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Accurate Determination of Lithium Isotopic Compositions in Geological Samples by Multi-collector Inductively Coupled Plasma-Mass Spectrometry

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Abstract: Accurate determination of lithium (Li)isotopic composition in natural geological samples is the basis for Li isotope geochemical studies. In this study, a method contained preparation of geological materials (water and rock) and accurate determination of Li isotopic composition was set up. The separation of Li from water and rock samples was implemented by a single column containing 1.5 mL of Bio-Rad AG 50W-X12 (200–400 mesh) resin, with 0.40 M HCl and 1.0 M HCl as eluents. Only 8.5 and 14 mL of eluents were used to separate Li from water and rock samples with this method, respectively. Blank signal of the operation procedure was (2.4 ± 0.1) mV, which was almost same as the 2.3 mV of the 2% HNO_3 signal used in this study. Experimental results showed that Li isotopic fractionation during leaching process was significant and deviation of δ^7Li values in these samples with incompletely recovered Li reached up to 50‰. Lithium isotopic ratios were determined by multi-collector ICP-MS (Nu Plasma II) using the sample standard bracketing (SSB) method. L-SVEC standard with similar Li concentration to samples (about 80 ng mL^{-1}) was used in this study. The external precision (2σ) of this technique, determined by repeated measurement of pure Li standard solutions and seawater was $< \pm 0.8$‰. The measured δ^7Li values of seawater and rock standards AGV-2, BCR-2 and GSP-2 were $+31.4$‰ ± 0.7‰ ($n = 18$), $+7.23$‰ ± 0.16‰ ($n = 4$), $+3.7$‰ ± 0.7‰ ($n = 8$) and -0.10‰ ± 0.18‰ ($n = 4$), respectively, similar to previously published values. This method could be used to accurately determine Li isotopic composition of various types of geological samples such as waters and rocks. The advantage of this method was that the amount of resin and reagent was reduced to 50% or less of the previous studies, thereby significantly improving the work efficiency and reducing the operation procedure blank.

Key Words: Lithium isotopic composition; Multi-collector inductively coupled plasma mass spectrometry; Lithium isotopic fractionation

1 Introduction

Lithium (Li) has two stable isotopes, ^6Li and ^7Li, with natural abundances of 7.52% and 92.48%, respectively[1]. Due to the large relative mass difference between the two isotopes (16.7%), the Li isotope is strongly fractionated in nature. The δ^7Li value of samples in the earth's surface environment varies from –20‰ to +45‰, covering almost the range of Li isotopic composition of all natural reservoirs[2]. Because Li has only one valence state (+1) in nature, its isotope fractionation is not directly influenced by the redox environment. In addition, Li isotopic behavior is almost not influenced by biological processes compared to other non-traditional stable isotopes (such as Mg, Si, B, etc.)[3]. Therefore, Li isotope plays an irreplaceable role in tracing some key geochemical processes. Accurate

determination of Li isotopic composition in different types of geological samples is the basis of Li isotopic geochemistry research, especially samples in earth's surface environment (such as water, soil and rock). As a result, an analytical method for the composition of Li isotopes in many different types of natural geological samples is urgently needed.

At present, Li isotopic ratio of geological samples was mainly determined by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and single analysis took approximately 8 min. The external precision (2σ) of this technique was usually better than ±1‰. However, Li in the sample should be separated from other metal cations before using MC-ICP-MS to analyze the Li isotopic ratio, otherwise the matrix effect would cause serious deviations in the analysis results. Generally, Li in sample was separated and purified using a cationic resin exchange column, but the types and volumes of eluents and the separation steps used by researchers were different. For example, some researchers used low concentrations of HCl or HNO_3 and also a mixture of HCl or HNO_3 with methanol or ethanol as eluents, and the volume of the total eluent was 25–190 mL and the Li-containing eluent was 15–80 mL[4–9]. Additionally, each sample was undergone different separation times (1–3 times) by the column. Although previous researchers established different separation methods for different types of samples, the application of each method had limitations. Therefore, to some extent, the application and development of Li isotopic geochemistry were limited.

In theory, a universal separation method for different types of samples can be achieved by increasing the amount of resin. However, the blank of Li actually produced by the operation procedure is ten times than theoretical calculation, and the extra blank of Li is mainly derived from the resin[10]. So the larger the amount of resin is used, the more Li blank is produced. Furthermore, the volume of eluent will increase as the amount of resin increases, and then it will take more time to evaporate the Li-containing eluent. Additionally, process of recycling resin will also consume more concentrated HCl or HNO_3. Therefore, these processes will lower the work efficiency and potentially increase blanks.

This study intended to establish a set of separation methods suitable for soil, rock (basalt, andesite, granite) and water samples (seawater, salt lake water, river water, hot springs), and reduced the amount of the resin and eluent used as much as possible. The resin employed was BioRad AG50W-X12 (200–400 mesh). The Li was eluted with 0.40 and 1.0 M HCl. The separation was 1 or 2 times. The separation method in this study greatly reduced the amount of eluent used compared with previous studies[4,7–9], improved work efficiency and reduced Li blanks. Li isotopic ratios were determined by MC-ICP-MS (Nu Plasma II) and the external precision (2σ) of this technique was better than ±0.8‰.

2 Experimental

2.1 Materials, reagents and standards

A column (PFA, Savillex), approximately 20 cm in length, was used for chemical separation. The resin used in this study was Bio-Rad AG 50W-X12 (200–400 mesh). PFA vessels (15 mL, from Savillex, USA) and Teflon beakers (10 mL) were used for solid sample dissolution and Li-containing eluent collection, respectively. Commercially ultra-pure (HNO_3, HCl) and superior pure (HF) acid were purified twice using the acid purification system (Savillex, DST-1000). Ultrapure water was produced by the Mili-Q Element ultrapure system (18.2 MΩ cm). The 0.40 M and 1.0 M HCl eluents were calibrated by acid-base titration after 4 times and 10 times dilution, respectively. The standard materials included L-SVEC (pure lithium carbonate from National Institute of Standards (NIST)), basalt BCR-2, andesite AGV-2 and granodiorite GSP-2 from US Geological Survey (USGS) and seawater (from the South China Sea).

2.2 Sample preparation

2.2.1 Preparation of water samples

The water samples in this study included sea water, salt lake water, hot spring water and river water samples. The concentration of Li solutions for analysis was 80 ng mL^{-1}. The volume of each sample solution should be enough to be analyzed at least three times, therefore, the total amount of Li in the water sample for purifying was no less than 160 ng (about 40 ng in single analysis). Water sample was transferred to a Teflon beaker, evaporated to dryness on a hot plate (120 °C), and then evaporated to dryness (120 °C) again after adding 1 mL of concentrated HNO_3. Finally, the evaporated sample was taken out from the hot plate and cooled slightly. Then 1 mL of 0.40 M HCl was added to dissolve the sample for next chemical separation.

2.2.2 Preparation of rock and soil samples

According to the content of Li in different samples, the samples were weighed accurately (20–50 mg) and loaded in PFA vessels. The steps for dissolving were as follows: (1) 4 mL of mixed acid (concentrated HF and concentrated HNO_3 mixed in 3:1, *V/V*) was added to the vessel (the amount of mixed acid could be increased or decreased according to the sample amount), and then the vessel was sealed and placed on a hot plate for 24 h (150 °C). (2) Open the lid and evaporate to dryness under 120 °C, then 1 mL of concentrated HNO_3 was added and followed by a 10 min ultrasonic processing, and then evaporated again (120 °C). This step should be repeated 2–3 times, until the precipitate changed from white to brown

and soluble in concentrated HNO_3. (3) 3 mL of concentrated HNO_3 was added to the precipitate in the digestion tank, heated on a hot plate (120 °C) for 12 h, and then evaporated to dryness (120 °C). (4) 3 mL of concentrated HCl was added to the vessel, and heated on a hot plate (120 °C) for 12 h until the solution was clear without impurities, and then was evaporated to dryness (120 °C) in the open state. Finally, 1 mL of HCl (1.0 M) was added to dissolve the precipitate for chemical separation.

2.3 Chemical separation

2.3.1 Separation of water samples

The purification of Li in the water sample was carried out using a one-step column separation method. (1) The column was cleaned by leaching sequentially with 6 M HCl and ultrapure water, and the resin was washed with 2 mL of HCl (6 M) and 2 mL of ultrapure water (repeat 3 times). Then the washed resin (1.5 mL) was loaded into the column carefully to ensure no bubbles. (2) The resin was conditioned with 2 mL of HCl (0.40 M). (3) Then the prepared samples were added into the column. (4) After the sample flowed through the column, 0.5, 0.5 and 2.5 mL of HCl eluent (0.40 M) were added successively, and the waste liquid was discarded. (5) 5 mL of M HCl (0.40) was added to the column and the Li-containing eluent was collected using a Teflon beaker which was cleaned with acid and ultrapure water. (6) The eluent collected in step 5 was evaporated to dryness (120 °C), and after cooling slightly, 2 mL of HNO_3 (2%) was added and transferred to a tube for Li isotope analysis.

2.3.2 Separation of rock and soil samples

Separation of Li from rock and soil samples was carried out using a two-step column separation method. The first step of the separation method was as follows. The column was cleaned by leaching sequentially with HCl (6 M) and ultrapure water, and the resin was washed with 2 mL of HCl (6 M) and 2 mL of ultrapure water (repeat 3 times). Then the washed resin (1.5 mL) was loaded into the column carefully to ensure no bubbles. The resin was conditioned with 2 mL of HCl (0.40 M) and the prepared samples were added to the column. After the sample was passed through the column, 0.5 mL and 1.0 mL of HCl eluents (1.0 M) were added successively. At last, 4.0 mL of HCl (1.0 M) was added to the column and the rinsed solution was collected by Teflon beaker. The second step was the same as in Section 2.2.1.

2.4 Analysis of Li content

The Li content in the eluent samples was determined by ICP-MS. The contents of major elements such as Na, K, Ca and Mg were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The Li isotopic composition of the samples was determined by MC-ICP-MS (Nu Plasma II). The purified samples were introduced into the instrument with 2% HNO_3 (*V/V*), ensuring Li concentrations were about 80 ng mL^{-1}. The test process used two Ferrari cups H9 and L6 to collect the signals of ^7Li and ^6Li, respectively. The main parameters during the operation of the instrument are shown in Table 1. Since Li only has two stable isotopes, internal calibration of mass fractionation is impossible to achieve during the process of analyzing, the analysis process should follow this sequence: blank—standard—blank—sample—blank—standard…… Prior to analysis of each sample, the instrument should be cleaned with 2% HNO_3 until the signal value of ^7Li was below 10^{-3} V (signal/noise ratio was approximately 10^4).

The experimental procedures above were performed at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, and sample preparation process was completed in the clean room.

The test results are expressed as $δ^7Li$, which are calculated by the formula (1), where the ($^7Li/^6Li$) standard is the average of the two standards $^7Li/^6Li$ adjacent to the sample, and the Li isotope standard is L-SVEC.

$$δ(^7Li/^6Li) = [(^7Li/^6Li)_{Sample} − (^7Li/^6Li)_{Standard}]/(^7Li/^6Li)_{Standard} × 1000‰ \qquad (1)$$

3 Results and discussion

3.1 Separation of Li from sample matrix

The cation exchange resin method can easily separate Li from other metal cations except Na[4]. In the periodic table, Li and Na belong to the first main group (group IA), which have similar chemical properties and similar partition coefficients between the resin and acidic medium. The content of Na in the natural sample is much higher than Li, so it is difficult to completely separate Na in the process of separation and purification, which is also a hot topic discussed by researchers[4,7]. If the method could effectively separate Li and Na, the content of other metal ions in the Li solution after separation and purification can be negligible. Therefore, the separation method for Li in different samples always focuses on how to separate Li from Na efficiently.

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

Instrument	Parameters
RF power	1300 W
Cool gas	13 L min^{-1}
Auxiliary gas	0.8 L min^{-1}
Intensity of Li	4 V mL ng^{-1}
Sample gas	0.1 mL min^{-1}
Pressure of analytical chamber	$< 1 × 10^{-6}$ Pa

3.1.1　Separation of Li from water samples

The leaching curve was established based on seawater, L-SVEC, river water and salt lake water samples. According to the leaching curve (Fig.1), Li started to be rinsed out at the 5 mL of eluent and was completely rinsed out at the 8th mL of eluent. However, Na began to be rinsed out at the 10 mL, indicating that Li and Na could be completely separated. Although the sample types varied greatly, Li was eluted in the same volume range, except for the salt lake water. Therefore, the collected volume range of Li was set to 3.5–8.5 mL. The recovery of Li was 98.6%–102.3% (average 100.6%, $n = 30$), suggesting that Li was recovered completely. The contents of other major cations (K, Na, Ca, Mg, Fe, Mn and Al) in Li solutions were almost lower than the detection limit (0.01 M). It was concluded that Li in the water samples could be effectively separated from other metal cations by the chemical separation method in this study. In addition, the Li blank signal ((2.4 ± 0.1) mV) of operation procedure was almost identical to that of 2% HNO_3 used (2.3 mV), which was determined by MC-ICP-MS.

3.1.2　Separation of Li from rock and soil samples

The pretreated sample was added to the column and collected according to the separation method of Li in the water sample. However, the results showed that the expected recovery rate of 100% was not achieved and recovery rates of some sample were only about 50%. Although the recovery rate of some samples was close to 100%, the Na content was abnormally high. Therefore, the separation method of Li in the water sample was not suitable for separating Li in rock and soil samples directly, because the rock and soil samples were more complex and contain more matrix ions than the water samples.

Some researchers usually used multiple (2–4) different exchange columns to separate Li from solid samples such as rocks to remove different kinds of metal cations, and finally obtain relatively pure Li solution[10,11]. In this study, a two-step exchange method was used. At the first step, most of the cations were removed, but excess Na and a small amount of other cations were still in the Li solution. At the second step, the cations such as Na were removed according to the separation method of Li in the water sample, and the separation of Li was completed finally. To improve efficiency, 1.0 M HCl was used as the eluent for the first step. The results indicated that the ranges of Li eluted from three types samples (rock standard: BCR-2; soil sample: GD-21; pure lithium carbonate: L-SVEC) were basically identical, and Li was eluted at the 3 mL, rinsed out at 5 mL completely, and the recovery rates were all about 100% (Fig.2A).

Since most cations had been removed in the first step, the Li elution curve of second step was established according to the separation method of water sample. The results showed that the Li leaching curve of second step was almost the same as that of the water sample. At the 5 mL, Li was rinsed out, and was completely rinsed out at the 8 mL; while Na was rinsed out from the 11 mL (Fig.2B). Similarly, soil samples and rock samples with known Li content were dissolved and then loaded into the column. The leached solutions were collected after two steps separation. The Li content of the solutions was determined and the recovery rates were between 98.1% and 103.6% (average 100.8%, $n = 20$). Other major cations (such as K, Na, Ca, Mg, Fe and Al) in the solutions were also determined. The results showed that except for trace
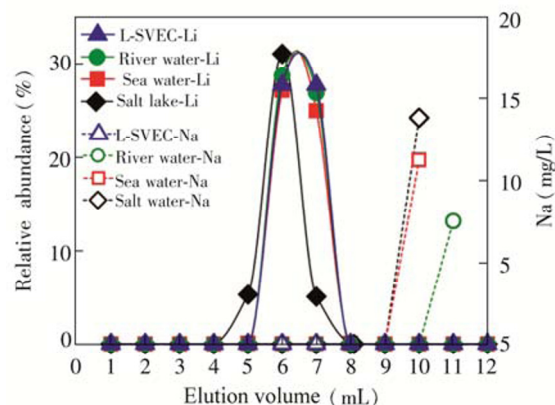

Fig.1　Elution profiles of Li for seawater, salt water, river water and L-SVEC
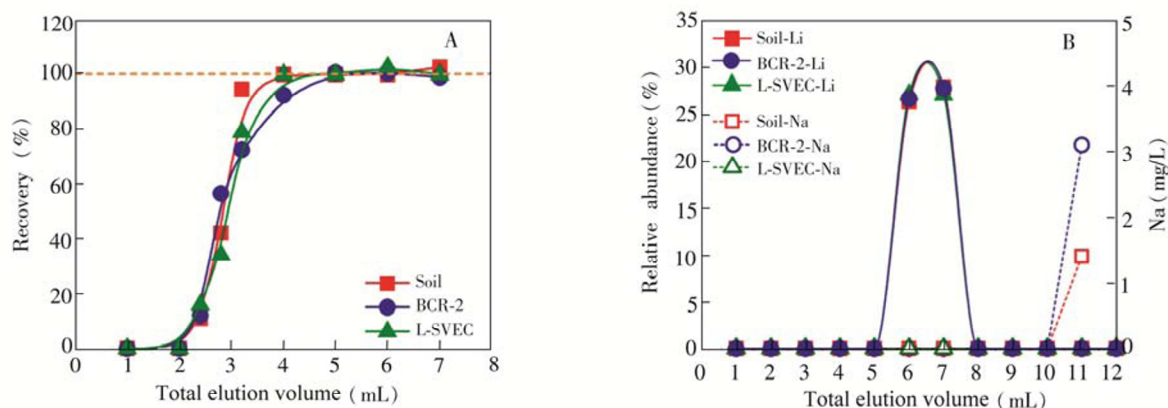

Fig.2　Elution profiles of Li for BCR-2, L-SVEC and soil sample ((A) and (B) represent the first and second column, respectively)

amounts of Fe and Al (maximum 0.02 mg L^{-1}), levels of other cations were almost lower than detection limit (0.01 mg L^{-1}). Additionally, the obtained Li solutions needed to be diluted to 80 ng mL^{-1} when the Li isotope was analyzed by MC-ICP-MS, so the contents of Fe and Al in the final solutions were negligible. Therefore, the two-step column separation method could effectively purify Li from rock and soil samples.

3.2　Matrix effect

The hydro-geochemical compositions of natural waters varied so greatly that the Na/Li (molar ratio) values differed by several orders of magnitude. Usually, river water had a Na/Li value of 103 and seawater could be up to 2×10^4. According to previous studies, when MC-ICP-MS was used to determine the Li isotope composition, excessive Na content would seriously affect the results of Li isotope analysis[4]. In this study, Na was quantitatively added to samples with their Li isotopic composition known (L-SVEC, δ^7Li=0) to obtain a series of solutions having Na/Li ratios of 1 to 5 (molar ratio), and then the Li isotopic compositions of solutions were determined. The results showed that with the increase of Na/Li ratio, Li isotopic ratio had a slight decrease. But the Li isotopic ratio was not affected by the Na content when the Na/Li ratio was less than 3 (Fig.3).

Tomascak et al[12] added Mg and Na to the purified Li solutions separated from seawater sample and the ratio of Na/Li (or Mg/Li) was 1–5, and the measured Li isotopic ratio of these samples did not change significantly. Wang et al[4] found that the determination of Li isotopic ratio was relatively stable when the Na/Li ratio of sample was lower than 5, but the Li isotopic ratio would increase when the Na/Li ratio was greater than 5. Su et al[7] found that when the Na/Li ratio was less than 20, it would not have a significant effect on the Li isotope ratio determination. However, Gou et al[9] believed that it was also feasible to determine the Li isotope ratio when Na/Li was 50–128 (mass ratio). In this study, the Na/Li values of Li solutions separated from water samples, rocks and soil samples were all less than 0.1, so there was no influence on the determination of Li isotope ratio.

3.3　Li isotope fractionation during chemical separation

L-SVEC (δ^7Li = 0) was added into the column, and Li elution solutions of different stages were collected according to the elution curve which was established previously. For the first step of separation method of solid samples, the first 2.8, 3.2, 4.0, 5.0, 6.0 and 7.0 mL leaching solutions were collected, and then the Li isotopic composition was determined. As shown in Fig.4, the δ^7Li values of the first 2.8 and 3.2 mL were +16.4‰ and +5.8‰, indicating that the Li isotope was significantly fractionated during the leaching process and the δ^7Li value in early leaching solution was higher than L-SVEC before the leaching; while the δ^7Li of the first 4.0, 5.0, 6.0 and 7.0 mL was close to the L-SVEC. For the separation method of water samples, the 5th, 6th, 7th and 8th milliliter leaching solutions were collected separately, and then determined the isotopic composition. The Li isotopic ratio of the 5th and the 8th milliliter solutions were not obtained because the low Li content in these solutions. The δ^7Li value of the 6th and the 7th milliliter leaching solutions were +18.5‰ and −30.1‰, respectively, indicating that the Li isotope was significantly fractionated during the leaching process, too. The difference of δ^7Li value between 6th and 7th milliliter leaching solutions was close to 50‰, and the δ^7Li value in early leached solution was higher than that of L-SVEC before the leaching, and the δ^7Li value of late rinse solution was lower than that of L-SVEC.
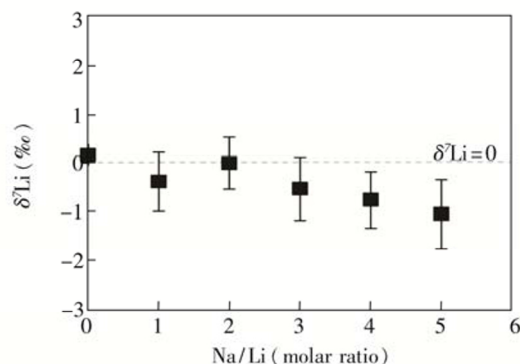

Fig.3　Effect of Na concentrations on Li isotope determination
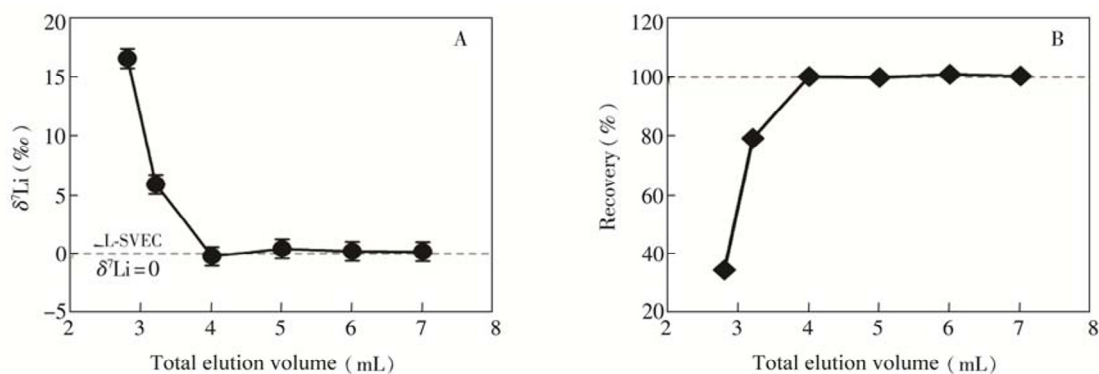

Fig.4 The δ^7Li value (A) and Li recovery rate (B) of eluent in different leaching stages

The above results showed that significant isotopic fractionation occurred during separation of Li using cation exchange resin, and ^{7}Li was preferentially eluted. This phenomenon was consistent with previous research. During the process of Li leaching from solid phase to liquid, ^{7}Li was preferentially eluted, while ^{6}Li tended to remain in the solid phase, resulting in Li isotopic fractionation[13]. Therefore, if Li was not completely recovered in the process of separating Li from the cationic resin, a deviation of ^{7}Li/^{6}Li from the actual value occurred, resulting in an error finally. For the first step of separation method of solid samples, the δ^7Li values of the first 4.0, 5.0, 6.0 and 7.0 mL leaching solutions were close to the L-SVEC, showing no fractionation. The reason was that Li was almost completely recovered when solutions were collected. Although fractionation occurred in the separation process, when the successively eluted solutions were mixed together, the δ^7Li value in mixed liquid was still consistent with L-SVEC. The result also conformed to the range of the elution curve of Li. From the early 4.0 mL, the recovery of Li eluent was close to 100%. Moriguti *et al*[10] studied Li isotope fractionation during separation and purification. They determined Li isotopic ratios in solutions with Li recovered incompletely, and also found that significant Li isotopic fractionation during the leaching process. The δ^7Li value in earlier eluted solution was relatively higher than that of in later solution, and the difference was up to about 200‰[10].

The δ^7Li values in the natural reservoirs differed by about 70‰. Therefore, if the recovery rate of Li was too low after chemical separation process, the determined Li isotopic ratio would have a serious deviation which could be reduced by ensuring recovery rate.

3.4 Mismatching effects of Li concentrations

The δ^7Li values of L-SVEC samples with different concentrations and sample/standard concentration ratio ranging from 0.5 to 2.5, were determined. The results varied from –0.4‰ to +0.2‰ (average –0.1‰ ± 0.9‰, 2σ, n = 13) (Fig.5), within the allowable range of determined error (0 ± 0.8‰), indicating concentration mismatch between sample and standard had no significant effect on δ^7Li value in this study, which was inconsistent with previous study results. They observed that if the sample and the standard Li concentration did not match, when the Li-isotope ratio was determined by MC-ICP-MS, the instrument discrimination effect would lead to different degrees of measurement error[7,9,14]. The contradiction may be caused by different assay instruments. This study used the Nu Plasma II, while others used the Neptune. For the mass discrimination effect, some researchers used 5% NaCl solution to eliminate the memory effect of Li and reduced the effect of concentration mismatch on the results[14]. In addition, some researchers controlled the sample/standard concentration ratio to 0.9–1.1 to reduce the

analysis error[9]. Although concentration mismatch in this study had no significant effect on results, the Li concentrations of the sample and standard were still controlled within 10% error range during the test.

3.5 Determination results of international standard substances and natural samples

To further verify the reliability of this analysis method, the Li isotopic composition of some natural samples (river water, salt lake water, hot spring water and soil) and international standard materials was determined. The δ^7Li value of seawater, AGV-2, BCR-2 and GSP-2 was +31.4‰ ± 0.7‰ (n = 18), +7.23‰ ± 0.16‰ (n = 4), +3.7‰ ± 0.7‰ (n = 8) and –0.1‰ ± 0.18‰ (n = 4), respectively. These results were in perfect agreement with the data reported by the previous researchers (Table 2). The accuracy of the repeated samples was better than 0.8‰, which was equivalent to the level of similar laboratories in the world, indicating the accuracy and precision of lithium isotope determination in this study were reliable.

4 Conclusions

A simple and efficient Li chemical separation method was established for various types of natural geological samples such as water samples and rocks, using AG 50W-X12 (200–400 mesh) resin and only HCl as leachate. Compared with previous studies, it greatly reduced the amount of eluent, improves efficiency and decreased the Li blanks in operation procedure. It was found that significant Li isotopic fractionation occurred during the leaching process, and ^{7}Li tended to preferentially be eluted. Therefore, it must be ensured that Li was completely recovered in the chemical separation process. The separation and purification method combined with MC-ICP-MS could accurately determine the Li isotopic composition of various types of geological samples. The determined results of some international reference materials were consistent with the data reported by previous studies, and the analytical precision reached the level of other laboratories in the world. Therefore, the data of Li isotope composition in the natural samples obtained by this method were credible.
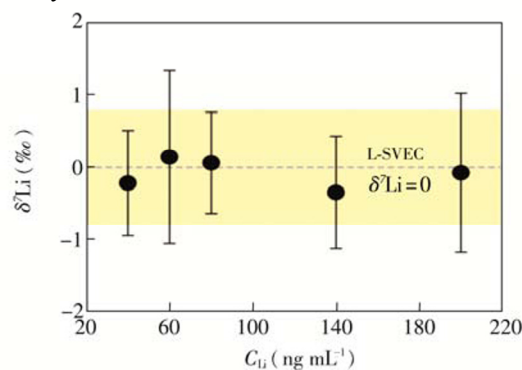

Fig.5　δ^7Li values of the L-SVEC with different concentrations of Li

Table 2   Standards and samples used for Li isotopic determination in experiment

Sample name	δ^7Li (Mean ± 2SD, ‰)	Reference	Sample name	δ^7Li (Mean ± 2SD, ‰)	Reference
Sea water	+30.0 ± 0.7	[10]	AGV-2	+5.13 ± 0.94	[7]
	+31.8 ± 1.9	[12]		+7.92 ± 0.34	[19]
	+29.3 ± 0.9	[15]		+6.1 ± 0.4	[23]
	+32.0 ± 0.2	[16]		+6.85 ± 0.2	[14]
	+31.1 ± 0.2	[17]		+6.83 ± 0.75	[9]
	+31.6 ± 1.0	[4]		+7.23 ± 0.16 ($n = 4$)	This study
	+31.2 ± 0.3	[18]	BCR-2	+4.08 ± 1	[24]
	+30.55 ± 0.45	[19]		+2.6 ± 0.3	[18]
	+30.91 ± 0.26	[20]		+2.7 ± 1.3	[3]
	+30.87 ± 0.15	[14]		+3.5 ± 0.2	[25]
	+31.3 ± 0.6	[21]		+3.7 ± 0.7 ($n = 8$)	This study
	+31.1 ± 0.7	[22]	Hot spring	+3.92 ± 0.56 ($n = 3$)	This study
	+31.4 ± 0.7 ($n = 18$)	This study	Salt lake water	+18.54 ± 0.47 ($n = 3$)	This study
GSP-2	−0.78 ± 0.25	[14]	River water	+8.83 ± 0.32 ($n = 3$)	This study
	−0.10 ± 0.18 ($n = 4$)	This study	Soil sample	−1.89 ± 0.64 ($n = 3$)	This study

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