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

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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. δ^7Li 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 δ^7Li 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.

Keywords: Lithium isotopes; Ion-exchange chromatography; Multiple-collector ICPMS; International reference rock standards; Matrix effects

1. 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) [1]. However, it has been further enhanced by the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) [2]. The ionic radius of Li^+ (≈0.59 Å) is similar to that of Mg^{2+} (≈0.57 Å). Therefore, lithium can substitute for magnesium in olivine, enstatite and diopside [3]. 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 [4], continental weathering rates [5,6], and as a tracer of subducted oceanic crust in the mantle [7,8].

Lithium has two stable isotopes, ^{6}Li and ^{7}Li, with a large relative mass difference of ~17%. Mass-dependent lithium isotope fractionation has been known since Taylor and Urey [9] 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 [10]. The first accurate and precise measurements of lithium isotopes were performed using TIMS [8,11–17]. However, the TIMS technique suffers from a highly instable instrumental fractionation and requires Li that is virtually free of matrix [17,18]. Therefore, complicated ion exchange procedures have to be applied to obtain very pure Li solutions [19]. Quadrupole ICPMS is able to measure isotope ratios on very small amounts of lithium but is limited to lower precision compared with MC-ICPMS [20,21]. Other techniques that have been used for the measurement of lithium isotopes include atomic absorption spectrometry

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[22,23], secondary ionization mass spectrometry [24] and laser-excited atomic fluorescence spectroscopy [25]. The advent of multiple-collector ICPMS offers the opportunity for small amounts of lithium to be analysed to high precision [2,26,27].

Most recently the procedures that have been developed to separate lithium from silicate rocks use large eluant volumes [2,27,28] and, therefore, are limited to relatively large sample amounts and are sensitive to (Mg, Fe)-rich rock matrices [29,30]. 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. 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 δ-values as δ^6Li. In this way positive δ-values are isotopically light and negative δ-values are isotopically heavy. This is the opposite of how δ-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 δ^7Li-notation in agreement with the recommendations [31]:

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

The lithium isotope composition is given in per mil relative to NIST SRM 8545 or L-SVEC ($^7\text{Li}/^6\text{Li} = 12.02 \pm 0.03$) [32]. Other standards are utilized sometimes, e.g., seawater [33,34] or IRM-016 [35]. 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.

2.1. L-SVEC preparation

Approximately 100 mg of L-SVEC powder (Li_2CO_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. [36] 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.

2.2. 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. Qi et al. [37] reported highly anomalous lithium isotope compositions (>1000‰) 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 h 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 6 M HCl. An aliquot (1/8th of the solution, equivalent to ~12.5 mg of the original sample powder) from the 6 M HCl solution was then evaporated and dissolved in 0.5 ml of 0.67 M HNO_3 in methanol. This is made from a 30% (v/v) solution of methanol, which dilutes concentrated HNO_3 to the desired concentration and is hereafter referred to as 0.67 M HNO_3/methanol. The final concentration of methanol in the solution is ~27%. This aliquot was used for Li separation by ion exchange chromatography.

2.3. Chromatography

The separation of lithium from other elements using mixtures of mineral acids and organic media is based on the previous work of Šulcek and co-workers [38,39]. 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 HNO_3; HCl may create Fe(III)-complexes that are not retained by cation resins and may therefore elute Fe together with lithium [40]. Moreover, HNO_3 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. [7]. Košler et al. [20] 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 [28] 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 6 M HCl and de-ionized water, then with 3 M 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 pre-conditioned with 2 ml 0.67 M HNO_3/methanol. The sample is loaded onto the resin in 0.5 ml of 0.67 M HNO_3/methanol. Subsequently cations are eluted with 1 M 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 1 M 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.

2.4. Mass spectrometry

Lithium isotope ratios were measured on Nu1700 (Nu Instruments), a new large-geometry high-resolution MC-ICPMS [41]. The Nu1700 is equipped with three 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 (Cetac) desolvator and ionized in argon plasma at 1400 W. The other instrument parameters are listed in Table 1.

Table 1
Instrumental settings and conditions

RF power (W)	1400
Nebulizer pressure (psi[a])	49
Auxiliary gas flow rate (L/min)	0.9
Coolant gas flow rate (L/min)	13.0
Nebulizer	Microconcentric
Spray chamber temperature (°C)	108
Membrane temperature (°C)	108
Sample uptake rate (μL/min)	80
Acceleration voltage (kV)	6
Resolution	∼700
Analyzer pressure (mbar)	2.3×10^{-9}

Conditions for DSN-100, only argon is used.
[a] 1 psi = 0.06895 kg cm^{-2}.

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 (10–14) × 10^{-9} A/ppm of Li in solution were obtained at an uptake of ≈80 μl/min. Samples were run at a mass resolution of 700–800 ($m/\Delta M$; ΔM 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 $^6LiH^+$ on mass ^{7}Li at a resolution of ∼1400 (required resolution 1010) but no hydrides have been detected. Each measurement consists of 40–60 cycles of 10 s of integration resulting in a total integration time of 400–600 s. Our standard procedure uses between 30 and 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 1000–3000 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% (2S.D.) based on multiple standard analyses.

3. Results and discussion

3.1. Separation of lithium

The first 8 ml of 1 M 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 [19,20]. 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 [42]. The process must be essentially an equilibrium fractionation between AG 50W-X8 resin and 1 M 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 [20]). 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

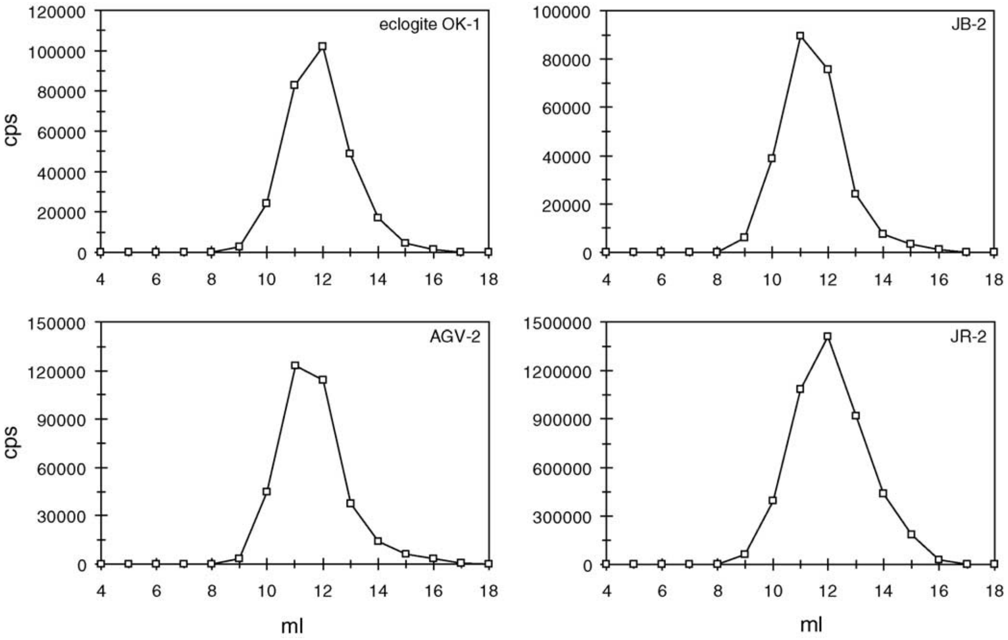

Fig. 1. Elution curve of lithium for silicate rocks. AG 50W-X8 ion exchange resin is used for: eclogite OK-1, basalt JB-2, andesite AGV-2 and rhyolite JR-2, respectively. Note that all Li eluted within 16 ml independent from the rock type. This is especially interesting for high-magnesium rocks. If any loss of Li is possible, then it could happen due to longer tailing of lithium. This would shift lithium isotope composition towards heavier values as previously well documented [19,20].

for which less than 100% lithium (within analytical errors) was recovered have not been taken for isotope analysis.

Chan et al. [30] 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) [43]; 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% SiO_2 and 0.04% MgO). Results of the column calibration are shown in Fig. 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 lherzolite 8520-9 [44] and a spodumene from a zoned pegmatite (Tin Mountain mine, Harney Peak, USA) [45]. Lithium is a trace element in olivine [3,46,47]. On the other hand, lithium in spodumene (nominally $LiAlSi_2O_6$) 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) 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 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

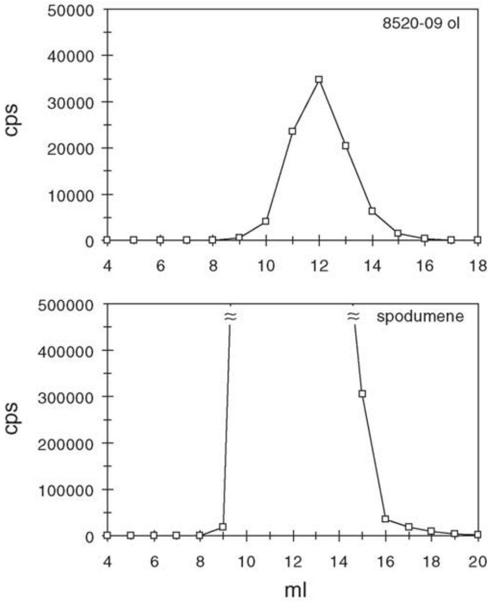

Fig. 2. Elution of lithium for mineral separates. (a) Olivine from lherzolite 8520-09 and (b) spodumene from Harney Peak (USA). Note that elution of lithium is within exactly the same volume as for rocks. Opening the window for spodumene is caused by large amount of lithium present in the sample.

change lithium elution parameters, i.e., the method is matrix independent for most silicate materials.

3.2. Instrumental mass fractionation

Nu1700 can accommodate the mass dispersion of $\sim$15% suitable for simultaneous detection of both lithium isotopes. However, all plasma source mass spectrometers suffer from a mass bias effect [48] 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 [2]. 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. 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 and 0.15‰ (2S.E.) whereas errors calculated from averages of at least four sample runs give $\leq$0.5‰ (2S.D.).

To ensure that the Nu1700 was functioning correctly, a lithium solution prepared from LiNO$_3$ (Merck) was measured before each analytical session. With the LiNO$_3$ the accuracy and precision of the mass spectrometer can be monitored, excluding any effects from column chemistry. The isotope composition of the LiNO$_{3,}$ measured over the past 12 months, is 0.91 ± 0.15‰ (2S.D., $n = 15$) 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.

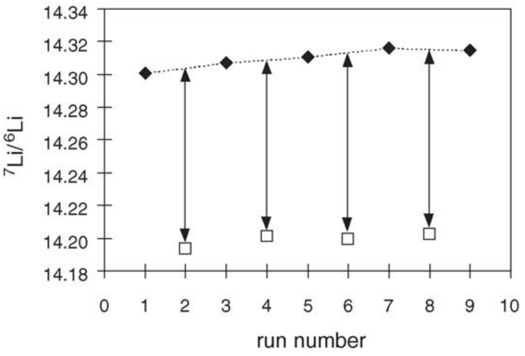

Fig. 3. Standard-sample-standard bracketing technique. ^{7}Li/^{6}Li ratios of four single sample measurements (squares) bracketed by five L-SVEC analyses (diamonds) are shown. Each symbol represents 40–60 single measurements. The slight increase of the sample ^{7}Li/^{6}Li ratios is corrected by a similar increase of the ratio for bracketing standard.

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 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 V (uptake rate 80 μl/min). The ^{7}Li/^{6}Li ratio of the background has been detected at $\sim$12.6, while measured ratios of L-SVEC varied between 13.8 and 14.4 depending on cones, gas flow conditions and lens settings. To find the best analysis procedure for lithium isotope measurements, L-SVEC solutions with concentrations ranging from 10 to 45 ppb are compared with a 50-ppb L-SVEC standard solution. The measured isotope ratios for these L-SVEC solutions vary by −3.5‰ for the 10 ppb solution relative to the 50-ppb solution for the DSN-100 when measured in standard mode (see Fig. 4). When the standard mode is employed together with the Aridus, lithium isotope ratios are altered by −2.0‰ (see Fig. 4). When the TRA mode is applied, isotope ratios are independent of sample concentrations (see Fig. 4). We conclude that the mass bias effect on lithium isotopes is, within error, concentration independent. It is likely that insufficient time elapses to wash out lithium between standard and sample analysis. Between samples and standards it has been washed with 2% HNO$_3$ for 120 s. Methods measuring zeros by deflecting ion beams cannot correct for any lithium memory independent from the used desolvator. Better results are achieved by measuring zeros using blank solution in TRA

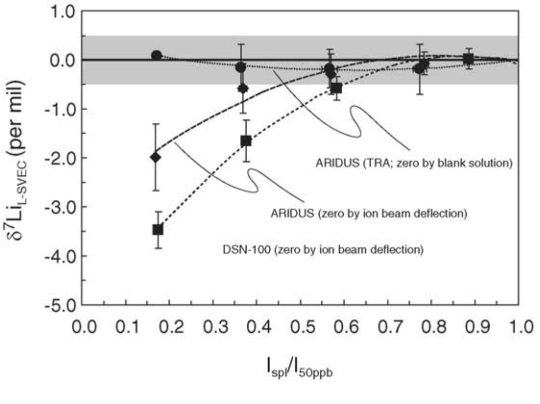

Fig. 4. Lithium isotope ratio measurements of L-SVEC solutions with different concentrations using an Aridus (Cetac) and DSN-100 (Nu Instruments) desolvating nebulizer for sample introduction. Plotted are isotope ratios versus concentration of the sample solution relative to 50-ppb L-SVEC solution as total beam intensity (I) ratios ($I_{\mathrm{spl}}/I_{50\mathrm{ppb}}$). 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 four single measurements. Errors are 2S.D.

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. 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., [49]). 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. 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 Nu1700 can be affected by matrix elements at only high concentrations (see also [50]). 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.

3.3. 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}Li/^{6}Li = 12.02 ± 0.03 [32]. 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 [51] and references therein). Galy et al. [36] have shown that Mg international reference material SRM 980 suffers from large amounts of heterogeneity in ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}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., Prague, Czech Rep.) together with our own aliquot that has been used as a bracketing solution. The results are shown in Fig. 6. All three aliquots were identical to our own within ±0.03‰. Thus, this standard would appear to be homogeneous and very suitable for high precision isotope ratio mass spectrometry.

3.4. International reference rocks

The data for international reference rocks from this study are presented in Table 2. The error of all averages is given as 2S.D. 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.

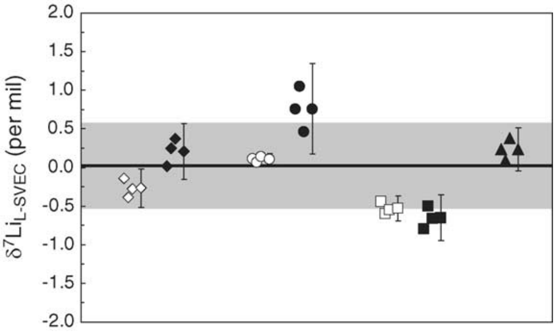

Fig. 5. The effects of matrix elements. L-SVEC solutions doped with Na (diamonds), Mg (circles), Al (squares), and a multi-element (Na, Mg, Al, Ca, K and Fe) matrix (triangle) are compared with pure L-SVEC solutions. Each symbol represents the average of four single measurements. The grey field gives 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 2S.D.

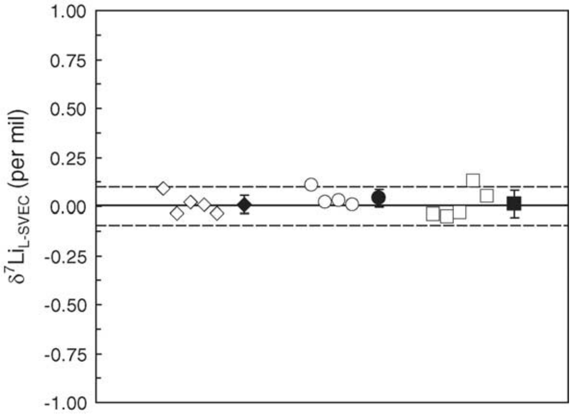

Fig. 6. Comparison of several selected L-SVEC aliquots. It is clear that this reference material is homogeneous in terms of lithium isotope composition. Open symbols represent individual runs; closed symbols are the averages of the respective runs with 2S.E. error bars (diamonds, P. Tomascak, δ^{7}Li = 0.01 ± 0.05‰; circles, J. Košler, δ^{7}Li = 0.04 ± 0.05‰; squares, R.H. James, δ^{7}Li = 0.01 ± 0.07‰; solid line is the average of our L-SVEC aliquot with dashed lines as 2S.E. error bars, δ^{7}Li = 0.003 ± 0.099‰).

Table 2
δ^7Li values for international reference rocks

	Li (ppm) measured	Li (ppm) recomm.	δ^7Li (‰)	2S.E.	n[a]	Average (2S.D.)	Other studies	
							δ^7Li (‰)	2S.D.
AGV-1	12.0	12.0	6.74	0.20	3			
BHVO-1	4.4	4.6	5.31	0.18	3		5.0[b]	1.4
							5.8[c]	1.6
							5.2[d]	0.5
BCR-1	12.5	12.9	2.56	0.06	2			
			2.19	0.33	2	2.38 (0.52)		
AGV-2	10.4	11.0	8.28	0.23	4			
			7.80	0.35	4			
			7.65	0.44	2			
			8.24	0.09	2			
	12.4		8.12	0.34	4			
	10.9		7.53	0.43	3	7.94 (0.64)		
BHVO-2	4.8	5.0	4.50	0.28	4			
	5.0		4.84		1			
	4.4		4.36	0.08	2			
			4.65	0.36	3			
	5.0		4.46	0.22	3			
	4.9		4.52	0.14	3			
	5.0		4.40	0.31	2			
	4.7		4.58	0.16	4			
			4.62	0.13	3	4.55 (0.29)	4.5[e]	1.0
JB-2	8.4	7.8	4.93	0.33	3			
	7.8		4.90	0.21	2			
	8.2		4.69	0.04	4			
	7.8		4.66	0.28	3			
			4.44	0.07	4		6.8[c]	0.2
	8.1		4.73	0.48	3		5.1[d]	0.4
			4.70		1		4.7[e]	1.0
			4.65	0.16	3		5.1[f]	1.1
			4.55	0.06	3		4.9[g]	0.7
	8.4		4.73	0.12	2	4.70 (0.29)	4.2[h]	0.3
JR-2	78.6	79.2	3.84	0.18	3		3.9[c]	0.8
							3.9[d]	0.4

recomm., recommended.

[a] Number of individual measurements.

[b] Bouman et al. [53].

[c] James and Palmer [15].

[d] Chan and Frey [14].

[e] Zack et al. [52].

[f] Tomascak et al. [2].

[g] Moriguti and Nakamura [19].

[h] Nishio and Nakai [27].

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 2.1 ml columns and using MC-ICPMS. Different volcanic rocks ranging from high MgO, low SiO_2 concentrations to high SiO_2, low MgO chemistry were selected (see also Section 3.1).

The δ^7Li value of 4.7 ± 0.3‰ (2S.D.) for JB-2 from this study (10 separate digestions of JB-2) is in good agreement with previously published values 5.1 ± 1.1‰ (2S.D.) [2] and 4.9 ± 0.7‰ (2S.D.) [19] and within analytical error of 4.3 ± 0.3‰ (2S.D.) [27]. However, this value is significantly different from a δ^7Li of 6.8 ± 0.2‰ (2S.D.) reported by James and Palmer [15]. A compilation of available data for JB-2 is given in Fig. 7.

For BHVO-2 a total of nine averages gives a δ^7Li of 4.55 ± 0.3‰ (2S.D.). This is in excellent agreement with δ^7Li of 4.5 ± 1.0‰ (2S.D.) reported by Zack et al. [52]. A δ^7Li value of 5.3 ± 0.2‰ (2S.E.) has been obtained for BHVO-1 which is in the middle of the range of published δ^7Li values from 5.0 to 5.8‰ [14,15,53]. Although both BHVO-1 and BHVO-2 come from the same lava flow, they are distinct by about 0.8‰ in δ^7Li and do not overlap within analytical error

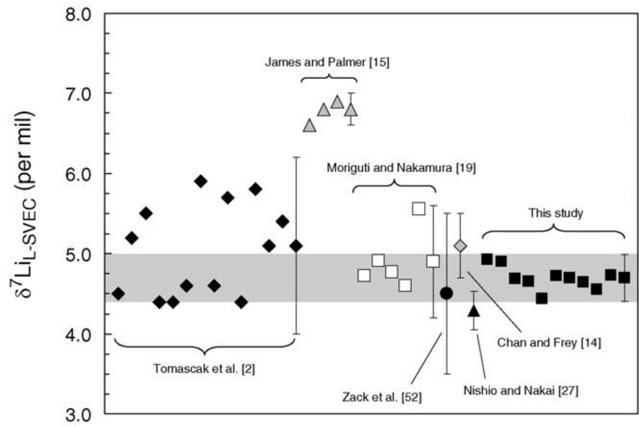

Fig. 7. Compilation of δ^7Li values for GSJ reference material JB-2 from the literature and this study. The grey bar shows ±2S.D. for JB-2 obtained from this study (0.29‰).

in our study. This may be explicable by some small-scale heterogeneity. Heterogeneity for lead isotopes has been reported for BHVO-2 [54].

For JR-2 a δ^7Li of 3.8 ± 0.2‰ (2S.E.) has been measured which is within analytical error the same as reported by James and Palmer [15] ($\delta^7\text{Li} = 3.9 \pm 0.8$‰; 2S.D.) and 3.9 ± 0.4‰ (2S.D.) reported by Chan and Frey [14] using TIMS techniques. It is interesting to note that this rhyolite still has a δ^7Li similar to that for pristine mantle rocks [55] consistent with no isotope fractionation during magmatic differentiation as reported by Tomascak et al. [7] for a sub-alkalic to alkalic basaltic rock suite.

A δ^7Li of 7.9 ± 0.6‰ (2S.D.) measured for AGV-2 is clearly above the δ^7Li range of fresh MORB mantle rocks [52]. The Li in AGV-1 and AGV-2 is slightly different. The δ^7Li value of AGV-1 (6.7 ± 0.2‰, 2S.E.) is substantially lower.

3.5. *Other reference materials and rocks*

Lithium abundances and isotope compositions of several other materials are summarized in Table 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 ($\delta^7\text{Li} = 35.3 \pm 0.8$‰, 2S.D.). 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 [56] and references therein). This may also be the source of the poorer reproducibility of this reference material.

A $\delta^7\text{Li} = -8.3 \pm 0.2$‰ (2S.D.) for the eclogite OK-1 is consistent with a MORB protolith [43] and fractionation of lithium isotopes related to subduction and dehydration as

Table 3
δ^7Li values for other rocks and standard materials

	Li (ppm) measured	Li (ppm) recomm.	δ^7Li (‰)	2S.E.	n[a]	Average	2S.D.
NIST 612	30.2	43.17[c]	35.07	0.47	3		
	35.5		34.79	0.25	4		
			35.55	0.39	3		
			35.62		1	35.26	0.79
Eclogite OK-1	10.1		−8.30	0.08	2		
(Münchberg, Germany)	9.3		−8.24	0.09	2		
	9.8		−8.16	0.11	4		
	10.3		−8.40	0.13	4	−8.27	0.20
8520-09 olivine (Mongolia)	1.4		3.60	0.36	3		
Spodumene (Harney Peak, USA)			7.23	0.15	3		
Li nitrate	0.04[b]		0.88	0.11	4		
			0.98	0.03	2		
			0.87	0.17	4		
			1.04	0.30	7		
			0.88	0.11	4		
			1.03	0.23	5		
			0.91	0.14	4		
			0.97	0.11	4		
			0.93	0.14	2		
			0.92	0.25	4		
			0.88	0.32	4		
			0.93	0.23	4		
			0.84	0.15	3		
			0.77	0.16	3		
			0.83	0.09	3	0.91	0.15

[a] Number of individual runs in one analytical session.
[b] Concentration matched to 40 ppb of L-SVEC.
[c] Pearce et al. [56].

proposed by Zack et al. [52] for eclogitic rocks from Trescolmen, Switzerland. Recently, even more negative δ^7Li values were reported for peridotitic rocks from far-east Russia that have been metasomatised by an eclogitic melt [57].

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) [46] and for mineral separates of peridotitic rocks from Kenya, France, Australia, Italy and Germany [3]. Isotope analysis of this olivine yielded $\delta^7\mathrm{Li} = 3.6 \pm 0.4‰$ (2S.E.). This is consistent with the conclusions, that δ^7Li of unmetasomatised mantle is $4.2 \pm 0.8‰$ [55] similar to values for peridotites reported by Chan et al. [30] and Brooker et al. [58]. Spodumene from Tin Mountain, Harney Peak, has $\delta^7\mathrm{Li} = 7.2 \pm 0.2‰$ (2S.E.). This is similar to lithium isotopes measured for I-type granites from Australia [59]. However, granites from the Harney Peak region are considered S-type, which are expected to have low δ^7Li 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 [45]. Further studies are required to solve this paradox.

4. Conclusions

We have presented lithium isotope data for seven 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 $\leq 0.5‰$ (2S.D.) 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 $\sim$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.

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