

Purification of High Aluminum Content Samples for Rapid and Precise Analysis of Lithium Isotopes

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ABSTRACT: The analysis of lithium isotopes in high-aluminum content samples was accompanied by significant tailing of Al on Li using the traditional single-column method regardless of using single HCl or HNO₃ as eluent. This hindered the precise determination of Li isotopes and made one-step column chromatographic separation of Li in silicate rocks challenging. Additional column procedures may be required to separate Li from Al in high Al samples, which would be time-consuming and result in reagent waste. In this study, the usage of a 10 mL 0.2 mol L⁻¹ HF and 0.5 mol L⁻¹ HCl mixed eluent significantly reduced the Al tailing to less than 1% of that observed with the traditional method. The proposed purification procedure is applicable to a wide range of geological samples or minerals (*e.g.*, silicates, seawater, sediments, and feldspars). Additionally, the matrix effect of Al and the Li concentration effect were investigated for accurate Li isotope analysis. The concentration effect, which was proved mainly led by the inappropriate treatment of the baseline. The real concentration effect yielded only a bias of 0.2‰ if normalized the solution of 20 ng g⁻¹ Li with that of 140 ng g⁻¹. In accounting for this, Li isotopes can now be analyzed quite accurately at variable concentrations during non-strictly concentration-matched conditions. The long-term external precision of δ⁷Li based on the international standard LSVEC was approximately ±0.2‰ (2SD), making it suitable for geological sample analyses. The proposed method was confirmed through the analysis of BCR-2, BHVO-2, AGV-2, BIR-1a, RGM-2, JF-1, SCo-1, GSP-2, GSR-6, and GSR-8. All the results agreed with previously published values. Besides, two in-house Li isotope solution standards CAGS-Li-P (6.25±0.25‰) and CAGS-Li-N (-15.02±0.18‰) were developed and routinely analyzed to monitor the instrumental mass bias.

INTRODUCTION

The lightest metal, lithium has two stable isotopes, ⁶Li and ⁷Li. The delta value, δ⁷Li (‰), is commonly used to express their difference, defined as:¹⁻⁴ $\delta^7\text{Li} (\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{standard}} - 1] \times 1000$. Due to the relatively large mass difference between ⁷Li and ⁶Li, Li isotopes fractionate in many geological processes, such as chemical weathering,^{5,6} magmatic differentiation,⁷ hydrothermal alteration,⁸ subduction processes,⁹ and crust-mantle interactions.¹⁰

Initial advancements in this field were made using thermal ionization mass spectrometry (TIMS).¹¹⁻¹⁶ However, due to the advantages of low sample consumption and high analysis precision of the multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), the available data on Li isotopes in diverse geological samples has substantially increased.^{4,17} Recently, Juzer *et al.* proposed using a single collector triple quadrupole ICP-MS (QQQ-ICP-MS) to measure δ⁷Li. This method also achieved high precision (~0.6‰, 2σ) and required sub-nanogram sample consumption.¹⁸

Fig. 1 Plot of the annual number of papers relevant to Li isotopes published between 1998 to 2022 from Web of Science (using keywords “Li isotopes” in the field of “Earth and Planetary Sciences”), and time spent for elution.

Table 1. Operating parameters of MC-ICP-MS (Nu Plasma II) for Li isotopic analyses

Mass Spectrometer set-up	
RF Forward power	1300W
RF Reflected power	1W
Cooling gas (Ar)	13 L min ⁻¹
Auxiliary gas (Ar)	1 L min ⁻¹
Mix gas (Ar)	1.2 L min ⁻¹
Skimmer cones	Ni dry cone
Sample uptake rate	~40 µL min ⁻¹
Integration time	3 s
Blocks	1
Cycles	100
Wash-out time	170 s
Cup configurations	
H9	⁷ Li ⁺
L6	⁶ Li ⁺

The ⁷Li/⁶Li ratios were typically determined using a sample-standard bracketing (SSB) method with MC-ICP-MS^{19–23} to correct the instrumental mass bias, which was also widely used for measuring the ratios of many non-traditional stable isotopes (e.g., B, Mg, Fe, Cu).³ Nevertheless, the SSB approach requires element concentrations in the purified samples and standards to be matched to achieve precise and accurate determination of isotope ratios.^{11,14,15,23–25} Interestingly, Lin *et al.* suggested that the analysis of Li isotopes by a 5% NaCl washing method obviates the need for strict matrix-matching.³

There has been a 300% increase in publications related to lithium isotopes in geosciences over the past decade, and the steps and time spent from sample preparation to mass spectrometer have reduced significantly in the last 20 years (Fig. 1).^{1,3,4,11,15,16,18,23,24,26–35} However, interferences of the matrix elements on Li in MC-ICP-MS, particularly Al, may cause significant instrumental mass bias.^{1,3,6,37} Thus, it is vital to completely separate Li from the matrix elements.^{12,24}

The aluminum would be eluted prior to Li off Bio Rad® AG 50W-X12 (100–200 mesh) cation exchange resin, however,

sometimes Li elution was accompanied by Al tailing when dealing with high-Al samples. Previous studies employed single-column methods with a large height-to-diameter ratio^{3,11,14,15,17,24,26–28,31,32} or multiple columns to address Al tailing.^{1,3,4,11,15,16,23,24,26–34} Nevertheless, considerable time and steps were required to purify samples in these methods. The single-step method generally requires a large volume of cation-exchange resin (e.g., AG50W-X8 or -X12) and acid,^{16,17,26,33,38–40} increasing the risk of contamination. The multi-step method is extremely time-consuming due to the requirement for evaporation and redissolution during the column separation steps,^{16,28} barring the methods modified by Zhu *et al.*⁴ and Choi *et al.*¹⁹ Zhu *et al.*⁴¹ had achieved great success in removing Al and High-Field-Strength Elements (HFSEs) by adding 0.3 mol L⁻¹ HF to the eluent, and they had a relatively low elution volume.⁴¹ However, they need to use 0.2 mol L⁻¹ HCl and 0.73 mol L⁻¹ HCl in the elution process, and the total cation quantities loaded is relatively smaller (7–70 mg rock powder) than that of this study (110–160 mg). More importantly, the peaks of Li, Na and Ca cannot be separated by the single column for carbonate, so they developed a two-column separation method for it. In this study, we explored a novel method to remove the influence of Al tailing on the test within the premise of ensuring accuracy and single-column procedure. Compared with the less effective single-long-column methods for high Al samples, where 0.5 mol L⁻¹ HCl was used as eluent, the proposed method,^{4,17,26,28,29,33,34} which employed a mixed acid (0.5 mol L⁻¹ HCl + 0.2 mol L⁻¹ HF),^{32,41} successfully separated lithium from matrix elements and HFSEs for various geological reference materials (e.g., BCR-2, BHVO-2, AGV-2, BIR-1a, RGM-2, JF-1, SCo-1, GSP-2, GSR-6, and GSR-8). The accuracy and precision of the Li isotope data with this purification procedure were evaluated with the measurements of well-studied geological reference materials, whose δ⁷Li values have been reported by international laboratories.

EXPERIMENTAL

Instrumentation. All experiments were conducted on a double-focusing MC-ICP-MS (Nu Plasma II, Nu Instruments, UK) and an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer Q-ICP-MS (Agilent Company, USA) at the Ministry of Natural Resources Key Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences. Sample and standard solutions were aspirated through a Desolvating Nebulizer System (DSN-100) (“dry plasma” mode) due to its advantages of low sample concentration and high signal.⁴² After careful adjustment and optimization of the instrument parameters, the measured aspiration rate of the nebulizer is 40±5 µL min⁻¹. The Nu Plasma II was equipped with six ion counters and sixteen Faraday cups. The ⁶Li and ⁷Li were analyzed with the two farthest Faraday cups [L6 and H9],^{15,43} respectively. Zoom optics were

Table 2. Column separation procedure for Li

Separation steps	Volume of elute and acid type		Volume (mL)
	Traditional	This study	
Conditioning	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	10 (2 mL×5)
Sample loading	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	1
Matrix rinsing	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl + 0.2 mol L ⁻¹ HF	10 (2 mL×5)
	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	9 (3 mL×3)
Check Li	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	1 mL
Li elution	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	20 (2 mL×10)
Check Li	0.5 mol L ⁻¹ HCl	0.5 mol L ⁻¹ HCl	1 mL
	6 mol L ⁻¹ HCl	6 mol L ⁻¹ HCl	12
	Milli-Q water	Milli-Q water	12
	6 mol L ⁻¹ HCl	6 mol L ⁻¹ HCl	12
	Milli-Q water	Milli-Q water	12
Column cleaning	6 mol L ⁻¹ HCl	6 mol L ⁻¹ HCl	12
	Milli-Q water	Milli-Q water	12
	6 mol L ⁻¹ HCl	6 mol L ⁻¹ HCl	12
	Milli-Q water	Milli-Q water	12

applied to ensure simultaneous collection of Li isotopes on the Faraday cups. All Faraday cups were equipped with 10¹¹Ω resistors. Detailed operating parameters are listed in the Table 1.

Reagents and solutions. All acids, samples, and standards were prepared with 18.2MΩ cm⁻¹ Milli-Q water (Millipore, Bedford, MA, USA). Concentrated HCl, HNO₃, and HF (analytical grade, Beijing Chemical Works, Beijing, China) were purified twice for HCl and once for HNO₃ and HF by sub-boiling distillation using DST-1000 acid purification systems (Savillex, Eden Prairie, USA). An analytical sequence (LSVEC, sample-1, LSVEC, sample-2, LSVEC, etc.) was used. The reference material LSVEC (Li₂CO₃ powder)⁴⁴ was obtained from the National Institute of Standards and Technology (NIST). Approximately 50 mg of powder was weighed, dissolved in 1 mL concentrated HNO₃, evaporated to dryness, and diluted in 500 mL 2% HNO₃ to produce a 20 ug g⁻¹ (Li) stock solution. The LSVEC standard solution used in the analysis was further diluted with 2% HNO₃ to 150 ng g⁻¹.

A variety of geological reference materials (GRMs) were chosen to evaluate the accuracy and precision of the Li isotopes measurement. These included AGV-2 (andesite), BCR-2 (basalt), BHVO-2 (basalt), BIR-1a (basalt), RGM-2 (rhyolite), JF-1 (feldspar), SCo-1 (shale), and GSP-2 (granodiorite) from the United States Geological Survey (USGS), GBW07108 (GSR-6, argillaceous limestone), GBW07108 (GSR-8, trachyte) GRMs from National Research Centre of Geoanalysis (NRCG) of China, and Atlantic Ocean seawater from the International Association for the Physical Sciences of the Oceans (IAPSO and OSIL). Two in-house standard Li solutions (CAGS-Li-P, CAGS-Li-N) were prepared and analyzed. Instrumental stability is crucial for obtaining accurate isotopic ratios using the SSB method. In this study, we alternately measured CAGS-Li-P, CAGS-Li-N, and LSVEC to evaluate the stability of the instrument at the beginning, middle, and end of each sequence. In this study, a column filled with Bio Rad® AG 50W-X12(100–200 mesh) cation exchange resin was used. The column dimensions were 8 mm inner diameter

and 12.5 cm long, with a resin volume of 7 mL (2.1 meq. mL⁻¹) for the columns, and the capacity was 14.7 meq. All solutions and reference materials were prepared in a Class-100 clean laboratory (Ministry of Natural Resources Key Laboratory of Isotope Geology) to minimize the blank contamination.

Sample preparation. For all geological reference materials (GRMs), 110 mg powders were digested in a mixture of 3 mL concentrated HF + 1mL concentrated HNO₃.^{4,45-50} Except for the BHVO-2, AGV-2 and BIR-1a, 160 mg were digested in Teflon beakers. The beakers were then boiled (120°C) for at least 24 h, and then evaporate to dryness. Subsequently, it was refluxed with aqua regia, boiled at 120°C overnight, and evaporated again. The dry residues were re-dissolved in 0.5 mol L⁻¹ HCl. The Li concentration of the digested sample was determined by an Agilent 7900 Q-ICP-MS before chemical separation. The sample was then diluted or concentrated to 150 ng g⁻¹ Li in 0.5 mol L⁻¹ HCl prior to the column purification.

Lithium is well mixed in the open ocean system with uniform concentration (174 ng g⁻¹ Li)⁴ and isotopic composition. Approximate 1.3mL of the seawater (OSIL Atlantic seawater and IAPSO standard seawater) standard sample was evaporated to dryness, and the residue was dissolved with 1mL of concentrated HNO₃ to remove any organic material. This was followed by the addition of 1mL HCl and further evaporation. The residues were then diluted with 1.5mL 0.5 mol L⁻¹ HCl, and a solution of 150 ng g⁻¹ Li in 0.5 mol L⁻¹ HCl would be obtained prior to the column purification.

Elution procedure. After a thorough evaluation of traditional methods and detailed optimization of elution parameters, a chemical procedure was established as follows: the column was initially preconditioned with 10 mL of 0.5 mol L⁻¹ HCl. Then, 1 mL of sample solution was loaded into the column. The column was rinsed with 10 mL of mixed acid (0.5 mol L⁻¹ HCl + 0.2 mol L⁻¹ HF) after sample loading. This step significantly reduced the tailing of Al and effectively separated HFSEs (e.g., Zr, Hf, Ta, Ti) for various geological reference materials compared with the traditional single column procedure. The columns were then washed with 9 mL of 0.5 mol L⁻¹ HCl to ensure the complete removal of anions (e.g., Br⁻, I⁻, SO₄²⁻) and HFSEs. Subsequently, 22 mL (1 mL+20 mL+1 mL) of 0.5 mol L⁻¹ HCl was passed through the column to elute Li, the first and the last 1 mL of elution were collected separately to check for any shifts in the Li elution peak. Then, 20 mL of eluent was evaporated to dryness and dissolved in 2% HNO₃ to achieve a concentration of 150 ng g⁻¹ for the MC-ICP-MS measurements. Finally, the washing steps alternated between 12 mL of 6 mol L⁻¹ HCl and 12 mL of Milli-Q water more than six times to fully remove Fe, Ca and REE. These details are listed in the Table 2.

Fig. 2 More than 18,000 Al/Li data of the whole rock. The differentiation of Al and Li are much larger in ultra-mafic, mafic, and acid igneous. (Data were downloaded from the GEOROC database (<https://georoc.eu/>) on 27 February 2023, using the following parameters: Precompiled Files=Rocks).

Fig. 3 $\delta^7\text{Li}$ shifted from pure Li due to the addition of varying amounts of Al. The typical analytical uncertainty of this study is $\pm 0.3\text{‰}$. Isotope measurements from Hu *et al.*³⁷ were performed on a Nu Plasma II under ‘wet’ plasma conditions. Isotope measurements from Li *et al.*¹ were performed on a Nu Plasma 3 under ‘Dry’ plasma conditions. The exact reason why our trend is opposite to the previous studies is not clear now, probably due to the differences of the instrumental parameters or the conditions of the ICP source.

RESULTS AND DISCUSSION

Matrix effect of Al on Li isotope analysis. Due to the limited cation exchange capacity of resin, the high ionic equivalent loaded on the column will decrease the efficiency of cation purification. This problem will not occur in seawater, because the main component H_2O (over 96%) can be removed by evaporation. However, for most silicate samples with high Al/Li (mass ratio between Al and Li in g g^{-1}) ratios (Andesite, Basalt, Basanite, Dacite, Granite, Rhyolite, *etc.*) (Fig. 2 and Fig. S1), if the matrix of Al was not removed sufficiently, the high Al/Li ratios would cause a large bias of Li isotope ratios.³⁷ We collected more than 18,000 Al/Li data of the whole rock (data downloaded from the GEOROC database [<https://georoc.eu/>] on 27 February 2023, using the following parameters: Precompiled Files=Rocks). Si and O can be volatilized after digested with HF. However, large

amounts of Ca, Mg, and Al remained in the solution after digestion, suppressing the purification efficiency of Li. This led to a long tailing of Al, which co-eluted with Li. The Al/Li ratios in the Li eluent ranged between ~ 100 to 2000 after treated by the traditional single column method in this study. According to the results of many experiments, generally the whole rock samples with Al/Li ratios exceeding 1000 would result in a tailing of Al. The matrix elements (Al) presented as the consequence of insufficient purification or imperfect column chemistry schemes, and the Al/Li ratios of these samples would still be exceeding 50 with the traditional single-column purification method.

In this study, we investigated the effects of matrix element Al on Li. These may cause mass biases for the isotopes in sample solutions versus pure standards, posing a particular challenge. Mixing GSB-Li solutions with different concentrations of GSB-Al (*e.g.*, Al/Li=0, 0.2, 0.5, 1, 2, 3, 5, 10, 20, 50) resulted in negative shifts of $\delta^7\text{Li}$, the bias of $\delta^7\text{Li}$ decreased systematically with the increase of Al/Li ratios and became significant when the ratios were greater than 2. The presence of Al with Al/Li ratios from 5 to 50 resulted in a relatively constant bias of over -1‰ $\delta^7\text{Li}$ (Fig. 3). The observed phenomenon was inverse to previous studies, which may cause by the difference of instrumental parameters or difference designs of the ICP source of MC-ICP-MS. We do believe our data including the results in Hu *et al.* and Li *et al.* are objectively existed. This issue remains to be solved in the future.

Cut the tail of Al elution curve. In this study, 1 mL sample was loaded on the resin. The traditional single-column purification procedure led to a long tailing of the Al element and matrix effect. Worse yet, the tailing of Al overlapped with the peak of Li, which posed a challenge for high Al samples. Interestingly, wash the resin after loading and before the collection of Li with a mixed acid ($0.5 \text{ mol L}^{-1} \text{ HCl} + 0.2 \text{ mol L}^{-1} \text{ HF}$) can easily overcome the problem of Al tailing. The F^- ions would be complexed with Al^{3+} ions, thus decrease the effective valence state of Al^{3+} ions.⁵¹ The anion AlF_6^{3-} seldom exchanges with cationic resin, hence, the tailing of Al was significantly reduced. The addition of 10 mL of $0.2 \text{ mol L}^{-1} \text{ HF}$ cut the tailing of Al and slightly shifted the elution peak backward, but did not change the elution range of Li (Fig. 4A). This step also achieved complete separation of the HFSEs effectively before Li elution was collected (Fig. 4B and Fig. S2). And the lithium was eluted prior to Na off in this study thoroughly, so the Na/Li ratios in the elution process was extremely low (< 1). The proposed column chemical protocol has the advantage of a short overall duration for Li column separation, especially for the high Al concentration samples, which could be completed in less than 3.5 hours. Most of the Al removal is accomplished through elution. Low concentration inorganic acid (HF and HCl) was used in this study. The $0.5 \text{ mol L}^{-1} \text{ HCl}$ is selected as the eluent instead of the $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ because the latter has the disadvantages of broadening the elution peak of Li and degrading the resin.¹⁴

Fig. 4 Elution profiles of BCR-2 using 0.5 mol L⁻¹ HCl as the eluent. (A) Elution curves of Al, Li and Na. (a) Elution curves of Al. (B, b) Elution curves of Ta, Hf, Zr, Ti. Solid lines are the elution curves of with 10mL 0.2 mol L⁻¹ HF + 0.5 mol L⁻¹ HCl procedure. Dashed lines are without HF. Total elution time for Li is less than 3.5 hours.

Fig. 5 $\delta^7\text{Li}$ of 10 ng g⁻¹, 20 ng g⁻¹, 40 ng g⁻¹, 60 ng g⁻¹, 80 ng g⁻¹, 100 ng g⁻¹, 120 ng g⁻¹ and 140 ng g⁻¹ normalized with 50 ng g⁻¹ concentration LSVEC. The typical analytical uncertainty of this study is $\pm 0.3\%$. Correction formula of concentration effect: $y = 0.0795\ln(x) - 0.3089$. (A) Comparison of Li isotope between baseline subtracted and non-subtracted. (B) Fig. B is a partial enlargement of Fig. A.

Unfortunately, Li isotope fractionation is not restricted to natural processes and occurs readily during sample preparation and analyses. As prematurely ending the Li leaching range could lead to a high $\delta^7\text{Li}$ (^7Li elutes out of the chromatographic column faster than ^6Li),^{14,29,52} we carefully measured the elution range of Li using Q-ICP-MS (Agilent 7900) to ensure that the Li recovery is $99.8 \pm 0.3\%$. Furthermore, we collected 1 mL of pre- and post-Li eluate fractions for all samples, respectively, to monitor if there is any loss of Li or shift of Li elution peak.

Concentration effect on Li isotope analysis. In order to examine the concentration effect of Li during the analysis process with MC-ICP-MS, we prepared various concentrations of LSVEC (10 ng g⁻¹, 20 ng g⁻¹, 40 ng g⁻¹, 60 ng g⁻¹, 80 ng g⁻¹, 100 ng g⁻¹, 120 ng g⁻¹ and 140 ng g⁻¹) using a 50 ng g⁻¹ concentration of LSVEC to correct the instrumental mass bias with the SSB (50 ng g⁻¹, 10 ng g⁻¹, 50 ng g⁻¹, 20 ng g⁻¹...50 ng g⁻¹, 140 ng g⁻¹, and 50 ng g⁻¹) method. A large deviation of $\delta^7\text{Li}$ was found if the baseline was

not subtracted, therefore, background had a great influence on the test due to the dark noise on the Faraday cups in the Nu Plasma II, yielding a negative value, typical a few millivolts (mV). When the sample concentration is lower than 10 ng g⁻¹, the deviation will exceed 20‰ (Fig. 5A). But when we deducted the baseline of 2% HNO₃, we can use a 50 ng g⁻¹ standard solution to correct the samples with Li concentration from 20 ng g⁻¹ to 140 ng g⁻¹, meanwhile, the deviation from the recommended value is less than 0.2‰. It can be expected when the sample concentration is lower than 10 ng g⁻¹, the bias would exceed -0.6‰ (Fig. 5B). The equation ($Y = 0.0795\ln(x) - 0.3089$) can be used to correct the fractionation caused by the concentration effect for accurate Li isotope analysis, if the concentration of sample and standard were not strictly matched (Fig. 5B). As the concentration of Li decreases, the deviation in the measured $\delta^7\text{Li}$ becomes more pronounced. This equation may not always be valid; however, it should be effective during one analytical section. Therefore, this study recommends to conduct the same experiment at the beginning of each analytical section if this method is required.

Table 3. $\delta^7\text{Li}$ values of standards used in this experiment

Sample	Original Al/Li	Measured Al/Li after purification		Measured $\delta^7\text{Li}$ (mean \pm 2SD‰)		Reported in literature	Ref.
		Traditional	This study	Traditional	This study		
SCo-1, shale Li: 45 $\mu\text{g/g}$	3044.44	91.02	0.24	-1.58 \pm 0.68‰ (n=5)	0.51 \pm 0.30‰ (n=6)	0.42 \pm 1.1‰ (n=13)	49
					-1.13 \pm 0.13‰ (n=4)*	0.70 \pm 0.30‰ (n=3)	49
						-1.9 \pm 0.20‰	50
JF-1, feldspars Li: 8.87 $\mu\text{g/g}$	7491.07	624.95	1.70	0.14 \pm 1.06‰ (n=4)	3.70 \pm 0.16‰ (n=9)	3.30 \pm 1.30‰	57
GSR-8, trachyte Li: 17.5 $\mu\text{g/g}$	4118.10	253.77	1.00	1.96 \pm 2.94‰ (n=5)	4.72 \pm 0.21‰ (n=8)	4.77 \pm 0.21‰ (n=6)	51
RGM-2, rhyolite Li: 58 $\mu\text{g/g}$	1166.85	73.76	0.19	1.04 \pm 1.36‰ (n=4)	2.69 \pm 0.11‰ (n=6)	2.75 \pm 0.15‰ (n=5)	3
	6596.50	632.64	1.66	0.73 \pm 1.72‰ (n=4)	3.14 \pm 0.20‰ (n=7)	2.8 \pm 0.2‰	1
BCR-2, basalt Li: 9 $\mu\text{g/g}$	8061.19	#1267.55	#12.23	5.40 \pm 1.66‰ (n=3)	#7.90 \pm 0.38‰ (n=7)	3.19 \pm 0.39‰ (n=6)	4
						3.10 \pm 0.90‰ (n=9)	54
						3.02 \pm 0.51‰ (n=7)	32
AGV-2, andesite Li: 11 $\mu\text{g/g}$	8061.19	#1267.55	#12.23	5.40 \pm 1.66‰ (n=3)	#7.90 \pm 0.38‰ (n=7)	3.10 \pm 0.20‰	1
						7.92 \pm 0.34‰ (n=7)	15
						7.94 \pm 0.64‰ (n=6)	23
GSP-2, granodiorite Li: 36 $\mu\text{g/g}$	2178.15	158.06	0.31	-2.67 \pm 0.96‰ (n=4)	-0.47 \pm 0.14‰ (n=4)	7.98 \pm 0.19‰	22
						7.00 \pm 0.30‰	1
						-0.56 \pm 0.55‰ (n=3)	32
BIR-1a, basalt Li: 3.6 $\mu\text{g/g}$	43055.56	#2045.33	#10.25	-3.48 \pm 1.62 (n=4)	#3.71 \pm 0.47‰ (n=4)	4.07 \pm 0.33‰ (n=6)	4
						3.30 \pm 0.60‰ (n=5)	55
						3.39 \pm 0.77‰ (n=9)	56
BHVO-2, basalt Li: 5 $\mu\text{g/g}$	15820.59	448 (#1377.35)	1.00(#12.47)	1.16 \pm 2.90‰ (n=4)	#4.50 \pm 0.44‰ (n=3)	4.50 \pm 0.24‰ (n=4)	3
						4.50 \pm 0.40‰ (n=5)	55
						4.63 \pm 0.16‰	22
OSIL, Seawater Li: 174 ng/g	0.05	0.05	0.05	30.37 \pm 0.36‰ (n=6)	30.28 \pm 0.32‰ (n=6)	4.70 \pm 0.20‰	1
						4.29 \pm 0.46‰ (n=7)	28
						4.50 \pm 0.54‰ (n=17)	59
IAPSO, Seawater Li: 174 ng/g	0.05	0.05	0.05	30.54 \pm 0.39‰ (n=7)	30.22 \pm 0.15‰ (n=7)	5.68 \pm 0.14‰ (n=7)	32
						30.88 \pm 0.12‰ (n=10)	22
						30.87 \pm 0.15‰ (n=15)	3
IAPSO, Seawater Li: 174 ng/g	0.05	0.05	0.05	30.54 \pm 0.39‰ (n=7)	30.22 \pm 0.15‰ (n=7)	31.00 \pm 0.10‰ (n=31)	58
						30.00 \pm 0.70‰ (n=5)	16
						31.14 \pm 0.20‰ (n=31)	14
						31.20 \pm 0.40‰	1

Except for the data marked by * (2 mol L⁻¹HCl), the reported data from this study were dissolved by HNO₃ and HF (1:3).

Notice that if the samples were overload for the 10 mL 0.2 mol L⁻¹HF, it could still result in a high Al/Li content after purification. Traditional: Al partly removed with traditional single column method; This study: Al fully removed with the addition of 0.2 mol L⁻¹HF.

Accurate determination of Li isotopes for natural materials.

Two in-house Li solutions (CAGS-Li-N, $\delta^7\text{Li}=-15.02\pm 0.18\%$, 2σ , n=40; CAGS-Li-P, $\delta^7\text{Li}=6.25\pm 0.25\%$, 2σ , n=40) analyzed over 5 months were used to judge the stability of the instrument (Fig. S3), and LSVEC ($\delta^7\text{Li}=0\pm 0.2\%$, 2σ , n>100, more than 2 years) was used to monitor the instrument mass bias of Li isotope analyses. To evaluate the flexibility of the proposed procedure, including its ability to treat high Al samples, a group of geological reference materials (GRMs) were analyzed, including BHVO-2, AGV-2, BIR-1a, RGM-2, JF-1, SCo-1, GSP-2, GSR-6, GSR-8, and seawater (OSIL, IAPSO). Li content differs greatly among these standards. The obtained $\delta^7\text{Li}$ values of BCR-2 (3.14 \pm 0.20‰, n=7), AGV-2 (7.90 \pm 0.38‰, n=7), BIR-1a (3.71 \pm 0.47‰, n=4), RGM-2 (2.69 \pm 0.11‰, n=6), JF-1 (3.70 \pm 0.16‰, n=9), SCo-1 (0.51 \pm 0.30‰, n=6), GSP-2 (-0.47 \pm 0.14‰, n=4), GSR-6 (-

1.88 \pm 0.09‰, n=6), GSR-8 (4.72 \pm 0.21‰, n=8) and OSIL (seawater) (30.28 \pm 0.32‰, n=6), IAPSO (seawater) (30.22 \pm 0.15‰, n=7) were similar to published data within uncertainty.^{1,3,4,15,24,29,33,53-63} We also dissolved SCo-1 with 2 mol L⁻¹ HCl, the obtained $\delta^7\text{Li}$ values of SCo-1 is similar to the reported values of -1.90 \pm 0.20‰ by Li *et al.* (Table 3)⁵⁴ Li isotope of SCo-1 depends on the acids used for digestion. Both Li isotope of the whole rock and the carbonate component agree with those reported in the literature. However, it is too early to state that our procedure is effective for carbonate samples, more studies should be done to verify it.

The analytical precision (2σ) of the samples that Al was fully removed (with 10mL 0.2 mol L⁻¹ HF and 0.5 mol L⁻¹ HCl elution) is obviously better than that of Al partly removed (with only

Fig. 6 (A) Comparison of $\delta^7\text{Li}$ measurements for frequently reported reference materials. Error bars are 2SD of the bracketing standard measurements. When $2\text{SD} \leq 0.3$, the error bars are invisible. (a) Fig. a is a partial enlargement of Fig. A. (B) $\Delta^7\text{Li} \text{‰}$ (Al partly removed - Al fully removed) has a negative correlation with Al/Li ratios, and the trend agrees with the experiments in Fig 3. (b) Fig. b is a partial enlargement of Fig. B.

10 mL 0.5 mol L⁻¹ HCl elution) samples. The former was almost better than 0.32‰. Except for the BHVO-2, AGV-2 and BIR-1a, which had a 2σ of 0.38~0.47‰, probably due to the sample overload for the 10mL of 0.2mol L⁻¹ HF, which results in a failure to completely remove of Al. The $\delta^7\text{Li}$ of many well-characterized GRMs showed only small differences between published values from different laboratories. These results were listed in Table 3. In this study, $\delta^7\text{Li}$ varied greatly, and had a large difference in 2SD between Al fully and partly removed samples (Fig. 6A). The partial Al removal occurred in GRMs if treated by the traditional single-column method. The Li isotopes bias of Al partly removed samples were in perfect agreement with the matrix effect experiments in this study (Fig. 3), where $\Delta^7\text{Li} \text{‰}$ (Al partly removed - Al fully removed) has the same negative correlation trend as Fig. 3 (Fig. 6B, b). According to this phenomenon, this study confirmed that the matrix effect of Al had a negative shift of $\delta^7\text{Li}$ in both natural samples and samples artificially added with Al in our laboratory conditions.

CONCLUSIONS

The 10 mL 0.2 mol L⁻¹ HF elution solution can effectively reduce the tailing of Al. This optimized method offers numerous advantages, including fewer steps, minimal use of material and time, low Al/Li ratios after purification, reducing the risk of

contamination from complicated experimental procedures, and with applicability to extensive geological samples (e.g., silicates, seawater, sediments, and feldspars). The measured $\delta^7\text{Li}$ values of international standard BCR-2 (3.14±0.20‰), AGV-2 (7.90±0.38‰), BIR-1a (3.71±0.47‰), RGM-2 (2.69±0.11‰), JF-1 (3.70±0.16‰), SCo-1 (0.51±0.30‰), GSP-2 (-0.47±0.14‰), GSR-6 (-1.92±0.16‰), GSR-8 (4.72±0.21‰) and seawater (30.28±0.32‰ for OSIL, 30.22±0.15‰ for IAPSO) are similar to previously published data within uncertainty. Additionally, we investigated the impact of varying Al/Li ratios using MC-ICP-MS under “Dry” plasma conditions. The Al/Li ratios should be decreased to achieve accurate Li isotopes composition. Furthermore, we examined the concentration effect, a technique that does not necessitate strict concentration matching if the baseline of the Faraday cups were subtracted properly. Besides, two in-house Li isotope solution standards CAGS-Li-N and CAGS-Li-P were routinely analyzed to monitor the instrumental mass bias and judge the stability of the instrumental, and there has more than 1000 mL Li solutions of CAGS-Li-P and CAGS-Li-N available, which can serve isotope laboratories at home and abroad for a long time.

ASSOCIATED CONTENT

The supporting information (Figs. S1–S3) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

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