

2.1 Historical Perspective

Lithium was discovered as an elemental species in 1817 by J.A. Arfvedson and isolated as a metal one year later by Sir H. Davy. The existence of two naturally occurring isotopes of lithium, ${}^6\text{Li}$ and ${}^7\text{Li}$, was unambiguously proven by A.J. Dempster (1921) and the atomic weight of Li and the individual isotope masses were first determined with reasonable accuracy and precision by F.W. Aston (1932) (few available data are referenced therein) at 6.928 ± 0.008 , 6.012, and 7.012 atomic mass units, respectively (atomic mass unit, *amu*, is defined as $1.660538921 \pm 73 \times 10^{-27}$ kg and corresponds to 1/12 of mass of unbound neutral ${}^{12}\text{C}$ in nuclear and electronic ground state; modern physics uses the term “unified atomic mass” abbreviated as ‘u’ or dalton). In the decades that followed this, however, only a few attempts to refine the absolute atomic weight as well as its uncertainty (see summary in Svec and Anderson 1965) were implemented. The actual atomic weights of ${}^6\text{Li}$ and ${}^7\text{Li}$ are 6.0151223 ± 5 and 7.0160040 ± 5 u, respectively. The actual atomic weight of Li, currently accepted by IUPAC, is 6.941 ± 0.002 (Wieser 2006) and it may well be that this level of precision will not improve significantly in the near future due to natural variations in ${}^7\text{Li}/{}^6\text{Li}$ exceeding ~ 80 ‰ (Tomascak 2004, this volume).

The natural variations of ${}^7\text{Li}/{}^6\text{Li}$ were not measured extensively or with clearly established reproducibility until late 1980s (Chan 1987). This article reported a method for chemical

separation and precise isotopic measurements with ~ 2.5 ‰ external uncertainty. Although earlier measurements which used mass spectrometry were performed on a range of terrestrial and extraterrestrial samples (e.g., Balsiger et al. 1968; Brown et al. 1977; Eugster and Bernas 1971; Krankowsky and Müller 1967; Michiels and De Bièvre 1983), data reported in these studies were usually expressed in absolute ${}^7\text{Li}/{}^6\text{Li}$ ratios with errors exceeding several per mil. This severely hampered data comparison and the overall utility of Li isotopes in geochemistry.

A major problem of early reports on Li isotopic compositions was the lack of a widely distributed reference material that would allow for reliable inter-laboratory comparison of measured isotopic ratios. In 1973, Flesch and co-workers isolated Li from “virgin” spodumene-rich ores from the granitic pegmatite at Kings Mountain, North Carolina, USA, and determined its isotopic composition at ${}^7\text{Li}/{}^6\text{Li} = 12.0192 \pm 0.0002$ (Flesch et al. 1973). The isolated Li was made available by the National Bureau of Standards (now NIST) as L-SVEC (since reassigned as SRM 8545). The availability of an external standard permitted calibration of measured ${}^7\text{Li}/{}^6\text{Li}$ and presentation of data relative to L-SVEC in permil deviations. Chan (1987) and several papers that followed employed the normalized ${}^6\text{Li}/{}^7\text{Li}$ ($\delta^6\text{Li}$). Since that time, though, the use of the $\delta^7\text{Li}$ value has prevailed, as it is consistent with the other major

stable isotopic systems (i.e., positive values reflect enrichment in the heavy isotope). This nominal $\delta^7\text{Li} = 0$ ‰ mimics the Li isotopic composition of global magmatic continental crust (Bryant et al. 2004; Magna et al. 2010; Teng et al. 2004, 2008, 2009). Considering that the $\delta^7\text{Li}$ values in mineral phases from worldwide granitic pegmatites vary greatly (e.g., Magna et al. 2013), the choice of this particular spodumene by Flesch et al. was quite serendipitous.

The L-SVEC reference standard has proven, perhaps fortuitously, robust, with proven Li isotopic homogeneity within better than ± 0.1 ‰ (2σ) for aliquots allocated to different laboratories (Magna et al. 2004). This is noteworthy in the view of homogeneity problems encountered for reference materials used in several other stable isotopic systems (e.g., NIST SRM 980 for Mg; Galy et al. 2003), Si isotopic discrepancies for IRMM-018 versus NBS-28 (see Reynolds et al. 2006 and discussion therein), or different values in newly marketed reference materials compared to older, exhausted resources, such as for Ca (note differences in $\delta^{44/40}\text{Ca}$ between SRM 915a and 915b; Heuser and Eisenhauer 2008). Recently, however, the L-SVEC reference material has run out and was replaced by the new IRMM-016 artificial material with $\delta^7\text{Li}_{\text{L-SVEC}} = -0.2$ to $+0.3$ ‰ (Aulbach and Rudnick 2009; Aulbach et al. 2008; Caciagli et al. 2011; Huang et al. 2010; Jeffcoate et al. 2004; Kasemann et al. 2005; Millot et al. 2004; Penniston-Dorland et al. 2010; Qi et al. 1997b; Simons et al. 2010; Teng et al. 2006; Zack et al. 2003). This can thus be considered identical within external analytical uncertainty of Li isotopic measurements and no further recalculation is required. Care should be exercised, however, to juxtapose L-SVEC and IRMM-016 when significantly different $\delta^7\text{Li}$ values emerge (e.g., < -0.5 ‰; Liu et al. 2010; Marks et al. 2007) that are slightly beyond the level of current analytical uncertainties.

Yet another problem for Li isotopic analyses is represented by laboratory-induced contamination that may seriously compromise the intrinsic $^7\text{Li}/^6\text{Li}$ in natural samples as these ratios often show large variations in commercially available Li materials (Qi et al. 1997a) and even minimal

exposure to such reagents may result in erratic $^7\text{Li}/^6\text{Li}$ (Košler and Magna 2014). Vigilance in areas of sample preparation is just as critical as in the chemistry laboratory (as discussed below) for the production of verifiable Li isotopic data. For example, in many rock processing facilities the preparation of samples for XRF or other flux-fusion methods has taken place. Traces of residual dust from Li-borate flux, even years later, threaten samples being processed for mineral separates or rock powders in such spaces.

2.2 Lithium Isolation by Cation Exchange Chromatography

Separation of Li from other elements in natural materials is challenging owing to M/Li ratios commonly in excess of 10^4 (e.g., Na/Li in seawater), as well as the similarity of the ion exchange partitioning of Li to some major cations. Pioneering work on partitioning of Li and other elements between ion exchangers and various types of elution media stressed the efficacy of mineral acids such as HCl and HNO_3 in separating Li (Strelow et al. 1974; Šulcek et al. 1965; Šulcek and Rubeška 1969), in particular when mixed with organic solvents (e.g., methanol and ethanol, although other organic elution media may be used for specific purposes; Kim 2001). All major subsequent analytical developments adopted this approach with different combinations of these mineral acids and simple alcohols.

A major consideration when ion exchange is applied to Li isolation is the large isotopic fractionation introduced during chromatographic separation as a consequence of greater affinity of ^6Li to stationary phase (Taylor and Urey 1938). As a result of incomplete Li recovery, unintended isotopic fractionation can be caused. For example, Moriguti and Nakamura (1998) and Košler et al. (2001) have shown that Li isotopic fractionation may reach several tens of percent with ^7Li eluting first and ^6Li tailing (Fig. 2.1) as a result of equilibrium fractionation of Li between the solid phase and solvent (Schauble 2004); thus, ~ 100 % yields are indeed essential. This differs from elements with more than two isotopes where

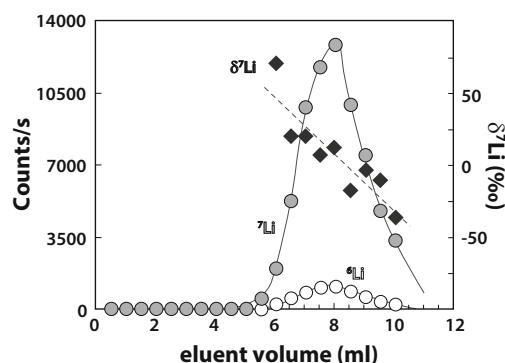


Fig. 2.1 Example of Li isotopic fractionation during ion exchange chromatography (after Košler et al. 2001). A progressive shift from isotopically heavy to light fractions during ongoing chromatographic isolation of Li, with a $\delta^7\text{Li}$ range of $\sim 100\%$ during elution. A failure to complete recovery of Li would result in the collection of a sample with an erroneous isotopic composition

internal corrections for incomplete recovery may be applied. Unfortunately for the laboratory geochemist, achieving quantitative recovery is not simply a matter of calibrating ion exchange columns. Position of the elution peak for Li from exchange columns is affected by the bulk chemical composition of the sample and the ion load to the column. Thus, separate elution recipes may be necessary for different sample types (Fig. 2.2). The reality of this issue was driven home by Chan et al. (1999), where biased $\delta^7\text{Li}$ results resulted in the publication of a correction (Chan et al. 2002). Analyses of rocks yielding distinct (and geologically reasonable) isotopic compositions were shown, after chemical separation issues were solved, to be isotopically homogeneous and with no anomalous samples.

The sensitivity of different instrumental methods to analyte solutions that lack complete purification is variable, but, for plasma-based methods, it is clear that significant amounts of contaminant elements may compromise the accuracy and precision of Li isotopic determinations. Hence, the quality of ion exchange separation is an important issue in sample preparation. The effects of imperfect separation of Li from other elements have been demonstrated by many studies (e.g., Huang et al. 2010; Jeffcoate et al. 2004; Magna et al. 2004; Moriguti and Nakamura

1998; Nishio and Nakai 2002; Rosner et al. 2007; Tomascak et al. 1999). In particular, the removal of Na, as the nearest major element to be eluted after Li, has received attention; avoiding or eliminating Na tailing in the Li fraction during chromatographic separation is the goal here. The extent to which contaminant elements may compromise successful isotopic analysis depends largely on the measurement technique. Whereas there is some degree of freedom in matrix concentrations for plasma-based techniques (Huang et al. 2010; Jeffcoate et al. 2004; Košler et al. 2001; Magna et al. 2004; Rosner et al. 2007; Tomascak et al. 1999), little tolerance is apparent with thermal ionization methods (Hoefs and Sywall 1997; James and Palmer 2000; Moriguti and Nakamura 1998; Xiao and Beary 1989).

Early attempts to measure Li isotopic compositions in natural samples required several hundreds of nanograms Li (e.g., Chan 1987; Chan and Edmond 1988; You and Chan 1996) but these requirements were alleviated with technical improvements; high-sensitivity ICP-based mass spectrometers now allow accurate analyses with less than 5 ng Li. The need to prepare such large samples, especially for relatively low-Li materials like mantle rocks, required large-volume columns packed with ion-exchange resins and large amounts of collection media (sometimes several hundred milliliters). This made early techniques rather time consuming and prone to elevated procedural blanks. With diminishing sample size came the capacity to analyze materials with very low Li abundance and/or samples of very small size, critical for high spatial resolution as well as when limited amounts of sample were available.

Exchange media with Li-specific characteristics are not available, unlike for certain elements or elemental groups (e.g., Dow AMBERLITETM for B, Sr. Spec for Sr and Pb, and Eichrom TRU Resin for actinides). The use of cation exchange resins such as AG50W-X8 appears to provide high efficiency in separating Li from other elements, but optimization of the geometry of chromatographic columns also plays a role in quality of element separation, blank suppression, and time cost.

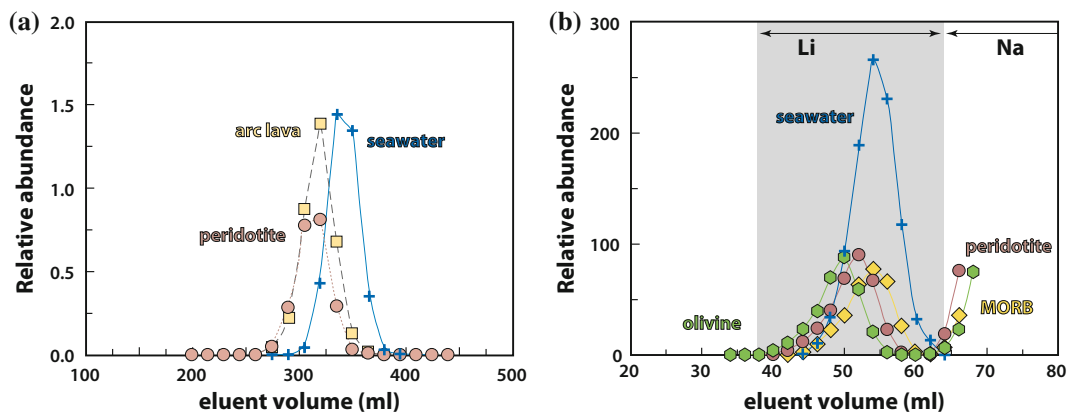


Fig. 2.2 Examples of the difference in cation exchange elution peaks for Li resulting from various matrices (e.g., peridotites and other silicate rocks, seawater). Improper

column calibration may lead to incomplete collection of the Li fraction (Chan et al. 1999, 2002)

Mixtures of mineral acids with methanol or ethanol provide better separation of Li from other elements than strictly inorganic eluants. The increasing concentration of alcohols at a given molarity of the respective mineral acid increases the separation factor between Li and Na (as the next element to elute), such that 80 % by volume methanol solution roughly triples the separation over 60 % methanol solution. This is counter-balanced by decreasing separation factor when the molarity of the respective acid increases. Therefore, a near-ideal formula entails low-molarity acid mixed in high percentage organic solvent. There is apparently little difference between HCl and HNO₃, the former providing slightly larger separation factor between Li and Na and the latter quantitatively eliminating some elements such as Fe, Zn and Cd, which may appear in HCl-based elution schemes (Strelow et al. 1974). One practical downside of the acid–organic mixture is the formation of small bubbles in the resin. This phenomenon restricts both choice of the internal diameter of a column (which cannot be too narrow) and the column material (e.g., non-wetting material like PFA Teflon versus quartz glass).

A glut of methods have been successfully employed in geochemistry and cosmochemistry: pure HCl (Chan 1987; James and Palmer 2000; Misra and Froehlich 2009; Moriguti and Nakamura 1998; Oi et al. 1997; Sahoo and Masuda

1995a, 1998), HCl–ethanol (Jeffcoate et al. 2004 in second step), pure HNO₃ (Hoefs and Sywall 1997 and Magna et al. 2006 in second step) and HNO₃–methanol (Huang et al. 2010; Choi et al. 2010; Košler et al. 2001; Magna et al. 2004; Nishio and Nakai 2002; Seitz et al. 2004; Tomascak et al. 1999). These studies encompass a wide variety in resin mesh size (100–200 vs. 200–400), cross-linkage (X8 vs. X12; see Schönbächler and Fehr 2014 for a more detailed review of issues related to ion exchange chromatography), and column size/volume, but they all seem to provide a reasonable means of Li separation. Inasmuch as no single method presents a clear best-case separation (i.e., one that minimizes reagents and time whilst maximizing ease of use and flexibility of sample type), there appears to be room for further analytical improvements. Perhaps in the near future a selective complexing agent or the use of other solvents (e.g., acetone) will further improve the process of Li separation for isotopic measurement.

2.3 Methodology of Li Isotopic Measurements

At present, a plethora of technical possibilities exists for measurements of Li isotopic compositions, but superior performance with respect to the accuracy and precision of isotopic data

collection is represented by plasma-based techniques (Q-ICPMS, SF-ICPMS, MC-ICPMS), thermal ionization (TIMS), and secondary ionization (SIMS). Although this instrumentation and its technical aspects are rather complex and expensive, these methods provide the data output required for geochemistry and cosmochemistry. Nevertheless, other methods have also been developed for specific purposes and we discuss them here briefly. Also, it is important to note the prevalence of the $\delta^6\text{Li}$ notation, where negative values represent isotopically heavier values, in most of the earlier publications. Following the Goldschmidt 2002 geochemical conference a more logical $\delta^7\text{Li}$ notation has uniformly been accepted (Coplen et al. 2002). The conversion can simply be performed with the following equation:

$$\delta^7\text{Li} = - \frac{\delta^6\text{Li}}{\left(1 + \left(\frac{\delta^6\text{Li}}{1000}\right)\right)}$$

This conversion must be performed for $\delta^6\text{Li}$ values outside the range ~ -10 to $\sim +10$ ‰. Within this range the sign-changed difference between $\delta^6\text{Li}$ and $\delta^7\text{Li}$ values results in shifts <0.1 ‰ whereas for $\delta^6\text{Li}$ values in the range of seawater (-31.0 ‰; Millot et al. 2004) the difference is ~ 1 ‰. It increases to $\sim +10$ ‰ at $\delta^7\text{Li} > 100$ ‰ and to ~ 40 ‰ at $\delta^7\text{Li} > 200$ ‰, found for anthropogenically fractionated samples (Millot et al. 2010; Négrel et al. 2010).

2.3.1 Mass Spectrometry-Based Methods of Widest Use

2.3.1.1 TIMS

Prior to the diversification of ICP and SIMS instruments, thermal ionization was the primary method of choice in yielding high-precision Li isotopic compositions for several decades. Indeed, the first absolute Li isotopic compositions were obtained by TIMS (Balsiger et al. 1968; Svec and Anderson 1965, 1966) or its modifications (Brown et al. 1977) and this

remains the only reliable method for determination of absolute Li isotopic abundances, as the plasma-based instruments always return mass-biased results and the instrumental fractionation is too great and variable to effectively correct back to absolute ratios. As such TIMS has represented a cornerstone for resolving even small differences in $\delta^7\text{Li}$ considering ± 1 ‰ errors that were routinely obtained (Chan 1987). It is unfortunate that, despite the generation of the L-SVEC standard in the early 1970s, TIMS studies throughout the 1970s and 1980s failed to measure this material, making it impossible to recalculate data to modern systematics.

Several strategies have been developed that employed polyatomic species, such as Li_2BO_2^+ (Bickle et al. 2000; Datta et al. 1992; Chan 1987; Sahoo and Masuda 1995b), LiNaBO_2^+ (Chan et al. 1992), Li_2F^+ (Green et al. 1988), or metal Li^+ ion (Ahmed et al. 2002; Jabeen et al. 2003; James and Palmer 2000; Michiels and De Bièvre 1983; Moriguti and Nakamura 1998; Sahoo and Masuda 1995a, 1998; Xiao and Beary 1989; You and Chan 1996). These approaches combined different loading procedures, utilizing $\text{Li}_2\text{B}_4\text{O}_7$, Li_3PO_4 , $\text{LiCl} + \text{H}_3\text{BO}_3$, LiOH , LiI , LiF , LiCl (but other possibilities were also explored, see Xiao and Beary 1989), with various filament configurations: single Re, Ta–Re or double Re, or triple Re filament assembly.

The developments by Chan et al. in measurement by TIMS, making use of the L-SVEC standard, broke the logjam and ushered in a new era of Li isotopic geochemistry. Studies using this technique introduced several first-order observations on the geochemical cycle of Li, making the first steps into this *terra incognita* (e.g., Chan et al. 1992, 1993, 1994; You et al. 1995). However, with the advent and rapid development of MC-ICPMS instrumentation (e.g., Halliday et al. 1995, 1998), TIMS techniques quickly became a somewhat obsolete approach for determination of Li isotopic compositions in natural samples considering the more time consuming mass spectrometry and lesser opportunity to monitor shifts in instrumental mass bias. Despite these drawbacks, TIMS

remains the only method capable of directly measuring the absolute Li isotopic abundances and as such, it will continue to have importance for precise validation of Li isotopic abundances in reference materials.

2.3.1.2 ICPMS

Despite the explosion in the use of plasma-based technologies in early 1980s, these methods did not find broad application to Li isotopic measurements until much later. The early generation of single-collector quadrupole ICP instruments was not well suited for isotopic determinations in geological samples but the few attempts returned data that were fully in the context of contemporaneous investigations (Grégoire et al. 1996; Vanhoe et al. 1991). Despite larger inaccuracy of Li isotopic measurements by this technique, it was applied to, for example, serious social–medical questions (Sun et al. 1987).

Košler et al. (2001) presented an improved quadrupole ICPMS protocol for determining Li isotopic compositions in natural samples (foraminiferal species) with external reproducibility approaching the $\pm 2\%$ (2σ) barrier which would be adequate for many geological applications. Further optimization has improved these statistical parameters (Carignan et al. 2007; Misra and Froehlich 2009). The higher sensitivity sector-field (single-collecting) ICPMS does not appear to represent significant improvement in accuracy and long-term precision of Li isotopic measurements compared to quadrupole instruments (Janoušek et al. 2010; Magna et al. 2010). Nonetheless, Li isotopic measurement by Q-ICPMS is not a “routine” practice, and as such the diversification of MC-ICPMS instruments leaves ICPMS a less used alternative today. However, for studies for which precision of $\pm 1.0\%$ is sufficient, it is a viable method that is certain to continue to be applied.

2.3.1.3 MC-ICPMS

With the advent of MC-ICPMS instrumentation and subsequent rapid developments in accurate, high-precision stable isotopic measurements (Halliday et al. 1995, 1998), it was only a matter of time before the tool was brought to bear on Li

isotopes (Tomascak et al. 1999). The possibility of monitoring the varying instrumental bias by alternating samples and reference materials (L-SVEC; Fig. 2.3) on short time scales (plus the capability of monitoring abrupt changes in instrumental bias) promoted a massive increase in number of available data for Li isotopic compositions in all manner of geological settings, as well as some of the first credible data on non-terrestrial materials (*cf.* Tomascak 2004 and later development discussed in several sections of this volume). The major advantages of this technique lie in rapid throughput of solute samples, possibility to monitor instrumental bias during the analytical session, and low consumption of material that may, under suitable circumstances (sample/noise ratio), utilize less than one nanogram of Li with sub-permil external reproducibility. Furthermore, MC-ICPMS appears less susceptible to undesired shifts in measured $^7\text{Li}/^6\text{Li}$ ratios resulting from the presence of matrix elements due to imperfect chemical separation of Li (e.g., Bryant et al. 2003; Jeffcoate et al. 2004; Magna et al. 2004; Nishio and Nakai 2002; Rosner et al. 2007; Tomascak et al. 1999). Despite the strong fractionation of Li isotopic ratios with MC-ICPMS compared to TIMS, the method of measuring samples bracketed by standards has effectively circumnavigated this problem.

The issue of accuracy and inter-laboratory comparison is only secured by the availability of reference rock materials. At present, several of these are utilized worldwide (e.g., the basalts BHVO-2, JB-2, BCR-2, and IRMM BCR-403 or IAPSO seawater) and many others have been characterized for their $\delta^7\text{Li}$ through multiple independent measurements. Considering this wide range of materials of distinctive chemical compositions, it may be a prerequisite to “matrix-match” complete analytical procedures with corresponding reference materials instead of relying solely on one reference material.

Technical approaches to the measurement by MC-ICPMS are diverse. Overall, solutes are aspirated into the plasma via low-flow nebulizers, nominally $30\text{--}100\ \mu\text{L min}^{-1}$, where the plasma may be “hot” ($\sim 1200\text{--}1400\ \text{W}$) or “cool”

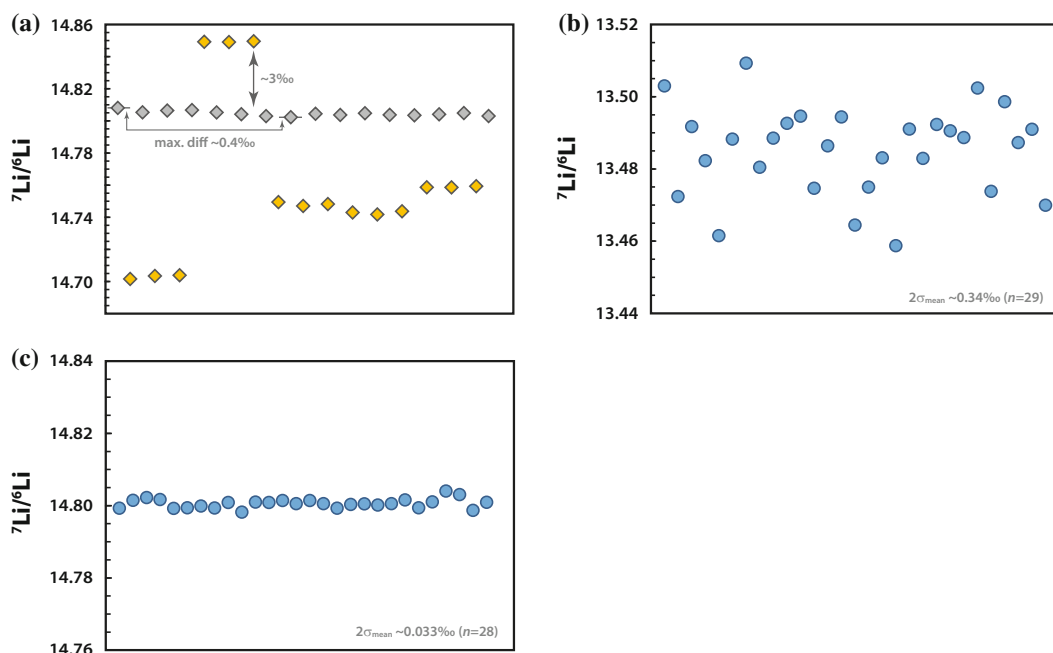


Fig. 2.3 Example of analytical sequences with standard-sample bracketing, as commonly used with MC-ICP-MS measurement (a). Calculation of the final $\delta^7\text{Li}$ may be performed in two ways: (i) relative to the average $^7\text{Li}/^6\text{Li}$ of two bracketing reference solution measurements irrespective of the actual measured $^7\text{Li}/^6\text{Li}$ (~ 14.80 for the depicted analytical sequence), or (ii) recalculating the measured values to the natural $^7\text{Li}/^6\text{Li}$ of ~ 12.1 . Both

alternatives should yield identical results. Stability of the instrumental bias is among the key factors for accurate determination of Li isotopic composition, here exemplified by a maximum $^7\text{Li}/^6\text{Li}$ variability of $\sim 0.4\text{‰}$ over >5 h. In b and c, example of noisy and stable measurement is apparent by a ~ 10 -fold difference in internal errors of the measurement of the same solution over two different analytical sessions, performed within 1 week

(~ 700 – 800 W; Bryant et al. 2003; Choi et al. 2013); aspiration is often aided by desolvation, resulting in more homogeneous droplet size just prior to dispersion in plasma. During an analytical session, a solution is introduced after the background signal level is reached that may require significant washout time, but alternative switch between sample and standard solution without rinsing was also explored (Rosner et al. 2007). This latter approach requires a complete signal intensity match to better than $\pm 5\%$ in order to avoid instrumental bias introduced by improperly balanced signals of bracketing standard and unknown sample (Huang et al. 2010; Magna et al. 2004; Rosner et al. 2007). The isobaric interferences from $^{12}\text{C}^{++}$, $^{14}\text{N}^{++}$ and $^6\text{LiH}^+$ appear to pose a minor problem and were indeed not detected at mass resolution of ~ 1400

(Magna et al. 2004) despite lower mass resolving power required to delimit these individual peaks. When Tomascak et al. (1999) introduced MC-ICPMS measurement protocols for Li isotopic measurements with the first generation instruments, a reproducibility of $\pm 1.1\text{‰}$ (2σ), basically equivalent to TIMS analysis, was achieved. Currently, the long-term reproducibility of MC-ICPMS measurements using more modern instruments appears to be at the $\pm \sim 0.3$ – 0.4‰ (2σ) level (Jeffcoate et al. 2004; Magna et al. 2004; Millot et al. 2004). Although short-term reproducibility may surpass this level, it is not apparent in the current literature that any group is able to do demonstrably better for true, long-term conditions.

At present the literature on Li isotopes is dominated by data generated with solution

MC-ICPMS. Recently, le Roux (2010) presented a laser ablation (LA) MC-ICPMS method. In this study, they performed in situ measurements of Li isotopic composition in reference glasses whose Li isotopes had been characterized by means of solution MC-ICPMS. It appears that combination of LA with MC-ICPMS may result in rapid determination of Li isotopic compositions on the sub-0.1 mm scale if followed by technical improvements in detection limits and sensitivity. For example, minerals with 10–20 ppm Li generated ~ 0.1 V signals on mass ^7Li against 6–8 V for 10 ppb Li solutions routinely obtained with solution MC-ICPMS. Also, diligent matrix matching appears to be essential for laser sampling, which demands a suite of homogeneous and well characterized glass reference standards. The recent report of Xu et al. (2013) showed the spatial capabilities coupled with high sample throughput weighed against still rather high analytical errors (mostly >1.8 ‰, 2σ) and poor reproducibility for a large selection of reference glass standards. It shows that this methodology yet awaits further detailed analytical efforts before it may become a fast and lower-cost analytical alternative.

2.3.1.4 SIMS

Although it may seem that implementation of laser ablation into MC-ICPMS could represent a new and straightforward in situ means of Li isotopic determination, SIMS technology is far ahead in terms of spatial resolution, sensitivity, and overall technical abilities in investigations of Li isotopic compositions. The first real attempts to measure Li isotopic compositions with a secondary or sputtering ion source were performed on meteorites (Gradsztajn et al. 1967; Poschenrieder et al. 1965) and lunar rocks (Eugster and Bernas 1971), although the precision and accuracy were apparently too low for any valuable scientific statements apart from the $^7\text{Li}/^6\text{Li}$ ratios identical to those found for terrestrial rocks within large uncertainties. Nevertheless, further measurements of Li isotopic compositions in geological samples were mostly obtained by TIMS and later MC-ICPMS; only relatively recently have studies utilizing SIMS

measurement of Li isotopes emerged (e.g., Barrat et al. 2005; Beck et al. 2004; Decitre et al. 2002; Chaussidon and Robert 1999; Kobayashi et al. 2004; Richter et al. 2003).

Whereas SIMS requires precise matrix matching for any elemental and/or isotopic determinations, little effort has been exerted for characterization of suitable geological reference materials in terms of Li isotopic compositions (Jochum et al. 2006; Kasemann et al. 2005). This appears a persistent problem and may require further experimental work. Such inferences are stressed by apparent matrix-induced fractionation of Li isotopes (Bell et al. 2009) which may indeed impart an additional uncertainty to in situ measurements unless these matrix effects are not disentangled correctly. It would follow that an instrumental mass fractionation factor may be estimated from false data and that not only must a mineral phase be matched, but also its major element composition should be more or less identical with unknown samples. These matrix effects may partly be responsible for a larger uncertainty linked to SIMS, that in most applications is limited to $\sim \pm 2$ ‰ (2σ). It is expected that this can be significantly reduced in carefully controlled experiments (Marks et al. 2008).

Marks et al. (2008) provided a detailed investigation and SIMS–MC-ICPMS cross-calibration of pegmatitic Na-rich arfvedsonite and aegirine in order to determine the matrix effects caused by SIMS. These authors found a significant difference in resulting $\delta^7\text{Li}$ of the two methods at the level of 4–5 ‰ (see also Kasemann et al. 2005), and differences on the order of nearly 10 ‰ for NIST 610, 612 and 614 glasses. Similarly, Bell et al. (2009) applied a differential matrix correction factor deduced from experimentally verified fractionation of Li isotopes in response to major chemical composition of olivines (Mg#). Recently, Su et al. (2015) have provided a detailed SIMS, ICPMS and MC-ICPMS comparison of multiple grains of olivine, clinopyroxene and orthopyroxene from ultramafic rocks collected in China, with the aim of establishing well-characterized mineral reference materials for in situ techniques. While laborious by nature, these analyses showed that

(i) SIMS results for olivine may strongly depend on Mg# [molar $\text{MgO}/(\text{MgO} + \text{FeO}) \times 100$] which would demand careful daily calibration over a range of Mg# values, and (ii) significant $\delta^7\text{Li}$ variations of several ‰ persisted between different laboratories and even between different sessions conducted in a single laboratory. This may, in part, be linked with different instrumental optimization parameters because the reported Li contents in mineral phases were shown to be reproducible.

The homogeneity in Li contents is also an important factor to consider, as has been underscored by inter-laboratory consistency of Li abundances in a natural quartz specimen (Audétat et al. 2015). Therefore, combined analytical tools may become a truly essential strategy for further SIMS studies of, for example, meteoritic constituents such as chondrules and calcium–aluminum-rich inclusions, considering both their small sizes and the important message they may carry since their formation in the earliest era of the Solar system. In fact, Li partitioning within single crystals of a mineral species may depend on major element composition, such as shown for plagioclase (Coogan 2011).

2.3.2 “Other” Analytical Methods

2.3.2.1 Atomic Absorption Spectrometry (AAS)

This technique has been successfully applied to rapid determination of Li isotopic compositions in the nuclear industry. Lithium-6 has large cross section for thermal neutrons (~ 942 barns) and the knowledge of ^6Li level is important for its burnup rate and for estimation of the production rate of tritium through the $^6\text{Li}(n,\alpha)^3\text{H}$ reaction. The possible usage of AAS for determining Li isotopic ratios was first explored by Wheat (1971) who employed a mono-isotope hollow cathode lamp. For AAS, it is essential to precisely know the Li content in unknown samples; Li isotopic ratios are calculated from measured absorbance of ^6Li (Meier 1982) but the linearity of these absorbance determinations, which is prerequisite for exact data acquisition, appears to

be disputed (Kushita 1986). Chapman and Dale (1976) reported on an AAS methodology for fast determination of $^7\text{Li}/^6\text{Li}$ in a range of samples which Chapman et al. (1980) suggested to approach analytical precision obtained by classical TIMS techniques. However, the data of Kushita (1986) show that this expectation was largely over-estimated.

In later progress, many problems were overcome (Wizemann and Niemax 2000), but the precision of Li isotopic determinations reached with AAS remains an issue. Moreover, results obtained for many natural samples (Meier 1982) that are likely to have non-extreme isotopic compositions (e.g., natural waters) show extremely light compositions. Therefore, the reliability of AAS (and also atomic emission spectrometry; ur Rehman et al. 2009) or laser-induced breakdown/atomic fluorescence (Smith et al. 1998) may be adequate for nuclear research, but geochemical applications require much more precise data, largely beyond capabilities of these techniques.

2.3.2.2 Nuclear- and Charged-Particle-Based Techniques

The general use of neutron activation analysis (NAA) in $^7\text{Li}/^6\text{Li}$ determination has been explored, with primary application to the nuclear industry. In principle, the abundance of one of the Li isotopes is determined precisely and total Li abundance is then measured by an independent method; the final $^7\text{Li}/^6\text{Li}$ can then be calculated (Wiernik and Amiel 1970). Wölflle and Neubert (1977) introduced an activation analysis method for simultaneous determination of ^6Li and ^7Li , and applied it to aqueous solutions, but the approach is less effective for natural samples. On the other hand, Rajan et al. (1980) applied nuclear techniques to $^7\text{Li}/^6\text{Li}$ determination of several stony meteorites, showing largely homogeneous Li isotopic compositions within ± 10 ‰ of terrestrial value (given by analysis of spodumene) which is broadly compatible with recent high-precision MC-ICPMS investigations (e.g., Seitz et al. 2007; see Chap. 3) but any inter-sample relations cannot be accounted for by this method. It may be that NAA techniques

(Chao and Tseng 1995; Itoh et al. 1993) and other more or less related methods, such as proton induced gamma-ray emission (Trompeter et al. 1999) or nuclear track detection (Kjellman et al. 1985), remain permissible methods for fast determination of Li contents in geological and other samples (see Räsänen 1992 for review), but they are less useful in determining Li isotopic compositions and their subtle variations at precisions of less than several permil, seriously limit their utility in the examination of a large range of geochemical processes.

2.3.2.3 Resonance Ionization and Other Techniques

Of the less-commonly applied methods to measure Li isotopes, resonance ionization mass spectrometry (RIMS), could offer an alternative to destructive methods (Suryanarayana et al. 1998) due to its extremely low detection limits (on the order of several tens femtograms of Li). The possible application of this technique to cosmochemical studies (Knight et al. 2007; Levine et al. 2009) could provide answers to some fundamental questions of the origin of the Solar system, presuming continued technical advancement. Laser spectroscopy was developed for studies of nuclear properties of different Li isotopes (Hergenröder et al. 1993; Nörtershäuser et al. 2011) but seems to be less applicable to geochemistry.

References

- Ahmed S, Jabeen N, ur Rehman E (2002) Determination of lithium isotopic composition by thermal ionization mass spectrometry. *Anal Chem* 74:4133–4135
- Aston FW (1932) The isotopic constitution and atomic weights of caesium, strontium, lithium, rubidium, barium, scandium and thallium. *Proc R Soc Lond A* 134:571–578
- Audétat A, Garbe-Schönberg D, Kronz A, Pettke T, Rusk B, Donovan JJ, Lowers HA (2015) Characterisation of a natural quartz crystal as a reference material for microanalytical determination of Ti, Al, Li, Fe, Mn, Ga and Ge. *Geostand Geoanal Res* 39:171–184
- Aulbach S, Rudnick RL (2009) Origins of non-equilibrium lithium isotopic fractionation in xenolithic peridotite minerals: examples from Tanzania. *Chem Geol* 258:17–27
- Aulbach S, Rudnick RL, McDonough WF (2008) Li-Sr-Nd isotope signature of the plume and cratonic lithospheric mantle beneath the margin of the rifted Tanzanian craton (Labait). *Contrib Mineral Petrol* 155:79–92
- Balsiger H, Geiss J, Groegler N, Wytenbach A (1968) Distribution and isotopic abundance of lithium in stone meteorites. *Earth Planet Sci Lett* 5:17–22
- Barrat JA, Chaussidon M, Bohn M, Gillet P, Göpel C, Lesourd M (2005) Lithium behavior during cooling of a dry basalt: an ion-microprobe study of the lunar meteorite Northwest Africa 479 (NWA 479). *Geochim Cosmochim Acta* 69:5597–5609
- Beck P, Barrat JA, Chaussidon M, Gillet P, Bohn M (2004) Li isotopic variations in single pyroxenes from the Northwest Africa 480 shergottite (NWA 480): a record of degassing of Martian magmas? *Geochim Cosmochim Acta* 68:2925–2933
- Bell DR, Hervig RL, Buseck PR, Aulbach S (2009) Lithium isotope analysis of olivine by SIMS: calibration of a matrix and application to magmatic phenocrysts. *Chem Geol* 258:5–16
- Bickle MJ, Chapman HJ, You C-F (2000) Measurement of lithium isotopic ratios as lithium tetraborate ions. *Int J Mass Spectrom* 202:273–282
- Brown HL, Biltz C, Anbar M (1977) A precision isotope ratio mass spectrometer for the analysis of $^6\text{Li}/^7\text{Li}$. *Int J Mass Spectrom Ion Phys* 25:167–181
- Bryant CJ, McCulloch MT, Bennett VC (2003) Impact of matrix effects on the accurate measurement of Li isotope ratios by inductively coupled plasma mass spectrometry (MC-ICP-MS) under “cold” plasma conditions. *J Anal Atom Spectrom* 18:734–737
- Bryant CJ, Chappell BW, Bennett VC, McCulloch MT (2004) Lithium isotopic compositions of the New England Batholith: correlations with inferred source rock compositions. *Trans R Soc Edinburgh—Earth Sci* 95:199–214
- Caciagli N, Brenan JM, McDonough WF, Phinney D (2011) Mineral-fluid partitioning of lithium and implications for slab-mantle interaction. *Chem Geol* 280:384–398
- Carignan J, Vigier N, Millot R (2007) Three secondary reference materials for lithium isotope measurements: Li7-N, Li6-N and LiCl-N solutions. *Geostandards Geoanal Res* 31:7–12
- Chan LH (1987) Lithium isotope analysis by thermal ionization mass spectrometry of lithium tetraborate. *Anal Chem* 59:2662–2665
- Chan LH, Edmond JM (1988) Variation of lithium isotope composition in the marine environment: a preliminary report. *Geochim Cosmochim Acta* 52:1711–1717
- Chan LH, Edmond JM, Thompson G, Gillis K (1992) Lithium isotopic composition of submarine basalts: implication for the lithium cycle in the oceans. *Earth Planet Sci Lett* 108:151–160
- Chan LH, Edmond JM, Thompson G (1993) A lithium isotope study of hot springs and metabasalts from

- mid-ocean ridge hydrothermal systems. *J Geophys Res* 98:9653–9659
- Chan LH, Gieskes JM, You C-F, Edmond JM (1994) Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California. *Geochim Cosmochim Acta* 58:4443–4454
- Chan LH, Leeman WP, You C-F (1999) Lithium isotopic composition of Central American Volcanic Arc lavas: implications for modification of subarc mantle by slab-derived fluids. *Chem Geol* 160:255–280
- Chan LH, Leeman WP, You C-F (2002) Lithium isotopic composition of Central American Volcanic Arc lavas: implications for modification of subarc mantle by slab-derived fluids: correction. *Chem Geol* 182:293–300
- Chao J-H, Tseng C-L (1995) Determination of low-level lithium in environmental water samples by neutron activation. *Appl Radiat Isot* 46:211–215
- Chapman JF, Dale LS (1976) The determination of lithium isotope abundances with a dual-beam atomic absorption spectrometer. *Anal Chim Acta* 87:91–95
- Chapman JF, Dale LS, Fraser HJ (1980) The atomic absorption spectrometric determination of lithium isotope abundances by direct measurement of the absorbance ratio. *Anal Chim Acta* 116:427–431
- Chaussidon M, Robert F (1999) Lithium nucleosynthesis in the Sun inferred from the solar-wind $^7\text{Li}/^6\text{Li}$ ratio. *Nature* 402:270–273
- Choi MS, Shin HS, Kil YW (2010) Precise determination of lithium isotopes in seawater using MC-ICP-MS. *Microchem J* 95:274–278
- Choi MS, Ryu J-S, Park HY, Lee K-S, Kil Y, Shin HS (2013) Precise determination of the lithium isotope ratio in geological samples using MC-ICP-MS with cool plasma. *J Anal Atom Spectrom* 28:505–509
- Coogan LA (2011) Preliminary experimental determination of the partitioning of lithium between plagioclase crystals of different anorthite contents. *Lithos* 125:711–715
- Coplen TB, Böhlke JK, De Bièvre P, Ding T, Holden NE, Hopple JA, Krouse HR, Lamberty A, Peiser HS, Révész K, Rieder SE, Rosman KJR, Roth E, Taylor PDP, Vocke RD Jr, Xiao YK (2002) Isotope-abundance variations of selected elements. *Pure Appl Chem* 74:1987–2017
- Datta BP, Khodade PS, Parab AR, Goyal AH, Chitambar SA, Jain HC (1992) Thermal ionisation mass spectrometry of Li_2BO_2^+ ions: determination of the isotopic abundance ratio of lithium. *Int J Mass Spectrom Ion Proc* 116:87–114
- Decitre S, Deloule E, Reisberg L, James RH, Agrinier P, Mével C (2002) Behavior of Li and its isotopes during serpentinization of oceanic peridotites. *Geochem Geophys Geosys* 3, paper number. doi:[10.1029/2001GC000178](https://doi.org/10.1029/2001GC000178)
- Dempster AJ (1921) Positive ray analysis of lithium and magnesium. *Phys Rev* 18:415–422
- Eugster O, Bernas R (1971) Li, B, Mg and Ti isotopic abundances and search for trapped solar wind Li in Apollo 11 and Apollo 12 material. *Proc Lunar Sci Conf* 2:1461–1469
- Flesch GD, Anderson AR, Svec HJ (1973) A secondary isotopic standard for $^6\text{Li}/^7\text{Li}$ determinations. *Int J Mass Spectrom Ion Phys* 12:265–272
- Galy A, Yoffe O, Janney PE, Williams RW, Cloquet C, Alard O, Halicz L, Wadhwa M, Hutcheon ID, Ramon E, Carignan J (2003) Magnesium isotope heterogeneity of the isotopic standard SRM980 and new reference materials for magnesium-isotope-ratio measurements. *J Anal At Spectrom* 18:1352–1356
- Gradsztajn E, Salome M, Yaniv A, Bernas R (1967) Isotopic analysis of lithium in the Holbrook meteorite and in terrestrial samples with a sputtering ion source mass spectrometer. *Earth Planet Sci Lett* 3:387–393
- Green LW, Leppinen JJ, Elliot NL (1988) Isotopic analysis of lithium as thermal dilithium fluoride ions. *Anal Chem* 60:34–37
- Grégoire DC, Acheson BM, Taylor RP (1996) Measurement of lithium isotope ratios by inductively coupled plasma mass spectrometry: application to geological materials. *J Anal Atom Spectrom* 11:765–772
- Halliday AN, Lee D-C, Christensen JN, Walder AJ, Freedman PA, Jones CE, Hall CM, Yi W, Teagle D (1995) Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *Int J Mass Spectrom Ion Proc* 146/147:21–33
- Halliday AN, Lee D-C, Christensen JN, Rehkämper M, Yi W, Luo X, Hall CM, Ballentine CJ, Pettke T, Stirling CH (1998) Applications of multiple collector-ICPMS to cosmochemistry, geochemistry and paleoceanography. *Geochim Cosmochim Acta* 62:919–940
- Hergenröder R, Veza D, Niemax K (1993) Detection limit and selectivity for lithium isotopes in continuous wave field ionization laser spectroscopy. *Spectrochim Acta (B)* 48:589–569
- Heuser A, Eisenhauer A (2008) The calcium isotope composition ($\delta^{44/40}\text{Ca}$) of NIST SRM 915b and NIST SRM 1486. *Geostand Geoanal Res* 32:311–315
- Hoefs J, Sywall M (1997) Lithium isotope composition of Quaternary and Tertiary biogenic carbonates and a global lithium isotope balance. *Geochim Cosmochim Acta* 61:2679–2690
- Huang K-F, You C-F, Liu Y-H, Wang R-M, Lin P-Y, Chung C-H (2010) Low-memory, small sample size, accurate and high-precision determinations of lithium isotopic ratios in natural materials by MC-ICP-MS. *J Anal Atom Spectrom* 25:1019–1024
- Itoh M, Yamada Y, Kiriya N, Komura K, Ueno K, Sakanoue M (1993) Neutron activation analysis of low level lithium in water samples. *J Radioanal Nucl Chem* 172:289–298
- Jabeen N, ur Rehman E, Ahmed S (2003) Determination of lithium isotopic composition by thermal ionization mass spectrometry in seawater. *J Radioanal Nucl Chem* 258:427–430
- James RH, Palmer MR (2000) The lithium isotope composition of international rock standards. *Chem Geol* 166:319–326
- Janoušek V, Erban V, Holub FV, Magna T, Bellon H, Mlčoch B, Wiechert U, Rappich V (2010)

- Geochemistry and genesis of behind-arc basaltic lavas from eastern Nicaragua. *J Volcanol Geotherm Res* 192:232–256
- Jeffcoate AB, Elliott T, Thomas A, Bouman C (2004) Precise, small sample size determinations of lithium isotopic compositions of geological reference materials and modern seawater by MC-ICP-MS. *Geostand Geoanal Res* 28:161–172
- Jochum KP, Stoll B, Herwig K, Willbold M, Hofmann AW, Amini M, Aarburg S, Abouchami W, Hellebrand E, Mocek B, Raczek I, Stracke A, Alard O, Bouman C, Becker S, Dücking M, Brätz H, Klemm R, de Bruin D, Canil D, Cornell D, de Hoog CJ, Dalpé C, Danyushevsky L, Eisenhauer A, Gao Y, Snow JE, Groschopf N, Günther D, Latkoczy C, Guillong M, Hauri EH, Höfer HE, Lahaye Y, Horz K, Jacob DE, Kasemann SA, Kent AJR, Ludwig T, Zack T, Mason PRD, Meixner A, Rosner M, Misawa K, Nash BP, Pfänder J, Premo WR, Sun WD, Tiepolo M, Vannucci R, Vennemann T, Wayne D, Woodhead JD (2006) MPI-DING reference glasses for in situ microanalysis: new reference values for element concentrations and isotope ratios. *Geochem Geophys Geosys* 7, paper number Q02008. doi:10.10129/02005GC001060
- Kasemann SA, Jeffcoate AB, Elliott T (2005) Lithium isotope composition of basalt glass reference material. *Anal Chem* 77:5251–5257
- Kim DW (2001) Chromatographic enrichment of lithium isotopes by hydrous manganese(IV) oxide. *Bull Korean Chem Soc* 22:503–506
- Kjellman N, Kristiansson K, Malmqvist L (1985) Selective determination of lithium and boron in minerals by means of an SSNTD-technique. *Nucl Instr Methods Phys Res A* 235:193–197
- Knight KB, Savina MR, Davis AM, Pellin MJ, Levine J, Grossman L, Simon S (2007) Application of RIMS to the study of beryllium chronology in early Solar System condensates. Workshop on the chronology of meteorites and the early Solar System, #4088
- Kobayashi K, Tanaka R, Moriguti T, Shimizu K, Nakamura E (2004) Lithium, boron and lead isotope systematics of glass inclusions in olivines from Hawaiian lavas: evidence for recycled components in the Hawaiian plume. *Chem Geol* 212:143–161
- Košler J, Magna T (2014) Developments in clean lab practices. In: McDonough WF (ed) *Treatise on geochemistry*, vol 15, 2nd edn. Elsevier Ltd., Oxford, pp 111–122
- Košler J, Kučera M, Sylvester P (2001) Precise measurement of Li isotopes in planktonic foraminiferal tests by quadrupole ICPMS. *Chem Geol* 181:169–179
- Krankowsky D, Müller O (1967) Isotopic composition and abundance of lithium in meteoritic matter. *Geochim Cosmochim Acta* 31:1833–1842
- Kushita K (1986) Atomic absorption spectrometric determination of the isotopic composition of lithium by an ultimate absorbance-ratio technique. *Anal Chim Acta* 183:225–230
- le Roux PJ (2010) Lithium isotope analysis of natural and synthetic glass by laser ablation MC-ICP-MS. *J Anal Atom Spectrom* 25:1033–1038
- Levine J, Savina MR, Stephan T, Dauphas N, Davis AM, Knight KB, Pellin MJ (2009) Resonance ionization mass spectrometry for precise measurements of isotope ratios. *Int J Mass Spectrom* 288:36–43
- Liu X-M, Rudnick RL, Hier-Majumder S, Sirbescu M-LC (2010) Processes controlling lithium isotopic distribution in contact aureoles: a case study of the Florence County pegmatites, Wisconsin. *Geochem Geophys Geosys* 11, paper number Q08014. doi:10.10129/02010GC003063
- Magna T, Wiechert UH, Halliday AN (2004) Low-blank separation and isotope ratio measurement of small samples of lithium using multiple-collector ICPMS. *Int J Mass Spectrom* 239:67–76
- Magna T, Wiechert U, Halliday AN (2006) New constraints on the lithium isotope compositions of the Moon and terrestrial planets. *Earth Planet Sci Lett* 243:336–353
- Magna T, Janoušek V, Kohút M, Oberli F, Wiechert U (2010) Fingerprinting sources of orogenic plutonic rocks from Variscan belt with lithium isotopes and possible link to the subduction-related origin of some A-type granites. *Chem Geol* 274:94–107
- Magna T, Novák M, Janoušek V (2013) Lithium isotopes in giant pegmatite bodies—implications for their sources and evolution. In: Geological Association of Canada and Mineralogical Association of Canada annual meeting, Winnipeg, Canada. Abstract volume, p 135
- Marks MAW, Rudnick RL, McCammon C, Vennemann T, Markl G (2007) Arrested kinetic Li isotope fractionation at the margin of the Ilímaussaq complex, South Greenland: evidence for open-system processes during final cooling of peralkaline igneous rocks. *Chem Geol* 246:207–230
- Marks MAW, Rudnick RL, Ludwig T, Marschall H, Zack T, Halama R, McDonough WF, Rost D, Wenzel T, Vicenzi EP, Savov IP, Altherr R, Markl G (2008) Sodic pyroxene and sodic amphibole as potential reference materials for *in situ* lithium isotope determinations by SIMS. *Geostand Geoanal Res* 32:295–310
- Meier AL (1982) Determination of lithium isotopes at natural abundance levels by atomic absorption spectrometry. *Anal Chem* 54:2158–2162
- Michiels E, De Bièvre P (1983) Absolute isotopic composition and the atomic weight of a natural sample of lithium. *Int J Mass Spectrom Ion Phys* 49:265–274
- Millot R, Guerrot C, Vigier N (2004) Accurate and high-precision measurement of lithium isotopes in two reference materials by MC-ICP-MS. *Geostand Geoanal Res* 28:153–159
- Millot R, Petelet-Giraud E, Guerrot C, Négrel P (2010) Multi-isotopic composition ($\delta^7\text{Li}$ – $\delta^{11}\text{B}$ – δ^{D} – $\delta^{18}\text{O}$) of

- rainwaters in France: Origin and spatio-temporal characterization. *Appl Geochem* 25:1510–1524
- Misra S, Froehlich PN (2009) Measurement of lithium isotope ratios by quadrupole-ICP-MS: application to seawater and natural carbonates. *J Anal Atom Spectrom* 24:1524–1533
- Moriguti T, Nakamura E (1998) High-yield lithium separation and the precise isotopic analysis for natural rock and aqueous samples. *Chem Geol* 145:91–104
- Nishio Y, Nakai S (2002) Accurate and precise lithium isotopic determinations of igneous rock samples using multi-collector inductively coupled plasma mass spectrometry. *Anal Chim Acta* 456:271–281
- Négrel P, Millot R, Brenot A, Bertin C (2010) Lithium isotopes as tracers of groundwater circulation in a peat land. *Chem Geol* 276:119–127
- Nörtershäuser W, Sánchez R, Ewald G, Dax A, Behr J, Bricault P, Bushaw BA, Dilling J, Domsbky M, Drake WF, Götze S, Kluge H-J, Kühl T, Lassen J, Levy CDP, Pachucki K, Pearson M, Puchalski M, Wojtaszek A, Yan Z-C, Zimmermann C (2011) Isotope-shift measurements of stable and short-lived lithium isotopes for nuclear-charge-radii determination. *Phys Rev A* 83, paper number 012516
- Oi T, Odagiri T, Nomura M (1997) Extraction of lithium from GSJ rock reference samples and determination of their isotopic compositions. *Anal Chim Acta* 340:221–225
- Penniston-Dorland SC, Sorensen SS, Ash RD, Khadke SV (2010) Lithium isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA. *Earth Planet Sci Lett* 292:181–190
- Poschenrieder WP, Herzog RF, Barrington AE (1965) The relative abundance of the lithium isotopes in the Holbrook meteorite. *Geochim Cosmochim Acta* 29:1193–1195
- Qi HP, Coplen TB, Wang QZ, Wang YH (1997a) Unnatural isotopic composition of lithium reagents. *Anal Chem* 69:4076–4078
- Qi HP, Taylor PDP, Berglund M, De Bièvre P (1997b) Calibrated measurements of the isotopic composition and atomic weight of the natural Li isotopic reference material IRMM-016. *Int J Mass Spectrom Ion Proc* 171:263–268
- Räsänen J (1992) Analysis of lithium by ion beam methods. *Nucl Instr Methods Phys Res B* 66:107–117
- Rajan RS, Brown L, Tera F, Whitford DJ (1980) Lithium isotopic composition in some stone meteorites. *Earth Planet Sci Lett* 51:41–44
- Reynolds BC, Georg RB, Oberli F, Wiechert U, Halliday AN (2006) Re-assessment of silicon isotope reference materials using high-resolution multi-collector ICP-MS. *J Anal At Spectrom* 21:266–269
- Richter FM, Davis AM, DePaolo DJ, Watson EB (2003) Isotope fractionation by chemical diffusion between molten basalt and rhyolite. *Geochim Cosmochim Acta* 67:3905–3923
- Rosner M, Ball L, Peucker-Ehrenbrink B, Bluzstajn J, Bach W, Erzinger J (2007) A simplified, accurate and fast method for lithium isotope analysis of rocks and fluids, and $\delta^7\text{Li}$ values of seawater and rock reference materials. *Geostandards Geoanal Res* 31:77–88
- Sahoo SK, Masuda A (1995a) High precision isotopic measurement of lithium by thermal ionization mass spectrometry. *Int J Mass Spectrom Ion Proc* 151:189–196
- Sahoo SK, Masuda A (1995b) Simultaneous measurement of lithium and boron isotopes as lithium tetraborate ion by thermal ionization mass spectrometry. *Analyst* 120:335–339
- Sahoo SK, Masuda A (1998) Precise determination of lithium isotopic composition by thermal ionization mass spectrometry in natural samples such as seawater. *Anal Chim Acta* 370:215–220
- Seitz H-M, Brey GP, Lahaye Y, Durali S, Weyer S (2004) Lithium isotopic signatures of peridotite xenoliths and isotopic fractionation at high temperature between olivine and pyroxenes. *Chem Geol* 212:163–177
- Seitz H-M, Brey GP, Zipfel J, Ott U, Weyer S, Durali S, Weinbruch S (2007) Lithium isotope composition of ordinary and carbonaceous chondrites, and differentiated planetary bodies: bulk solar system and solar reservoirs. *Earth Planet Sci Lett* 260:582–596
- Schauble EA (2004) Applying stable isotope fractionation theory to new systems. In: Johnson CM, Beard BL, Albarède F (eds) *Geochemistry of non-traditional stable isotopes*. *Rev Mineral Geochem* 55:65–111
- Schönbächler M, Fehr MA (2014) Basics of ion exchange chromatography for selected geological applications. In: McDonough WF (ed vol 15) *Treatise on geochemistry*, 2nd edn. Elsevier Ltd., Oxford, pp 123–146
- Simons KK, Harlow GE, Brueckner HK, Goldstein SL, Sorensen SS, Hemming NG, Langmuir CH (2010) Lithium isotopes in Guatemalan and Franciscan HP–LT rocks: insights into the role of sediment-derived fluids during subduction. *Geochim Cosmochim Acta* 74:3621–3641
- Smith BW, Gornushkin IB, King LA, Winefordner JD (1998) A laser ablation-atomic fluorescence technique for isotopically selective determination of lithium in solids. *Spectrochim Acta (B)* 53:1131–1138
- Strelow FWE, Weinert CHSW, van der Walt TN (1974) Separation of lithium from sodium, beryllium and other elements by cation-exchange chromatography in nitric acid-methanol. *Anal Chim Acta* 71:123–132
- Sun XF, Ting BTG, Zeisel SH, Janghorbani M (1987) Accurate measurement of stable isotopes of lithium by inductively coupled plasma mass spectrometry. *Analyst* 112:1223–1228
- Suryanarayana MV, Sankari M, Gangadharan S (1998) Determination of $^6\text{Li}/^7\text{Li}$ isotope ratio using two photon resonance three photon resonance ionization mass spectrometry. *Int J Mass Spectrom Ion Proc* 173:177–189
- Svec HJ, Anderson AR (1965) The absolute abundance of the lithium isotopes in natural sources. *Geochim Cosmochim Acta* 29:633–641
- Svec HJ, Anderson AR (1966) A mass spectrometer for the precise assay of the lithium isotopes. *J Sci Instrum* 43:134–137

- Su B-X, Gu X-Y, Deloule E, Zhang H-F, Li Q-L, Li X-H, Vigier N, Tang Y-J, Tang G-Q, Liu Y, Pang K-N, Brewer A, Mao Q, Ma Y-G (2015) Potential orthopyroxene, clinopyroxene and olivine reference materials for in situ lithium isotope determination. *Geostand Geoanal Res* 39:357–369
- Šulcek Z, Rubeska J (1969) Bestimmung des Lithiumspurengehaltes in Gesteinen. *Collect Czechoslovak Chem Commun* 34:2048–2056
- Šulcek Z, Povondra P, Štangel R (1965) Chromatographische Trennung der Lithium- und Natriumionen. *Collect Czechoslovak Chem Commun* 30:380–387
- Taylor TI, Urey HC (1938) Fractionation of the lithium and potassium isotopes by chemical exchange with zeolithes. *J Chem Phys* 6:429–438
- Teng F-Z, McDonough WF, Rudnick RL, Dalpé C, Tomascak PB, Chappell BW, Gao S (2004) Lithium isotopic composition and concentration of the upper continental crust. *Geochim Cosmochim Acta* 68:4167–4178
- Teng F-Z, McDonough WF, Rudnick RL, Walker RJ (2006) Diffusion-driven extreme lithium isotopic fractionation in country rocks of the Tin Mountain pegmatite. *Earth Planet Sci Lett* 243:701–710
- Teng F-Z, Rudnick RL, McDonough WF, Gao S, Tomascak PB, Liu Y (2008) Lithium isotopic composition and concentration of the deep continental crust. *Chem Geol* 255:47–59
- Teng F-Z, Rudnick RL, McDonough WF, Wu F-Y (2009) Lithium isotopic systematics of A-type granites and their mafic enclaves: further constraints on the Li isotopic composition of the continental crust. *Chem Geol* 262:370–379
- Tomascak PB (2004) Developments in the understanding and application of lithium isotopes in the Earth and planetary sciences. In: Johnson CM, Beard BL, Albarède F (eds) *Geochemistry of non-traditional stable isotopes*. *Rev Mineral Geochem* 55:153–195
- Tomascak PB, Carlson RW, Shirey SB (1999) Accurate and precise determination of Li isotopic compositions by multi-collector sector ICP-MS. *Chem Geol* 158:145–154
- Trompeter WJ, Reyes AG, Vickridge IC, Markwitz A (1999) Lithium and boron distributions in geological samples. *Nucl Instr Methods Phys Res B* 158:568–574
- ur Rehman E, ur Rehman S, Ahmed S (2009) ^6Li atom percentage determination by atomic absorption-emission spectrometry using a natural lithium hollow cathode lamp. *Appl Spectrosc* 63:971–973
- Vanhoe H, Vandecasteele C, Versieck J, Dams R (1991) Determination of lithium in biological samples by inductively coupled plasma mass spectrometry. *Anal Chim Acta* 244:259–267
- Wheat JA (1971) Isotopic analysis of lithium by atomic absorption spectrophotometry. *Appl Spectrosc* 25:328–330
- Wiernik M, Amiel S (1970) Determination of lithium and its isotopic composition by activation analysis and measurement of ^8Li and ^{17}N . *J Radioanal Chem* 5:123–131
- Wieser ME (2006) Atomic weights of the elements 2005 (IUPAC technical report). *Pure Appl Chem* 78:2051–2066
- Wizemann HD, Niemax K (2000) Measurement of $^7\text{Li}/^6\text{Li}$ isotope ratios by resonant Doppler-free two-photon diode laser atomic absorption spectroscopy in a low-pressure graphite furnace. *Spectrochim Acta (B)* 55:637–650
- Wölflé R, Neubert A (1977) Determination of isotopic composition of lithium by neutron activation analysis; comparison with mass spectrometry. *J Radioanal Chem* 39:375–384
- Xu R, Liu Y, Tong X, Hu Z, Zong K, Gao S (2013) In-situ trace elements and Li and Sr isotopes in peridotite xenoliths from Kuandian, North China Craton: Insights into Pacific slab subduction-related mantle modification. *Chem Geol* 354:107–123
- Xiao YK, Beary ES (1989) High-precision isotopic measurement of lithium by thermal ionization mass spectrometry. *Int J Mass Spectrom Ion Proc* 94:101–114
- You C-F, Chan LH (1996) Precise determination of lithium isotopic composition in low concentration natural samples. *Geochim Cosmochim Acta* 60:909–915
- You C-F, Chan LH, Spivack AJ, Gieskes JM (1995) Lithium, boron and their isotopes in sediments and pore waters of Ocean Drilling Program Site 808, Nankai trough: implications for fluid expulsion in accretionary prisms. *Geology* 23:37–40
- Zack T, Tomascak PB, Rudnick RL, Dalpé C, McDonough WF (2003) Extremely light Li in orogenic eclogites: the role of isotope fractionation during dehydration in subducted oceanic crust. *Earth Planet Sci Lett* 208:279–290

Advances in Lithium Isotope Geochemistry

Tomascak, P.B.; Magna, T.; Dohmen, R.

2016, XI, 195 p. 51 illus., 16 illus. in color., Hardcover

ISBN: 978-3-319-01429-6