〔Note〕

Improved Method for Seawater Lithium Isotopic Ratio Determination Using MC-ICP-MS

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We developed a simple, accurate, and sensitive analytical method for determination of the lithium isotopic ratio of seawater, using a multi-collector ICP mass spectrometer 〔MC-ICP-MS〕. The method involves a single-step column separation, and improvements in sensitivity and precision are achieved by the use of an X-type skimmer cone and relatively low plasma RF power on MC-ICP-MS. With this method, the δ^7Li value in standard seawater 〔NASS-5〕 was measured to be $+30.97 \pm 0.31$ ‰ 〔2σ〕, which is consistent with the reported value in previous studies. We obtained δ^7Li $= +30.82$ ‰ of surface seawater from the East China Sea, which is the same as those for open oceans, suggesting that the surface seawater is not influenced by meteoric water from the Eurasian Continent. As the sampling location is in the flow passage of the Kuroshio Current, the value represents the δ^7Li value of the Kuroshio Current.

Key Words : Li isotopic ratio, Seawater, MC-ICP-MS

1. Introduction

Lithium 〔Li〕, which is fluid mobile, has two isotopes, ^{6}Li 〔7.52 %〕 and ^{7}Li 〔92.48 %〕, the ratios of which vary widely in environmental samples. Li isotope ratios are useful for tracing weathering and hydrothermal alteration [1,2], fluid migration in the earth's crust [3] and material recycling between the mantle and crust [4,5]. In particular, knowledge of Li isotope ratios in seawater leads to important information for estimating the behavior of water mass. Nonetheless, the reported data for seawater have been limited [6-13], and that of the East China Sea has not been reported yet. The limitation of the data is due to a troublesome procedure of Li isolation and a regent purification [8], which require skillful techniques using analyzing devices [14], and a use of hydrogen fluoride 〔HF〕, which is difficult to handle [8]. In order to overcome these problems, this study reports a simple, accurate, and sensitive mass spectrometric analysis for the lithium isotope ratio of seawater without HF and a regent purification. Along with the report of the method, a measured Li isotope ratio for the East China Sea is reported with the developed method.

2. Experimental procedures

2.1 Solution preparation

EL-grade CH$_3$OH 〔Methanol for the Electronics Industry,

99.9 %; Kanto Chemical Co., Inc., Tokyo, Japan〕 was diluted with ultrapure water to prepare a 30 % CH$_3$OH solution. EL HNO$_3$ 〔Nitric acid for the Electronics Industry, 70 %; Kanto Chemical Co., Inc., Tokyo, Japan〕 was diluted with the 30 % CH$_3$OH to prepare a 0.67 M solution of HNO$_3$ in aqueous CH$_3$OH. EL CH$_3$OH was diluted with ultrapure water to prepare an 80 % CH$_3$OH solution, which was used to dilute EL HNO$_3$ to produce a 1 M solution of HNO$_3$ in aqueous CH$_3$OH 〔1 M HNO$_3$/CH$_3$OH〕. These HNO$_3$ solutions were used as eluents for Li separation. To dissolve the separated Li just before analysis by ICP-MS, we prepared a 0.3 M HNO$_3$ solution by diluting EL HNO$_3$ with ultrapure water. For washing the resin in the separation column, 6 N HCl was prepared by dilution of EL HCl 〔Hydrochloric acid for the Electronics Industry, 36 %; Kanto Chemical Co., Inc., Tokyo, Japan〕 with ultrapure water. Finally, a standard solution for determination of Li isotope ratios was prepared by dissolving L-SVEC 〔Li isotopes in lithium carbonate; 0.2694 g〕, which is a reference material for the Li isotope ratio prepared by H. Svec, Iowa State University [15], in 100 mL of approximately 0.3 M HNO$_3$, and measured the whole weight to be 101.2643 g for 499.8 ppm stock solution. We diluted the stock solution to 50 ppb with 0.3 M HNO$_3$; the 50 ppb solution was analyzed before and after each sample solution was analyzed, and the results were used to determine the Li isotope ratios of the sample solutions.

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2.2　Column preparation

Quartz wool was stuffed into the toe of a column with an internal diameter of 7 mm, and a cation exchange resin（2.2 mL, BioRad AG50W-X8, 200-400 mesh）was added on top of the wool to a height of *ca*. 5.5 cm. The resin was washed with 30 mL of 6 M HCl and 20 mL of ultrapure water and then stored in ultrapure water to prevent it from drying out.

2.3　Elution curve determination

An aliquot of seawater（5 mL）was placed in a Savillex® vial and evaporated to dryness at 100 ℃ on a hot plate. After the residue cooled to room temperature, it was dissolved in 0.5 mL of 0.67 M HNO_3/CH_3OH. The resin in the column was washed with 4 mL of 6 M HCl and 4 mL of ultrapure water and subsequently conditioned with 2 mL of 0.67 M HNO_3/CH_3OH. The sample（dissolved in 0.5 mL of 0.67 M HNO_3/CH_3OH）was loaded onto the resin; then 25 mL of 1 M HNO_3/CH_3OH was added to the column in 1 mL increments, and each 1-mL fraction was collected up to a total volume of 25 mL. The flow rate was *ca*. 15 min mL^{-1}. The eluted fractions were evaporated to dryness at 80 ℃ on a hot plate for several hours, and the residue was dissolved in 10 mL of 0.3 M HNO_3 for analysis by means of ICP-MS.

2.4　Collection and preparation of seawater samples

On June 2, 2002, a research vessel（R/V）*Hakuho* [16] sampled surface seawater in the East China Sea（ECS）on board with a bucket, and it was put through a filter（pore size：0.45 μm）. The sampling site is located at 24° 56.85'N, 122° 58.47'E, which is in the flow passage of the Kuroshio Current [16]. As a standard material, NASS-5 was used, which is fifth in a series of ocean water for trace metals distributed by National Research Council of Canada [17]. The seawater was taken in the North Atlantic at a depth of 10 m, 35 km southeast of Halifax, Nova Scotia province, Canada, filtered through 0.45 μm acrylic copolymer filters, and then acidified to pH 1.6 with ultrapure nitric acid.

NASS-5（*n* = 3）, blanks（*n* = 2）and an ECS sample（*n* = 1）were subjected to chromatographic separation. Aliquots（5 mL）of NASS-5 and ECS were placed in 7-mL Savillex® vials with screw caps and evaporated to dryness at 100 ℃. The residues were cooled to room temperature and dissolved in 5 mL of 0.67 M HNO_3/CH_3OH.

The resin in the column was washed with 4 mL of 6 M HCl and 4 mL of ultrapure water, and then conditioned with 2 mL of 0.67 M HNO_3/CH_3OH（**Fig. 1**）. A sample（dissolved in 0.5 mL of 0.67 M HNO_3/CH_3OH）was loaded dropwise on the column; 7 mL of 1 M HNO_3/CH_3OH was added to remove unnecessary cations; and then 9 mL of 1 M HNO_3/CH_3OH was added to recover Li. The eluate was evaporated to dryness at 80 ℃ on a hot plate, and the
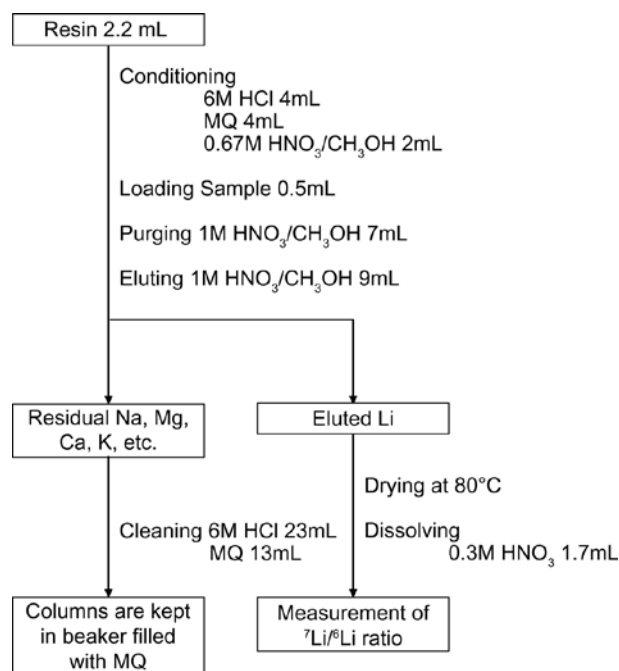

Fig. 1　Flow chart of the Li purification step used in this study

residue was dissolved in enough 0.3 M HNO_3 to bring the Li concentration to 50 ppb.

2.5　ICP-MS measurement

Li and other element concentrations of each 1-mL fraction were analyzed on a quadrupole ICP-MS system（*XSERIES 2*; Thermo Fisher Scientific, Bremen, Germany）, and elution curves were produced. For determination of the recovery test, Li concentrations were measured by the standard addition method. The precisions were within 3 %.

Li isotope ratios were measured by MC-ICP-MS（*Neptune Plus*; Thermo Fisher Scientific, Bremen, Germany）. For determination of analytical conditions, the sensitivities were compared with one another under each condition as a background value, as shown in **Table 1**. Then the stabilities of the measured values for 50 ppb L-SVEC were compared under two different conditions of a radiofrequency（RF）power（1200 and 800 W）. Each measurement consisted of 60 cycles of a 2-s integration procedure. The uptake time was 4 min, and the rinse time with 0.3 M HNO_3 was 3 min. Peak centering was performed before the first acquisition. The $^7Li/^6Li$ ratio is expressed as $\delta\,^7Li$, which is the deviation in parts per thousand relative to the L-SVEC standard（$^7Li/^6Li$ = 12.02 ± 0.03）:

$$\delta\,^7Li\,(‰)\ =\ \{(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{L\text{-}SVEC} - 1\}\ \times 1000 \tag{1}$$

Table 1 Comparison of the analytical intensity under different operating conditions

Plasma RF power (W)	1200	1200	1000	800
Extraction voltage (kV)	-2	-2	-2	-1.85
Skimmer cone	H type	X type	X type	X type
Gas flow rate (L min^{-1})				
Plasma Ar	15	15	15	15
Auxiliary Ar	0.8	0.8	0.8	0.75
Nebulizer Ar	1.04	1.175	1.052	0.925
Intensity signal (V)[a]				
The highest value	0.34	4.3–4.6	4.5	3.8–4.0
Background value	<0.01	<0.01	<0.01	<0.01

[a] The highest value and background value of intensity signal (V) were measured on mass 7 using a 50 ppb L-SVEC Li standard and 3% HNO_3, respectively.

3. Results and discussion

3.1 Elution curves

The elution curves are shown in **Fig. 2**. For all elements, the intensity（cps）was normalized by the intensity of the first fraction. None of the elements except Li eluted between 8 and 16 mL, and the intensity of Li was substantially larger than the intensities of the other elements, except Na. Na did not elute before the 20-mL fraction, and thus Na and Li could be clearly separated if the 8-16-mL fraction was recovered. None of the major elements in seawater, such as Mg, Ca and

K, eluted in this fraction（Fig. 2）. This method is based on Magna *et al.*（2004）, in which using CH_3OH and HNO_3 for an eluent, Li and other alkali（earth）metals show a large different retention, leading to successful separation between these elements [18].

3.2 Blank values and recovery ratios for column separation

Blank values and recovery ratios for column separation of NASS-5 are shown in **Table 2**. Prior to calculation of the recovery ratio, the Li concentration in NASS-5 was determined to be 21.2 μM by means of the standard addition method. The Li concentration in the blank samples was less than 1 nM, which is negligible. The average recovery ratio for the NASS-5 samples was 102.8 ± 0.8 %（$n = 3$）, indicating the Li was completely recovered within an analytical error of 3 %. There is no problem regarding the recovery ratios for the column separation in this study.

3.3 Cool plasma MC-ICP-MS

The ^{7}Li intensities of 50 ppb L-SVEC and background（BG）values measured 3 min after the start of 0.3 M HNO_3 uptake are shown in Table 1. Changing the skimmer cone from an H-type to an X-type increased the sensitivity by more than 10 times. Lowering the RF power（cool plasma）did not lower the BG value, in contrast to what was shown by Choi *et al.*（2013）but did lower the sensitivity（highest value, Table 1）. We evaluated the stability of the measured values during uptake of 50 ppb L-SVEC at the two different RF powers（**Fig. 3**）. At RF = 1200 W（hot plasma）,
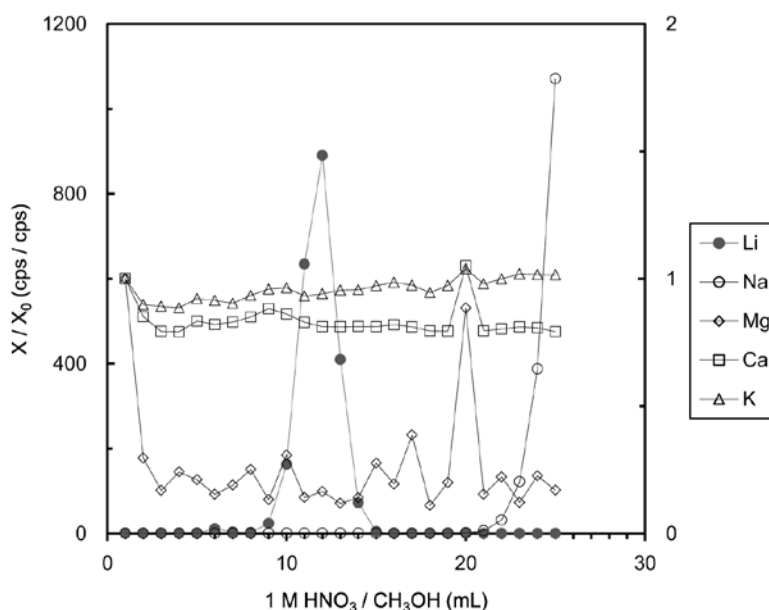

Fig. 2 Acquired elution curves for Li, Na, Mg, Ca, and K. The solid lines for Na and Li are indicated by a scale on a left axis, and the dotted lines for Mg, Ca, and K are indicated by the one on a right axis. The 25 mL of 1 M HNO_3/CH_3OH was added to the column with 1 mL step-by-step addition, and each 1-mL fraction was collected up to a total volume of 25 mL

Table 2 Blank and recovery ratio during column separation of Li from NASS-5

Sample	Li μM	Recovery %	δ^7Li ‰	2σ ‰
Blank	<0.001			
	<0.001			
Nass-5[*]	21.8	103%	+31.1	0.002
	21.7	102%	+31.0	0.002
	22.0	104%	+31.0	0.002

[*]Nass-5 : 21.2 μM determined by standard additional method using ICP-MS in this study.

Fig. 3 Stability of measured ^{7}Li/^{6}Li ratios for a 50 ppb L-SVEC solution at RF powers of 800 W（open circles）and 1200 W（crosses）. In this case, different from a sample analysis, analyses of standard materials bracket analysis of unknown sample were not carried out, so that a raw ratio between an intensity of ^{7}Li and that of ^{6}Li is shown for 8 or 9 analyses

scattering of ±0.8 ‰ was observed, whereas at RF = 800 W（cool plasma）, scattering of only ±0.3 ‰ was achieved. The ^{7}Li sensitivities for the hot and cool plasmas were 4.3 V（BG value = 7 mV）and 4 V（BG value = 10 mV）, respectively. The hot plasma was better in terms of both sensitivity and BG value. In terms of precision, however, the cool plasma was remarkably better.

To calibrate the drift of mass fractionation during measurement, we used the standard-sample bracketing technique, which requires a stepwise shift in proportion to time spent. If the measured values of the standard show a stepwise shift, the shift would be a function to use for calibration. However, the shift was not so systematic with time under the hot plasma condition（Fig. 3）, which is not appropriate for analysis of Li isotope ratios. Choi *et al.*（2013）did not discuss the difference in precision between hot and cool plasmas, but on the basis of the comprehensive evaluation conducted in this study, we conclude that cool plasma is more suitable for analysis of Li isotope ratios.

3.4 Seawater analysis

The Li isotope ratios we obtained for seawater by means of the cool plasma method are +30.97 ± 0.31 ‰（n = 7）for NASS-5 standard seawater, and +30.82 ± 0.002 ‰（n = 1）for surface seawater in the ECS（**Table 3**）. The δ^7Li values of NASS-5 have been reported to be +30.63 ± 0.17 ‰ [6-8], and the measured values are consistent with the reported values within analytical certainty. That of the ECS is equivalent to those of open oceans; +30.71 ± 1.85 ‰ for Pacific Ocean [6, 9, 19-21], +31.03 ± 0.99 ‰ for Atlantic Ocean [6-9, 22, 23], and +30.37 ± 1.37 ‰ for Mediterranean Sea [9-13]（Table 3）. The δ^7Li value of seawater in open oceans has been reported as +30.77 ± 0.43 ‰ and is homogenous at the level of analytical precision for the methods currently used to measure it, although that in coastal areas shows a
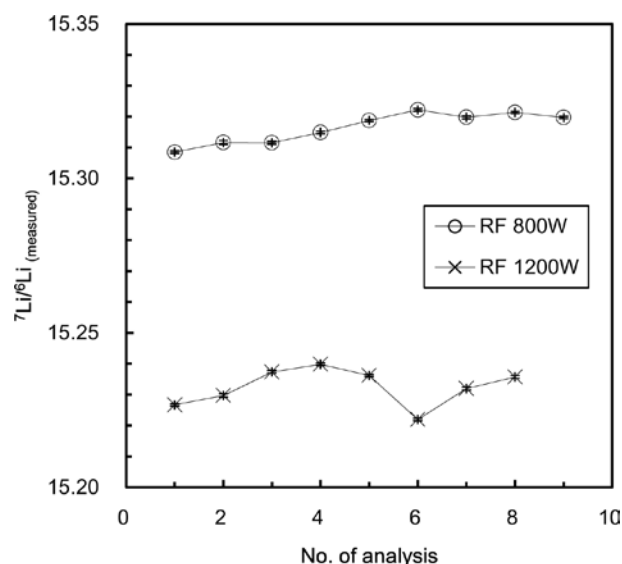
locality [6].

Into the ECS, a large amount of meteoric water from the Eurasian Continent flows [24], and the ECS is a marginal sea; the Ryukyu Island arc at the eastern to southeastern margin, Taiwan at the southern margin, and the Japanese islands at the northeastern margin. Whether or not a δ^7Li value of such a marginal sea is consistent with those of open oceans is important to know for discussion of the closed condition of the marginal sea. On the other hand, the Kuroshio Current has flowed into the ECS since the Last Glacial Maximum [25]. The Kuroshio Current is one of the largest currents in the world, and it has influence on the environments around the flow passage. It is very important to understand the flow passage of the Kuroshio Current when environments around the flow passage are discussed. The measured δ^7Li value for the ECS in the present study would represent that of the Kuroshio Current, since the sampling point was close to the flow passage of the Kuroshio Current and the δ^7Li value was consistent with those of open oceans without the influence of meteoric water（Table 3）. This datum should provide important knowledge in manifesting the behavior of the Kuroshio Current in the future.

4. Conclusion

In this study, we evaluated a simple, accurate, and sensitive method for determining the Li isotope ratios in

Table 3　δ ⁷Li values published for seawater from different ocean, along with external reproducibilities（2σ）and number of individually processed aliquots（n）

Area	Material	Ave	2σ	n	Reference
East China Sea	Sample	30.82	0.002	1	This study
Atlantic Ocean	NASS-5	30.97	0.31	7	This study
		30.63	0.44	3	Rosner et al. (2007)
		30.72	0.17	10	Huang et al. (2010)
		30.55	0.45	15	Choi et al. (2013)
	IAPSO	30.84	0.19	3	Rosner et al. (2007)
	Sample	31.17	0.16	16	Jeoffcoate et al. (2004)
		31.20	1.8	28	Millot et al. (2004)
		31.00	0.5	31	Millot et al. (2004)
		32.10	1.13	4	Hall et al. (2005)
Pacific Ocean	Sample	30.00	0.7	5	Moriguti and Nakamura (1998)
		31.93	1.2	3	Tomascak et al. (1999)
		29.30	0.9	3	Nishio and Nakai (2002)
		31.03	1.7	3	Bryant et al. (2003)
		31.13	0.18	2	Jeoffcoate et al. (2004)
		30.86	0.27	2	Rosner et al. (2007)
Mediteranean Sea	Sample	31.12	0.22	8	Jeoffcoate et al. (2004)
		29.60	0	2	Pistiner and Henderson (2003)
		29.70	0.42	4	Bouman et al. (2004)
		30.60	0.8	22	Kisakurek et al. (2004)
		30.85	1.4	1	Wunder et al. (2006)

seawater. First, we carried out a simple single-step chromatographic separation with a resin volume of 2.2 mL and an elution volume of 16 mL. The use of an X-cone instead of an H-cone increased the sensitivity more than 10 fold. The use of an RF power of 800 W decreased the sensitivity and increased the BG value, compared with those observed at an RF power 1200 W, but the precision was higher at the lower RF power. Using this method, we measured the Li isotope ratio of standard seawater to be + 30.97 ± 0.31 ‰（$n = 7$）, which is consistent with the reported ratios of standard seawater. Moreover, the Li isotope ratio of surface seawater in the ECS was measured to be + 30.82 ± 0.002 ‰（$n = 1$）, which is consistent with the reported values of seawater in open oceans. It suggests that surface seawater is not affected by meteoric water from the Eurasian Continent. Furthermore, the sampling site was near the flow passage of the Kuroshio Current so that the value would be expressive of the δ ⁷Li value of the Kuroshio Current.

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マルチコレクター ICP-MS を用いた海水中のリチウム同位体比分析法の開発

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要　旨

　本論文では，マルチコレクター ICP-MS を用いた海水中のリチウム同位体比の簡便で正確，かつ感度のよい分析方法を報告する．まず，分離は一段階のカラム分離だけで行い，X タイプのスキマーコーン及び低レベルに抑えたプラズマを用いることによって，精度と感度も確保した．本方法を用いて測定した標準海水（NASS-5）は，これまでの報告値とよく一致している．さらに，これまで明らかにされていない東シナ海の表層海水中のリチウム同位体比も測定した．得られた値は，外洋の値と一致しており，採取した場所が大陸からの陸水の影響を受けていないことを示唆している．また，採取した場所が黒潮の流路にあることも鑑みると，今回明らかになった値は黒潮の値を示していると考えられる．今後の水塊の移動過程や起源の研究において，こういった知見は大きな意義を持つ．

キーワード：リチウム同位体比，海水，マルチコレクター ICP-MS

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