{Li}$ for fertile Vitim garnet lherzolite of $+3.8\%$ (Seitz et al., 2004). This is also similar
to data for peridotites from Zabargad Island (Egypt), which yield $\delta^7\text{Li} \approx 4-5\%$ for the
terrestrial mantle (Chan et al., 2002b; Brooker et al., 2004). All these results are consistent
with the predicted upper mantle value of close to $+4\%$ (Chan, 2003).
In contrast, a whole-rock analysis of a fertile San Carlos spinel lherzolite given by SEITZ et al. (2004) gave light $\delta^7$Li = -1.1‰. The whole-rock data for this San Carlos sample appear inconsistent with the Li concentration and isotope composition determined from mass balance of the three major minerals analysed. Therefore, it would appear that some poorly understood effect is biasing the result from the whole rock. Our Li isotope data for mineral separates provide some evidence of heavier $\delta^7$Li in clinopyroxene although more data are needed to place better constraints on inter-mineral fractionation. The extensive study of SEITZ et al. (2004) yielded different results for reasons that are presently unclear. Olivines from their study are heavier in terms of Li isotope compositions than co-existing clinopyroxene and orthopyroxene but span a substantial range of $\delta^7$Li from 1.4 to 4.5‰. Co-existing orthopyroxenes were isotopically lighter and clinopyroxenes were in most cases isotopically the lightest major mineral. Although this could reflect variously depleted and metasomatised mantle as suggested by SEITZ et al. (2004), a more likely explanation for the observed light Li isotope signatures in pyroxenes would encompass late stage diffusion. That such a process can lead to significant shifts in $\delta^7$Li has been shown for silicate melts (RICHTER et al., 2003) as well as for solid-liquid systems, as documented in peridotitic lithologies where $\delta^7$Li variations as large as 10‰ were observed (LUNDSTROM et al., 2005). The latter study also proved experimentally that Li isotope fractionation on the order of tens of per mil is readily achievable in a very short-term timescale by diffusion and showed that scatter in $\delta^7$Li data for clinopyroxenes is more pronounced than for olivines. This is consistent with fast Li diffusion in clinopyroxene as recently observed (COOGAN et al., 2005).

ELLIOTT et al. (2004) sketched a possibility that heavy mantle Li may be caused by viscous coupling of hydrated isotopically heavy mantle with complementary dehydrated subducted slab. Some heterogeneity in the mantle does indeed exist as sampled by MORBs and OIBs at various locations. Fresh MORB analyses are sparse but show significant heterogeneity in $\delta^7$Li from +1.5 to 5.6‰ (CHAN et al., 1992; MORIGUTI and NAKAMURA, 1998b; TOMASCAY and LANGMUIR, 1999) -- even greater than for OIB with $\delta^7$Li values from +2.5 to 5.8‰ (TOMASCAY et al., 1999b; CHAN and FREY, 2003; MAGNA et al., 2004a). OIBs may be derived as unrepresentative small-volume melts from plumes rising from the core-mantle boundary, ultimately fed by subducted slabs (BAKER and JENSEN, 2004). Thus, they
Fig. 5.7: Li abundances vs. $\delta^7$Li of peridotitic rocks and mineral separates. Closed symbols – olivines; grey symbols – clinopyroxenes; open symbols – orthopyroxenes. Diamonds – San Carlos; squares – Vitt; triangles – Atsagin-Dush; reversed triangles – Tariat; circle – Kilbourne Hole. Solid star represents one harzburgite (8520-30), open stars display spinel lherzolites (8520-12, 8520-19, 8520-20); all are from Atsagin-Dush, Mongolia.

may not represent typical upper mantle compositions (ELLIOTT et al., 2004). MORBs represent shallow mantle melting of depleted lherzolites with interspersed mafic veins (LUNDSTROM et al., 2000). As large volume melts they should be more representative than OIB. However, the question arises of how much variably fractionated Li resulting from recycling is affecting the compositions if metasomatism from recycled components is selectively affecting the compositions of pyroxene, a phase that is preferentially melted during basalt production.

To summarise, the existing data for the Earth’s upper mantle are consistent with a $\delta^7$Li $\sim+4\%$. Non-metasomatised peridotites appear to be strikingly uniform in their Li isotope composition. Four such whole-rock peridotites as well as one peridotitic standard from this study are extremely homogeneous in their $\delta^7$Li ($-4.1\%$) varying at $\pm0.4\%$ (2$\sigma$), consistent with the upper mantle $\delta^7$Li at $4.2\%$ defined by CHAN (2003). Similar results are found for olivines of spinel lherzolites that average at +3.6\% and are identical with the mantle value.
We therefore suggest that the Earth’s upper mantle has δ⁷Li ~+4‰ as inferred from our olivine and whole-rock peridotite data. The Li content of the upper mantle as inferred from non-metasomatised spinel lherzolites of this study is ~1.6 ppm and is in excellent agreement with the estimate of Ryan and Langmuir (1987) and Sun and McDonough (1989).

Whether the upper mantle is also representative of the lower mantle is less clear. The deep mantle may differ in δ⁷Li as inferred from the slab dehydration and Li isotope fractionation model of Zack et al. (2003). Therefore, the possibility exists that the mantle is stratified with respect to Li isotopes. This would be caused by progressive ⁷Li depletion in the deep mantle due to its loss from the dehydrated subducted slab. A metasomatic overprint in clinopyroxenes has been shown in some mantle xenoliths from the Far East Russia and Japan (Nishio et al., 2004) which carry extremely negative δ⁷Li values inherited from metasomatism by eclogitic melts. The existence of light domains in the mantle is consistent with data for clinopyroxenes from ultramafic xenoliths. Nishio et al. (2004) explained this feature by metasomatic overprint with Li from subducted highly altered basalts that yielded extremely negative values. Similarly, a relationship between light Li and assimilation of subducted crust has been assumed on the basis of glass inclusions analysis in olivines and orthopyroxenes from Iblean plateau tholeiites (Gurenko and Schmincke, 2002). Recently, extremely negative δ⁷Li values have been found in glass inclusions of olivines from Hawaiian lavas (Kobayashi et al., 2004). Kobayashi et al. (2004) have attributed these light values to a recycled component, supported also by B and Pb isotopes. Therefore, recycling does appear to transfer a fractionated Li component into the mantle. What its average composition is remains unclear. How different the bulk upper mantle and bulk lower mantle are as a result of recycling is under-constrained.

5.5.4 Lithium isotope composition of Mars and Vesta

Two martian meteorites give distinct δ⁷Li of 3.9‰ (Zagami) and 5.0‰ (Nakhla). Zagami is a basaltic martian meteorite and most likely reflects the composition of the source material within the martian mantle, whereas Nakhla is a clinopyroxenite cumulate that closely resembles shallow ultramafic intrusives (Harvey and McSween, 1992). Study of light lithophile elements (Li, B) performed on pyroxenes from martian basalts (Zagami, Shergotty) provided evidence for incompatibility of Li in major mineral phases of martian basalts which has been explained by fluid degassing (Herd et al., 2004). The parental melt of Shergotty is
supposed to have high Li abundances >20 ppm based on recent mineral-melt partitioning data estimated for martian pyroxenes (HERD et al., 2005). A similar study of light lithophile elements distribution (Li, Be, B) in pyroxenes from nakhlites and shergottites led LENTZ et al. (2001) to conclude that the parental magmas of shergottites had significant water contents whereas the parental magmas of Nakhla were rather dry. Core-to-rim decreases in Li abundances in pyroxenes of Zagami have been explained by possible involvement of late-stage fluids (LENTZ et al., 2001) that could also potentially fractionate Li isotopes. Indeed, low-temperature alteration hydrous phases, e.g. “iddingsite” (a mixture of smectites and ferrihydrites), gypsum, calcite and halite have been found in nakhlites (BUNCH and REID, 1975). The high δ⁷Li of Nakhla may therefore be related to the former presence of water on Mars. Significant changes in δ⁵Li between pyroxene cores and rims could be caused by the presence of water during petrogenesis of martian basalts (BECK et al., 2004). However, a recent detailed ion-microprobe study of distribution of Li and its isotopes in olivine and pyroxene phenocrysts in lunar meteorite NWA 479 revealed large variations of δ⁷Li within single crystals (BARRAT et al., 2005). It has been concluded that diffusive isotope fractionation is responsible for observed Li isotope patterns. By analogy, martian meteorite NWA 480 studied previously (BECK et al., 2004) could also reflect a similar process rather than degassing. However, further work is necessary to verify this.

Eucrites are thought to be excavated from asteroid 4 Vesta by an impact (MELOSH, 1984). Eucrites have high Li abundances compared to martian and terrestrial basalts. Basaltic eucrites possibly represent large-degree melts from chondritic source (BLICHERT-TOFT et al., 2002). Given its incompatibility, the high Li content is therefore surprising (Table 5.1). An unlikely explanation is that the terrestrial and martian mantles are relatively depleted in Li because of crust formation. This would require that about half of the terrestrial lithium resides in the crust. Although Li is enriched in crust there is little evidence that Li in the crust can account for half the abundance of the terrestrial mantle. There is also no evidence that Li is lost to the core. The most likely explanation might be that the asteroid 4 Vesta is internally heterogeneous. The Li abundances of eucrites are in fact very similar to high-Ti mare basalts of the Moon. The δ⁷Li value of studied eucrites (see Table 5.1) averages at +3.7‰, identical within error to Mars (Zagami), the Moon and the Earth’s upper mantle (see above). This provides strong evidence that whatever the reason for the high Li abundance of eucrites, it does not relate to a process that produces large isotope fractionation.
5.5.5 Lithium isotope composition of chondrites

Two chondrites have also been measured (see Figure 5.2 and Table 5.1). The carbonaceous CV3 chondrite Allende gives $\delta^{7}\text{Li} = +3.1\%$ whereas a lower $\delta^{7}\text{Li} = +1.5\%$ has been obtained for the L6 chondrite Bruderheim. These results are in accord with a more comprehensive study of chondrites, which reports a range from $-4$ to $+3\%$ (McDONOUGH et al., 2003). Recently, ZACK et al. (2003) demonstrated that metamorphic dehydration at slightly higher temperatures will shift the Li isotope composition of rocks toward negative values, as low as $-11\%$. The variation among chondrites may reflect aqueous alteration on parent bodies with isotopically light Li in the residual metamorphosed chondrites (e.g. Bruderheim) and isotopically heavy Li related to chondrites with high aqueous alteration index (Orgueil, Allende; JAMES and PALMER, 2000; McDONOUGH et al., 2003). The isotopically light Li of chondrites may reflect the bulk solar system $\delta^{7}\text{Li}$, assuming that if anything aqueous processing has shifted some samples to heavier compositions. The bulk silicate Earth is expected to have an average $\delta^{7}\text{Li}$ value of $+4\%$, estimated from MORB (e.g. CHAN et al., 1992). A solar system with $\delta^{7}\text{Li} \sim 0\%$ (McDONOUGH et al., 2003) or $\delta^{7}\text{Li} \sim 2\%$ (W. McDonough, personal communication to ANH, 2005) would imply either that the planet formation process involves some small but significant Li isotope fractionation or there is a currently unidentified isotopically light reservoir within the Earth.

5.6 Conclusions – inner solar system Li isotope compositions

From these preliminary studies some very clear basic conclusions can be drawn.

(1) Basaltic and ultramafic rocks from the Earth, Moon, Mars and Vesta yield broadly similar Li isotope compositions consistent with a mantle source composition of $\delta^{7}\text{Li} \sim +4\%$. There is no reason why each upper mantle should appear to be the same in its Li isotope composition unless each entire terrestrial planetary object is also identical with $\delta^{7}\text{Li} \sim +4\%$. Therefore, a first order conclusion is that the Earth’s lower mantle is unlikely to be different in composition from its upper mantle given the similarity between this and other inner solar system upper mantles.

(2) The terrestrial, martian and some low-Ti lunar mare basalts have very similar Li abundances whereas eucrites have high Li abundances similar to high-Ti basalts. This
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indicates a heterogeneous interior of Vesta. The reason for this is unclear at present but may be related to differentiation during a magma ocean stage.

(3) The Earth, Moon, Mars and Vesta have different structure and composition of their respective crusts and cores. They also have dramatically different geology that includes a long history of subduction of isotopically fractionated Li into the Earth's mantle. However, none of these differences appear to have resulted in major changes in the Li isotope composition of the bulk planetary mantles.

(4) The Li isotope variation among lunar rocks reflects magmatic differentiation during the lunar magma ocean stage. Lithium isotope fractionation is likely caused by crystallisation of olivine, pyroxene and feldspar from the magma ocean and produces a relatively large isotope effect.

(5) There is no evidence for lithium isotope fractionation related to the depletion of volatiles in the inner solar system. This is similar to the result obtained for K (HUMAYUN and CLAYTON, 1995).

(6) There is also no indication that the Moon-forming Giant Impact resulted in Li isotope fractionation. Therefore, the effects found for Fe (POITRASSON et al., 2004) may be caused by fractionation during vaporisation of iron metal.

(7) Chondrites, as indicated by the results of this and an earlier study, are isotopically light compared with differentiated planetary bodies of the inner solar system. This is consistent with results of a more comprehensive study on chondrites (McDONOUGH et al., 2003). Therefore, there appears to be an important fractionation that takes place in the accretionary disc or in chondrite parent bodies during their thermal metamorphism and aqueous alteration.

Acknowledgement – We kindly thank Dmitri Ionov for providing splits of mineral separates from Vitim and Tariat peridotitic xenoliths, Mark Rehkämper for split of Kilbourne Hole sample and Albrecht von Quadt for splits of two peridotitic standard rocks. We appreciated discussions with Thorsten Kleine, Ingo Leya, Bill McDonough, Rainer Wieler and Helen Williams. Felix Oberli is acknowledged for maintenance of Nu1700. The manuscript benefited from careful and stimulating reviews by Tim Elliott and one anonymous reviewer. We are grateful to David Price for editorial handling, SNF and ETH funded this study.
Chapter 6

Summary and outlook
6.1 Summary and outlook

In this project a new method for low-blank separation and isotope measurements of lithium (Li) was set up which has subsequently been applied to terrestrial rocks, meteorites and lunar samples. These included continental arc volcanic rocks (primitive olivine tholeites, magnesian basaltic andesites, evolved andesites and dacites), ocean island basalts from Iceland and Jan Mayen, Mongolian spinel peridotite xenoliths and their minerals, and a set of samples from inner solar system bodies (Moon, Mars, eucrites, chondrites). For most of these Li isotope data have been complemented by trace element abundance measurements. The main achievements are summarised in the following:

1) A new method for separation of Li from a wide variety of silicate rocks was developed that employed a single-step cation-exchange chromatography and mixture of 1M HNO₃ blended with 80% methanol as elution media for concomitant separation of Li from other major and minor elements. Use of low quantities of elution media (~16 ml) resulted in insignificant and negligible contributions of blank Li. The robustness of the method has been proven by identical elution schemes for variety of rocks with distinct silica contents (basalts to rhyolites). The isotope homogeneity of Li international standard (L-SVEC) has been verified based on aliquots from three international labs compared to the aliquot used at ETH; the level of L-SVEC uniformity is better than 0.05‰ (2σ). No significant matrix effect on Li isotope measurements due to the presence of large amounts of major elements (e.g. Na, K, Mg, Ca, Al and Fe) has been observed. The external reproducibility of δ⁷Li as assessed by multiple replicate measurements of the reference rocks JB-2 and BHVO-2 is ± 0.3‰ (2σ). Several other reference rocks provide long-term reproducibility better than 0.5‰ (2σ) and differences between distinct generations of reference rocks (e.g. BHVO-1 vs. BHVO-2 and AGV-1 vs. AGV-2) are greater than the analytical error. The latter thus provides evidence of small-scale heterogeneity in the various generations of rock standards. An improvement of the analytical method has been presented for Li separation from individual mineral species of peridotitic rocks that employed small volumes of cation exchange resin combined with 0.5M HNO₃ as elution media. It provided additional purification of Li from the large amounts of Cr present in clinopyroxenes. Future innovation in Li analytical chemistry could be provided by extending the diversity of organic media and/or searching for Li-selective ion-exchange resins. Characterisation of
Li isotope compositions of a wider variety of reference rocks would certainly be helpful for inter-laboratory comparison that is now covered by a restricted number of available well-characterised standards. Recent developments in secondary ionisation mass spectrometry (SIMS; CHAUSSIDON and ROBERT, 1998, 1999; DECITRE et al., 2002; KASEMANN et al., 2005) allow closer insights into variations of Li isotopes within individual minerals and also chondrules (BECK et al., 2004, 2006; BARRAT et al., 2005; CHAUSSIDON et al., 2006; JEFFCOATE et al., 2007). Improvements of this alternative analytical technique in terms of accuracy and precision of measuring Li isotopes could be important for further research on a micron scale.

2) Subduction zones represent complex geological environments. Stable isotopes are becoming an important tool to unravel and quantify the material transport in subduction zones, i.e. which materials are recycled to the surface regions and which are subducted into the deep mantle. Seawater alteration preferentially adds $^7$Li to ocean-floor basalts. Therefore, isotopically heavy Li is subducted into the mantle. Although Li is mobilised during dehydration, there is no clear correlation with other parameters of fluid mobility. Comparison of several arcs clearly shows distinct across-arc profiles providing further evidence that Li in subduction zone volcanics is not a simple mixture of mantle and recycled crustal Li (MORIGUTI and NAKAMURA, 1998b; CHAN et al., 2002b; LEEMAN et al., 2004). In the southern Cascadia subduction zone Li isotopes are decoupled from fluid mobile elements (as indicated by e.g. Ba/Nb, Sr/Y) suggesting continuous isotope fractionation during subduction and in the mantle wedge. The high-alumina olivine tholeiites that originated from near-anhydrous melting of the spinel peridotite are isotopically lighter in Medicine Lake volcanics compared to Mt. Shasta lavas. This provides evidence for a heterogeneous mantle although both HAOT suits are enriched in fluid mobile elements (e.g. Sr, Pb and Li) relative to MORBs. The timing of this metasomatic enrichment is unclear but the anhydrous character of these lavas requires non-uniform mantle with predominantly light Li beneath Medicine Lake. Basaltic andesites and magnesian andesites show a large range in $\delta^7$Li with lighter values for Medicine Lake volcanics. Two fluid compositions with primarily heavy Li isotope signature are reported for Mt. Shasta BA lavas that have distinct Sr isotope ratios (MORB-like vs. "sediment-labelled"). Different fluids with light $\delta^7$Li<0.9‰ have been deduced from analysis of Medicine Lake BA lavas. Indistinguishable Sr isotope ratios for
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Medicine Lake BA lavas and “sediment-labelled” Mt. Shasta BA lavas provide evidence for a similarity in the sources of hydrous Medicine Lake and Mt. Shasta lavas. The depletion of lavas in $^7$Li follows the concept of progressive loss of heavy Li into the overlying mantle wedge (Zack et al., 2003). Light signatures away from the arc trench are interpreted as a slab signature that is the direct consequence of continuous Li isotope fractionation during dehydration and subduction. Nevertheless, a better understanding of processes beneath Mt. Shasta region is rendered difficult by a lack of precise information on Li partitioning and, in particular, isotope fractionation among major minerals and fluid phases for the whole range of p-T conditions and should be improved by acquiring relevant data (e.g. Lynton et al., 2005; Marschall et al., 2006). Diffusion-driven fractionation of Li isotopes may be an important mechanism that could provide explanation for isotopically heavy fluids or melts and, in parallel, isotopically lighter minerals generally (Lundstrom et al., 2005; Jeffcoate et al., 2007) or, more specifically, in arc settings (TomascaK et al., 2002). The extent of this fractionation between clinopyroxene and coexisting fluid is reduced with increasing temperature but can still be resolved at T>900°C (Wunder et al., 2006).

3) Some noble gas data of Earth’s interior require “hidden” reservoirs deep within Earth (Stuart et al., 2003). Such regions should recharge the upwelling mantle plumes with a characteristic $^3$He-enriched signature, which is often considered as remnants from the formation times of the Earth. Alternatively, ancient recycled oceanic lithosphere has been called upon as a source of high $^3$He/$^4$He ratios (Anderson, 1998). Coupled Li-He isotope data from picritic basalts from Hengill area, Iceland, suggest an alternative explanation for high $^3$He abundances that runs contrary to theories of “hidden” noble gas reservoirs at the base of the Earth’s lower mantle and/or in D” layer. It is suggested that the observed inverse and linear Li-He relationship is most likely generated in the mantle. Isotopically heavy Li carried by the low-$^3$He/$^4$He lavas could reflect a portion of ancient recycled oceanic lithosphere in the source of the Icelandic plume. This is corroborated by positive Eu anomaly and super-chondritic Sr/Nd which requires involvement of plagioclase in the earlier history although none of the lavas contain feldspar as a phenocryst phase. High-$^3$He/$^4$He lavas have low $\delta^7$Li but are diverse in terms of REE systematics. The $(La/Sm)_N$ of Enriched lavas are similar to that of the upper mantle whereas Depleted lavas show homogeneous $(La/Sm)_N$ consistent with the estimate of the depleted mantle. The Jan
Mayen lavas show particular enrichment in incompatible trace elements combined with limited variations in $\delta^7\text{Li}$. This enrichment is suggestive of incorporation of a mantle domain with EM2 affinity. Hot-spot origin of Jan Mayen cannot be ruled out at present based on Li isotope data. Overall, the data for Iceland and Jan Mayen suggest a globally uniform $\delta^7\text{Li} \sim +4\%$ independent of trace element enrichment or depletion. A recent study of distribution of Li isotopes in a suite of East Pacific Rise lavas (Elliott et al., 2006) provides an alternative explanation for the origin of the recycled component in MORB which is supposedly a result of entrainment of fluid-modified subarc mantle into the source region of MOR basalts. Hence, these diverse opinions reflect the need for further studies.

4) A study of Li isotopes in non-terrestrial materials indicates a homogeneous composition of differentiated inner solar system bodies whereas chondrites may be isotopically slightly lighter. Thus, the planet formation processes may have a small effect on Li isotopes. The large range in $\delta^7\text{Li}$ among lunar rocks reflects extreme degrees of crystallization (>95%) of the lunar magma ocean. The early- and late-stage cumulates with variable amounts of major minerals with isotopically different Li will produce basalts with distinct $\delta^7\text{Li}$. The presence or absence of clinopyroxene may be a major factor controlling the Li isotope compositions of the mare basalts. The bulk Moon $\delta^7\text{Li}$ value at $+3.8\%$ has been inferred from lunar rocks showing the least Eu depletion. The lunar crust represented by ferroan anorthosite seems to yield an extremely heavy Li isotope signature that may reflect equilibrium fractionation during plagioclase segregation from the early lunar magma ocean. The lunar regolith may have recorded the implantation of the isotopically heavy solar wind as evidenced by progressive enrichment in $^7\text{Li}$ within finer fractions of a lunar soil. Pristine peridotitic rocks provide evidence for a $\delta^7\text{Li} \sim +4.0\%$ for the Earth’s upper mantle. This is further supported by a limited range of $\delta^7\text{Li}$ measured for a worldwide collection of olivines from spinel lherzolites. There is no resolvable difference in estimated $\delta^7\text{Li}$ between terrestrial spinel peridotites and basaltic rocks and/or meteorites from Moon, Mars and Vesta despite large differences in the volatile content of these bodies. This provides evidence for uniform $\delta^7\text{Li}$ of mantles of the inner solar system planets. Available data for chondrites tend to reveal small but resolvable Li isotope fractionation within the accretionary disc or chondrite parent bodies. Extending the Li isotope database to chondritic meteorites of various petrologic classes may further
contribute to our knowledge of the processes in the young inner solar system (McDonough et al., 2003, 2006; Seitz et al., 2006b). The Moon currently represents an open field for exploration by Li isotopes because there was so far no attempt for detailed study of Li isotopes in the lunar materials. Relation of the lunar crust and the lunar mantle may be deconvoluted using Li isotopes for a larger suite of lunar crustal rocks. Evolution and cessation of the Lunar Magma Ocean could be explored further with Li isotope data for other lunar rocks and in particular mineral phases. Characterisation of Li isotope compositions for variety of other rock types (Mg-suite, low-Ti and high-Ti mare basalts, KREEP basalts) could further evaluate the processes that lead to genesis of these important lunar magmatic phases.
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