

A Revisited Purification of Li for 'Na Breakthrough' and its Isotopic Determination by MC-ICP-MS

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The accurate and precise determination of Li isotopic composition by MC-ICP-MS suffers from the poor performance of traditional column chromatography. Previously established chromatographic processes cannot completely remove Na in complex geological samples, which is currently interpreted to be a result of Na breakthrough. In this study, Na breakthrough during single-column purification was found to differ between simply artificial Na-containing sample solutions, where a little Na residue was found, and silicate rocks, where a large amount of breakthrough occurred. A revised two-step column purification for Li using 0.5 and 0.3 mol l⁻¹ HCl as eluents was designed to remove the Na. This modified method achieves high-efficiency Li purification from Na and consequently avoiding high Na/Li ratio interference for subsequent MC-ICP-MS analyses. The proposed method was validated by the analysis of a series of reference materials, including Li₂CO₃ (IRMM-016, -0.10‰), basalt (BCR-2: 2.68‰; BHVO-2: 4.39‰), andesite (AGV-2: 6.46‰; RGM-2: 2.59‰), granodiorite (GSP-2: -0.87‰) and seawater (CASS-5, 30.88‰). This work reports early Na appearance prior to the elution curves in chromatography and emphasises its influence for subsequent Li isotope measurement. Based on the findings, the established two-step method would be more secure than single-column chemistry for Li purification.

Keywords: Na breakthrough, Li isolation, Li isotopes, MC-ICP-MS.

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Lithium has two stable isotopes, ⁶Li and ⁷Li, with relative terrestrial abundances of 7.52% and 92.48% (Chan 1987, Berglund and Wieser 2011), respectively, and is commonly used as a trace element in studies of geofluids and geological materials. The large mass difference between the two isotopes results in significant isotope fractionation (approximately 110‰) (Chan and Edmond 1988, Moriguti and Nakamura 1998), making Li isotopes ideal tools for the study of hydrothermal alteration processes, continental weathering, subducted oceanic crust, sources of ore-forming fluids and cosmochemistry (Pistiner and Henderson 2003, Tomascak 2004, Tang *et al.* 2007, Sauzéat *et al.* 2015, Richard *et al.* 2018).

Multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) is a favoured technique for Li isotope measurement but it is susceptible to interference from other elements, particularly Na (Tomascak *et al.* 1999, Magna *et al.* 2004, Misra and Froelich 2009, Macpherson *et al.*

2015). Up to 4‰ instrumental mass-dependent deviations may be produced with Na/Li mass ratios up to ~ 500 and Ca/Li and Mg/Li ratios up to ~ 250 (Macpherson *et al.* 2015). Isolation of Li from the sample matrix is therefore essential for precise isotopic measurements.

Previous studies have shown that the separation of Li from Na is the most critical analytical step because Na is a major element in most rocks and has a distribution coefficient (*K_d*) similar to that of Li between stationary and mobile chromatographic phases (Table S1; Strelow 1960, Strelow *et al.* 1974). The separation factor between Li and Na is negatively correlated with the acid concentration and positively correlated with the organic solvent content of the mobile phase, with larger volumes of stationary phase (resin) improving separation (Strelow 1960, Strelow *et al.* 1974, You and Chan 1996, Tomascak *et al.* 1999, Hall *et al.* 2005, Wang *et al.* 2006). The efficient purification of Li from geological samples (including carbonates, clay, igneous

rocks and seawater) remains challenging in isotopic analyses. Gao and Casey (2012) loaded 15 and 10 ml volumes of cation-exchange resin into two successive chromatographic columns, which were eluted by 0.2 mol l⁻¹ HCl to purify Li from Na. However, this method required up to 130 ml eluent volumes and incurred Li losses and cross-contamination. In addition, large volumes of cation-exchange resin result in a decrease in the flow velocity of the mobile phase (eluent), increasing time required for separation (> 10 h for one chromatographic process). An eluent of 1 mol l⁻¹ HNO₃ in 80% methanol has also been widely used to isolate Li from the matrix with smaller resin volumes (2 ml) (Tomascak *et al.* 1999, Košler *et al.* 2001, Nishio and Nakai 2002, Rosner *et al.* 2007, Huang *et al.* 2010, Lin *et al.* 2015). However, mixtures of acid and organic solvents (methanol or ethanol) result in low eluent flow rates, degradation of resin, possible sources of contamination from organic solvent and potential environmental pollution from the release of methanol.

Here we describe a chromatographic method for Li purification involving Dowex® 50WX8 resin (Alfa Aesar, Shanghai, China) and acid eluates. This paper focuses on difficulties during the purification and aims at optimisation to separate Li from Na. Lithium recoveries were determined and δ⁷Li values of geological reference materials compared with published values.

Experimental procedure

Reagents

Commercially available HCl, HNO₃ and HF were treated with Savillex DST-1000 purification systems (America). Ethanol (EtOH) for high-performance liquid chromatography (HPLC) was used without further purification. Ultrapure water (resistivity ≥ 18.2 MΩ cm) was produced from laboratory tap water using two-stage purification systems (ELGA, High Wycombe, UK). All PTFE beakers and chromatography columns were cleaned in an acid reflux system (TraceClean; Milestone, Bergamo, Italy). All experiments were performed in a Class-1000 clean laboratory.

Standard solutions

Approximately 50 mg Li₂CO₃ (IRMM-016; Institute for References and Measurements, Europe) was weighed into a 7-ml PFA beaker and dissolved in 2 ml 2% v/v HNO₃. Then, the solution was evaporated to dryness on a hot plate at 120 °C, and the residue re-dissolved in 20 ml 2% v/v HNO₃, to produce a 400 µg g⁻¹ Li standard stock solution. A single-element standard solution of Li (1000 mg l⁻¹; Alfa

Aesar) was diluted to required concentrations and used to establish Li elution curves.

Sample description and preparation

The main constituents of the samples, which include granite (reference material ACE), granodiorite (GSP-2), andesite (AGV-2 and RGM-2), basalt (BCR-2 and BHVO-2), seawater (CASS-5), and saline lake water (JH), are listed in Table S2.

Rock samples: The Li and total matrix contents of the basalts were 9 µg g⁻¹ and 21.25 meq g⁻¹ for BCR-2, and 5 µg g⁻¹ and 23.4 meq g⁻¹ for BHVO-2, respectively. Previous studies have found that high Mg and Fe contents, such as those occurring in peridotite, pyroxenite and other mantle materials (You and Chan 1996, James and Palmer 2000, Chan *et al.* 2002, Chan 2004), may reduce Li recovery through the shift of Li elution curves (Chan *et al.* 2002). Attention must therefore be paid to resin and eluent volumes when analysing mantle materials, as discussed in section dealing with results of column 1 (below).

Powdered rock samples (50–100 mg) were digested in 2 ml 14.4 mol l⁻¹ HNO₃ plus 2 ml 24 mol l⁻¹ HF at 180 °C in a microwave digestion system (ETHOS ONE; Milestone) for ~ 2 h. Siliceous materials in samples were converted to volatile SiF₄. Digested samples were transferred to 7-ml PTFE beakers and heated to dryness on a hot plate at 120 °C. Residues were dissolved in 1 ml 16 mol l⁻¹ HNO₃ and heated to dryness, and this process was performed twice to ensure the removal of fluoride. A total of 1 ml of 12 mol l⁻¹ HCl was added and evaporated to dryness before residues were re-dissolved in 2 ml 0.5 mol l⁻¹ HCl in preparation for column chromatography. Rock solutions used for development of elution curves were added to 10 µg of Alfa Aesar Li standard solution to accomplish the requirement for Li determination in sample fractions.

Natural fluids: Seawater reference material CASS-5 (National Research Council of Canada) and saline lake water (JH, collected from NW China in January 2015 and preserved with 2% HNO₃) were used as natural fluids. The Li and total matrix contents were 0.174 µg g⁻¹ and 1.07 meq g⁻¹ for the seawater and 7.825 µg g⁻¹ and 9.00 meq g⁻¹ for the lake water, respectively. The Na content was higher in saline fluids than in rocks (Table S2).

Liquids were filtered through disposable 0.20-µm syringe filters (Tianjin Fuji Science and Technology, Tianjin, China) before 1 ml seawater and 0.1 ml saline lake water were

evaporated to dryness in 7-ml PTFE beakers at 80–100 °C, and the residue was re-dissolved in 2 ml 0.5 mol l⁻¹ HCl.

Ion-exchange procedures

Lithium separation from geological samples is usually achieved using sulfonic (-SO₃H) strong-acid cation-exchange resins such as AG or DOWEX 50WX8 or 50WX12. The absorption capacity of the resin is important in achieving good separation, with the optimal total cation content of loaded solutions < 10–15% of the total exchange capacity of the resin (Korkisch and Worsfold 1989, James and Palmer 2000, Zagrodni 2007, Gao and Casey 2012, Schönbacher and Fehr 2014). Mantle rocks and minerals commonly contain < 10 µg Li g⁻¹ and a high matrix metal content. MC-ICP-MS analysis requires at least 50 mg of rock powder; 50 mg of basalt contains ~ 1.2 meq of total metals. Analytical grade Dowex[®] 50WX8 cation-exchange resin (200–400 mesh; Alfa Aesar) was used for Li purification in this study. A volume of 7 ml of DOWEX[®] 50WX8 (200–400 mesh) resin has a capacity of 12.6 meq (1.8 meq ml⁻¹), meaning that a 7 ml resin volume is appropriate for the first column in this case.

The resin was first cleaned to remove trace metals and organic contaminants by soaking overnight in ultrapure

water (floating particles were removed) and washing with four resin volumes of 6 mol l⁻¹ HCl and ten volumes of ultrapure water in a borosilicate glass column (40 mm internal diameter).

The Li purification was undertaken using two sequential ion-exchange columns. Column conditions and resin handling procedures are summarised in Table 1.

Column 1 (internal diameter: 8 mm) was tested with both 0.15 mol l⁻¹ HCl and 0.5 mol l⁻¹ HCl for Li isolation. Two identical columns were successively loaded with 30 ml 2 mol l⁻¹ HCl, 30 ml ultrapure water and 7 ml cation-exchange resin. After loading, resin columns were cleaned with 42 ml 6 mol l⁻¹ HCl, followed by 21 ml ultrapure water. The columns were then treated with 5 ml 0.5 mol l⁻¹ HCl or 10 ml 0.15 mol l⁻¹ HCl to initialise column conditions. Next, sample solutions were loaded onto the columns with 2 ml 0.5 mol l⁻¹ HCl or 10 ml 0.15 mol l⁻¹ HCl, respectively. Finally, the Li absorbed in the above 2 columns (column 1) was separately eluted by 0.5 or 0.15 mol l⁻¹ HCl.

Column 2 (internal diameter: 5 mm) was tested with a range of eluents and resin volumes. After cleaning with 6 ml 2 mol l⁻¹ HCl and 6 ml ultrapure water, five identical

Table 1.
Scheme of cation-exchange chromatography used for Li purification

Procedure					
Batch processing for the resin			Soak in ultrapure water overnight and rinse with 4 column volumes of 1:1 v/v HCl and 10 column volumes of ultrapure water		
Step	Solution		Volume		
Column wash	2 mol l ⁻¹ HCl		2 column volumes (30 ml -column 1 and 6-column 2)		
Column wash	Ultrapure water		2 column volumes (30 and 6 ml)		
Resin loading	DOWEX 50WX8		7 ml and 2.5 ml		
Resin re-cleaning	1:1 v/v HCl		6 resin volumes (42 and 15 ml)		
Resin re-cleaning	Ultrapure water		3 resin volumes (21 and 7.5 ml)		
Column 1 (i.d. 8 mm)					
Resin volume	7 ml	7 ml			
Resin condition	10 ml 0.15 mol l ⁻¹ HCl	5 ml 0.5 mol l ⁻¹ HCl			
Sample loading	10 ml 0.15 mol l ⁻¹ HCl	2 ml 0.5 mol l ⁻¹ HCl			
Elution	0.15 mol l ⁻¹ HCl	0.5 mol l ⁻¹ HCl			
Column 2 (i.d. 5 mm)					
Resin volume	2.5 ml	2.5 ml	2.5 ml	1 ml	1.5 ml
Resin condition	5 ml 0.15 mol l ⁻¹ HCl	5 ml 0.15 mol l ⁻¹ HCl	5 ml 0.15 mol l ⁻¹ HCl	5 ml 0.15 mol l ⁻¹ HCl	5 ml 0.15 mol l ⁻¹ HCl
Sample loading	2 ml 0.15 mol l ⁻¹ HCl	2 ml 0.15 mol l ⁻¹ HCl	3 ml 0.15 mol l ⁻¹ HCl	3 ml 0.15 mol l ⁻¹ HCl	3 ml 0.15 mol l ⁻¹ HCl
Elution	0.15 mol l ⁻¹ HCl	0.3 mol l ⁻¹ HCl	0.5 mol l ⁻¹ HCl + 50% EtOH	0.5 mol l ⁻¹ HCl + 30% EtOH	0.5 mol l ⁻¹ HCl + 50% EtOH

columns were loaded with 1, 1.5, 2.5, 2.5 ml or 2.5 ml resin. Each column was flushed with 15 ml 6 mol l⁻¹ HCl, followed by 7.5 ml ultrapure water. The columns were treated with 0.15 mol l⁻¹ HCl to initialise resin conditions for the introduction of sample solutions. Different eluents (0.15 mol l⁻¹ HCl, 0.3 mol l⁻¹ HCl, 0.5 mol l⁻¹ HCl in 30% EtOH and 0.5 mol l⁻¹ HCl in 50% EtOH) were passed through different columns, as described in Table 1.

Eluates were evaporated to dryness at 120 °C, and the residue re-dissolved in 2% v/v HNO₃ for MC-ICP-MS analysis. The resin was reconditioned with ten bed volumes of 6 mol l⁻¹ HCl, washed with ultrapure water and stored in dilute HCl before reuse.

Analysis

Lithium and Na elution curves were derived by atomic absorption spectrophotometry analysis. Other element mass fractions were determined by quadrupole ICP-MS (NEXION300X, Waltham, MA, USA) at the State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Beijing, China. Precision (2s) for all element mass fractions was better than ± 10%.

Lithium isotope ratios were determined using a double-focussing MC-ICP-MS (Neptune, Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The sample introduction system included a PFA nebuliser and quartz spray chamber. The detection system was equipped with eight movable Faraday cups and a fixed cup. ⁶Li⁺ and ⁷Li⁺ were collected in the low-mass Faraday cup (L4) and the high-mass cup (H4), respectively.

Instrumental mass discrimination was corrected using the sample-calibrator bracketing approach, with calibrator and sample solutions containing 50 µg l⁻¹ Li. Between successive measurements, 2% v/v HNO₃ was aspirated for at least 3 min to remove background signals, with 5% NaCl solutions used to reduce the instrumental background and memory effect when the background signal was > 0.01 V (Lin *et al.* 2015). The operational parameters are listed in Table 2. Lithium isotope compositions were reported in the usual per mil delta notation relative to IRMM-016, where

$$\delta^7\text{Li} = \left[\left(\frac{{}^7\text{Li}/{}^6\text{Li}}{\text{sample}} \right) / \left(\frac{{}^7\text{Li}/{}^6\text{Li}}{\text{std}} \right) - 1 \right] \quad (1)$$

Deviation from extended ⁷Li/⁶Li measurement of IRMM-016 was < 0.20‰ (n = 19), with no systematic discrepancy in isotope ratios detected.

Results and discussion

Column 1

The first ion-exchange process, using Column 1, was intended to remove most of the Na in solution (Figure S1). Chromatographic purification of Li has previously been achieved with mobile phases of 0.5 mol l⁻¹ HCl (Chan 1987), 0.15 mol l⁻¹ HCl (Moriguti and Nakamura 1998) and 0.2 mol l⁻¹ HCl (James and Palmer 2000, Wang *et al.* 2006, Gao and Casey 2012), with the former two being selected for application here (Table 1). Lithium was eluted before Na using either 0.5 mol l⁻¹ HCl or 0.15 mol l⁻¹ HCl, as shown in Figure 1. The elution curves indicate that Li elution occurred over volumes of 19–34 ml with 0.5 mol l⁻¹ HCl and 82–115 ml with 0.15 mol l⁻¹ HCl (Figure 1), while the Na peak commenced at 40 ml with the former and 145 ml with the latter. Volume intervals for Li and Na elution peaks were separated by 5–6 ml with 0.5 mol l⁻¹ HCl and 25–30 ml with 0.15 mol l⁻¹ HCl. Use of 0.15 mol l⁻¹ HCl required three times the volume compared with 0.5 mol l⁻¹ HCl, increasing the time required for purification and the likelihood of Li blank contamination. The optimal choice of eluent was therefore considered to be 0.5 mol l⁻¹ HCl.

In the present study, the high Mg and Fe contents of BCR-2 and BHVO-2 did not significantly modify the Li elution peak position in curves from other rock samples. However, the Li elution peak position was shown to move in previous studies (You and Chan 1996, James and Palmer 2000, Chan *et al.* 2002, Chan 2004). To ensure complete collection of Li, the eluent was collected from 15 to 38 ml (Figure 1b), a wider range than indicated by the elution curves (19–34 ml). The step is reasonable because James and Palmer (2000) and Chan *et al.* (2002) reported that Li elution peaks shift to earlier eluent volumes in silicate samples enriched in Mg and Fe, which has been interpreted from the fact that relatively low Li content requires larger samples (up to 75 mg) that occupy more than the total cation content of 20% of resin capacity, with a corresponding reduction in ion selectivity.

Na breakthrough and its influence

Figure 1 shows that a small amount of Na constantly eluted before the main Na elution peaked. Similar behaviour was observed by Hoecke *et al.* (2015) and Li *et al.* (2018). Hoecke *et al.* (2015) concluded that this phenomenon was due to contamination from the resin. However, in this study no such contamination was evident when pure Li solutions were passed through the column (Figure 1). From the elution curves of column 1 (Figure 1b),

Table 2.
MC-ICP-MS operating parameters

Operating specification		Data acquisition		Neptune cup configuration			
RF power (W)	1300	Resolution setting	Low	Cup	L4	C	H4
Nebuliser Gas Flow (l min ⁻¹)	13	Uptake time	80 s	Mass/nuclide	⁶ Li	6.491 u	⁷ Li
Auxiliary Gas Flow (l min ⁻¹)	0.58–0.70	Blocks	30	Amplifier resistance (Ω)	10 ¹¹	10 ¹¹	10 ¹¹
Sample uptake (ml min ⁻¹)	0.1	Cycles/block	1				
Sampler and skimmer cone	Ni sampler, X skimmer	Total data acquisition time	130 s				
		Total measurement time	8 min				

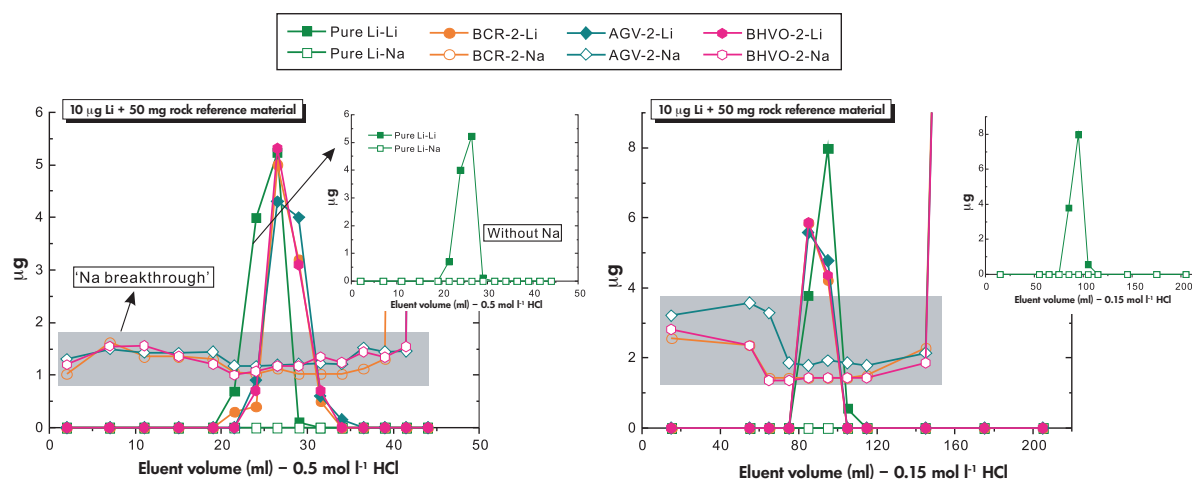


Figure 1. Elution curves of Li and Na with 0.5 and 0.15 mol l⁻¹ HCl as eluents using 7 ml resin volume. [Colour figure can be viewed at wileyonlinelibrary.com]

the Na residue present in the eluent collected from 15 to 38 ml was expected to be ~ 14 µg, much higher than total Li calculated from the sample mass and its Li content. Even if the test portions contained 500 ng of Li, Na:Li ratios in collected eluents were 28, which must be avoided as discussed in the section dealing with Column 2 (below).

Sodium has a much lower K_d value between the resin and mobile phase than other major elements, such as Fe, K and Mg (Table S1), indicating that a proportionally smaller amount of Na is distributed on the stationary phase under equilibrium conditions; that is, more of the stationary phase is required to adsorb Na. Most Na⁺ in solutions substitute for exchangeable H⁺ linking to cross-linked polystyrene with sulfonic acid functional groups in the resin column during sample loading, while a small part as the result of Na⁺ overload does not interact with the resin. Therefore, the part without interaction is free without resin structure adsorbed

and is directly flushed down by the following eluents before the initiation of its main elution peak in the curves. It has been suggested that Na/Li, Mg/Li and Ca/Li ratios in collected solutions could rise up to 20 after a single chromatographic process, especially for some high-Na saline waters and high-Mg silicate rocks (Magna *et al.* 2004, Jeffcoate *et al.* 2004, Huang *et al.* 2010, Gao and Casey 2012, Tian *et al.* 2012). Sodium breakthrough also seems to occur in previous studies, even when the total resin capacity was sufficiently large for total adsorption.

In order to quantify the Na breakthrough, a series of experiments was conducted with artificially varied Na content (100, 500, 1000, 2500, 5000 and 10000 µg) and a fixed Li content (10 µg). Figure 2 clearly shows that each curve has a relevant Na breakthrough before its main peak. The minimum breakthrough presents in the 100 µg Na curves and shows that Na collected in each fraction gradually varies from initial

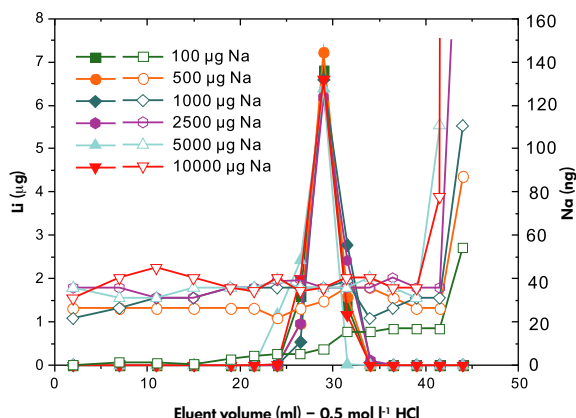


Figure 2. Elution curves for quantitative Na breakthrough with 0.5 mol l⁻¹ HCl as the eluent using 7 ml resin volume. [Colour figure can be viewed at wileyonlinelibrary.com]

0 ng to about 60 ng with the progress of rinsing. Furthermore ~ 25 ng Na is present in each fraction of 500 µg Na curves. Moreover, 1000–10000 µg Na curves have 35–40 ng Na in each fraction before and during the Li elution peak. Thus, during the purification of a Na dominated matrix, Na content in the collected eluents could reach to 400 ng, which would require at least 1.6 µg g⁻¹ Li in the sample to ensure Na/Li < 5 (see section 'Recovery and matrix effects'). However, the Na in each fraction is up to 1.4 µg for 50 mg silicate rocks which contain about 1000–2500 µg Na (recalculated from Table S2) and other matrix, as illustrated in Figure 1. Given that the amount of Na expected in silicate rocks is relatively consistent, at least 56 µg g⁻¹ Li in samples is required to ensure the measurement accuracy and precision for complex silicate samples.

The experiments clearly show orders of magnitude of Na early breakthrough during purification of different matrices, suggesting more attention should be paid to the Na disturbance during chromatographic processes.

Column 2

After initial purification, additional removal of Na residue from sample solutions should be undertaken to avoid matrix effects and matrix accumulation in sampler and/or skimmer cones during analysis, giving rise to a higher blanks and signal instability. Many other methods accomplish the ultimate Li-Na separation by using a mixture of an organic solvent and a mineral acid as the eluent (Moriguti and Nakamura 1998, Jeffcoate *et al.* 2004, Teng *et al.* 2004, Tian *et al.* 2012). Equilibrium distribution coefficient

experiments of cation-exchange selectivity have demonstrated that the separation factor α_{Na-Li} is positively correlated with the organic solvent content in the mobile phase (Strelow 1960, Strelow *et al.* 1974, Figure 3a). Moreover, eluents added with EtOH or MeOH behave better in Li-Na separation efficiency than single mineral acids under the condition of same resin volume (Moriguti and Nakamura 1998, Tian *et al.* 2012, Figures 3 and 4). Moriguti and Nakamura (1998) and Tian *et al.* (2012) used 0.5 mol l⁻¹ HCl in 30% ethanol as the mobile phase to separate Li from Na in their third column, and this mobile phase was obviously more effective than 0.15 mol l⁻¹ HCl in their second column. However, addition of 30% EtOH did not lead to complete separation in this study (Figure 3b). Addition of 50% ethanol to a 0.5 mol l⁻¹ HCl eluent improved the separation, with better separation using a resin volume of 2.5 ml (Figure 3d) than 1.5 ml (Figure 3c). However, using this eluent resulted in the sampler cones of the MC-ICP-MS being covered by carbonised materials after two weeks of operation (Figure S2) and reduced instrument stability, similar to Moriguti and Nakamura (1998). The carbonisation indicates that the measured solutions are full of organic materials, possibly due to degradation of the resin by the organic solvent or the organic solvent itself. Thus, mixtures of mineral acids and organic solvents are therefore not optimal eluents, and diluted mineral acids are used in preference.

As seen in Table S1 and Figure 4, low concentration single mineral acids can also have large enough discrepancies in the Na-Li distribution coefficients to achieve effective separation. The elution curves show that Li elution was located between 14 and 20 ml with 0.3 mol l⁻¹ HCl, and 24–36 ml with 0.15 mol l⁻¹ HCl, while the Na peak was initially detected at 24 ml with the former and 44 ml with the latter, respectively. Obviously, 0.3 mol l⁻¹ HCl and 0.15 mol l⁻¹ HCl have similar Li-Na volume intervals, but the former only required half of the elution volumes and time consumption compared with the latter. Here, 0.3 mol l⁻¹ HCl is proposed as the mobile phase to separate Li from residual Na (Figure 4).

Application of the complete chromatographic separation (Column 1 and Column 2) to rock reference materials showed that showed all samples had Na: Li < 5 and most had Na: Li < 1 (Table 3). Since any matrix element (Na, Al, Mg and Fe, etc.) may change the isotope ratios of samples to compare with the standard (Tomascak *et al.* 1999 and Magna *et al.* 2004), all major elements with distribution coefficients similar to Li were monitored. Figure 5 shows that the sum of all other elements makes up less than 10% of the lithium, indicating that the procedure efficiently purified Li from not only Na but also other major elements.

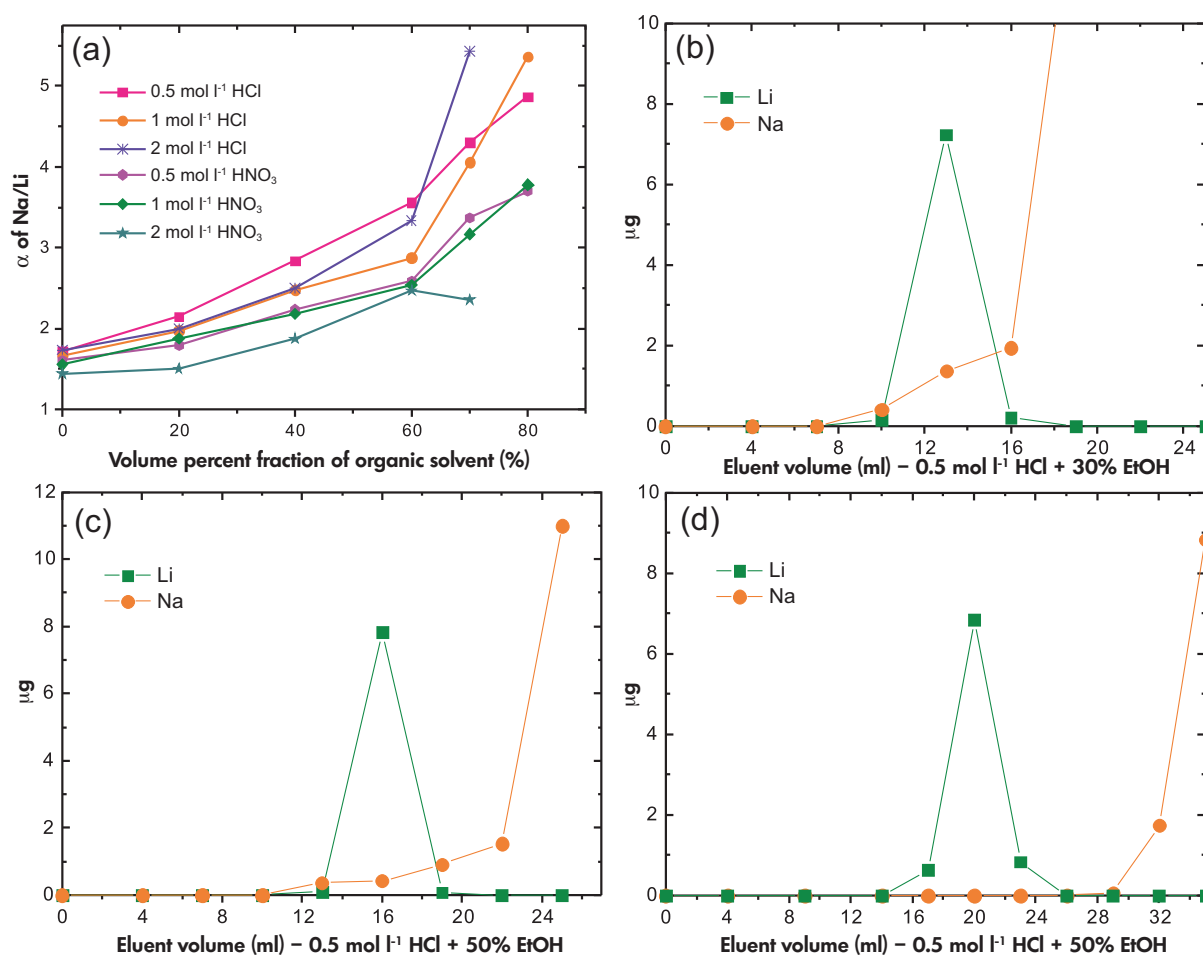


Figure 3. (a) Relationship between Na-Li separation factor (α) and volume per cent fraction of organic solvent; (b) elution curves with 0.5 mol l⁻¹ HCl + 30% EtOH as the eluent using 1 ml resin volume; (c) elution curves with 0.5 mol l⁻¹ HCl + 50% EtOH as the eluent using 1.5 ml resin volume; (d) elution curves with 0.5 mol l⁻¹ HCl + 50% EtOH as the eluent using 2.5 ml resin volume. The separation factor (α) was calculated from Strelow (1960) and Strelow *et al.* (1974). [Colour figure can be viewed at wileyonlinelibrary.com]

Recovery and matrix effects

Moriguti and Nakamura (1998), Košler *et al.* (2001) and Jeffcoate *et al.* (2004) found that Li isotopes are significantly fractionated during elution, because of the preferential partitioning of ⁷Li into the mobile phase. Thus, complete recovery of Li is essential to avoid chromatographic fractionation effects. Here, the recovery of Li was monitored by quadrupole ICP-MS, with Li recovery (%) = ((Li content before chromatography)/(Li content after chromatography) × 100). A series of artificial standard solutions with precisely known Li concentration (based on CASS-5 and BCR-2) was used to study chromatographic recovery, with results indicating a mean recovery of 104.7 ± 4.5% (Table 3). No isotopic fractionation was observed through comparison of $\delta^7\text{Li}$ values for IRMM-

016 and Alfa Aesar Li standard solutions before and after chromatography.

It is essential to monitor matrix effects for the Li isotope measurement. The instrument bias in relation to matrices is significant in published works. Nishio and Nakai (2002) estimated Li isotope deviation in a single focusing MC-ICP-MS produced by residual Na, Mg and Fe matrix effects, suggesting that a decrease of approximately 3‰ in $\delta^7\text{Li}$ values was generated when the concentrations of other ions were more than double that of Li. Tian *et al.* (2012) showed that the Li isotope ratios exhibited significant negative deviations when the Na/Li ratios were more than 20. However, a positive deviation caused by Na matrix was reported in Li *et al.* (2018). Given residual Na in the final solution could result in higher or lower Li isotope ratios

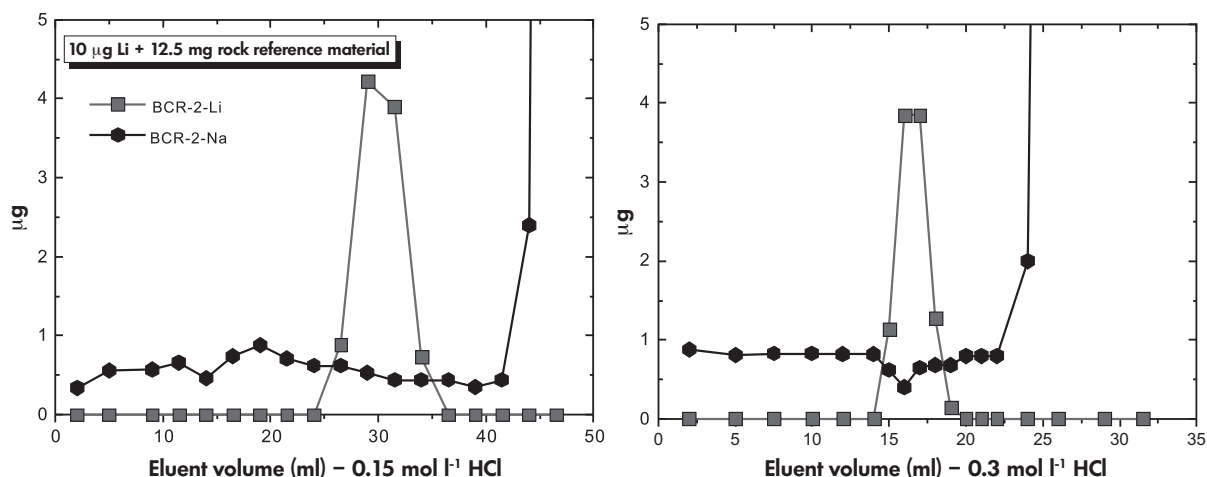


Figure 4. Elution curves of Li and Na with 0.15 mol l⁻¹, 0.3 mol l⁻¹ HCl and 0.5 mol l⁻¹ HCl + 50% EtOH as eluents using 2.5 ml resin volume.

Table 3.
Lithium recovery and isotope ratios obtained after ion-exchange chromatography

Sample		Li-b1	Li-a1	Li-b2	Li-a2	Na/Li	Li recovery (%)	$\delta^7\text{Li}$ (‰)	2s	
IRMM-016	0.2 µg Li	.bld.	.bld.	.bld.	.bld.		103	-0.01	0.07	
IRMM-016	0.3 µg Li	.bld.	.bld.	.bld.	.bld.		106	-0.07	0.08	
IRMM-016	0.5 µg Li	.bld.	.bld.	.bld.	.bld.		104	-0.23	0.47	
Alfa Li	0.5 µg Li	.bld.	.bld.	.bld.	.bld.		106	80.49	0.00	
BCR-2	20 mg basalt	.bld.	.bld.	.bld.	.bld.	3.5	107	2.56	0.13	
BCR-2	20 mg basalt	.bld.	.bld.	.bld.	.bld.	0.26	98	2.67	0.20	
BHVO-2	50 mg basalt	.bld.	.bld.	.bld.	.bld.	0.54	101	4.39	0.96	
AGV-2	20 mg andesite	.bld.	.bld.	.bld.	.bld.	0.75	103	6.11	0.57	
CASS-5	1 ml seawater	.bld.	.bld.	.bld.	.bld.	0.36	114	30.91	0.16	
Alfa Li		Without chromatography (n = 6)							80.87	0.17
Total procedure blank (ng)		0.25–0.7 ng (n = 3)								

.bld.—below detection limit of quadrupole ICP-MS. Li-b1 Li fraction before the collected eluents for column 1; Li-a1 Li fraction after the collected eluents for column 1. Li-b2 Li fraction before the collected eluents for column 2; Li-a2 Li fraction after the collected eluents for column 2.

measured by MC-ICP-MS, matrix effects were examined by doping Li standard solutions (50 µg l⁻¹ Li) with various Na concentrations and comparing Li isotope ratios with that of a pure IRMM-016 solution. The doped Na matrices produced negligible systemic deviation on ⁷Li/⁶Li ratios (Figure 6). To achieve a satisfactory precision and accuracy, the analysis using our instrument under operating conditions requires the Na/Li ratio in samples to be < 5.

Analysis of reference materials

The performance of the two-column procedure was evaluated by analysing the reference materials ACE (granite), GSP-2 (granodiorite), AGV-2 and RGM-2 (andesites), BCR-2

and BHVO-2 (basalts), CASS-5 (seawater) and JH (natural salt water), with results shown in Table 4 and Figure 7. These materials provide a range of chemical compositions (Table S2), thus testing the procedure over a wide range of matrix compositions. Their range of Li contents is also wide, from 4.5 to 11 µg g⁻¹ for rocks and 0.175 to 7.825 µg g⁻¹ for fluids, with a corresponding range of Li isotope ratios.

The Li isotope compositions of basalts BCR-2 and BHVO-2 have been reported to be homogeneous with a $\delta^7\text{Li}$ variation of < 1‰ (Figure 7a). The mean $\delta^7\text{Li}$ values of BCR-2 and BHVO-2 determined here were $2.64 \pm 0.10\text{‰}$ (n = 5) and $4.39 \pm 0.23\text{‰}$ (n = 3), consistent with reported values of 2.6–3.5‰ and 4.1–5.5‰, respectively (Zack *et al.* 2003,

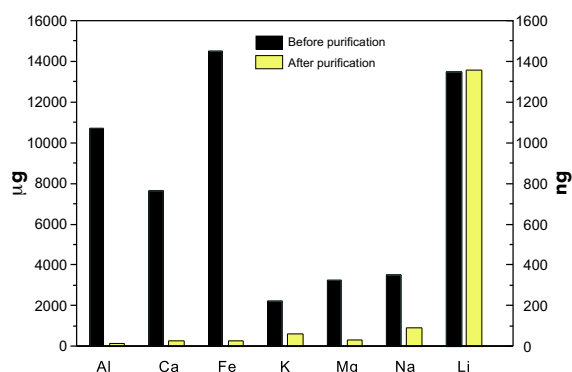


Figure 5. Lithium and other major elements in final solutions after the two-step chemical procedure. [Colour figure can be viewed at wileyonlinelibrary.com]

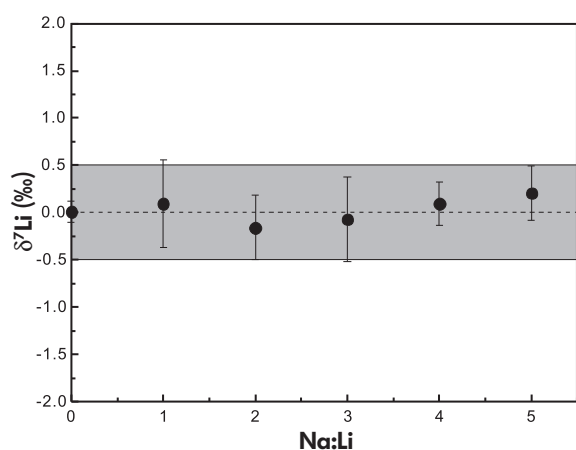


Figure 6. Influence of Na/Li ratio on measured lithium isotopic composition of IRMM-016 reference solution.

Jeffcoate *et al.* 2004, Kasemann *et al.* 2005, Magna *et al.* 2006a, b, 2008, Marschall *et al.* 2007, Rosner *et al.* 2007, Huang *et al.* 2010, Pogge von Strandmann *et al.* 2011, 2012, Vlastélic *et al.* 2011, Gao and Casey 2012, Brant *et al.* 2012, Penniston-Dorland *et al.* 2012, Genske *et al.* 2014, Ryu *et al.* 2014, Lin *et al.* 2015, Bohlin *et al.* 2018). Regarding AGV-2, several researchers thought it heterogeneous in terms of Li isotopic composition (Tian *et al.* 2012, Lin *et al.* 2015, Gou *et al.* 2017). The $\delta^7\text{Li}$ value for AGV-2 in this study was $6.57 \pm 0.63\text{‰}$ ($n = 6$), agreeing with the reported values of 5.68–6.85‰ by Su *et al.* (2011), Tian *et al.* (2012), Lin *et al.* (2015) and Gou *et al.* (2017), but much lower than the reported 7.92–8.14‰ by Magna *et al.* (2004, 2006a, b) and Huang *et al.* 2010 (Figure 7a). Analysis of RGM-2 yielded a $\delta^7\text{Li}$ value of $2.59 \pm 0.33\text{‰}$ ($n = 4$), consistent with a published value of 2.75‰ (Lin *et al.*

Table 4. Summary of Li isotope compositions of replicate sample preparations

Sample (type)	Date	$\delta^7\text{Li}$	2s	
BCR-2 (basalt) 9 ± 2 µg g ⁻¹	2016/10	2.64	0.42	
	2016/11	2.64	0.14	
	2017/03	2.69	0.31	
	2017/09	2.56	0.13	
	2017/09	2.67	0.20	
	2019/06	2.89	0.00	
Mean		2.68	0.22	
Literature range		2.6–3.5		
BHVO-2 (basalt) 5 µg g ⁻¹	2016/10	4.39	0.69	
	2016/11	4.27	0.36	
	2018/10	4.5	0.17	
	Mean		4.39	0.23
	Literature range		4.1–5.5	
	AGV-2 (andesite) 11 µg g ⁻¹	2016/10	6.11	0.57
2016/11		6.20	0.53	
2017/03		6.89	0.33	
2017/03		6.22	0.53	
2017/03		6.89	0.19	
2017/09		6.11	0.57	
2017/09		6.47	0.01	
2017/09		6.66	0.22	
2017/09		6.66	0.22	
2019/06		6.50	0.75	
2019/06	6.26	0.02		
2019/06	6.73	0.23		
Mean		6.46	0.60	
Literature range		5.68–6.85		
Literature range		7.92–8.14		
RGM-2 (andesite) 57–63.2 µg g ⁻¹	2019/03	2.65	0.42	
	2019/06	2.34	0.36	
	2019/06	2.67	0.05	
	2019/06	2.68	0.51	
	2019/06	2.59	0.33	
Mean		2.75		
AC-E (granite) 88 µg g ⁻¹	2017/09	3.48	0.07	
	2018/10	3.5	0.17	
Mean		3.49	0.03	
GSP-2 (granite) 36 µg g ⁻¹	2019/03	-1.00	0.56	
	2019/06	-0.92	0.94	
	2019/06	-0.69	0.09	
	2019/06	-0.87	0.32	
Literature range		-0.78 to -0.86		
CASS-5 (seawater) 0.174 µg ml ⁻¹	2016/09	30.69	0.06	
	2016/10	31.49	0.79	
	2016/10	30.84	0.41	
	2017/09	30.91	0.16	
	2018/10	30.8	0.23	
	2018/10	30.6	0.59	
	2019/06	30.73	0.74	
Mean		30.87	0.59	
Literature range		29–32		
JH (salt lake water) 7.825 µg ml ⁻¹	2017/09	29.15	1.16	
	2017/09	28.84	0.3	
Mean		28.99	0.43	

Each value was obtained through the whole sample preparation.

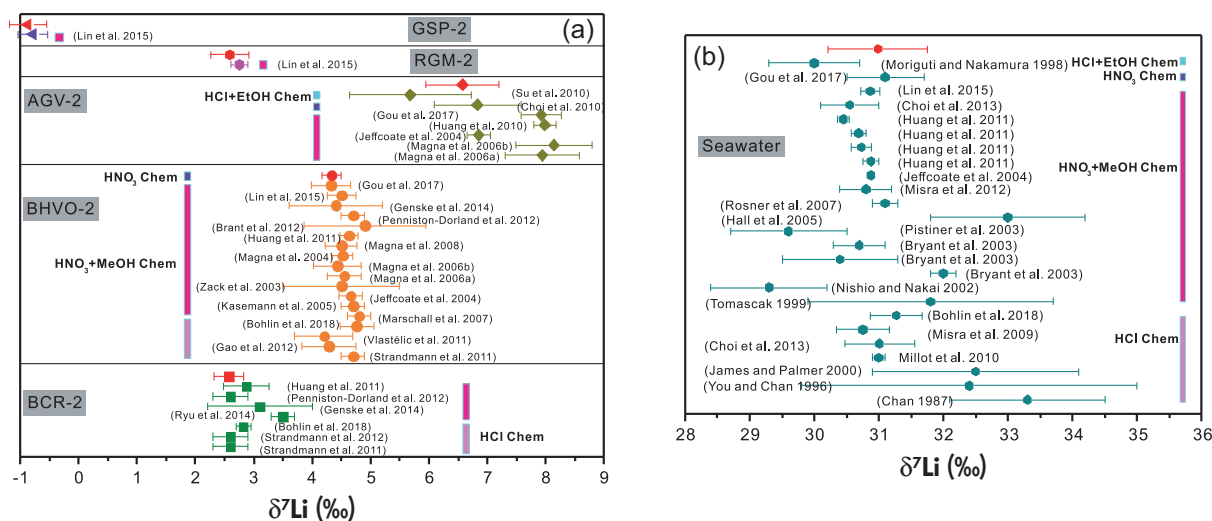


Figure 7. (a) Lithium isotope composition of rock reference materials BCR-2, BHVO-2, AGV-2, RGM-2 and GSP-2; (b) Lithium isotope compositions of seawater. [Colour figure can be viewed at wileyonlinelibrary.com]

Table 5.
Summary of published lithium separation methods

Step	Resin volume	Resin	Eluent	Collected volume (ml)	Collected position (ml)	Test	Reference
1	~ 20 ml	AG 50WX8	0.15 mol l ⁻¹ HCl	60	120–180	MC-ICP-MS	Wang <i>et al.</i> (2006)
2	2.7 ml	AG 50WX12	0.2 mol l ⁻¹ HCl	36	24–42	TIMS	James and Palmer (2000)
2	2.7 ml	AG 50WX12	0.2 mol l ⁻¹ HCl	36	24–42	TIMS	James and Palmer (2000)
2	15 ml	AG 50WX8	0.2 mol l ⁻¹ HCl	135	27.5–162.5	MC-ICP-MS	Gao and Casey (2012)
2	5 ml	AG 50WX12	0.2 mol l ⁻¹ HCl	85	7.5–92.5	MC-ICP-MS	Gao and Casey (2012)
1	100 ml	AG 50WX8	0.5 mol l ⁻¹ HCl	100	240–340	MC-ICP-MS	Chan (1988)
1	15 ml	AG 50WX8	0.5 mol l ⁻¹ HCl	26	38–64	TIMS	You and Chan (1996)
1	8 ml	AG 50WX8	0.5 mol l ⁻¹ HCl	22.5	15–37.5	MC-ICP-MS	Hoecke <i>et al.</i> (2015)
1	8 ml	AG 50WX12	0.5 N HNO ₃	32	18–60	MC-ICP-MS	Gou <i>et al.</i> (2017)
2	7 ml	Dowex 50WX8	0.5 mol l ⁻¹ HCl	37	15–38	MC-ICP-MS	This work
2	2.5 ml	Dowex 50WX8	0.3 mol l ⁻¹ HCl	37	10–24	MC-ICP-MS	This work

2015). The $\delta^7\text{Li}$ value obtained for ACE ($3.49 \pm 0.03\text{‰}$; $n = 2$) is consistent with reported values for I-type granites ($1.9\text{--}8.0\text{‰}$) (Teng *et al.* 2004). The measurement result for GSP-2 ($-0.87 \pm 0.32\text{‰}$; $n = 3$) is similar to the reported range of $-0.86\text{--}0.78\text{‰}$ (Lin *et al.* 2015).

The Li isotope composition of modern seawater is considered to be homogenous due to the long residence time of Li in seawater (~ 3 Ma; Bryant *et al.* 2003), with published $\delta^7\text{Li}$ values of $29\text{--}33\text{‰}$ (Edmond *et al.* 1979, Chan 1987, Huh *et al.* 1998, Moriguti and Nakamura 1998, Bryant *et al.* 2003, Pistiner and Henderson 2003, Choi *et al.* 2010 and Choi *et al.* 2013, Millot *et al.* 2010, Misra and Froelich 2012, Gou *et al.* 2017). Modern seawater is therefore suitable for use as a Li isotope reference material. Here, $\delta^7\text{Li}$

values measured in seawater were $30.88 \pm 0.63\text{‰}$ ($n = 6$) (Table 4), consistent with reported values (Figure 7b). The saline lake water (JH) yielded $\delta^7\text{Li}$ values of $28 \pm 0.63\text{‰}$ ($n = 3$), similar to those of seawater. Lithium sources for salt lakes in inland China include weathering, evaporation and the consequent precipitation of saline minerals, resulting in Li enrichment and contributing to heavier isotopic compositions (Xiao *et al.* 1994).

Comparison with other methods

The Li isotope compositions of CRMs purified by different methods do not display systematic variations, although the various methods used differ in time commitment and reagent consumption (Table 5). The two-step method proposed in this

study required collection of 37 ml total eluents, much less than 100 ml in Chan (1987), 60 ml in Wang *et al.* (2006) and 220 ml in Gao and Casey (Table 5). The time required was less than 5 and 4.5 h for column 1 and column 2, respectively, significantly shorter than the > 20 h Li purification by the two-step chromatographic column of Gao and Casey (2012) and 24 h of Wang *et al.* (2006). James and Palmer (2000) achieved a good separation between Li and Na by repeating same column chromatographic process and collecting a relatively small volumes of eluents (36 ml). However, its elution curves are susceptible to sample matrix, especially for Mg- or Fe-rich silicate samples and seawater, which is similar to the shift of elution curves in Chan (1987), You and Chan (1996) and Chan *et al.* (2002). Hoecke *et al.* (2015) separated Li from Na using a single resin column and 0.5 mol l⁻¹ HCl, but the fractions containing Na residual were attributed to resin contamination and were not further treated. Our study shows that early breakthrough of Na should be paid more attention, especially when single-column purification (e.g., Hoecke *et al.* 2015, Gou *et al.* 2017) is undertaken. In our proposed method, the second step is designed to remove Na residual after the first column chromatography, achieving Li purification from different sample matrices with relatively low volumes of eluents and time.

Conclusions

The proposed two-column method provides quantitative recovery of Li and is suitable for the determination of Li isotope ratios in geological materials and natural fluids with satisfactory analytical precision and accuracy. Our experiments showed that Na early breakthrough occurred even when there was sufficient resin capacity, which requires more consideration if Li purification is undertaken using a single column. However, sample solutions purified from the two-column method proposed here have Na/Li ratios much less than 5, ensuring analysis by MC-ICP-MS without interference. Lithium isotopic compositions of RMs determined by this method were consistent with previously published values.

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Supporting information

The following supporting information may be found in the online version of this article:

Figure S1. (a) Schematic diagram of the ion exchange column. (b) Interaction process of sample loading and elution.

Figure S2. MC-ICP-MS cone after the determination of sample solutions treated by the organic solvent EtOH (ethanol).

Table S1. Distribution coefficients in different acid solutions.

Table S2. Chemical composition of rock and water reference materials.

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