REGULAR PAPER

**Determination of Li Abundances in Chondrules, Bulk Chondrites,
and Standard Rocks by Direct-Loading Isotope
Dilution Mass Spectrometry**

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Precise isotope dilution technique of Li, along with other alkalis, alkaline earths and iron, for tiny silicate materials (having as low as 10 pg Li) is described. Samples were decomposed by acids, equilibrated with mixed spikes including ^6Li and directly loaded on a mass spectrometer filament without chemical separation. Li and other lithophiles were measured by successive heating procedures. Results of precise Li analyses are presented for 7 Allende chondrules, 5 bulk chondrites and three standard rocks, JB-1, JB-2, and BCR-1.

1. Introduction

Lithium along with Be and B has an anomalously low cosmic abundance as a light element and has been argued for its origin in stellar environments.¹⁾ Bulk analyses of Li have been systematically carried out for meteorites in two to three decade in several laboratories.²⁾⁻⁵⁾ However, except for a few cases,⁵⁾⁻⁷⁾ individual meteoritic components such as chondrules have rarely been analyzed.

Lithium was reported to show abundance features similar to those for Mg for bulk meteorites,⁸⁾ but has not been sufficiently clarified for its cosmochemical properties. Although neutron activation analysis has been applied to determination of Li in meteorites,⁵⁾ its application to a trace analysis of Li for meteoritic components such as chondrules (Li ~ 2 ppm) have been limited. In view of current discoveries of heterogeneous distributions of elements and isotopes in primitive meteorites, it is important to clarify micro-distributions of trace elements and thus analysis of trace Li is considered to be of potential importance. In this connection, ion probe can be applicable. However, it is still of limited use in "bulk" elemental analyses for somewhat "larger" samples.

Previously, we have developed direct-loading isotope dilution mass spectrometry (DL-IDMS) technique of rare earth elements and other lithophiles for microgram-sized meteoritic materials.⁹⁾ Extending our previous works, we have established the DL-IDMS

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technique of Li and applied it to individual chondrules, bulk chondrites and standard rocks in this work.

2. Experimental

A ^6Li enriched metal ball (purity: 99.954%) immersed in kelocine medium was obtained from Oak Ridge National Laboratory (ORNL). The ^6Li metal was carefully cleaned by removing surface materials completely using a blade cutter and dissolved in distilled water (Li $\sim$ 3500 ppm). A diluted ^6Li -enriched spike solution was prepared by adjusting acidity (1 N-HCl) and concentrations (Li $\sim$ 7 ppm) and stored in a teflon bottle. For isotope dilution analyses, composite spike solutions including enriched isotopes of ^6Li , ^{41}K , ^{87}Rb , ^{84}Sr , and ^{136}Ba were prepared. Spike solutions of ^{25}Mg , ^{42}Ca , and ^{56}Fe had been prepared separately.⁹⁾

For isotopic reference, three laboratory standard solutions ($\text{LiCl}\cdot\text{H}_2\text{O}$ reagent [Merck; purity 99.99%], the Allende bulk meteorite and Allende barred-olivine chondrule) were prepared. Because of hygroscopic properties of $\text{LiCl}\cdot\text{H}_2\text{O}$, much cautions were paid for weighing procedure. For determination of Li concentration in ^6Li -enriched spike solution, three mixed solutions having different relative amounts of Li reagent standard and ^6Li -enriched spike solutions were prepared and six separate runs were carried out for the mixed solutions.

Sample decomposition procedures and mass spectrometric runs (using JEOL JMS-05RB mass spectrometer) are similar to those previously described.⁹⁾ For the standard rocks, about 10 $\sim$ 50 μg -sized samples were directly loaded on filaments. On the other hand, about 30 μg -sized meteorite samples were used. In order to evaluate the reproducibility, replicate analyses of the bulk Allende meteorite (Sample B) were carried out for different sizes (100 μg for B-1, 10 μg for B-2).

3. Results and Discussion

3.1 Isotopic analyses by direct-loading mass spectrometry

Isotopic analyses were carried out using a double filament mode; Re-center and Ta-side filaments. Samples were loaded in nitride or chloride form and measured as metallic Li ion. Run currents under working conditions were 2.0 A (center) and 0.15 $\sim$ 0.17 A (side) for analyses for spike and reagent standards, and 2.5 A (center) and 0.22 $\sim$ 0.28 A (side) for direct-loading analyses of chondrules, bulk meteorites and standard rocks. To correct the discrimination caused by an electron multiplier, a square root of 6/7 was multiplied to the observed $^6\text{Li}/^7\text{Li}$ ratio.

During the repeated runs, it was noted that the run current for a chloride form was generally lower than that for nitride form. The $^6\text{Li}/^7\text{Li}$ ratios obtained by using a chloride form were 0.0754 ± 0.0004 (1 σ), and systematically lower than those by using a nitride form (mean value: 0.07899 ± 0.00009). On the other hand, the $^6\text{Li}/^7\text{Li}$ ratios obtained by direct-loading technique for Allende bulk and chondrule samples were even higher than those of reagent standards, ranging from 0.0810 ± 0.0009 to 0.0828 ± 0.0012 (Table 1).

Compared to chemical reagent runs, direct-loading runs of Li require much higher heating temperature and yield more stable Li signals. Such features have been also

Table 1. $^6\text{Li}/^7\text{Li}$ Ratios Determined by Direct-Loading Mass Spectrometry of Allende Bulk and Chondrule Samples, Compared with Those of Terrestrial Standards

Run No.	Samples	Weight ^a	$^6\text{Li}/^7\text{Li}$ ratio ^b
Run 1	Allende bulk	100 μg (Li: 0.13 ng)	0.0828 ± 0.0012
Run 2	Allende bulk	100 μg (Li: 0.13 ng)	0.0810 ± 0.0009
Run 3	Allende bulk	100 μg (Li: 0.13 ng)	0.0823 ± 0.0013
Run 4	Allende BO ^c	470 μg (Li: 0.94 ng)	0.0816 ± 0.0007
Run 5	Allende BO	370 μg (Li: 0.74 ng)	0.0822 ± 0.0015
		Weighted mean	0.0818 ± 0.0004
	Literature data: NBS ⁽¹⁾		0.0828 ± 0.0001
	NBS ⁽²⁾		0.0820 ± 0.0001
	IUPAC (1989) ⁽³⁾		0.0811 ± 0.0023

^a Weight of samples loaded on filaments.^b Errors are 1σ .^c BO: barred olivine chondrule. Fig. 1. The relative intensities of ^7Li , ^{23}Na , ^{39}K , and ^{85}Rb as a function of heating duration, for 10 μg -sized BCR-1.

noted in cases of REE and other elements for direct-loading runs.⁹⁾ As mentioned previously, in order to obtain a high efficiency of Li signals, matrix effects must be carefully controlled. Particularly, for high alkali samples, the influence of large amount of Na and K are significant on vaporization and ionization of Li. For example, results for BCR-1 are shown in Fig. 1. It is pointed out that Na signal was always much (2~3 order magnitude) higher than that of Li, and that Na (and K) always interfered ionization of Li. Therefore prolonged heating steps were required to minimize these interferences before heating up to reach to the best stable signals of Li. Otherwise, Li signals decay out quickly before Na and K decaying. Finally, the best Li signals can be obtained with reasonable heating schedule, which is similar to the cases for Mg, Ba, and Sr runs.⁹⁾

It was found that the mass fractionation occurred more extensively during the

Table 2. ${}^6\text{Li}/{}^7\text{Li}$ Ratio for ${}^6\text{Li}$ -Enriched Spike Solution

Run No.	Weight ^a	${}^6\text{Li}/{}^7\text{Li}$ ratio ^b
Run 1	Li: 1000 (ng)	21.54 ± 0.20
Run 2	Li: 1000 (ng)	21.66 ± 0.30
Run 3	Li: 1000 (ng)	21.64 ± 0.21
Run 4	Li: 1000 (ng)	21.50 ± 0.21
	Weighted mean	21.57 ± 0.11
	Corrected ^c	22.35
ORNL		22.15

^a Weight of samples loaded on samples.^b Errors are 1σ ^c After corrected for mass fractionation.Table 3. Li Concentration (in ppm) for ${}^6\text{Li}$ -Enriched Spike Solution

Samples	Sp/Std ^a	Weight ^b	Li concentration ^c
S(I)	1.0/1.0	Li: 1000 ng	7.625 ± 0.070
S(I)	1.0/1.0	Li: 500 ng	7.565 ± 0.071
S(I)	1.0/1.0	Li: 500 ng	7.615 ± 0.021
S(II)	1.0/0.5	Li: 200 ng	7.546 ± 0.025
S(II)	1.0/0.5	Li: 100 ng	7.553 ± 0.030
S(III)	0.5/1.0	Li: 100 ng	7.588 ± 0.033
		Weighted mean	7.581 ± 0.013

^a The proportion of the weight of spike solution to that of standard solution in the mixed solution.^b Weight of samples loaded on filaments.^c Errors are 1σ .

reagent run rather than the direct-loading run. For the direct-loading run, Li exists as minor component on a filament and may thus be stabilized by other major elements such as Mg, Ca, Fe, *etc.* As shown in Table 1, the mean value of ${}^6\text{Li}/{}^7\text{Li}$ ratio for Allende chondrules and bulk sample is 0.0818 ± 0.0004 . This value is in good agreement with the recommended value of IUPAC (1989)¹⁰⁾ and also those of recent precise Li measurements.^{11), 12)} The ${}^6\text{Li}/{}^7\text{Li}$ ratios in bulk meteorites are normally constant, typically 0.0813 as reported by Shima and Honda.¹³⁾

From the above discussion, the ${}^6\text{Li}/{}^7\text{Li}$ ratios obtained by direct-loading runs for Allende samples are considered to represent the least fractionated one and thus employed as a reference value for isotope dilution calculation in this work. The mean ${}^6\text{Li}/{}^7\text{Li}$ ratio obtained for nitride form is 0.07899 ± 0.00009 . Then the fractionation factor of 0.966 is calculated relative to that of direct-loading value of Allende. The correction factor of 1.036 is therefore employed for correction of values obtained for reagent and spike solutions.

3.2 Calibration of ${}^6\text{Li}$ -enriched spike solution

For concentration calibration of ${}^6\text{Li}$ -enriched spike solution, the isotopic analyses of spike solution were, at first, carried out. The results of the ${}^6\text{Li}/{}^7\text{Li}$ ratios in nitride form are shown in Table 2. The mean value of 21.57 ± 0.07 obtained in this work is systematically lower than the ORNL value (22.15). Considering that this ratio was obtained in the reagent runs, a lower value may be caused by mass fractionation. Then

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Table 4. Comparison of Analytical Results of Lithium Abundances (in ppm) for Standard Rocks

Sample	Weight (μg) ^a	This work ^b	Literature
JB-1	50	11.4 $\pm$ 0.08	11.5 ^d
	50	11.1 $\pm$ 0.09 ^c	
	Weighted mean	11.3 $\pm$ 0.06	
JB-2	50	8.23 $\pm$ 0.11	8.0 ^d
BCR-1	50	13.8 $\pm$ 0.13	13.5 $\pm$ 1.7 ^c
	20	13.7 $\pm$ 0.08 ^c	12.9 $\pm$ 0.4 ^f
	10	14.0 $\pm$ 0.13 ^c	
	Weighted mean	13.8 $\pm$ 0.06	

^a Weight of samples loaded on filaments.

^b Errors are 1σ .

^c Replicate analyses for the same split solution.

^d From Ando *et al.*¹⁴⁾

^e From the mean value compiled in Gladney *et al.*¹⁵⁾

^f From the value obtained by isotope dilution method compiled in Gladney *et al.*¹⁵⁾

Table 5. Results for Bulk Samples of Chondrites and Allende Chondrules

Sample	Type ^a	Weight ^b (mg)	Weight ^c (μg)	Li (ppm)	Na (ppm)	K (ppm)	Rb (ppm)	Sr (ppm)	Ba (ppm)	Mg (%)	Ca (%)	Fe (%)
Bulk meteorites												
Allende A ^d	CV	9.6	30	1.51	n.a. ^e	335	1.19	19.8	6.36	12.4	1.81	11.1
B-1		41.2	100	1.33	n.a.	301	1.19	n.a.	n.a.	n.a.	n.a.	n.a.
B-2		41.2	10	1.30	n.a.	303	1.21	n.a.	n.a.	n.a.	n.a.	n.a.
Ningqiang	CK	16.4	30	1.78	n.a.	317	1.21	10.9	4.72	14.2	1.43	22.9
Murchison	CM	11.1	30	1.65	n.a.	545	1.82	12.9	4.82	12.3	1.43	18.2
Allegan	H5	15.5	30	2.18	n.a.	867	2.04	11.3	4.25	17.0	1.34	15.1
Etter	L5	10.0	30	1.89	n.a.	650	2.04	11.8	4.16	11.6	1.07	16.6
Allende chondrules												
SN-1	PO	6.95	30	1.34	2915	300	1.03	10.1	3.60	17.9	1.30	23.3
SN-2	POP	7.57	30	1.87	7879	800	3.80	7.61	3.93	19.8	1.24	5.09
SN-7	POP	3.31	30	1.31	9433	604	1.99	18.5	5.03	14.8	1.83	8.45
SN-8	POP	2.15	30	1.82	7758	776	2.45	34.5	5.71	15.3	3.16	14.2
SN-14	BO	4.55	30	1.63	5397	462	1.74	11.4	5.30	18.6	1.31	19.8
H-1	POP	10.5	30	2.38	5952	708	2.56	10.6	4.34	24.7	2.04	11.0
H-374	PO	4.88	30	1.36	2796	305	1.03	9.81	3.68	19.2	1.14	23.1

^a PO: porphyritic olivine, POP: porphyritic olivine and pyroxene, BO: barred olivine.

^b Weights of bulk chondrites decomposed or total weights of chondrules.

^c Weights of samples loaded on filaments.

^d Samples A and B were taken from a common powder split but decomposed separately. B-1 and B-2 are replicate analyses for the sample B.

^e Not analyzed.

the correction factor of 1.036 was applied to the observed $^6\text{Li}/^7\text{Li}$ ratios of individual runs. The $^6\text{Li}/^7\text{Li}$ ratio of ^6Li -enriched spike solution after the above correction is now in agreement with the value given from ORNL.

Calibration of the Li concentration in ^6Li -enriched spike solution using mixed spike-standard solutions was then carried out. The results are shown in Table 3. The Li concentrations determined for spike solutions were in agreement within 1%. A mean

Fig. 2. Li isotopic compositions for reagent Li standard, Allende bulk, and chondrule samples compared with IUPAC (1989)¹⁰⁾ and NBS literature data.^{11), 12)} Errors represent one standard deviation from the mean values. The dark area is one standard deviation error from the grand mean for Allende samples.

Li concentration of the stock solution ($\text{Li } 7.581 \pm 0.013$ ppm) was used for later analyses of standard rocks, bulk meteorites, and chondrules.

3.3 Direct-loading analyses for standard rocks, bulk meteorites, and chondrules

Results for DL-IDMS of GSJ and USGS standard rocks (JB-1, JB-2 and BCR-1) and bulk meteorites are given in Tables 4 and 5. In order to evaluate the reproducibility, replicate analyses of standard rocks (JB-1 and BCR-1) and the Allende meteorite were carried out. It is found that the results agree within 2~3% with each other. A slightly larger deviation in Li values was observed even for the same powder split of Allende, which may be due to the heterogeneous distribution of Li-enriched components such as CAIs.⁴⁾ For standard rocks, our value for JB-2 is 3% higher than the literature value, but those for JB-1 are in good agreement with those given in Ando *et al.*¹⁴⁾ On the other hand, our BCR-1 value is in good agreement with the mean value (13.5 ± 1.7) compiled in Gladney *et al.*¹⁵⁾ but 7% higher than the mean value obtained by isotope dilution method (12.9 ± 0.4) given by the same author.

Although our results of standard rocks are a little dispersed from the literature data, no systematical differences were observed. Therefore the interlaboratory biases were not found. A total procedural blank of Li is 0.09 pg. The contribution of the Li blank to the sample was less than 0.01% and therefore was negligible. The contribution of other element blanks to the samples were less than 1%. In view of the blank contribution, spike calibration and reproducibility, the precision of our analyses for standard rocks and meteorite samples is believed to be better than 3%.

For meteorite samples, the abundances of other alkali metals (K and Rb), alkaline earths (Mg, Ca, Sr, and Ba), and Fe were successively determined. Lithium abundances in bulk meteorites range from 1.30 to 2.18 ppm and therefore are within the typical

range of bulk chondrites. Except for a few case, most of other elements also show typical abundances for bulk chondrites. However, Fe abundances of Allende and Allegan and Mg and Ca abundances of Etter are too low for bulk chondrites. The reason of these low values is not understood. It may be possible that sampling heterogeneities exist and/or possible misleading mass spectrometric processes may not be ruled out.

Seven individual Allende chondrules were analyzed in this work. Li abundances range from 1.31 to 2.38 ppm with a mean of 1.67 ppm. Previously some Li abundance data have been reported for chondrules from unequilibrated chondrites including Allende,⁵⁾⁻⁷⁾ but data for individual chondrules have not been presented. They range from 0.9 to 3.1 ppm with one exception. Our mean value of Allende chondrules is consistent with their results, and is similar to the Allende whole rock values, as previously reported for several chondrites.^{5), 7)} Our data show that Li abundances in individual chondrule vary by less than a factor of 2. It is thus pointed out that the Li concentrations are less variable in chondrules, which is in contrast with the large variations for other alkali metal and alkaline earth elements.

In this work, only seven chondrules were analyzed for Li. To establish more general abundance feature for chondrules, further systematic analytical works would be required in future.

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