

# Simultaneous Measurement of Lithium and Boron Isotopes as Lithium Tetraborate Ion by Thermal Ionization Mass Spectrometry

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A method for the measurement of  $\text{Li}_2\text{BO}_2^+$  ions by thermal ionization mass spectrometry employing a Daly ion-counting system was examined. By solving simultaneous quadratic equations of intensity ratios ranging between  $m/z$  55 and 57, and between  $m/z$  56 and 57, precise and accurate measurement of lithium and boron isotope ratios can be carried out simultaneously. The intensity ratio between  $m/z$  54 and 57 can be used to check the internal consistency of the lithium and boron isotope ratios obtained. The isotopic fractionation rate with the species  $\text{Li}_2\text{BO}_2^+$  was low. Prior to measurement, a two-column ion-exchange process was used to separate lithium from the sample matrix and then to convert  $\text{LiCl}$  into  $\text{LiOH}$ , which subsequently reacts with  $\text{H}_3\text{BO}_3$  to form lithium tetraborate. Lithium and boron isotope ratios were successfully measured simultaneously with precisions (relative standard deviations) of 0.05% for lithium and 0.01% for boron.

**Keywords:** Lithium; boron; isotopic composition; Daly ion-counting system; thermal ionization mass spectrometry

## Introduction

The determination of lithium and boron isotope ratios in natural materials is of interest in geochemical exploration as a guide to hydrothermal alteration. It also has useful applications in the exploration of ore deposits and geothermal reservoirs.<sup>1</sup> Lithium and boron have not only experienced natural variations in their isotopic abundances but have also been subject to extensive mass separation for technological applications. Variations in the isotopic abundance can be traced to a variety of causes including natural mass fractionation, isotopic effects during chemical treatment, isotopic fractionation in the instrument, or due to segregated nuclear reactions. In the last example, the products and depleted parents are prevented from re-entering the general pool of elements for remixing. In addition, lithium and boron are important because of the nuclear spallation effect on both elements and the high lithium content of iron meteorites.

The isotopic composition of lithium has been studied by many workers.<sup>2-11</sup> Reported values show a spread of several per cent. in the isotopic abundance ratio in lithium reagents and natural lithium-bearing minerals. The most precise assays to date involve standardization of reference materials and the atomic mass of lithium. Flesch *et al.*,<sup>3</sup> for example, reported the absolute  $^6\text{Li}/^7\text{Li}$  ratio as  $0.0832 \pm 0.0002$  from a high-purity  $\text{Li}_2\text{CO}_3$  sample, manufactured by The Lithium Corporation of America, whereas Michiels and de Bievre<sup>4</sup> reported this ratio as  $0.08137 \pm 0.00034$  from a natural lithium sample. Both groups measured the ratio from commercial natural lithium samples using conventional mass spectrometers. Isakov *et al.*<sup>6</sup> reported a range of 6.77–9.28‰ in mica samples analysed by mass spectrometry. It should be noted that the  $^6\text{Li}/^7\text{Li}$  abundance ratio can be subject to relatively

large natural variations owing to the large mass ratio between 6 and 7. A few researchers have recommended the iodide<sup>2-5</sup> or chloride<sup>7</sup> salts of lithium as filament loading forms. Some have specially designed mass spectrometers suitable only for lithium isotope analysis.<sup>7</sup>

Theoretical and experimental data have shown that the ratio of molecular to atomic species volatilized is a major factor in the fractionation rate, particularly for triple filament sources in which the evaporation and ionization processes are spatially separated.<sup>8</sup> The large relative mass difference between the two lithium isotopes, because of the low atomic mass, makes the control of isotope fractionation particularly difficult in the precise isotopic analysis of lithium. Several thermal ionization mass spectrometric methods have been developed using both single and multiple filament techniques. In order to obtain reproducible results, the volatilization rate of each atomic and molecular species must be constant or controllable during the analysis and reproducible from one loading to the next. However, it is difficult to determine the volatilization rates in thermal ionization mass spectrometry because neutral species are not detectable. One approach for circumventing this difficulty is to use a molecular species that greatly reduces the fraction of lithium vaporized as atomic  $\text{Li}^+$  ions or neutral atomic or low molecular mass species and the extent of isotopic fractionation during the measurement.

In a triple filament procedure,  $\text{LiI}$  has been used<sup>2-5</sup> as the loading material and its high molecular mass reduced the fractionation factor. Similarly, another triple filament procedure for the isotopic analysis of lithium is based on the measurement of the  $\text{Li}_2\text{F}^+$  ion with a precision of 0.2%.<sup>8</sup> Lithium fluoride is one of the most stable compounds of lithium. More recently, lithium isotope ratios have been measured, with lithium loaded as the tetraborate ( $\text{Li}_2\text{BO}_2^+$ ), by using both single<sup>9</sup> and double filament procedures.<sup>10</sup> The measurement of  $\text{Li}_2\text{BO}_2^+$  reduces isotopic fractionation for the single filament procedure and a precision (relative standard deviation) of 0.13% was achieved. Chan<sup>9</sup> observed a peak at mass 55, but an accurate measurement of masses 54 and 55 was not possible. In the double filament procedure, with lithium loaded as  $\text{Li}_2\text{B}_4\text{O}_7$ , the measurement of the  $\text{Li}^+$  ion was achieved with a precision better than 0.1%. When adjusting the conditions of filament assembly and geometry, it is possible to obtain  $\text{Li}^+$  ions stronger than  $\text{Li}_2\text{BO}_2^+$  ions. However, such a problem is beyond the scope of this paper.

Refined thermal ionization mass spectrometry and ultra-clean chemical separation techniques have been the primary focus of our efforts to analyse lithium isotopes. Previous work using similar techniques facilitated the measurement at mass 55 but could not measure mass 54 using a multicollector system.<sup>11</sup> In this paper, we describe clean separation techniques prior to improved mass spectrometric analysis. A Daly ion-counting system was used, which allows measurement of the four possible nuclear isotopic species of  $\text{Li}_2\text{BO}_2^+$  at masses 54, 55, 56 and 57, in addition to small efficient loadings on the

filament and stable ionization efficiencies at reduced temperatures.

## Experimental

### Instrument and Apparatus

A VG (VG Isotech, Cheshire, UK) Sector 54-30 thermal ionization mass spectrometer equipped with a Daly ion-counting system was used. The detection system was linear and accurate to 0.04% under the conditions used here. Ion count rates were corrected by using background correction. The counting time used for an isotopic species was 5 s for masses 54, 55, 56 and 57. Each redundant piece of data consists of the average of seven ratio measurement sets while the final ratio is the mean of 15 data sets.

### Reagents and Materials

A cation-exchange column was prepared by packing a 2 cm i.d. Pyrex column with AG 50W-X8 (200–400 mesh) resin (Bio-Rad Laboratories, Richmond, CA, USA) to a height of 8 cm. The resin was pre-cleaned by soaking in 6 mol dm<sup>-3</sup> HCl and washed with distilled water prior to packing into a column. The resin in the column was converted into the H<sup>+</sup> form by passing 10 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> HCl through it, followed by washing with distilled water until the washings were free from chloride.

An anion-exchange column was prepared by packing a similar column to a height of 6 cm with AG 1-X8 (200–400 mesh) resin (Bio-Rad Laboratories). The resin was pre-cleaned by soaking in 6 mol dm<sup>-3</sup> HNO<sub>3</sub> and washing with distilled water prior to packing into a column. The exchanger was converted into the OH<sup>-</sup> form by repeated washing with 1 mol dm<sup>-3</sup> NaOH (Suprapur grade; Merck, Darmstadt, Germany). As this column was used for the conversion of LiCl into LiOH, extra care was taken to prevent contamination.

Ultrapure HCl and HNO<sub>3</sub>, purchased from Wako Pure Chemical Industries (Osaka, Japan), were further purified by carrying out up to three sub-boiling distillations. Aqueous solutions were prepared from distilled water from a Milli-Q water purification system (with a resistivity of 18 MΩ cm).

A lithium isotopic standard [National Institute of Standards and Technology (NIST) L-SVEC lithium carbonate] and a boron isotopic standard [NIST Standard Reference Material (SRM) 951 boric acid] were used for the synthesis of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.

In all the experiments lithium was separated from a mixture by cation-exchange chromatography. For the standards, a cation-exchange column was not necessary. In order to check the effect of the cation-exchange column on lithium isotope composition, both cation- and anion-exchange columns were employed. A solution containing lithium was passed through the cation-exchange column to separate any other cations present in the solution. Lithium was eluted from the column using 0.5 mol dm<sup>-3</sup> HCl. The column was then washed with Milli-Q water to ensure that lithium was not retained on the column. The eluate was preconcentrated to a small volume in a Teflon beaker by evaporation almost to dryness at a low temperature. The main aim was to convert the LiCl solution into LiOH for the synthesis of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. Therefore, this step helped to reduce the amount of chloride loaded onto the anion-exchange column. Subsequently, the LiCl solution was passed through the anion-exchange column, which had been preconditioned with 1 mol dm<sup>-3</sup> NaOH, thus converting LiCl into LiOH. Lithium carbonate can be used for the synthesis of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. However, LiOH was found to be the best choice for the synthesis of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> in this work.

### Instrumental Procedure

Prior to sample loading, zone-refined rhenium ribbon (ESPI Marz Grade, 99.996%) filaments were de-gassed at 4.0 A in an evacuated chamber (<1.0 × 10<sup>-6</sup> Torr; 1 Torr = 133.322 Pa) for 1 h.

In the single filament procedure, 0.5 µg of lithium (as LiOH) and 1 µl of 1 mg g<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> were found to be the optimum values. The mass ratio of LiOH to H<sub>3</sub>BO<sub>3</sub> taken is nearly stoichiometric in relation to Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. A 1 µl volume of 1 mg g<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> was taken and deposited onto the rhenium filament using a micropipette. The droplets were dried at a current of 0.8 A. After evaporation of H<sub>3</sub>BO<sub>3</sub> to dryness, 0.5 µg of lithium (as LiOH) was loaded onto the same filament. The LiOH sample solution was dried with a current of 0.8 A passing through the filament. The filament was further heated for 10 s at 1.8 A, and held for 5 min at 0.8 A before introduction into the mass spectrometer.

Mass spectrometric analysis was started when the ion-gauge pressure in the instrument reached 1.0 × 10<sup>-8</sup>–2.0 × 10<sup>-8</sup> Torr. Liquid nitrogen was added to the cold finger over the source. An accelerating voltage of 8 kV was used. In this procedure, Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> ions were thermally ionized from Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> on the same filament and monitored at masses 54, 55, 56 and 57. After ensuring that the instrumental calibration between magnetic field strength and atomic mass scale was stable, the sample was slowly heated and de-gassed under vacuum using a filament current of 0.7 A for 3 h. The filament current was then increased very slowly until a Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> signal started to appear. Once the Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> ion signals appeared, the system was allowed to stabilize until the signal ceased to increase with time. Generally, the signal from a 0.5 µg load of lithium increases from approximately 120 000–150 000 counts s<sup>-1</sup> to 250 000–300 000 counts s<sup>-1</sup> by the end of a run (after 2 h). The baseline was determined at the beginning of a set of measurements. Typical baseline count rates varied from 0 to 8 counts s<sup>-1</sup> at mass 55.5. The target intensity was focused at <2.0 × 10<sup>-13</sup> A for measurement. The selection of ion beams was made by varying the magnetic field, and the ion beams were focused on masses 54, 55, 56 and 57. Data acquisition was started after stable emission and at a desired signal strength (≈2.0 × 10<sup>-12</sup> A) using an ion-counting pulse system. After the completion of each set comprising a pre-set number (7) of measurements, the instrument measures the baseline after beam focusing and peak centring. The computer automatically adjusts the filament current to maintain a smooth increase in the ion current. The integration time was

**Table 1** Possible nuclide combination species of the Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> molecular ion

Mass number	Species
54	( <sup>6</sup> Li) <sub>2</sub> <sup>10</sup> B ( <sup>16</sup> O) <sub>2</sub>
55	<sup>6</sup> Li <sup>7</sup> Li <sup>10</sup> B ( <sup>16</sup> O) <sub>2</sub> ( <sup>6</sup> Li) <sub>2</sub> <sup>10</sup> B ( <sup>16</sup> O) ( <sup>17</sup> O) ( <sup>6</sup> Li) <sub>2</sub> <sup>11</sup> B ( <sup>16</sup> O) <sub>2</sub>
56	( <sup>7</sup> Li) <sub>2</sub> <sup>10</sup> B ( <sup>16</sup> O) <sub>2</sub> <sup>6</sup> Li <sup>7</sup> Li <sup>11</sup> B ( <sup>16</sup> O) <sub>2</sub> ( <sup>6</sup> Li) <sub>2</sub> <sup>11</sup> B <sup>16</sup> O <sup>17</sup> O ( <sup>6</sup> Li) <sub>2</sub> <sup>10</sup> B ( <sup>17</sup> O) <sub>2</sub> <sup>6</sup> Li <sup>7</sup> Li <sup>10</sup> B <sup>16</sup> O <sup>17</sup> O ( <sup>6</sup> Li) <sub>2</sub> <sup>10</sup> B <sup>16</sup> O <sup>18</sup> O
57	( <sup>7</sup> Li) <sub>2</sub> <sup>11</sup> B ( <sup>16</sup> O) <sub>2</sub> <sup>6</sup> Li <sup>7</sup> Li <sup>10</sup> B <sup>16</sup> O <sup>18</sup> O ( <sup>6</sup> Li) <sub>2</sub> <sup>11</sup> B <sup>16</sup> O <sup>18</sup> O ( <sup>7</sup> Li) <sub>2</sub> <sup>10</sup> B <sup>16</sup> O <sup>17</sup> O ( <sup>6</sup> Li) <sub>2</sub> <sup>11</sup> B ( <sup>17</sup> O) <sub>2</sub> ( <sup>6</sup> Li) <sub>2</sub> <sup>10</sup> B <sup>17</sup> O <sup>18</sup> O <sup>6</sup> Li <sup>7</sup> Li <sup>11</sup> B <sup>16</sup> O <sup>17</sup> O <sup>6</sup> Li <sup>7</sup> Li <sup>10</sup> B ( <sup>17</sup> O) <sub>2</sub>

5 s, whereas the magnetic settlement time was 2 s. Typically, 100–150 ratios were obtained during a sample run with the ion current increasing from  $2.9 \times 10^{-12}$  to  $4.3 \times 10^{-12}$  A. Results were discarded if they consisted of less than 70 reproducible ratios.

## Results and Discussion

### Determination of $^6\text{Li}/^7\text{Li}$ Ratio

The relative ion intensity measurement is made for the molecular ion of  $\text{Li}_2\text{BO}_2^+$  produced from  $\text{Li}_2\text{B}_4\text{O}_7$ . Considering the isotopic abundances of the constituent elements, *e.g.*, lithium, boron and oxygen, 36 isotopically distinct  $\text{Li}_2\text{BO}_2$  molecules having mass numbers ranging from 54 to 61 are obtained. The possible species with nuclide combinations corresponding to  $\text{Li}_2\text{BO}_2^+$  ions of masses 54–57 are given in Table 1. Theoretical ion intensity ratios and abundances of  $\text{Li}_2\text{BO}_2$  molecules are summarized in Tables 2 and 3.

Even if the contributions of the isotopes  $^{17}\text{O}$  and  $^{18}\text{O}$  are ignored, this does not have a significant effect on the results of the calculations. In order to maintain mathematical exactness, however, the contributions of these trace oxygen isotopes to the 'isobaric' molecular ions are quantitatively taken into account in the present calculations. Specifically, the ion with mass number 54 contains exclusively two  $^{16}\text{O}$  atoms. It is self-evident that  $\text{Li}_2\text{BO}_2^+$  ions involving two  $^{16}\text{O}$  atoms are the 'dominant' species for ions with mass numbers 55, 56 and 57. Isobaric contributions of molecular ions involving  $^{17}\text{O}$  and/or  $^{18}\text{O}$  to the bulk intensities ( $I$ 's) are calculated as 0.002, 0.010 and 0.050%, corresponding to mass numbers 55, 56 and 57, respectively. Hence the following equations for the measured ion intensity ratios for  $I_{54/57}$ ,  $I_{55/57}$  and  $I_{56/57}$  should hold:

$$\frac{I_{54}}{I_{57}} \times 1.00050 = \frac{(^6\text{Li})_2^{10}\text{B}(^{16}\text{O})_2}{(^7\text{Li})_2^{11}\text{B}(^{16}\text{O})_2} \times \frac{^{10}\text{B}}{^{11}\text{B}} = X^2Y \quad (1)$$

$$\frac{I_{55}}{I_{57}} \times 1.00047 = \frac{2 \times ^6\text{Li}^7\text{Li}^{10}\text{B}(^{16}\text{O})_2}{(^7\text{Li})_2^{11}\text{B}(^{16}\text{O})_2} + \frac{(^6\text{Li})_2^{11}\text{B}(^{16}\text{O})_2}{(^7\text{Li})_2^{11}\text{B}(^{16}\text{O})_2} = 2XY + X^2 = X(X + 2Y) \quad (2)$$

$$\frac{I_{56}}{I_{57}} \times 1.00040 = \frac{2 \times ^6\text{Li}^7\text{Li}^{11}\text{B}(^{16}\text{O})_2}{(^7\text{Li})_2^{11}\text{B}(^{16}\text{O})_2} + \frac{(^7\text{Li})_2^{10}\text{B}(^{16}\text{O})_2}{(^7\text{Li})_2^{11}\text{B}(^{16}\text{O})_2} = 2X + Y \quad (3)$$

where  $X = ^6\text{Li}/^7\text{Li}$  and  $Y = ^{10}\text{B}/^{11}\text{B}$ .

Chan<sup>9</sup> has calculated  $X$  ( $^6\text{Li}/^7\text{Li}$ ) by substituting the known value of  $Y$  ( $^{10}\text{B}/^{11}\text{B}$ ) using eqn. (3).

As with measurements obtained by other methods, the solution obtained here can reflect the effect of fractionation. The potentially unique advantage of the proposed method is that it can provide an approach for investigating the relationship between the simultaneous effects of 'in situ' fractionation of boron and lithium isotopes. Therefore, we have solved simultaneous quadratic equations to determine the isotopic composition of lithium and boron in the  $\text{Li}_2\text{BO}_2$  molecular

ion. Taking into consideration eqns. (2) and (3) as a set of simultaneous equations, we obtain

$$X^2 + 2XY = \alpha \quad (4)$$

and

$$2X + Y = \beta \quad (5)$$

where  $\alpha$  and  $\beta$  are the product of the measured intensity ratios and the isobaric correction factors.

Mathematically, the simultaneous quadratic equations give two values. Needless to say, one of them has no physical meaning. Therefore,

$$X = \frac{2\beta - (4\beta^2 - 4 \times 3 \times \alpha)^{1/2}}{2 \times 3} \quad (6)$$

Once  $X$  has been calculated,  $Y$  can be calculated using eqn. (3). From these values, eqn. (1) can be checked and compared with the measured value. This provides a verification of the extent of isotope fractionation.

In order to test the precision and accuracy of the thermal ionization mass spectrometric method used in this work, measurements of  $\text{Li}_2\text{BO}_2^+$  ions at masses 54, 55, 56 and 57 were carried out individually using ten filaments. Each filament was loaded with 0.5  $\mu\text{g}$  of NIST L-SVEC lithium carbonate and the results are presented in Table 4. Applying eqns. (2) and (3), the averages of the intensity ratios shown in Table 4 yield  $X = 0.082289$  and  $Y = 0.24779$ .

Different methods for loading the lithium samples onto the filament were attempted. For example,  $\text{LiCl}$  and  $\text{LiNO}_3$  samples were mixed with  $\text{H}_3\text{BO}_3$ , but the results were not satisfactory. However, a mixture of  $\text{LiOH}$  and  $\text{H}_3\text{BO}_3$  produced the most stable isotope ratio measurements for lithium. In general,  $\text{LiOH}$  reacts chemically with  $\text{H}_3\text{BO}_3$  to

**Table 3** Mathematically calculated mass spectrum distribution abundances of the  $\text{Li}_2\text{BO}_2$  molecule

Mass number	Abundance (%)
54	0.11141
55	3.19650
56	28.00990
57	68.24387
58	0.16427
59	0.27356
60	0.00022
61	0.00027

**Table 4** Measured isotope ratios of NIST L-SVEC  $\text{Li}_2\text{CO}_3$  as the  $\text{Li}_2\text{BO}_2^+$  ion

No.	54/57	55/57	56/57
1	0.00167	0.04748	0.41203
2	0.00167	0.04753	0.41219
3	0.00167	0.04752	0.41221
4	0.00167	0.04751	0.41212
5	0.00168	0.04754	0.41225
6	0.00168	0.04756	0.41233
7	0.00167	0.04753	0.41220
8	0.00168	0.04755	0.41224
9	0.00167	0.04751	0.41217
10	0.00168	0.04757	0.41229
Average	0.001674	0.04753	0.41220
$s^*$	0.000005	0.000026	0.000085
$s_r^\dagger$ (%)	0.31	0.021	0.050

\*  $s$  = Standard deviation.

$^\dagger s_r$  = Relative standard deviation.

**Table 2** Abundance ratios of  $\text{Li}_2\text{BO}_2^+$

Theoretical ratio	Abundance ratio
54/57	0.00163
55/57	0.04684
56/57	0.41044
58/57	0.00241
59/57	0.00401
60/57	0.000003
61/57	0.000004



form  $\text{Li}_2\text{B}_4\text{O}_7$ . Therefore,  $\text{H}_3\text{BO}_3$  followed by  $\text{LiOH}$  was loaded directly onto the filament to form  $\text{Li}_2\text{B}_4\text{O}_7$ , the most stable loading form, which produces a strong  $\text{Li}_2\text{BO}_2^+$  signal. This permits lithium isotope ratio measurements to be made with high precision.

According to our experiments, the recommended B/Li atomic ratio for stable and precise lithium isotope ratio measurements ranges from 2 to 2.5, corresponding to, or higher than, the stoichiometric B/Li ratio.

The ionization filament temperature is a crucial parameter which governs the rate of fractionation. This has been demonstrated by most researchers in this field. At optimum sample vaporization temperatures, lithium evaporates primarily as molecular species containing boron. In our studies, it was observed that the fractionation was higher at temperatures above  $850^\circ\text{C}$ .

In order to check the blank before sample loading, a de-gassed filament was loaded with  $\text{H}_3\text{BO}_3$  only, and without any lithium sample. It did not produce any detectable  $\text{Li}_2\text{BO}_2^+$  ion signals under the conditions used for lithium isotope ratio measurements. This verified that there was no background from the filament material under these conditions.

The analysis was, therefore, carried out with a low signal intensity at low temperature to reduce fractionation, and the isotope ratio measured as a function of time showed negligible variations. For precise measurement of lithium isotope ratios, the amount of sample and control of the filament temperature are important factors to be considered.

As mentioned above, we observed ratios of  $0.082289 \pm 0.000043$  and  $0.24779 \pm 0.00032$  for  $^6\text{Li}/^7\text{Li}$  ( $X$ ) and  $^{10}\text{B}/^{11}\text{B}$  ( $Y$ ), respectively. The isotopic ratio obtained ( $^{10}\text{B}/^{11}\text{B} =$

$0.24779$ ) agrees well with the certified value ( $^{10}\text{B}/^{11}\text{B} = 0.2473 \pm 0.0002$ ).<sup>12</sup> It would be significant to calculate  $X^2Y$  from the values obtained for  $X$  and  $Y$  from eqns. (2) and (3), because, as mathematically derived above [eqn. (1)],  $X^2Y$  corresponds to  $I_{54}/I_{57}$  multiplied by the correction factor. Evaluation based on  $X = 0.082289$  and  $Y = 0.24779$  gives  $X^2Y = 0.001678$ , while the observed mean value for the corrected  $I_{54}/I_{57}$  ratio is  $0.001675$ , which is in good agreement with the calculated value for  $X^2Y$  within the experimental uncertainty. The uncertainty of  $\pm 0.02\%$  for  $\alpha$  results in uncertainties of  $\pm 0.076$ ,  $\pm 0.18$  and  $\pm 0.048\%$  for  $X$ ,  $Y$  and  $X^2Y$ , respectively. In turn, the uncertainty of  $\pm 0.02\%$  for  $\beta$  results in uncertainties of  $\pm 0.01$ ,  $\pm 0.13$  and  $\pm 0.17\%$  for  $X$ ,  $Y$  and  $X^2Y$ , respectively. This suggests that the degree of isotopic fractionation during the measurements was negligible. Further, it endorses the high linearity of the Daly ion-counting system for intensity ratio magnitudes of  $10^5$ – $10^6$  and the high dependability and internal consistency of the  $X$  and  $Y$  values obtained.

The same method was applied to high-purity Sumitomo  $\text{Li}_2\text{CO}_3$  samples. Results of these analyses are given in Table 5. Taking the correction factor into consideration, we found  $X = 0.082415$  and  $Y = 0.24775$ . The results are similar and the isotope ratio of boron is identical. The Sumitomo sample was similar to the standard lithium sample, and the same  $\text{H}_3\text{BO}_3$  was used in both instances. The results obtained in this work were compared with those obtained by other workers, and are summarized in Tables 6 and 7. The proposed method is reproducible and has an analytical precision (relative standard deviation) of  $0.05\%$  for lithium and  $0.01\%$  for boron.

## Conclusions

This study demonstrates that precise measurement of the isotope ratios of lithium and boron can be carried out by using a thermal ionization mass spectrometer equipped with a Daly ion-counting detection system. The sample loading procedure, purity of chemical form and control of the filament temperature are the salient features in achieving precise measurement of ratios. In order to apply this technique to the measurement of samples, it is essential to achieve quantitative recovery and clean separation of lithium from other inorganic ions during the separation process. In order to apply the technique to the precise measurement of boron isotope ratios, the boron in the sample should preferably be in the form of

**Table 5** Analytical reproducibility for the Sumitomo  $\text{Li}_2\text{CO}_3$  sample

	54/57	55/57	56/57	$^6\text{Li}/^7\text{Li}$	$^{10}\text{B}/^{11}\text{B}$
	0.00168	0.04761	0.41242	0.08243	0.24754
	0.00168	0.04762	0.41244	0.08245	0.24752
	0.00167	0.04759	0.41238	0.08239	0.24758
Average	0.00167	0.047606	0.41241	0.08242	0.24755
$s^*$	0.000005	0.000015	0.00003	0.000031	0.000031
$s_r^\dagger$ (%)	0.34	0.032	0.007	0.037	0.012

\*  $s$  = Standard deviation.

$^\dagger s_r$  = Relative standard deviation.

**Table 6** Comparison of lithium isotopic composition of NIST L-SVEC standard

Researcher	Measured ion	Loaded as (chemical) form	$^6\text{Li}/^7\text{Li}$ ratio ( $X$ )	Reference
Flesch <i>et al.</i>	$\text{Li}^+$	$\text{LiI}$	$0.0832 \pm 0.00033$	3
Chan	$\text{Li}_2\text{BO}_2^+$	$\text{Li}_2\text{B}_4\text{O}_7$	$0.08282 \pm 0.0001$	9
Lamberty <i>et al.</i>	$\text{Li}^+$	$\text{LiI}$	$0.08214 \pm 0.00009$	5
Green <i>et al.</i>	$\text{Li}^+$	$\text{LiF}$	$0.08201 \pm 0.00013$	8
Xiao and Beary	$\text{Li}^+$	$\text{Li}_2\text{B}_4\text{O}_7$	$0.082212 \pm 0.000019$	10
Sahoo and Masuda	$\text{Li}_2\text{BO}_2^+$	$\text{Li}_2\text{B}_4\text{O}_7$	$0.082289 \pm 0.000043$	This work

**Table 7** Comparison of boron isotopic composition of NIST SRM 951 boric acid

Researcher	Measured ion	Loaded as (chemical) form	$^{10}\text{B}/^{11}\text{B}$ ( $Y$ )	Reference
Spivack and Edmond	$\text{Cs}_2\text{BO}_2^+$	$\text{Cs}_2\text{B}_4\text{O}_7$	$0.24718 \pm 0.00024$	13
Xiao <i>et al.</i>	$\text{Cs}_2\text{BO}_2^+$	$\text{Cs}_2\text{B}_4\text{O}_7$	$0.24689 \pm 0.00011$	14
Nakamura <i>et al.</i>	$\text{Cs}_2\text{BO}_2^+$	$\text{Cs}_2\text{B}_4\text{O}_7$	$0.24684 \pm 0.00035$	15
Zeininger and Heumann	$\text{BO}_2^-$	$\text{H}_3\text{BO}_3 + \text{La}(\text{NO}_3)_3$	$0.2489 \pm 0.0002$	16
Sahoo and Masuda	$\text{Li}_2\text{BO}_2^+$	$\text{Li}_2\text{B}_4\text{O}_7$	$0.24779 \pm 0.00032$	This work

either borate or  $\text{H}_3\text{BO}_3$ . The  $\text{Li}_2\text{BO}_2^+$  ion beam technique described here for the isotopic analysis of lithium and boron can be applied to samples of either element of whatever origin. One advantage of the technique is that no isotope standard is required.

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