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Measurement of lithium isotopic ratios as lithium tetraborate ions

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Abstract

Determination of ${}^6\text{Li}/{}^7\text{Li}$ ratios using Li_2BO_2^+ ions analysed by thermal ionisation mass spectrometry with ion counting has been investigated by numerical simulation and experiment. It is possible to solve for one or more of the ${}^6\text{Li}/{}^7\text{Li}$ ratio, ${}^{10}\text{B}/{}^{11}\text{B}$ ratio and fractionation if one or more of the ratios of the 54, 55, 56, 57, 58 and 59 masses of Li_2BO_2^+ are measured. Monte Carlo simulation of data sets suggests that within-sample precision on measurement of Li_2BO_2^+ mass ratios is largely limited by counting statistics and should result in precision as good as 0.25% (1σ) on the ${}^6\text{Li}/{}^7\text{Li}$ ratio. However repeatability of ${}^6\text{Li}/{}^7\text{Li}$ and ${}^{10}\text{B}/{}^{11}\text{B}$ ratios gives precisions no better than approximately $\pm 3\%$ (1σ) and the probable cause is fractionation of the ${}^6\text{Li}/{}^7\text{Li}$ ratio on the filament due to the large Li^+ ion beam produced during analysis of Li_2BO_2^+ . Plots of variation of sample fractionation with time confirms that fractionation is primarily controlled by varying ${}^6\text{Li}/{}^7\text{Li}$ ratio rather than varying fractionation of Li_2BO_2^+ or ${}^{10}\text{B}/{}^{11}\text{B}$ ratio. (Int J Mass Spectrom 202 (2000) 273–282) © 2000 Elsevier Science B.V.

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1. Introduction

Analysis of lithium isotopic compositions is of significance to geochemistry and cosmochemistry in addition to the technological applications of the separated isotopes. Lithium has two natural stable isotopes, ${}^6\text{Li}$ and ${}^7\text{Li}$. The large relative mass difference results in large variations in the isotopic ratio in nature but also makes Li very susceptible to fractionation during both chemical preparation of samples and analysis by thermal ionisation mass-spectrometry. Improvements in chemical separation procedures have minimised fractionation

during sample preparation [1], but monitoring fractionation during analysis has not so far proved possible. Loading Li as part of a heavy molecule and analysing the isotopic ratio of the Li^+ beam at carefully controlled conditions has given isotopic compositions repeatable to better than 0.5% although the results from individual operators differ by up to 2.6% [1–10]. Chan [1] and Sahoo and Masuda [6] analysed Li isotopic compositions from the ion Li_2BO_2^+ , which yields masses from 54 to 60. With this method it is theoretically possible to correct for fractionation if two or more mass ratios are measured and the B isotopic composition is known or to calculate both Li and B isotopic compositions and fractionation if three or more mass ratios are measured.

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In this article we evaluate the possibility of fractionation-corrected Li isotopic analysis using Li_2BO_2^+ ions. Monte Carlo numerical techniques are used to investigate the optimal B isotopic spike, optimal analytical routines and error propagation. Analyses of the National Bureau of Standards (NBS) L-SVEC Li carbonate using ion-counting are used to test the method, particularly the success of fractionation corrections. Our main conclusion is that it is not possible to correct for fractionation resulting from loss of the much large Li^+ beam.

2. Theory

It is possible to solve for Li, B and O isotopic composition as well as fractionation from analyses of the isotopic ratios of the eight masses of Li_2BO_2^+ . First we present the method and discuss the results of theoretical calculations of the likely analytical sensitivity and error propagation based on Monte Carlo techniques. We discuss estimates of fractionation and its significance, the optimal errors in calculated Li and B isotopic compositions given counting statistics and the optimal B isotopic composition to minimise propagated errors in calculation of Li isotopic composition. Table 1 lists the combinations of Li, B and O isotopes that make up masses of Li_2BO_2^+ and the calculated fractions of the constituent molecules for Li with the isotopic composition of the L-SVEC standard (${}^6\text{Li}/{}^7\text{Li} = 0.08282$) and boron with ${}^{10}\text{B}/{}^{11}\text{B} = 0.05072$. Following Chan [1] and Sahoo and Masuda [6] it is convenient to simplify the probability expression for each mass by dividing by ${}^7\text{Li}_2{}^{11}\text{B}{}^{16}\text{O}_2$. The measured isotopic ratio R_{ij}^m of two masses (i and j) of Li_2BO_2^+ can then be expressed as

$$R_{ij}^m = g(F)f({}^6\text{Li}/{}^7\text{Li}, {}^{10}\text{B}/{}^{11}\text{B}, {}^{18}\text{O}/{}^{16}\text{O}, {}^{17}\text{O}/{}^{16}\text{O}) \quad (1)$$

where g describes the dependence of fractionation on the fractionation factor F and the function f , the true ratio of the two masses, is given by the ratio of sums of the probabilities of the masses listed in Table 1. The contributions of ${}^{17}\text{O}$ and ${}^{18}\text{O}$ to masses 54, 55, 56 and 57 are less than one part in 10^4 and uncertainty in

oxygen isotope composition does not contribute significantly to the analytical uncertainty using these masses. The dominant factors in masses 58 and 59 are multiplied by ${}^{18}\text{O}/{}^{16}\text{O}$. In the discussion below we assume that ${}^{17}\text{O}/{}^{16}\text{O}$ varies linearly with ${}^{18}\text{O}/{}^{16}\text{O}$. Eq. (1) may be solved for as many of the unknowns, ${}^6\text{Li}/{}^7\text{Li}$, ${}^{10}\text{B}/{}^{11}\text{B}$, ${}^{18}\text{O}/{}^{16}\text{O}$ and the fractionation factor, F , as isotope ratios of Li_2BO_2^+ have been measured, if the fractionation function, g , is defined.

The fractionation of a species such as Li_2BO_2^+ depends on the ionisation mechanism. If the species is evaporated as the whole molecule, then fractionation of an isotopic ratio R_{ij} may be approximated by the linear relationship (e.g., see Russell et al. [12])

$$g(F) = (1 + F\Delta m_{ij}) \quad (2)$$

where $\Delta m_{ij} = m_i - m_j$ is the mass difference and F is the fractionation factor. Fig. 1 illustrates the apparent variation of the isotopic ratio ${}^6\text{Li}/{}^7\text{Li}$ calculated from 54/57, 55/57, 56/57, 58/57 and 59/57 ratios with the linear fractionation factor, F [Eq. (2)], with no correction for fractionation. The marked sensitivity of the calculated ${}^6\text{Li}/{}^7\text{Li}$ ratios to fractionation should be noted. The calculated ${}^6\text{Li}/{}^7\text{Li}$ ratio from 56/57 changes by 2.5‰ and that from 55/57 changes by 1.7‰ for 1‰ variation in F .

The nonlinear set of equations (1) are conveniently solved by the Newton–Raphson method for some or all of the unknowns ${}^6\text{Li}/{}^7\text{Li}$, ${}^{10}\text{B}/{}^{11}\text{B}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ and the fractionation factor, F , given measurements of a selection of Li_2BO_2^+ isotopic ratios. To test the sensitivity of the solutions to random errors, investigate error propagation and establish the most favourable analytical protocols, synthetic data sets have been created with random, normally distributed errors calculated using Monte Carlo techniques. Errors calculated as proportional to counting statistics are close to those of the measurements presented below. The results portrayed in Fig. 2 show, as expected, that as the number of unknowns increases the error on the estimated ${}^6\text{Li}/{}^7\text{Li}$ ratio increases. In particular solution for all three ratios (${}^6\text{Li}/{}^7\text{Li}$, ${}^{10}\text{B}/{}^{11}\text{B}$ and ${}^{18}\text{O}/{}^{16}\text{O}$) and fractionation yields standard errors on ${}^6\text{Li}/{}^7\text{Li}$ ratios of $\sim 2.5\%$ for the analytical conditions detailed in Fig. 2.

Table 1
Combinations of Li, B and O isotopes which constitute masses of Li_2BO_2^+

Mass number	Species	Probability ^a $/^7\text{Li}_2^{11}\text{B}^{16}\text{O}_2$	Fraction of mass in L-SVEC	Mass fraction
54	$^6\text{Li}_2^{10}\text{B}^{16}\text{O}_2$	X ² Y	1.00	0.000281
55	$^6\text{Li}^7\text{Li}^{10}\text{B}^{16}\text{O}_2$	2XY	0.55	
	$^6\text{Li}_2^{10}\text{B}^{16}\text{O}^{17}\text{O}$	2X ² YR17	1.7×10^{-5}	
	$^6\text{Li}_2^{11}\text{B}^{16}\text{O}_2$	X ²	0.45	0.012327
56	$^7\text{Li}_2^{10}\text{B}^{16}\text{O}_2$	Y	0.23	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{16}\text{O}_2$	2X	0.77	
	$^6\text{Li}_2^{11}\text{B}^{16}\text{O}^{17}\text{O}$	2X ² R17	2.4×10^{-5}	
	$^6\text{Li}_2^{10}\text{B}^{17}\text{O}_2$	X ² YR17 ²	2.3×10^{-10}	
	$^6\text{Li}^7\text{Li}^{10}\text{B}^{16}\text{O}^{17}\text{O}$	4XYR17	2.9×10^{-5}	
	$^6\text{Li}_2^{10}\text{B}^{16}\text{O}^{18}\text{O}$	2X ² YZ	6.6×10^{-6}	0.174783
57	$^7\text{Li}_2^{11}\text{B}^{16}\text{O}_2$	1	1.00	
	$^6\text{Li}^7\text{Li}^{10}\text{B}^{16}\text{O}^{18}\text{O}$	4XYZ	3.4×10^{-5}	
	$^6\text{Li}_2^{11}\text{B}^{16}\text{O}^{18}\text{O}$	2X ² Z	2.8×10^{-5}	
	$^7\text{Li}_2^{10}\text{B}^{16}\text{O}^{17}\text{O}$	2YR17	3.8×10^{-5}	
	$^6\text{Li}_2^{11}\text{B}^{17}\text{O}_2$	X ² R17 ²	9.7×10^{-10}	
	$^6\text{Li}_2^{10}\text{B}^{17}\text{O}^{18}\text{O}$	2X ² YZR17	5.3×10^{-10}	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{16}\text{O}^{17}\text{O}$	4XR17	1.2×10^{-4}	
	$^6\text{Li}^7\text{Li}^{10}\text{B}^{17}\text{O}_2$	2XYR17 ²	1.2×10^{-9}	0.807969
58	$^7\text{Li}_2^{11}\text{B}^{16}\text{O}^{17}\text{O}$	2R17	0.46	
	$^7\text{Li}_2^{10}\text{B}^{16}\text{O}^{18}\text{O}$	2YZ	0.13	
	$^7\text{Li}_2^{10}\text{B}^{17}\text{O}_2$	YR17 ²	4.4×10^{-6}	
	$^6\text{Li}^7\text{Li}^{10}\text{B}^{17}\text{O}^{18}\text{O}$	4XYZR17	7.9×10^{-6}	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{16}\text{O}^{18}\text{O}$	4XZ	0.41	
	$^6\text{Li}_2^{11}\text{B}^{17}\text{O}^{18}\text{O}$	2X ² ZR17	6.5×10^{-6}	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{17}\text{O}_2$	2XR17 ²	1.4×10^{-5}	
	$^6\text{Li}_2^{10}\text{B}^{18}\text{O}_2$	X ² YZ ²	8.9×10^{-7}	0.001325
59	$^7\text{Li}_2^{11}\text{B}^{17}\text{O}_2$	R17 ²	3.5×10^{-5}	
	$^7\text{Li}_2^{11}\text{B}^{16}\text{O}^{18}\text{O}$	2Z	1.00	
	$^7\text{Li}_2^{10}\text{B}^{17}\text{O}^{18}\text{O}$	2YZR17	1.9×10^{-5}	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{17}\text{O}^{18}\text{O}$	4XZR17	6.2×10^{-5}	
	$^6\text{Li}^7\text{Li}^{10}\text{B}^{18}\text{O}_2$	2XYZ ²	8.6×10^{-6}	
	$^6\text{Li}_2^{11}\text{B}^{18}\text{O}_2$	X ² Z ²	7.0×10^{-6}	0.003309
60	$^7\text{Li}_2^{11}\text{B}^{17}\text{O}^{18}\text{O}$	2ZR17	0.63	
	$^7\text{Li}_2^{10}\text{B}^{18}\text{O}_2$	YZ ²	0.087	
	$^6\text{Li}^7\text{Li}^{11}\text{B}^{18}\text{O}_2$	2XZ ²	0.28	
61	$^7\text{Li}_2^{11}\text{B}^{18}\text{O}_2$	Z ²	1.0	2.0×10^{-6} 3.4×10^{-6}

^a X = $^6\text{Li}/^7\text{Li}$ (0.08282), Y = $^{10}\text{B}/^{11}\text{B}$ (0.05072), Z = $^{18}\text{O}/^{16}\text{O}$ (0.002048) and R17 = $^{17}\text{O}/^{16}\text{O}$ (0.000377)

If three unknowns (F, $^6\text{Li}/^7\text{Li}$ and $^{10}\text{B}/^{11}\text{B}$) are calculated from five peaks or two unknowns (F and $^6\text{Li}/^7\text{Li}$) from two or three peaks, the standard error on $^6\text{Li}/^7\text{Li}$ decreases to $\sim 1\%$. If fractionation is ignored and only $^6\text{Li}/^7\text{Li}$ calculated as an unknown the estimated

standard errors vary between 0.2‰ and 0.35‰ with limited improvement from analysis of multiple peaks (Fig. 2B). However it should be noted that to reproduce such results fractionation would need to be kept within a range of $\pm 0.1\%$. It should be emphasised

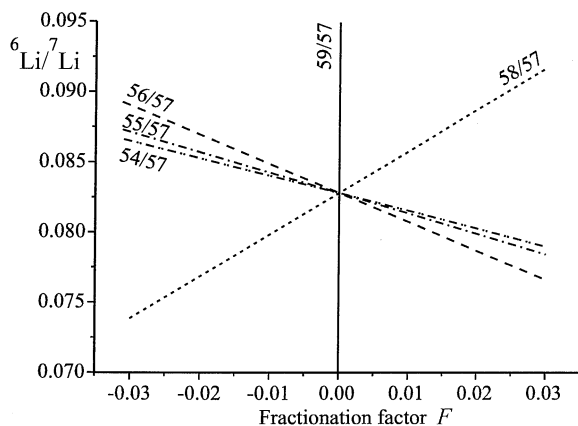


Fig. 1. Illustration of variation in ${}^6\text{Li}/{}^7\text{Li}$ isotopic ratios calculated from isotopic ratios of Li_2BO_2^+ subject to fractionation where the fractionation is not taken into account. Assumes a linear fractionation law as in equation. Note that ${}^6\text{Li}/{}^7\text{Li}$ ratio calculated from 56/57 ratio changes by $\sim 2.5\%$ for $F = 1\%$. Li_2BO_2^+ isotopic ratios calculated assuming ${}^6\text{Li}/{}^7\text{Li} = 0.08282$, ${}^{10}\text{B}/{}^{11}\text{B} = 0.247$, ${}^{18}\text{O}/{}^{16}\text{O} = 0.002048$ and ${}^{17}\text{O}/{}^{16}\text{O} = 0.000377$.

that these theoretical errors represent the minimum attainable for the conditions and ignore a number of systematic errors, including errors on background counts and potential uncertainty in oxygen and boron isotopic ratios where these are used in the calculations.

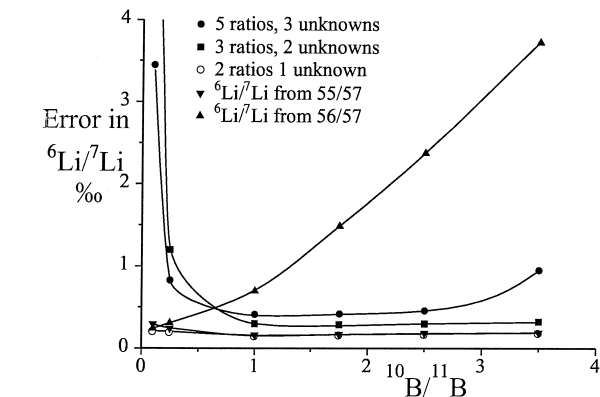
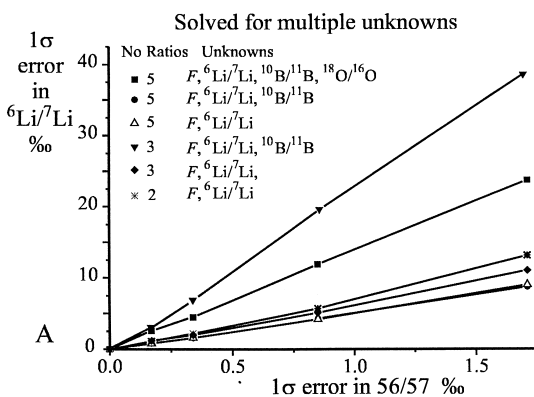


Fig. 3. Standard error in calculated ${}^6\text{Li}/{}^7\text{Li}$ ratio against ${}^{10}\text{B}/{}^{11}\text{B}$ ratio. Calculated as Fig. 2 except B isotope ratio varied and intensity of largest mass (57 for ${}^{10}\text{B}/{}^{11}\text{B} < 0.84$ and 56 if ${}^{10}\text{B}/{}^{11}\text{B} > 0.84$) assumed 10^{-13} A. Sets of 2, 3 and 5 ratios as in caption to Fig. 2.

The error analysis in Fig. 2 was calculated with samples spiked with B from standard reference material (SRM) 951 with a ${}^{10}\text{B}/{}^{11}\text{B}$ ratio of ~ 0.248 . The boron isotope ratio that minimises the error in the calculated ${}^6\text{Li}/{}^7\text{Li}$ ratio depends on which Li_2BO_2^+ mass ratios are used, but for most combinations ${}^{10}\text{B}/{}^{11}\text{B}$ ratios between 1 and 3 minimise the calculated errors (Fig. 3).

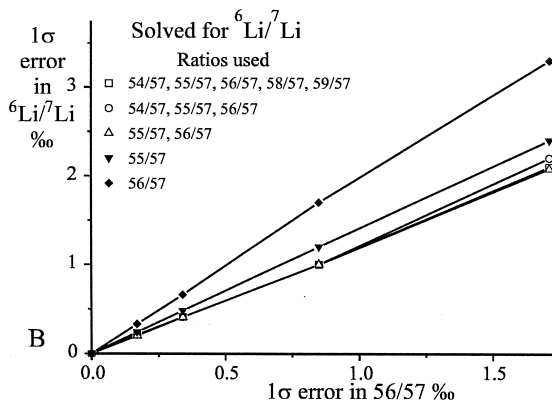


Fig. 2. Standard errors on unknowns (fractionation F , ${}^6\text{Li}/{}^7\text{Li}$, ${}^{10}\text{B}/{}^{11}\text{B}$ and ${}^{18}\text{O}/{}^{16}\text{O}$) calculated from 50 sets of analyses of Li_2BO_2^+ mass ratios calculated by Newton-Raphson solutions to equations plotted against error in 56/57 ratio. Errors on Li_2BO_2^+ ion ratios calculated by Monte Carlo method assuming errors on masses proportional to square root of number of counts with 8 s counts on masses 54, 55, 56, 58 and 59 and 3 s on mass 57 and intensity of 57 beam of 10^{-13} A with ${}^6\text{Li}/{}^7\text{Li} = 0.083$, ${}^{10}\text{B}/{}^{11}\text{B} = 0.248$ and ${}^{18}\text{O}/{}^{16}\text{O} = 0.002044$. Analysis of 50 cycles gives a standard error on the 56/57 ratio of 0.17% and error propagation with these errors and with these errors multiplied by factors of 2, 5 and 10 are shown as symbols on diagrams. Fractionation factor, $F = 0.01 \pm 0.01$ (1σ) for solutions in Fig. 2A which solve for fractionation and $F = 0$ in Fig. 2B which solve only for ${}^6\text{Li}/{}^7\text{Li}$. In Fig. 2A 5 ratios include masses 54, 55, 56, 58 and 59 over 57, 3 ratios 54, 55 and 56 over to 57 and 2 ratios 55/57 and 56/57.

Table 2
Analyses of Li₂BO₂⁺

Run No	No. ratios	¹⁰ B/ ¹¹ B	Li		se ^a		se		se		se		se	
			Load ng	B/Li molar	54/57	%	55/57	%	56/57	%	58/57	%	59/57	%
1570	90	0.248			0.001698	0.87	0.047898	0.22	0.413747	0.14	0.002585	0.55	0.004320	0.53
1571	127	0.248			0.001692	0.69	0.047838	0.20	0.413324	0.10	0.002585	0.51	0.004321	0.44
1642	195	0.248			0.001692	0.53	0.047885	0.16	0.413665	0.09	0.002522	0.40	0.004203	0.37
1643	150	0.248			0.001698	0.66	0.047960	0.30	0.413851	0.18	0.002547	0.44	0.004252	0.45
1644	150	0.248			0.001701	0.50	0.048004	0.16	0.414231	0.10	0.002590	0.37	0.004329	0.35
1645	150	0.248			0.001676	0.52	0.047604	0.14	0.412755	0.08	0.002590	0.37	0.004340	0.32
1736	150	0.248			0.001694	1.33	0.047875	0.35	0.413253	0.17	0.002595	1.07	0.004349	0.85
1737	150	0.248			0.001688	1.43	0.047889	0.33	0.413263	0.19	0.002603	1.22	0.004346	0.94
Average							0.047869	2.49	0.413511	1.10				
3270	50	0.252	500	1	0.001695	3.42	0.047980	0.59	0.415824	0.29	0.002578	1.84	0.004251	1.96
3271	70	0.252	500	1	0.001721	1.20	0.048566	0.55	0.417747	0.23	0.002609	1.08	0.004300	1.00
3272	170	0.252	500	1	0.001728	0.78	0.048679	0.17	0.418078	0.08	0.002615	0.71	0.004321	0.47
3273	110	0.252	500	2	0.001720	0.93	0.048507	0.29	0.417615	0.13	0.002615	0.78	0.004322	0.68
3275	80	0.252	500	2	0.001732	0.99	0.048722	0.28	0.418208	0.11	0.002625	0.82	0.004345	0.74
3277	110	0.252	500	10	0.001730	0.82	0.048730	0.23	0.418240	0.09	0.002690	1.06	0.004417	0.78
3278	120	0.252	500	10	0.001728	1.18	0.048696	0.21	0.418003	0.10	0.002672	1.05	0.004406	0.68
3284	50	0.252	100	2	0.001682	1.68	0.048536	0.59	0.417435	0.24	0.003003	6.90	0.004771	4.85
3285	40	0.252	100	2	0.001691	2.89	0.048602	0.43	0.417596	0.15	0.003045	5.77	0.004850	4.02
3286	50	0.252	100	10	0.001691	2.01	0.048058	0.90	0.416080	0.33	0.002635	1.33	0.004300	1.36
3287	40	0.252	100	10	0.001717	1.60	0.048649	0.38	0.417906	0.19	0.002726	3.28	0.004419	2.07
Average							0.048520	5.34	0.417521	1.96				
3420	100	3.5	100	2	na		0.558369	0.81	3.580107	0.31	na		na	
3421	120	3.5	100	2	na		0.562273	0.99	3.583382	0.46	na		na	
3422	120	3.5	100	2	na		0.561541	0.61	3.597626	0.43	na		na	
3423	170	3.5	100	2	na		0.568640	0.46	3.599383	0.21	na		na	
3424	100	3.5	100	2	na		0.565964	0.80	3.609151	0.30	na		na	
3425	170	3.5	100	2	na		0.566180	0.38	3.593375	0.22	na		na	
3452	130	3.5	100	2	na		0.562841	0.68	3.603078	0.29	na		na	
3453	110	3.5	100	2	na		0.566376	0.66	3.601542	0.28	na		na	
3454	120	3.5	100	2	na		0.566628	0.55	3.597480	0.28	na		na	
3457	200	3.5	100	1	na		0.536358	0.59	3.595866	0.29	na		na	
Average							0.561517	16.66	3.596099	2.43				

^a se = standard error, na = not analysed. Runs 1570 to 1737 comprised L-SVEC and SRM951 B standard but size of Li and B loads not known. Runs 3270 to 3287 used L-SVEC and dilithium tetraborate and runs 3420 to 3457 used L-SVEC and ¹¹B enriched spike.

3. Analytical methods

A variety of samples and preparation methods were utilised. A mixed solution containing the SRM L-SVEC standard and SRM951 B standard was provided by Chan (Louisiana State University, LA, USA). This solution contained ~47 ng/g of B and ~49 ng/g of Li and was used for runs 1570 to 1737 (Tables 2 and 3). Subsequently separate solutions of AA standard lithium hydroxide monohydrate (LiOH · H₂O) or dilithium tetraborate (Li₂B₄O₇) and orthoboric acid (H₃BO₃) were used to make solutions containing 10 ng/μl Li and 30 ng/μl B

(runs 3270 to 3287). Dilute L-SVEC solution (1 ng/μl) was also mixed with an ¹¹B-enriched solution (6 ng/μl, ¹¹B/¹⁰B = 3.531) prepared by dissolving ¹¹B and ¹⁰B powders in very dilute nitric acid (runs 3420 to 3457). For some trials the Li and B solutions were mixed during loading on the filament with the larger amount of B solution gradually loaded and dried down before the final addition of the Li solution. All samples were loaded onto the filament in 0.5 μl aliquots and dried initially at 1.0 A, increasing to 1.5 A for 20 s. Once all the solution was loaded the filament was raised to 1.8 A for a further 10 s.

Table 3
Calculated $\delta_{\text{Li}}/\text{Li}$, Fractionation and $^{10}\text{B}/^{11}\text{B}$ values

Run No	Li ng	B/Li ¹ molar	55/57 ²			56/57 ¹			2 peaks 1 unknown ¹			2 peaks 2 unknowns ¹			3 peaks 2 unknowns ¹					
			$^{10}\text{B}/^{11}\text{B}$	$\delta_{\text{Li}}/\text{Li}$	1σ %	No ³	$\delta_{\text{Li}}/\text{Li}$	1σ %	No	$\delta_{\text{Li}}/\text{Li}$	1σ %	No	Fract	$\delta_{\text{Li}}/\text{Li}$	1σ %	No	Fract	$\delta_{\text{Li}}/\text{Li}$	1σ %	No
3270	500	1	0.2520	0.081920	0.47	47/49	0.082010	0.65	50/52	0.081970	0.43	45/49	-0.00060	0.081704	1.08	55/58	-0.00067	0.081723	1.14	57/58
3271	500	1	0.2520	0.082950	0.32	29/31	0.083190	0.45	29/31	0.083010	0.30	29/31	-0.00236	0.082225	0.85	88/94	-0.00257	0.082235	0.84	90/94
3272	500	1	0.2520	0.083000	0.14	144/150	0.083140	0.19	157/166	0.083070	0.13	110/116	-0.00240	0.082529	0.44	210/220	-0.00258	0.082504	0.43	213/220
3273	500	2	0.2520	0.082720	0.24	102/110	0.082900	0.31	101/107	0.082770	0.26	102/109	-0.00248	0.082236	0.58	122/128	-0.00269	0.082222	0.58	124/128
3275	500	2	0.2520	0.082980	0.24	99/101	0.083130	0.29	93/95	0.083090	0.22	77/80	-0.00220	0.082553	0.56	121/127	-0.00235	0.082546	0.54	123/127
3277	500	10	0.2520	0.083100	0.19	83/86	0.083210	0.23	105/110	0.083140	0.18	82/86	-0.00202	0.082733	0.53	119/123	-0.00236	0.082662	0.47	117/123
3278	500	10	0.2520	0.083020	0.18	99/102	0.083040	0.25	132/136	0.083050	0.17	97/101	-0.00107	0.082571	0.50	210/220	-0.00129	0.082551	0.50	207/216
3284	100	2	0.2520	0.082950	0.28	30/31	0.082940	0.54	37/38	0.082970	0.32	30/31	-0.00091	0.082692	0.72	40/43	-0.00299	0.082084	0.78	55/58
3285	100	2	0.2520	0.082860	0.37	38/40	0.082920	0.36	34/34	0.082920	0.28	31/33	-0.00062	0.082479	0.91	70/72	-0.00217	0.082116	0.84	74/76
3286	100	10	0.2520	0.082090	0.75	45/46	0.082160	0.79	45/47	0.082100	0.71	44/46	-0.00194	0.081870	1.14	46/48	-0.00195	0.81812	1.08	48/50
3287	100	10	0.2520	0.082990	0.27	32/33	0.083130	0.44	30/31	0.083040	0.29	30/31	-0.00143	0.082487	0.68	56/58	-0.00194	0.082426	0.60	56/58
Mean				0.082780	4.64	11/11	0.082888	4.97	11/11	0.082830	4.88	11/11		0.082371	3.98	11/11		0.082262	3.74	11/11
1570			0.2477	0.082722	0.82	10/10	0.083019	0.73	9/10	0.082987	0.71	9/10	-0.00404	0.082220	1.03	10/10	-0.00373	0.081864	1.09	22/23
1571			0.2477	0.082773	0.25	17/17	0.082946	0.41	17/17	0.082924	0.38	17/17	-0.00277	0.082414	0.60	16/17	-0.00314	0.082308	0.76	16/17
1642			0.2477	0.082850	0.32	13/13	0.083073	0.49	13/13	0.083045	0.45	13/13	-0.00342	0.081901	0.79	31/32	-0.00459	0.082044	0.83	18/18
1643			0.2477	0.082513	0.43	10/10	0.082727	0.43	11/11	0.082700	0.42	11/11	-0.00306	0.082044	0.68	10/10	-0.00378	0.081941	0.50	10/10
1644			0.2477	0.082993	0.182	11/12	0.083252	0.34	14/15	0.083215	0.31	14/15	-0.0043	0.082213	0.58	25/25	-0.00446	0.082007	0.52	29/30
1645			0.2477	0.082991	0.199	10/11	0.08323	0.25	9/10	0.083200	0.23	9/10	-0.00363	0.082238	0.39	35/37	-0.00451	0.082089	0.43	35/36
1736			0.2477	0.082941	0.5	5/5	0.082859	0.65	10/10	0.082934	0.3	5/5	-0.00037	0.082636	1.83	9/10	-0.00061	0.082741	2.24	10/10
1737			0.2477	0.082913	0.54	5/5	0.082893	0.47	8/8	0.082921	0.45	5/5	0.000398	0.082980	1.82	9/9	-0.00075	0.082732	1.76	9/9
Mean				0.082837	1.97	8/8	0.083000	2.19	8/8	0.082991	2.01	8/8		0.082331	4.17	8/8		0.082216	4.21	8/8
3452	100	2	3.531	na			na			0.082230	0.61	116/120	0.01197	0.082074	0.75	86/90		na		
3453	100	2	3.531	na			na			0.082365	0.62	115/120	0.01256	0.082409	0.72	77/80		na		
3454	100	2	3.531	na			na			0.082718	0.53	114/120	0.01369	0.082674	0.58	113/120		na		
3457	100	1	3.531	na			na			0.082271	0.52	189/198	0.01413	0.082323	0.80	190/198		na		
3420	100	2	3.531	na			na			0.082189	0.72	96/100	0.01792	0.082677	0.80	118/120		na		
3421	100	2	3.531	na			na			0.082039	0.96	124/130	0.01722	0.082528	0.93	121/130		na		
3422	100	2	3.531	na			na			0.082124	0.57	117/120	0.01398	0.082292	0.63	95/100		na		
3423	100	2	3.531	na			na			0.083010	0.45	164/170	0.01309	0.082874	0.53	162/170		na		
3424	100	2	3.531	na			na			0.082635	0.78	98/100	0.00994	0.081954	0.82	97/100		na		
3425	100	2	3.531	na			na			0.082327	0.45	258/270	0.01479	0.082469	0.50	258/270		na		
Mean			3.531	na			na			0.082391	3.7	10/10		0.082427	3.40	10/10		na		

Table 3 (continued)

Run No	Li mg	B/Li molar	5 peaks 2 unknowns			3 peaks 3 unknowns			5 peaks 2 unknowns			5 Peaks 3 unknowns										
			$^{10}\text{B}/^{11}\text{B}$	$^6\text{Li}/^7\text{Li}$	$^{10}\text{B}/^{11}\text{B}$ %	$^6\text{Li}/^7\text{Li}$ %	Fract	$^6\text{Li}/^7\text{Li}$ %	No	$^{10}\text{B}/^{11}\text{B}$ %	$^6\text{Li}/^7\text{Li}$ %	Fract	$^6\text{Li}/^7\text{Li}$ %	No	$^{10}\text{B}/^{11}\text{B}$ %	No						
3270	500	1	0.2520	0.081990	0.46	46/49	0.00005	0.081781	0.65	0.252187	0.53	56/59	0.01444	0.084223	0.90	56/59	0.02427	0.083942	0.88	0.258045	0.95	58/59
3271	500	1	0.2520	0.083030	0.29	29/31	-0.00012	0.082554	0.57	0.252609	0.40	74/79	0.01681	0.085549	0.79	78/79	0.02894	0.085175	0.77	0.259883	0.57	75/79
3272	500	1	0.2520	0.083100	0.13	109/116	-0.00013	0.082713	0.26	0.252623	0.20	212/220	0.01765	0.085856	0.38	204/212	0.03027	0.085460	0.37	0.260332	0.31	202/212
3273	500	2	0.2520	0.082780	0.25	102/110	-0.00011	0.082432	0.44	0.252654	0.24	121/128	0.01767	0.085676	0.53	105/110	0.03071	0.085244	0.51	0.260415	0.40	111/118
3275	500	2	0.2520	0.083100	0.22	77/80	-0.00012	0.082814	0.34	0.252523	0.24	101/107	0.01920	0.086133	0.49	109/114	0.03234	0.085722	0.47	0.260737	0.36	107/113
3277	500	10	0.2520	0.083180	0.17	81/86	-0.00013	0.082904	0.30	0.252520	0.24	95/98	0.02812	0.087912	0.71	84/85	0.04652	0.087373	0.67	0.264239	0.50	82/85
3278	500	10	0.2520	0.083080	0.17	96/101	-0.00006	0.082821	0.32	0.252309	0.25	140/147	0.02836	0.087879	0.48	35/38	0.04574	0.087381	0.50	0.263549	0.57	37/38
3284	100	2	0.2520	0.083010	0.33	30/31	-0.00015	0.082591	0.46	0.252729	0.41	33/35	0.07167	0.096009	6.97	42/43	0.10971	0.095523	4.95	0.278957	2.28	35/35
3285	100	2	0.2520	0.082930	0.33	33/34	-0.00011	0.082398	0.53	0.252609	0.40	63/66	0.08329	0.098240	6.04	30/31	0.11619	0.096751	4.50	0.279416	1.81	31/31
3286	100	10	0.2520	0.082130	0.70	44/46	-0.00005	0.081978	0.83	0.252523	0.44	46/48	0.01855	0.085225	1.29	45/46	0.03258	0.084853	1.25	0.260745	0.60	43/46
3287	100	10	0.2520	0.083070	0.28	30/31	-0.00012	0.082736	0.34	0.252572	0.34	37/39	0.02884	0.087821	1.94	39/41	0.04786	0.087264	1.85	0.264787	1.52	41/42
Mean				0.082855	4.90	11/11		0.082520	4.34	0.252533	0.62		0.086253	15.4	9/11		0.085824	14.4	0.260993	7.64	8/11	
1570			0.2477	0.085724	0.71	10/10	-0.00016	0.082205	1.06	0.248588	0.38	21/22	0.03607	0.088114	0.77	10/10	0.03309	0.085076	0.61	0.257450	0.94	17/17
1571			0.2477	0.085626	0.29	15/16	-0.00014	0.082573	0.51	0.248447	0.36	16/17	0.03370	0.087831	0.64	16/16	0.02990	0.085207	0.45	0.256514	0.78	17/17
1642			0.2477	0.084398	0.38	23/23	-0.00022	0.082416	0.46	0.248783	0.46	17/17	0.02082	0.085624	0.44	24/26	0.01800	0.083698	0.48	0.253939	0.69	26/26
1643			0.2477	0.085021	0.46	10/10	-0.00016	0.082234	0.28	0.248602	0.32	10/10	0.02949	0.086869	0.70	10/10	0.02586	0.084464	0.32	0.255595	0.62	9/10
1644			0.2477	0.085895	0.35	22/22	-0.00025	0.08249	0.41	0.248879	0.29	20/21	0.03644	0.088287	0.36	25/26	0.03206	0.085283	0.36	0.257439	0.46	26/26
1645			0.2477	0.085853	0.22	25/26	-0.00022	0.082524	0.30	0.248783	0.22	26/26	0.03593	0.088170	0.37	36/37	0.03172	0.085259	0.31	0.257314	0.32	34/36
1736			0.2477	0.082961	0.24	5/5	-0.00002	0.082787	1.25	0.247851	1.02	10/10	0.02647	0.087150	1.26	7/7	0.03222	0.085739	1.38	0.256188	0.90	6/7
1737			0.2477	0.082934	0.36	8/8	-0.00003	0.082790	1.00	0.247881	0.81	9/9	0.02553	0.087121	1.11	5/5	0.03354	0.085850	1.16	0.255974	0.68	8/9
Mean				0.084801	14.7	8/8		0.082502	2.66	0.248477	1.61	8/8	0.087396	10.3	8/8		0.085072	8.20	0.256302	4.64	8/8	

¹ B/Li mole ratio times stoichiometric in Li_2BO_2^+ loaded.² Li_2BO_2^+ peak analysed, note recovery of precise $^6\text{Li}/^7\text{Li}$ from single Li_2BO_2^+ peak not possible with $^{10}\text{B}/^{11}\text{B} = 3.531$, 2 peaks include 55/57 and 56/57, 3 peaks 54/57, 55/57 and 56/57.³ Ratio of number of peak-jumping cycles used in statistics to total number analysed rejecting up to 10% of data.

Note Li and B sample size not available for runs 1570 to 1737.

na = not analysed.

In the mass spectrometer, samples were warmed to 1.0 A over a minimum of 20 min, then the current was increased gradually to the point where the Li_2BO_2^+ was first detected and then slowly to running conditions with the largest mass (57 or 56) set at an intensity of $\sim 10^{-13}$ A. Analyses were by peak switching using a Daly ion-counting system on a VG Sector 54 thermal ionisation mass spectrometer. Background counts were generally less than ~ 5 cts/s but on some samples backgrounds were significant and exhibited a linear variation from ~ 8 cts/s at mass 54.5 to ~ 26 cts/s at mass 58.5. Correction for the variable background was statistically significant for the smaller peaks (54, 58 and 59). The linearity of the ion-counting system between currents of 10^{-15} and 10^{-13} A is better than 1‰ determined by analysis of a range of standards of known isotopic composition (Sr, Nd and Pb).

4. Results

4.1. Precision

Means and standard errors on the mean of sets of Li_2BO_2^+ analyses are listed in Table 2. Sample loads for these results contained 100 to 500 ng Li and one to ten times as much boron on a molecular basis. Sample loads for runs 1570 to 1737 were also in this range, but the records of these samples and the solutions were lost in a laboratory fire. All the analyses were run with the largest peak set at an intensity of 10^{-13} A (mass 57 for SRM-951 and samples with similar boron isotope ratios, and mass 56 for the synthetic boron standard with $^{10}\text{B}/^{11}\text{B} = 3.5$). The result listed is that with the most precise standard error allowing rejection of up to 10% of the data. The precision on individual loads is mostly within a factor of two of that estimated from the counting statistics on the Monte Carlo simulations discussed above. For $^{10}\text{B}/^{11}\text{B} \sim 0.25$ this is 0.17‰ and for $^{10}\text{B}/^{11}\text{B} \sim 3.5 \sim 0.2\%$ on 50 cycles on the 56/57 mass ratio. Samples generally lasted 3–4 h but start to fractionate significantly in the latter parts of the analysis as discussed below. Smaller samples (0.5

to 10 ng) lasted shorter times and gave precision in the range 3‰ to 10‰ on 56/57 mass ratio. The standard deviation of repeat analyses (i.e., repeat sample loads) is approximately 10 times that of the standard error estimate on individual loads. This poor repeatability is attributed to variable fractionation.

4.2. Fractionation

Fractionation during ionisation of a complex ion such as Li_2BO_2^+ may be controlled by a variety of factors in addition to a simple mass dependant bias. If Li_2BO_2^+ evaporates as the ion then the masses which control fractionation are those analysed. However, if fractions of the molecule evaporate and subsequently combine to form Li_2BO_2^+ , then the appropriate mass ratio which controls fractionation will be different from that analysed. If a significant number of Li or B ions evaporate off the filament the remaining load may become fractionated. The mass ratio controlling fractionation may be inferred from the co-variation of two variably fractionated isotopic ratios plotted normalised to their unfractionated values (cf. [12]). Writing an equation for the pair of isotope ratios (i/j and k/j) and eliminating F gives

$$R_{kj}^m/R_{kj}^c = (R_{ij}^m/R_{ij}^c) \frac{\Delta m_{kj}}{\Delta m_{ij}} + \left(1 - \frac{\Delta m_{kj}}{\Delta m_{ij}}\right) \quad (3)$$

where R_{kj}^c is the isotope ratio of masses k and j and R_{kj}^m is the measured isotope ratio of masses k to j which is affected by fractionation. The slope of R_{kj}^m/R_{kj}^c against R_{ij}^m/R_{ij}^c reflects the mass differences controlling fractionation. Where R^c is not known, the error in the estimated slope (that is the mass-difference ratio $\Delta m_{kj}/\Delta m_{ij}$) from assuming an incorrect value for R^c is proportional to the error multiplied by the difference in mass-difference between the two sets of ratios and is insignificant in the examples discussed below.

Fig. 4 illustrates fractionation trends for two analyses (runs 3273 and 3275, Table 2) with the 55/57 and 56/57 ratios normalised to their means in each analysis. The data follow the fractionation trend expected if the $^6\text{Li}/^7\text{Li}$ ratio of the Li in the load varies rather

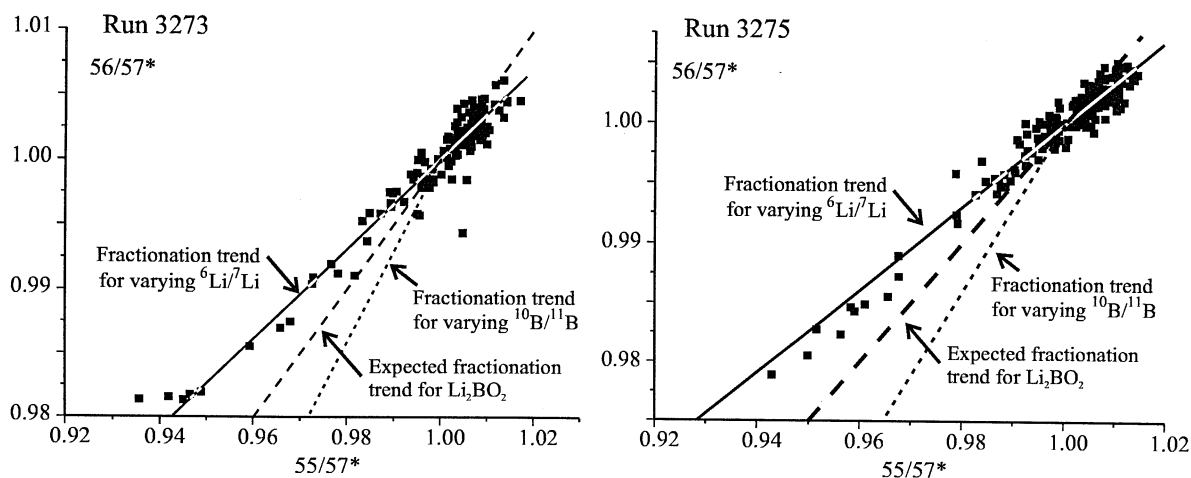


Fig. 4. Examples of fractionation in runs 3273 and 3275. Results from each cycle plotted as ratio to mean. Note analyses early in run have relatively high values which change slowly at first but exhibit large fractionations towards end of run (see Fig. 5). Data lie along trend caused by varying ${}^6\text{Li}/{}^7\text{Li}$ ratio rather than that expected for fractionation of Li_2BO_2^+ or ${}^{10}\text{B}/{}^{11}\text{B}$ as shown.

than the predicted fraction trend of Li_2BO_2^+ with slope of 0.5 or the trend predicted for variations in ${}^{10}\text{B}/{}^{11}\text{B}$ on the filament. Li_2BO_2^+ emission from the filament is accompanied by a relatively large Li ion beam as noted by Xiao and Beary [4] and Moriguti and Nakamura [5]. The systematic decrease in 55/57 and 56/57 ratios with time is consistent with preferential loss of ${}^6\text{Li}$ from the filament and a plot of 55/57 ratio against cycle number (Fig. 5) shows that the sample

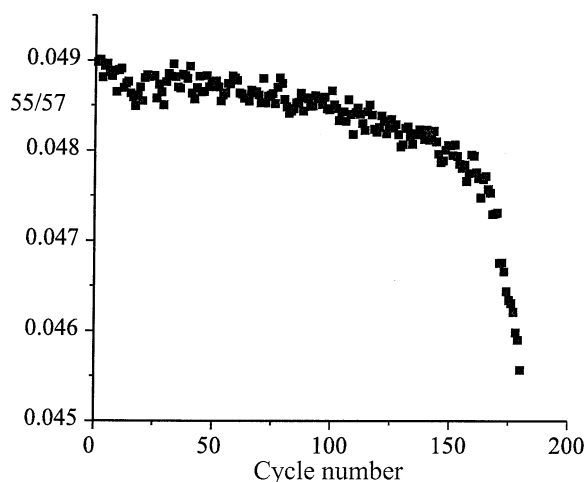


Fig. 5. Variation of 55/57 ratio with time (cycle number) for Run 3275. Total run (180 cycles) took 301 min.

fractionates slowly through most of the analysis but at an accelerating rate in the last 1/6th of the analysis. Xiao and Beary [4] observed that the ${}^6\text{Li}/{}^7\text{Li}$ ratio of the Li ion beam decreases with time consistent with preferential evaporation/ionisation of ${}^6\text{Li}$ from the filament.

The preferential loss of ${}^6\text{Li}$ is the probable explanation for the variability of ${}^6\text{Li}/{}^7\text{Li}$ ratios calculated from multiple runs of various standards (Table 3). Although individual analyses give internal precisions ($1 \times$ standard errors) between 0.1‰ and 1‰, means of repeat analyses have standard deviations greater than 2‰ and generally $\sim 4\%$ (Table 3). The results in Table 3 show that little is gained by analysis of multiple peaks. Including the fractionation correction reduces the estimated ${}^6\text{Li}/{}^7\text{Li}$ ratio and including the small masses 58 and 59 generally degrades the precision. The best sets of analyses (based either on the 55/57 or 56/57 singly, together, or on 55/57, 56/57 and 54/57 with or without fractionation correction) give results with a standard deviation (about the mean of the set of runs) of about 2‰ and the average of all the more precise sets (0.08273) has a standard deviation of 3.7‰ (Fig. 6). Note that the results from runs 3270 to 3287 exhibit two outliers (runs 3271 and 3286) which, when excluded, improve the scatter of the remaining runs to $\sim 2\%$. The consistency of analyses with enriched ${}^{10}\text{B}/{}^{11}\text{B}$ is com-

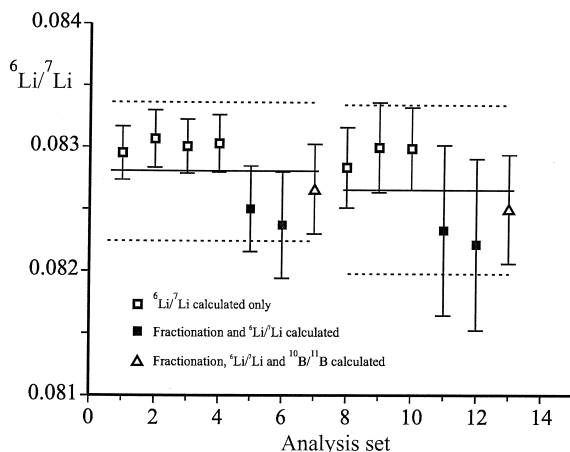


Fig. 6. Comparison of ${}^6\text{Li}/{}^7\text{Li}$ ratios calculated assuming (1) no fractionation and given ${}^{10}\text{B}/{}^{11}\text{B}$ (open square symbols), (2) calculating fractionation and ${}^6\text{Li}/{}^7\text{Li}$ for given ${}^{10}\text{B}/{}^{11}\text{B}$ (filled square symbols) and (3) calculating fractionation, ${}^6\text{Li}/{}^7\text{Li}$ and ${}^{10}\text{B}/{}^{11}\text{B}$ from three peaks (triangles). Sample set R1 gives means and standard errors from runs 1570 to 1737 (L-SVEC) and sample set R3 from runs 3270 and 3287 but omitting outliers in runs 3270 and 3286 (AA standard). Error bars are 2σ . Line is mean of all data and dotted lines two standard deviations of data about line.

parable to that with normal ${}^{10}\text{B}/{}^{11}\text{B}$ (Table 3). For runs 1570 to 1737 with SRM-951 boron, a value of 0.2477 (Sahoo and Masuda, 1995) was assumed for the ${}^{10}\text{B}/{}^{11}\text{B}$ ratio which differs by 3‰ from the mean value recovered ($0.2485 \pm 1.6\%$, 1σ) calculating fractionation, ${}^6\text{Li}/{}^7\text{Li}$ and ${}^{10}\text{B}/{}^{11}\text{B}$ as unknowns. For runs 3270 and 3287 a laboratory reagent of unknown natural boron isotopic composition was used. The calculations of ${}^6\text{Li}/{}^7\text{Li}$, or fractionation and ${}^6\text{Li}/{}^7\text{Li}$ only, from these runs assumed a ${}^{10}\text{B}/{}^{11}\text{B}$ ratio of 0.252 from the mean of the calculation of ${}^{10}\text{B}/{}^{11}\text{B}$ using three Li_2BO_2^+ peaks.

The results of this study suggest that the best estimates of ${}^6\text{Li}/{}^7\text{Li}$ are no more precise than approximately $\pm 3\%$ (1σ) but the range of values measured for the ${}^6\text{Li}/{}^7\text{Li}$ ratio of L-SVEC ($0.08265 \pm 4.1\%$, 1σ for runs 1570 to 1737 and $0.08241 \pm 3.5\%$ for runs 3452 to 3425) is similar to the range of published estimates (0.0820 to 0.0832, see Sahoo and Masuda, [11]). The probable cause of errors an order-of-magnitude less good than the propagation of measurement errors would suggest, is fractionation of the Li remaining on the filament due to the relatively large Li^+ beam.

5. Conclusions

${}^6\text{Li}/{}^7\text{Li}$ and ${}^{10}\text{B}/{}^{11}\text{B}$ may theoretically be analysed to sub-per-mil precision by measurement of multiple peaks of the ion Li_2BO_2^+ by thermal ionisation and using ion-counting detection. However the relatively large Li^+ beam emitted simultaneously with the smaller Li_2BO_2^+ beam causes the Li remaining on the filament to fractionate and precision of repeat analyses of ~ 100 ng Li loads is not better than $\sim 3\%$ at 1σ . Improvement in analysis of Li isotopic compositions may be possible if it proves possible to ionise a molecular complex with two or more masses without an accompanying Li ion beam or if direct correction of fractionation proves possible in plasma-source mass-spectrometers.

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