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Accurate determination of lithium isotope ratios by MC-ICP-MS without strict matrix-matching by using a novel washing method

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The accurate determination of Li isotopic ratios by MC-ICP-MS has traditionally been hampered by the high background and severe memory effect of Li. In this study, a novel method to efficiently reduce the high background and memory effect of Li was developed. It was found that the Li background can be significantly reduced by a factor of 15 to 70 by using a 5% NaCl rinse solution. In addition, the "mismatching effects" reported previously, which are caused by different acid and Li concentrations between the sample and standard, were eliminated once the Li background was efficiently reduced, suggesting that the crux of the two types of matrix effects is actually the high Li instrumental background and memory effect. Applying the background reduction technique, a method without strict matrix-matching was developed for the accurate and precise determination of Li isotopic ratios. The proposed method was validated by the analysis of eight reference materials with satisfactory results, even when the Li concentration in the samples was not matched with that of standards. The external precision of this method is better than $\pm 0.25\%_0$ (2SD) for δ^7Li, suitable for the identification of small fractionation of Li isotopes occurring in geological processes. With the proposed method, there is no need to match the Li and acid concentration of the sample and standard, which significantly reduced the sample preparation time and increased the sample throughput.

Introduction

Lithium has two stable isotopes (^{6}Li and ^{7}Li) with a large mass difference of $\sim 16.7\%$, consequently Li isotopes could be largely fractionated in many geological processes, such as weathering, magmatic differentiation, hydrothermal alteration and global scale crust–mantle recycling.[1–6] To better distinguish the Li isotopic compositional variations, a delta value defined as δ^7Li ($\%_0$) $= [(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{standard}} - 1] \times 1000$ is commonly used to express the difference. The determination of the ^{7}Li/^{6}Li ratio is generally implemented by a sample-standard bracketing (SSB) method with multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).[7–13] The SSB method is capable of correcting the instrumental signal drift and mass bias, and is commonly used to measure many isotopic ratios of non-traditional stable isotopes (*e.g.*, boron, magnesium, iron and copper). However, this method requires the strict-matching of the element and acid concentration in the sample and standard.[7,8,10,12,14–16] Therefore, it is not only time consuming in

sample preparation for matching but also increases risks for the accurate and precise determination of isotopic ratios.

Most recent studies of Li were implemented by MC-ICP-MS because it has several distinct advantages such as requiring smaller sample size, higher sensitivity and shorter measurement time. However, MC-ICP-MS is susceptible to instrumental and memory effect-related background interference[7,11] and isobaric interference of ^{12}C^{++} on ^{6}Li$^+$, and ^{14}N^{++} and ^{6}LiH$^+$ on ^{7}Li$^+$.[12,14,15] It has been demonstrated that the isobaric interference of ^{12}C^{++} and ^{14}N^{++} is negligible when measuring the ion counts of mass 6.5 and 7.5 (^{13}C^{++} and ^{15}N^{++}).[7,8,11] However, the memory effect-related background of Li is difficult to eliminate and can compromise the accuracy and precision of the results.[7,11,12,16] Most commonly, extending the washing time can reduce the Li backgrounds somewhat to 20–200 mV of ^{7}Li.[7,17,18] However, such a prolonged and aggressive washout procedure increases the time interval between the sample and the bracketing standard, which could damage the smooth accomplishment of the SSB method and thus hinder the effective correction of the instrumental drift.[18] Furthermore, it has been shown that the Li background increases gradually under running conditions,[7] and the "subtracted background" may thus differ from the true background.[19,20] The subtle difference could result in a significant change in the δ^7Li of samples due to the significant difference of Li isotopic compositions between the natural

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samples (δ^7Li = $-10\permil$ to $50\permil$)[21] and the backgrounds (δ^7Li = $-200\permil$ to $-450\permil$).[7,11]

Here, we describe a novel method for reducing the Li background and memory effect. The Li background can be reduced by a factor of 15–70 compared to the conventional method. Furthermore, it was found that the effects induced by the mismatch of acid and Li concentrations between the samples and standards were truly caused by the high Li instrumental background and memory effect of Li. With such low Li background achieved, a method without strict matrix-matching was developed for the accurate, precise and efficient determination of Li isotopic ratios in geological samples. To verify the robustness of the method, eight standards encompassing a wide range of matrices and Li concentrations were analyzed.

Experimental

Instrumentation

Experiments were conducted on a double focusing MC-ICP-MS (Neptune *Plus*, Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, the China University of Geosciences, Wuhan. The Neptune *Plus* is equipped with seven ion counters and nine Faraday cups, and all Faraday cups are equipped with 10^{11} Ω resistors. The distance between the two farthest cups (L4 and H4) equaled a relative mass dispersion of $\sim$17%,[9] which was theoretically capable of simultaneous measurements of ^{6}Li and ^{7}Li ($\sim$16.7% mass difference). However, the two ion counters on the corresponding cups in our instrument impede it; thus, zoom optics were applied to make the simultaneous analysis of ^{6}Li and ^{7}Li feasible. Amplifier rotation was applied to correct any gain calibration errors and improve the external precision, according to Weyer and Schwieters[22] and Chu *et al.*[23] Baseline and gain were performed every analytical day. The sample solution was introduced using the standard introduction system (low-flow PFA nebulizer ($\sim$50 μL min^{-1}) and quartz glass spray chamber) coupled with an autosampler (ASX-112FR, Cetac Technologies, Omaha, Nebraska, USA). With the introduction system, the newly designed X skimmer cone and Jet sample cone, a mean ^{7}Li signal of about 65–80 V (650–800 pA)

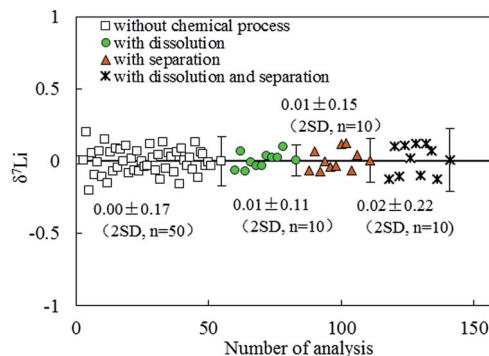**Fig. 1** Measured δ^7Li values of the L-SVEC solution without any chemical process, only with dissolution, only with separation, and with dissolution and separation. The error bars represent two standard deviations of the measurements.

per μg g^{-1} Li was routinely obtained. The detailed operating parameters are listed in Table 1.

Instrumental stability is the key to obtain accurate isotopic ratios using the SSB method. In our experiment, the ^{7}Li/^{6}Li of L-SVEC varied between 14.64 and 15.12 with a mass bias of approximately 20.3–24.2% compared with the certified Li ratios (12.17 (ref. 24)). The variation in the mass discrimination over $\sim$10 min was better than 0.01$\permil$. Additionally, the data of the L-SVEC solution analyzed over 3 months demonstrate that the long reproducibility of the instrument is better than 0.17$\permil$ (2SD, $n = 50$) over this time period (Fig. 1). The mass fractionation of Li caused by dissolution or/and separation was also evaluated systematically (Fig. 1). To ensure the data quality, the sample should be re-analyzed if the difference of ^{7}Li/^{6}Li in the two bracketing standards is larger than 2$\permil$.[10]

An analytical sequence (blank, L-SVEC, blank, sample 1, blank, L-SVEC, blank, sample 2, blank, *etc.*) was used. It is necessary to measure the "on peak" background before and after every sample and standard, because the background is too high (30–110 mV, ^{7}Li) to neglect. The high background is largely formed in the instrument, because the backgrounds obtained during the column separation (the other main source of the Li background) were assumed to be insignificant (35.8 $\pm$ 13.2 pg, $n = 8$). Moreover, the "mass spectrometer background" was never completely removed but increased gradually under normal running conditions.

Reagents and solutions

Ultrapure water (18.2 MΩ cm^{-1}) was acquired using a Milli-Q Element system (Millipore, Bedford, MA, USA). Commercially available nitric acid and hydrofluoric acid were further purified twice using a DST-1000 acid purification system (Savillex, Eden Prairie, USA), and hydrochloric acid (HCl) was prepared by dilution of Suprapur® grade hydrochloric acid (Merck KGaA, Darmstadt, Germany) with deionized water. Methanol (CH$_3$OH, 98% metal basis) was purchased from Sigma-Aldrich and purified using a 120 mL PFA sub-boiling system (Savillex, Eden Prairie, MN, USA), which consists of two 120 mL PFA bottles connected at right angles by a threaded PFA block. Methanol

Table 1 Operating parameters of MC-ICP-MS for Li isotopic analysis

Instrument	Neptune *plus*	
Mass resolution	Low ($\sim$400)	
RF power	1254 W	
Guard electrode	On	
Cool gas	16 L min^{-1}	
Auxiliary gas	0.84 L min^{-1}	
Sample gas	0.889 L min^{-1}	
Integration time	4.194 s	
Cycles/blocks	5 cycles/6 blocks	
Cones	Jet sampler cone + X skimmer cone	
Zoom optics	Focus quad: -4 V; dispersion quad: 17.6 V	
Sensitivity	65–80 V for ^{7}Li at 1 μg g^{-1}	
Background (2% HNO$_3$)	Without NaCl	30–110 mV
	With NaCl	1.5–2 mV

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Table 2 Sample digestion scheme

Step	Operation
Step 1	Powdered samples were weighed in 7 mL Teflon beakers. 1 mL HNO_3 + 3 mL HF were added. The tightly capped beaker was placed in an ultrasonic bath for 10 minutes and then was heated at 150 °C on a plate for 24 h
Step 2	The beaker was opened and the solution was evaporated at ∼120 °C to dryness, which is refluxed with 2.5 mL concentrated HNO_3. Then the beaker was heated at 150 °C for 12 h
Step 3	The residue was re-dissolved by adding 3 mL concentrated HCl and capped and heated at ∼120 °C for 12 h
Step 4	The final solution was evaporated to dryness, then diluted by 1 mL 0.67 mol L^{-1} HNO_3/30% methanol (v/v) prior to column purification

Table 3 Column separation procedure for Li

Separation steps[a]	Volume of elute and acid type	Volume/mL
Conditioning	0.67 mol L^{-1} HNO_3/30% methanol (v/v)	2
Sample loading	0.67 mol L^{-1} HNO_3/30% methanol (v/v)	1
Matrix rinsing	1 mol L^{-1} HNO_3/80% methanol (v/v)	4
Li elution	1 mol L^{-1} HNO_3/80% methanol (v/v)	11 (5–15)
Column cleaning	6 mol L^{-1} HCl	10
	H_2O	5
	3 mol L^{-1} HCl	5
	H_2O	5

[a] The whole procedure takes about 7–8 hours.

Fig. 2 Elution profiles of Li and Na of AGV-2, GSP-2 and BHVO-2.

was placed in the feed bottle and heated using two heating lamps to allow the methanol to evaporate slowly, with the vapor condensing in the water-cooled collecting bottle. Approximately 50 g methanol (placed in the feed bottle) were purified to 25 g (generally, 10 hours were needed). All the acids or acid–methanol mixtures used for column elution were prepared by gravimetric dilution and titrated using analytical-reagent grade Na_2CO_3 to determine the exact strength. 5 g NaCl powder (≥99.99% metals basis, Sigma-Aldrich) was weighed and diluted using deionized water to obtain 5% NaCl solution.

The reference material L-SVEC (Li_2CO_3, powder) was purchased from the National Institute of Standards and Technology (NIST). About 50 mg of L-SVEC was weighed and dissolved in 2 mL of concentrated HNO_3, evaporated to dryness and diluted in 500 mL 2% HNO_3 to obtain a 20 µg g^{-1} stock solution. The L-SVEC standard solution used in the analysis can be further diluted by 2% HNO_3. IRMM-016 lithium carbonate is also available as a fine powder from the Institute for Reference Materials and Measurements (IRMM).

A series of geological reference materials and a seawater standard were used as test samples for Li isotope ratio measurements, including AGV-1 (andesite), AGV-2 (andesite), BHVO-2 (basalt), GSP-2 (granodiorite) and RGM-2 (rhyolite) from United States Geological Survey (USGS); JG-2 (granite) from the Geological Survey of Japan (GSJ) and NASS-6 seawater obtained from National Research Council Canada (NRCC).

All acids and standards were prepared under class 100 clean laboratory conditions to minimize the lithium blank- and cross-contamination.

Sample preparation and analysis

∼50 mg of rock powders were digested by mixing 3 mL HF + 1 mL HNO_3 in Teflon vessels on a hotplate (∼120 °C), followed by the replenishment of the dried residue with 3 mL of HCl until the solutions were clear[8,13,16,17,25–27] (Table 2); $HClO_4$ is needed when insoluble fluorides are present in the final sample solution.[10,14,28] ∼3 g seawater samples were evaporated on a hotplate

at 90 °C until dry, and 2 mL of concentrated HNO_3 was added to remove the organic material.[8] After evaporation, the samples were re-dissolved in 1 mL of 0.67 mol L^{-1} HNO_3/30% methanol (v/v) prior to purification.

The purification of Li was achieved using a one-step column separation method modified by Huang et al.[8] and Magna et al.,[16] whereas the AG50W-X8 cation exchange resin (100–200 mesh, 2 mL) and a boron-silicate glass column (0.6 cm ID × 21.5 cm bed height, 10 mL reservoir) were used. The resin was washed by leaching sequentially with 0.15 mol L^{-1} HF,[29] 6 mol L^{-1} HCl, 3 mol L^{-1} HCl, and 1 mol L^{-1} HNO_3 in 80% v/v CH_3OH (ref. 7) and ultrapure H_2O before being loaded into the glass columns. The columns were further cleaned with 6 mol L^{-1} HCl, 3 mol L^{-1} HCl and ultrapure H_2O alternatively as detailed in Table 3 and then conditioned with 2 mL of 0.67 mol L^{-1} HNO_3 in 30% v/v CH_3OH. The details of the separation procedure are listed in Table 3. The columns were routinely calibrated by applying a series of silicate standards (∼50 mg AGV-2, GSP-2 and BHVO-2) (Fig. 2). All eluents (1 mol L^{-1} HNO_3 in 80% v/v methanol, 18 mL) were continuously collected every 1 mL and the recovery (Li recovery (%) = [Li in the selected elution interval]/[Li in the

solution before column separation] × 100%)[10] was 101.5 ± 1.5% (2SD, n = 5) using 11 (5–15) mL eluents. The collected solution was dried and then diluted to 4 mL of 2% HNO_3 prior to MC-ICP-MS measurements.

Results and discussion

A novel method for reducing the Li background and memory effect

The Li instrumental background and memory effect of Li are much more troublesome for the accurate and precise determination of Li isotopic ratios using the SSB method by MC-ICP-MS.[7,8,11,15] The Li instrumental background was not only difficult to be washed out (1 mV h^{-1}) but also was gradually increasing under the running conditions.[7] Consequently, although 3–5 minutes of washing time was used,[9,10,17,30] it was impossible to remove the Li background completely. In order to reduce the background as low as possible in the MC-ICP-MS analyses, specific washing strategies were applied for these elements (e.g., Li, B, Pb and Hg) with serious memory effects.[20,31–39] For example, Pistiner and Henderson[40] observed that the memory effect of Li can be significantly decreased with the addition of N_2 into the Ar-plasma.

During preliminary experiments, diluted seawater was introduced into the MC-ICP-MS for Li ratio measurements followed by 2% HNO_3 for rinsing. Unexpectedly, it was noted that the Li background was significantly reduced in 2% HNO_3 after seawater, suggesting that the seawater matrix, most likely NaCl, is responsible for the observed Li background reduction. Thus, 5% NaCl solution was investigated in an attempt to reduce the Li background. At the start of the analytical sequence, a 5% NaCl solution was introduced into ICP for 1 min. As shown in Fig. 3a, the Li background (^{7}Li) did not increase, but it decreased to 1.5–2 mV from 30–110 mV with 2% HNO_3 rinsing within a few minutes. The intensity of the "mass spectrometer background" was reduced from 1.69% to 0.02% of the sample intensity. Meanwhile, Li signal intensity in the samples shows no obvious change before and after the uptake of the NaCl solution (Fig. 3a). The low Li background can be maintained for 3 hours, wherein approximately 20 samples can be measured by

the SSB method (Fig. 3b). Most importantly, in this 3-hour period, low and constant Li background can be obtained using only 2% HNO_3 for rinsing for 1.5 min. With this new washing method, the background (30–110 mV, ^{7}Li) obtained by the common procedure (washed for 3–5 minutes with diluted HNO_3) is lowered by a factor of 15–70. This low Li background can be achieved and maintained by introducing 5% NaCl solution into the ICP for 1 min every 3 hours. Na and Li belong to the same family in the periodic table of elements, and thus have similar chemical properties. It is speculated that a thin "Na coating film" may have formed in the inlet system by introducing a concentrated NaCl solution, which could prevent/alleviate the deposition of Li. However, the exact mechanisms for this effect require further investigation which is beyond the scope of this study.

Mismatching effects of acid and Li concentrations: matrix effect or memory effect?

The matching of analyte and acid concentrations between the sample and the standard is critical when applying the SSB method for the accurate and precise determination of non-traditional stable isotopes, such as Cu,[41] Zn,[42] Mg[43–45] and Fe.[46] Li is no exception;[7,11,13,16,47] Bryant et al.,[12] found that samples with higher acid concentrations have lower δ^7Li values, and a larger difference (~6‰) in the δ^7Li is observed when the HNO_3 concentration ranges from 0.28 mol L^{-1} to 0.75 mol L^{-1} regardless of the power of ICP used. In addition to the acid concentration, the mismatch of the Li concentration between the sample and the standard can lead to serious mass discrimination as well.[11,12] All of these mismatching effects can be regarded as special cases of matrix effects.[48] However, Bryant et al.,[12] noted that the impact of Li concentration mismatch can be alleviated by reducing baseline interference. Magna et al.,[16] speculated that the mass bias effect of the Li isotopes is concentration independent, instead, the true reason is that the insufficient time elapses to wash out Li between the standard and sample during the measurements.

To investigate the mechanism of the mass bias effects caused by the mismatch of the Li and acid concentrations between the sample and standard, experiments were conducted
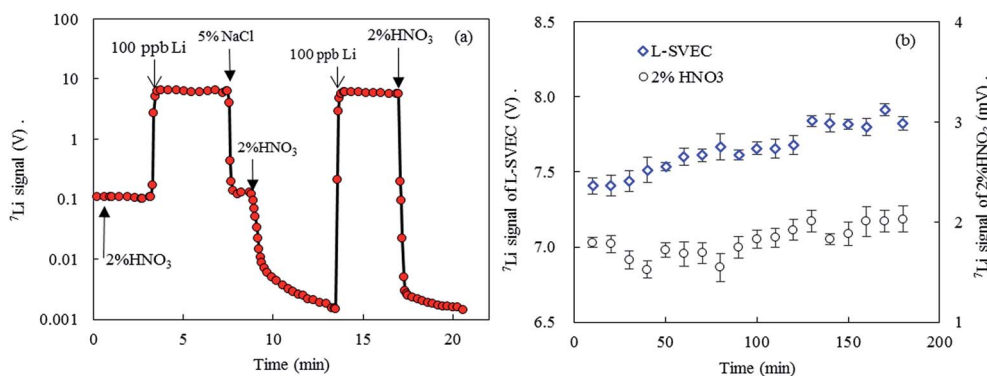

Fig. 3 (a) Variations in Li background upon washing with 2% HNO_3 after introducing a 5% NaCl solution for 1 minute. (b) Variations in the ^{7}Li signals of the L-SVEC solution (100 ng g^{-1} Li) and of 2% HNO_3 over 3 hours after washing with a 5% NaCl solution once. The error bars represent two standard deviations of the measurements.
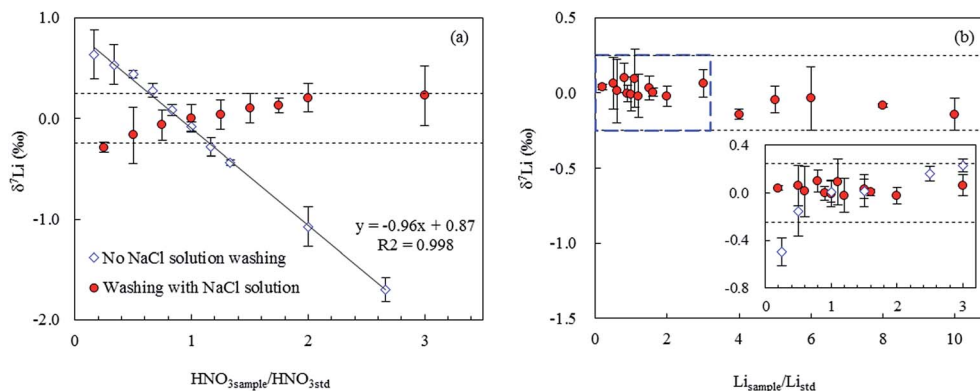
Fig. 4 Variations in the δ^7Li in the L-SVEC solutions as a function of increasing HNO_3 (a) and Li concentrations (b) with and without washing using the 5% NaCl solution.

under two conditions: (1) washing using NaCl solution and (2) no NaCl washing. For the "acid-related" mass bias, nine 100 ng g^{-1} L-SVEC solutions prepared in different HNO_3 concentrations (mass fraction) (0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4% and 6%) were analyzed and bracketed by the 100 ng g^{-1} L-SVEC standard in 2% HNO_3. L-SVEC solutions with Li concentrations ranging from 10 ng g^{-1} to 500 ng g^{-1} were analyzed to test the effects of the Li concentrations, and the solution with a Li concentration of 50 ng g^{-1} was used as the standard.

Washing using NaCl solution. Unlike the previous results,[12] no significant mass bias of Li was found with the varied acid concentrations ranging from 0.5% to 6% when the background was significantly reduced to 1.5–2 mV by the injection of the NaCl solution (Fig. 4a). Additionally, the Li concentration-related mass bias and a more negative δ^7Li value[8,11,12] for the instrumental background were not observed within analytical uncertainty, even though the Li concentration ratios of the samples and the standards ranged from 0.2 to 10 (Fig. 4b).

No NaCl washing. When the NaCl solution was not applied, the relationship between the δ^7Li values and the acid concentrations was similar to that reported by Bryant et al.,[12] whereas the δ^7Li varied significantly even when the acid concentration in the samples slightly differed from that in the standard. Moreover, the δ^7Li values correlate linearly with the ratios of $HNO_{3sample}$/HNO_{3std} (Fig. 4a), which may represent a mixing trend of the sample and the background. A significant mass bias introduced by the mismatch of the Li concentration between the sample and the standard was observed (Fig. 4b), similar to that reported by Rosner et al.,[11] and Huang et al.[8]

Overall, the mass bias that was previously believed to be due to the mismatch of the acid and Li concentrations was not observed when the background was reduced to a very low level. Our experiments confirm that the instrumental background with a more negative δ^7Li value was actually due to a memory effect and high background. These observations confirm that a method without strict matrix-matching can be employed for the accurate and precise determination of Li isotopic ratios if the Li high background and memory effect are efficiently eliminated.

Accurate and precise determination of Li isotope ratios in natural materials without strict matrix-matching

By applying the above novel washing method, the Li isotopic ratios of natural materials can be obtained without strict matrix-matching. In order to test the robustness of the method, six rock reference materials ranging from andesite to basalt (AGV-1, AGV-2, BHVO-2, GSP-2, JG-2 and RGM-2), one seawater (NASS-6) material and one lithium carbonate (IRMM-016) material were analyzed. The Li contents of these samples are varied significantly, so that the ultimate Li concentrations are different when the weight of all the rock samples is 50 mg (3 g for the seawater) and the final volume of digest is 4 mL (Table 4). The Li concentration of the bracketing L-SVEC standard is kept constant ~100 ng g^{-1}. Although the Li concentration of samples is not the same as that of the standard, the results obtained agree well with the reported values. External precision of the method is better than 0.25‰ (2SD) (Table 4).

The comparison of data precision and accuracy amongst different techniques is not straightforward because the results are highly dependent on various parameters, but a rough comparison with the previously reported data is needed to evaluate the accuracy of the newly developed method. The measured δ^7Li value of the basalt, BHVO-2 (4.50 ± 0.24‰, 2SD, $n = 4$), agrees well with all the previous studies within the uncertainties (4.1–5.5‰).[1,7,8,14,16,25,49–65] And the measured value is similar to the weighted average of all the reported values obtained by TIMS, ICP-MS and MC-ICP-MS (4.59 ± 0.11‰), which may be the best preferred reference data of BHVO-2. The measured δ^7Li values of granite, JG-2 (0.15 ± 0.15‰, 2SD, $n = 5$), and granodiorite, GSP-2 (−0.78 ± 0.25‰, 2SD, $n = 5$), are consistent with the published data within the uncertainty.[7,28,40,49,50,56,66–68] Granites generally contain refractory accessory minerals (e.g., zircon and rutile) that are difficult to be digested using the open vessel acid digestion method.[69,70] It is thus difficult to obtain the complete recovery of those trace elements highly enriched in the refractory minerals (e.g., Zr and Hf in zircon). However, Li is not enriched in these refractory minerals, and thus the influence of the digestion method on the recovery of Li is generally very limited. However, the bomb method[71] should be applied to reach the complete dissolution

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Table 4 δ^7Li values of the standards used in this experiment

Table 4 (Contd.)

Sample	δ^7Li (mean ± 2SD‰)		
	This work	Reported	Ref.
IRMM-016, Li-carbonate, Li: 100 ng g^{-1}	0.00 ± 0.16 ($n = 10$)	0.14 ± 0.20	50
		−0.10 ± 0.20	76
		0.05 ± 0.12	8
		0.18 ± 0.38	77
		0.15	51
		−0.5 ± 1.3*	50
		−0.5 ± 0.9	78
		−0.2 ± 0.5	79
		−0.8 ± 0.4†	80
AGV-1, andesite, Li: 138 ng g^{-1}	5.50 ± 0.25 ($n = 6$)	4.60 ± 0.70	78
		6.74 ± 0.35	16
AGV-2, andesite, Li: 134 ng g^{-1}	6.85 ± 0.20 ($n = 5$)	7.92 ± 0.34	14
		7.98 ± 0.19	8
		7.94 ± 0.64	16
		5.68 ± 1.04	72
		8.14 ± 0.93	58
GSP-2, granodiorite, Li: 450 ng g^{-1}	−0.78 ± 0.25 ($n = 5$)	−0.74 ± 0.2	77
		−0.86 ± 0.24	77
RGM-2, rhyolite, Li: 738 ng g^{-1}	2.75 ± 0.15 ($n = 5$)	RGM-1	74
		2.59 ± 0.15	
JG-2, granite, Li: 537 ng g^{-1}	0.15 ± 0.15 ($n = 5$)	0.20 ± 0.15	7
		0.10 ± 0.80	49
		−0.10 ± 0.80	49
		0.07 ± 0.22	56
		−0.22 ± 0.13	56
		0.19 ± 0.20	66
		0.2 ± 0.2	50
		−0.6 ± 0.8*	50
		0.3 ± 0.62	81
		−0.4 ± 0.2*	28
		−0.7 ± 0.8	40
		0.3 ± 1.6†	68
		0.2 ± 0.1	68
		0.07 ± 0.22	56
		−0.22 ± 0.13	56
		−0.21 ± 0.54	56
		−0.27 ± 0.14	56
		−0.31 ± 0.22	67
		0.03 ± 0.48†	67
Weighted average ± 1SD		−0.02 ± 0.11	
BHVO-2, basalt, Li: 60 ng g^{-1}	4.50 ± 0.24 ($n = 4$)	4.4 ± 0.8	49
		4.1 ± 0.8	49
		4.2 ± 0.8	49
		4.7 ± 0.8	49
		4.9 ± 0.8	49
		4.5	51
		4.29 ± 0.46	25
		4.55 ± 0.29	16
		4.7 ± 0.2	50
		4.70 ± 0.22	7
		4.63 ± 0.16	8
		4.2 ± 0.5	65
		4.48 ± 0.31	53
		4.52 ± 0.18	59
		4.43 ± 0.58	58
		4.5 ± 0.27	57
		4.58 ± 0.32	56
		4.8 ± 0.2	60
		4.9 ± 0.8*	63
		4.7 ± 0.2	64
		4.1 ± 0.2	55
		4.58 ± 0.58	54
		4.9 ± 0.3†	52
		4.46 ± 0.37	14
		4.3 ± 1.2	62
		4 ± 0.9	61
		4.7 ± 0.2	61
		5.5 ± 0.7†	1
Weighted average ± 1SD		4.59 ± 0.11	
NASS-6, seawater, Li: 112 ng g^{-1}	30.87 ± 0.15 ($n = 15$)	30.73 ± 0.15	8
		30.64 ± 0.44	11
		29.30 ± 0.92	10
		31.8 ± 1.9	13
		29.97 ± 0.72*	29
		31.1 ± 0.2	7
		31.14 ± 0.2	50
		31.2 ± 0.3	82
		32.0 ± 0.2	12
		30.4 ± 0.9	29
		30.55 ± 0.45	14
Weighted average ± 1SD		31.07 ± 0.33	

The Li concentrations are the ultimate concentrations of Li in the solutions. Except for these data marked by † (ICP-MS) and * (TIMS), the reported data from the literature were analyzed by MC-ICP-MS.

of granites in case any Li-rich refractory accessory minerals are present. Analyses of andesite, AGV-1 and AGV-2 collected from the same location, show that AGV-2 has a much higher δ^7Li value (6.85 ± 0.20‰, 2SD, $n = 5$) than AGV-1 (5.50 ± 0.25‰, 2SD, $n = 6$). The obtained δ^7Li value of AGV-2 is similar to the reported value of 5.68 ± 1.04‰ by Tian et al.,[72] but it is much lower than other reported values (7.92‰ to 8.14‰).[8,14,16,58] It is thus inferred that AGV-2 may be heterogeneous in terms of Li isotopic composition, as suggested by Su et al.[73] The δ^7Li value of RGM-2 (2.75 ± 0.15‰, 2SD, $n = 5$), first reported in this work, is consistent with the value of RGM-1 (collected from the same location as RGM-2) within the uncertainty reported by Schuessler et al.[74] The obtained δ^7Li value of IRMM-016 (0.00 ± 0.16‰, 2SD, $n = 10$) in our experiments is identical to that of L-SVEC.[16] The new reference seawater sample, NASS-6, yields a δ^7Li value of 30.87 ± 0.15‰ (2SD, $n = 15$), agreeing well with the recommended values of the reference seawater NASS-5 from the Atlantic (30.55–30.73),[8,11,14] seawater from the Pacific (29.3–31.8)[10,13,29] and the weighted average of all the reported values (31.07 ± 0.33‰), which confirms that the Li isotopic composition of seawater is homogeneous on a large scale.[11,75]

Generally, in order to minimize errors in background correction, the Li concentration of samples should be the same as that of standards. However, with the low and constant Li background achieved with NaCl washing, there is no need to spend time in sample preparation for matching the Li concentration. In addition, the mass bias effects of the acid concentration mismatch can be eliminated with the proposed new NaCl washing method (Fig. 4a).

Conclusions

A 5% NaCl solution can be used as an agent to reduce the Li instrumental background and memory effect of Li. With the NaCl washing method, the washing efficiency was increased 2–3 times and the Li background was reduced by a factor of 15–70. With an efficiently reduced Li background, the mass bias that was previously believed to be caused by the mismatching acid and Li concentrations between the sample and standard was not observed. The results obtained in this study confirm that both types of concentration mismatch-related matrix effects are actually due to the high Li instrumental background and memory effect of Li. Based on this conclusion, the analyses of 8 reference materials, including rocks, seawater and Li-carbonate, give δ^7Li values that agree well with the recommended values without the strict concentration-matching. The method can save time in sample preparation for matching and reduce the risk of deteriorating the accuracy and precision of Li isotopic ratios. Moreover, the low Li instrumental background and negligible memory effect can pave the way for the accurate and precise measurement of low-Li samples.

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