Precise boron isotopic analysis of complex silicate (rock) samples using alkali carbonate fusion and ion-exchange separation

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Abstract

We describe a technique for determining the boron isotopic composition of low-B silicate rocks which until recently have been difficult to analyze. The method involves an alkali carbonate fusion for sample dissolution, ion-exchange chromatography for boron purification, and PTIMS analysis using $Cs_2BO_2^+$. Our procedure combines several previously published methods in a unique manner to simultaneously (1) achieve state-of-the-art precision and accuracy, and (2) expedite analysis with respect to competing methods. Because isotopic fractionation corrections typically are based on concurrent analyses of the SRM-951 boric acid reference standard, these data do not provide a true measure of analytical accuracy or interlaboratory biases. In this study, analytical precision and accuracy were evaluated independently through replicate analyses of the JB-2 basalt reference standard, with completely independent chemical extractions of boron in each case. The average corrected $^{11}B/^{10}B$ ratio obtained is 4.0728 ± 0.0019 (2σ external uncertainty), which corresponds to a $\delta^{11}B$ value of +7.23 ± 0.47‰. This result agrees closely with data obtained by Nakamura et al. [Nakamura, E., Ishikawa, T., Birck, J.L., Allègre, C., 1992. Precise boron isotopic analysis of natural rock samples using a boron–mannitol complex. Chem. Geol. 94, 193–204.] using the HF digestion method. We strongly recommend that JB-2 be analyzed routinely in future boron isotopic studies to facilitate assessment of analytical uncertainties and interlaboratory biases. © 1997 Elsevier Science B.V.

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1. Introduction

Owing to improvements in analytical methods, the last decade has seen a rapid increase in the number of studies of the isotopic composition of boron in natural samples (cf. Leeman et al., 1991; Barth, 1993; Aggarwal and Palmer, 1995; Palmer and Swihart, 1996). At present, three distinct ap-

proaches to boron isotopic analysis are in common practice: positive thermal ionization mass spectrometry (PTIMS), negative thermal ionization mass spectrometry (NTIMS), and secondary ionization mass spectrometry (SIMS, or ion microprobe). Each of these methods has advantages and disadvantages, but for highest accuracy and precision, PTIMS using Cs-borate is preferable. This method introduces negligible mass fractionation during the course of an analysis owing to the large mass numbers (308, 309) analyzed, and samples of ~ 1 μg B can be analyzed

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with a precision of 0.4‰ or better (Ramakumar et al., 1985; Spivack and Edmond, 1986; Xiao et al., 1988; Leeman et al., 1991; Nakamura et al., 1992; Ishikawa and Nakamura, 1994; Gaillardet and Allègre, 1995). For comparison, NTIMS and SIMS methods allow analysis of smaller amounts of boron with minimal sample processing but with worse precision; for the NTIMS method typical 2-sigma precision is between ±1–2‰ (Vengosh et al., 1989) and ±0.7‰ (Hemming and Hanson, 1992), whereas precision is near ±4‰ for the SIMS method (Chaussidon and Albarède, 1992).

For PTIMS analysis of silicates, the method of boron extraction has proved to be the most challenging aspect. Treatment of the sample must (1) extract boron with yields approaching 100% to avoid isotopic fractionation, and (2) purify this boron extract to reduce matrix interferences which potentially can reduce ionization efficiency and/or produce fractionation effects on the filament. Primarily due to difficulties in both chemical separation and isotopic measurement, relatively few high precision (< 0.5‰) boron isotopic analyses are available in the literature for silicate rocks (Spivack and Edmond, 1986; Palmer, 1991; Nakamura et al., 1992; Ishikawa and Nakamura, 1994; Smith et al., 1997). More importantly, the analytical procedures employed have not been widely evaluated using international rock standards, although this clearly is desirable to evaluate accuracy and interlaboratory biases.

The first modern rock analyses involved use of a pyrohydrolysis extraction method (Spivack and Edmond, 1986; Spivack et al., 1987) that is best suited for relatively boron-rich materials. This method is less effective for aluminosilicate rocks with low boron contents (< 50 ppm B) because it requires a large amount of sample, a long time to extract all boron from the rock, and a large volume of water. An alternative procedure was developed by Nakamura et al. (1992) for extraction and purification of boron from silicate samples with low boron contents. Their method incorporates a HF acid sample digestion step followed by successive ion-exchange separations; it has the advantages that the reagents involved are easily purified, and that boron extraction is complete. However, because of the acidic milieu and the consequent high volatility of boron compounds, mannitol complexation of boron and

painstaking attention are required at all stages to avoid potential boron losses during multiple evaporation steps and/or contamination by boron in the ambient air. Using this method, the boron isotopic composition of a certified rock standard (island arc tholeiitic basalt, JB-2) was first presented by Nakamura et al. (1992).

We have developed a simple, yet efficient method of boron extraction and purification based on an alkali carbonate fusion for sample dissolution, ion-exchange chromatography for boron purification, and Cs-borate PTIMS analysis. This method offers a comparatively simple chemical treatment for silicate samples, largely in an alkaline environment where risks of boron loss, contamination, or isotopic fractionation are minimized. The precision and accuracy of the method is tested against the SRM-951 boric acid standard (U.S. National Institute of Standards and Technology) and against the JB-2 rock standard (Geological Survey of Japan).

2. Experimental methods

2.1. Boron extraction

Extraction of boron from aluminosilicates was accomplished via a fusion technique modified after the method of Kiss (1988). Purified K_2CO_3 was used as the flux because its high solubility facilitates rapid aqueous leaching of the resulting fusion cakes. Finely powdered samples (ca. 0.2–1.0 g) were mixed with purified K_2CO_3 with a flux-to-rock ratio of 5:1, then fused in Pt–Ir (95%–5%) crucibles at ~1000°C (K_2CO_3 melting point = 891°C). After cooling, the fusion cakes were dissolved in 5–6 ml ultrapure H_2O at room temperature and transferred into polypropylene tubes. An insoluble phase, comprising transition metal hydroxides and alkaline earth carbonates, is present in many natural samples (e.g., volcanic rocks). This solid material was separated by centrifuging for 20 min, washed repeatedly with ultrapure H_2O, and all washings combined with the original supernate. Boron was wholly contained in the soluble phase as indicated by recovery tests; under the alkaline conditions of extraction boron exists largely as borate ions. The advantages of this method are that it is rapid and that relatively large

amounts of sample can be processed, enabling rocks with low boron concentrations to be analyzed.

2.2. Chemical purification

Before introduction of the sample into the mass spectrometer it is necessary to separate boron from matrix impurities to avoid suppression of ionization of the boron species analyzed and to maintain a good vacuum in the mass spectrometer. Separation of boron was carried out by a three step ion-exchange separation procedure as described below.

2.2.1. Reagents and boron blanks

Trace boron was removed from the K_2CO_3 reagent (Suprapur® Merck) using several passages through Amberlite resin columns ($h = 50$ mm, $r = 5$ mm) in the basic form; a blank of 7.6 ng/g was obtained for the batch of reagent used in this study. All other reagents used were prepared as suggested by Leeman et al. (1991). NH_4OH was prepared as a saturated solution by bubbling NH_3 gas from a cylinder through chilled H_2O. Mannitol and Cs_2CO_3 aqueous solutions (100 μM/ml) were both purified through Amberlite resin columns. Ultrapure graphite (Johnson Matthey, 200 mesh) is suspended in 50% ethanol–50% H_2O to give 40 mg graphite/g.

Boron blanks were determined by isotope dilution using [10]B-enriched SRM-952 boric acid. Blanks in the reagents ordinarily used for Sr, Nd and Pb analyses were as follows: two-bottle sub-boiling distilled H_2O (1.4 ng/ml), two-bottle sub-boiling distilled 6.6 N HCl (1.3 ng/ml), 6 N NH_4OH (1.5 ng/ml), mannitol solution and Cs_2CO_3 (0.03 ng/ml). Using these reagents, the theoretical blank for the whole chemical treatment (44 ng) is in close agreement with measured procedural blanks for the entire chemical separation (37–50 ng). Variations in the measured $\delta^{11}B$ value as a function of blank contribution in the processed boron aliquot (Fig. 1) indicate that deviations of the observed $\delta^{11}B$ from the true isotopic composition lie within the range of typical mass spectrometric uncertainties ($\leq \pm 0.2‰$) for blank levels below $\sim 2\%$. Thus, for ordinary reagents, a minimum of ~ 2 μg of sample boron should be processed to maintain a negligible blank contribution; with moderate precautions, the blank can be ignored for samples containing more than 5 ppm boron.
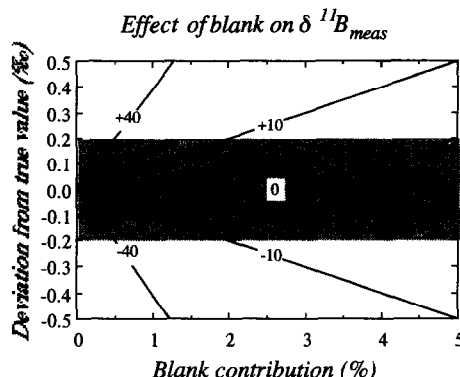

Effect of blank on $\delta^{11}B_{meas}$

Fig. 1. The effect of blank on the measured composition of a sample. Curves are shown for hypothetical blanks with $\delta^{11}B$ ranging from -40 to $+40‰$ (approximate extremes for terrestrial boron; a range of -10 to $+10‰$ is more likely in the laboratory). Assuming a sample with $\delta^{11}B = 0‰$, deviations from this 'true' value are indicated as a result of variable blank additions (as percent of total boron). For blank composition of $\pm 10‰$, a 2% blank contribution will result in a shift of only 0.2‰ in measured $\delta^{11}B$, which is within typical limits of analytical precision (shaded area).

However, considerable reduction of water and acid blanks is achieved by sub-boiling distillation of reagents in the presence of mannitol (cf. Nakamura et al., 1992). The feed water containing mannitol (0.4 g/l) was sub-boiled at a temperature below $\sim 80°C$ using a Teflon two-bottle still; 6.6 N HCl solution was similarly purified in the presence of mannitol (2 g/l). Following this treatment our H_2O and 6.6 N HCl reagents gave blank levels of 0.26 ng/ml and 0.16 ng/ml, respectively, confirming that volatilization of boron in acidic solutions is suppressed by mannitol (Feldman, 1961; Ishikawa and Nakamura, 1990). Using these reagents, the calculated total procedural blank (10.3 ng) is again similar to measured levels (11.6 ng). For comparison, Nakamura et al. (1992), using no boron-specific resin, obtained total procedural blanks similar to their calculated reagent blanks that are only slightly lower (3–4 ng) than those attainable with the fusion method. Thus, with ultrapure reagents isotopic analysis of samples with as little as 1 ppm boron is feasible with a negligible blank effect. Of course, blank corrections can be applied if the blank composition is known.

Independent column blanks were determined in the course of repeated usage and washing of the

ion-exchange resins; the resulting blank levels (ca. 6–10 ng of boron for 5 ml of eluate) are significantly higher than obtained for fresh, previously unused Amberlite resin (~ 1 ng). The implication is that some boron is permanently absorbed onto the columns after exposure to a sample. Thus, to completely avoid the possibility of contamination, the Amberlite resin was replaced after each processed sample. Our observation that procedural blank levels using fresh columns are similar to calculated reagent blanks indicates that external contamination is negligible.

2.2.2. Removal of K_2CO_3

The first step of sample purification involved use of Amberlite IRA 743 (50 mesh) boron-specific ion-exchange resin as first described by Kiss (1988), modified by Leeman et al. (1991). Subsequently, we have significantly reduced the column size and carefully calibrated reagent requirements to produce maximum (near 100%) boron yields needed for optimal isotopic work. Approximately 0.3 ml of resin was loaded onto heat-shrink Teflon columns ($h = 20$ mm, $r = 2$ mm) and cleaned at least twice with 5 ml of 6.6 N HCl. After two further cleanings with ultrapure water, the resin was conditioned with 2 ml 2 N NH$_4$OH and 3 ml ultrapure water. Flow rates through the ion-exchange resin were adjusted to less than 0.5 ml/min.

Following centrifugation, 1–2 ml of sample solution was loaded onto the column. No precipitate was observed at this stage. The sample was washed with 2 ml ultrapure water followed by 2 ml 2 N NH$_4$OH, then another 3 ml ultrapure water. Boron was eluted by the addition of 5 ml 2 N HCl and collected in concave bottom Savillex® PFE Teflon beakers containing 2 μmoles of mannitol for each μmole of boron processed (Feldman, 1961; Ishikawa and Nakamura, 1990; Leeman et al., 1991). Elution curves for our columns (Fig. 2) indicate a total boron recovery of 98%. The eluate was evaporated at low temperature ($< 68°C$) in the presence of mannitol to avoid volatilization of boron (see later discussion).

This first step provides an initial stage of purification and allows loading the sample leacheate onto the resin in basic form thereby precluding an evaporation step or formation of precipitates (e.g., silica gel-like compounds form upon acidification). The
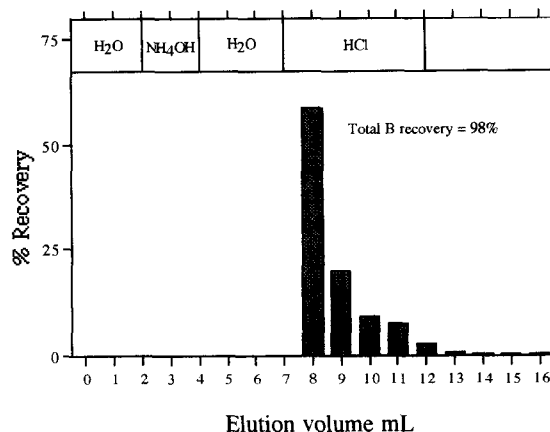

Fig. 2. Schematic diagram of the anion column elution procedure with reagent type shown at the top and reagent volume at the bottom. One ml aliquots of the HCl eluent were collected successively and analyzed for boron content via isotope dilution. Percent recovery is shown as a function of eluate volume.

final boron eluate contained ~ 7 μg of potassium for each gram of K_2CO_3 processed through the column. Because combination of potassium with boron can suppress the formation of $Cs_2BO_2^+$ during mass spectrometric analysis, further purification of the sample solution is necessary.

2.2.3. Removal of cations

The second purification step involves separation of boron from cations using AG 50W-X8 (200–400 mesh) cation-exchange resin; 2.5 ml of resin was loaded onto polypropylene columns ($h = 30$ mm, $r = 5$ mm). The resin bed was cleaned twice using 5 ml of 6.2 N HCl, then conditioned using 3 ml of 0.02 N HCl. The dry sample from the previous step was dissolved in 1 ml 0.02 N HCl and loaded onto the cation column. Under these conditions, the major cations are retained on the column whereas B readily passes through. The boron fraction was immediately collected in a Savillex® PFE Teflon beaker, and total elution was obtained by loading another 3 ml of 0.02 N HCl after the loading of the sample. We use 0.02 N HCl in this step instead of water to avoid a boron elution tail.

Boron recovery at this stage exceeded 99%. However, a non-negligible amount of potassium remains in the eluate (typically ~ 40 ng relative to an initial gram of K_2CO_3). The boron sample obtained at this

stage sometimes had a brownish color (probably due to cation resin impurities). In the mass spectrometric analysis of such samples we have observed a considerable reduction of the $Cs_2BO_2^+$ ion current, as previously noted by Nakamura et al. (1992). Similar organic impurities were also observed by Hemming and Hanson (1994); whereas these were not eliminated by use of UV radiation, they could be removed by using an ultra-filtration apparatus. We found that a third column step is also effective in removing organic material while nearly eliminating potassium and trace cations.

2.2.4. Final purification of boron

The boron samples, in HCl solution following the preceding cation-exchange elution, are adjusted to alkaline pH (10–12) by addition of NH_4OH. As emphasized by Aggarwal and Palmer (1995), this step is crucial to convert all boron to the $B(OH)_4^-$ form, which is the species absorbed onto the Amberlite resin (Kiss, 1988). At lower pH values, some fraction of boron in solution occurs as $B(OH)_3$, which may not be quantitatively absorbed on the resin; partial loss of this species can result in fractionation of the boron isotopic ratio (cf. Kakihana et al., 1977).

These pH-adjusted solutions are loaded onto clean and preconditioned Amberlite resin columns ($h = 20$ mm, $r = 2$ mm) and the column procedure in the first step is repeated. Following evaporation in the presence of mannitol, the final sample residues should have a white color. At this point the sample is ready for mass spectrometric analysis.

2.2.5. Boron recovery tests

Total recovery for the combined fusion/ion-exchange procedure is approximately 95–98% based on repeated tests using SRM-951. The efficiency of boron extraction was further evaluated by processing two rock standards (JB-2 and RGM-1) through the fusion and subsequent purification steps. The amount of recovered boron was measured via either isotope dilution or inductively coupled plasma emission spectroscopy (ICP–ES) methods; these data are compared (Table 1) with boron determinations via prompt-gamma neutron activation (PGNA) in untreated powders of the same standards (cf. Leeman and Sisson, 1996). The close agreement between

Table 1
Boron recovery study

	JB-2 ppm B	RGM-1 ppm B
After chemical separation (*equiv. rock concentration*)		
ICP–ES	27.1 (95%)	26.0 (94%)
		26.8 (96%)
		27.2 (98%)
Isotope dilution	26.95 (95%)	
	28.04 (98%)	
Recommended values (Govindaraju, 1994)	30	28
PGNA (Leeman and Sisson, 1996)	28.5 ± 1.8	27.8 ± 2.1

In parentheses percent recovery relative to average PGNA values.

PGNA vs. ICP–ES or isotope dilution results (typically within 5%) indicates that boron recovery, for combined fusion/ion exchange, is on the order of 94–98%, which is significantly higher than that obtained using NaOH as a fluxing agent (Musashi et al., 1990). The loss of boron (2–6%) is consistent with the observed boron tail in the Amberlite column elution. It should be noted that the apparent discrepancies between our determinations and the independent analyses of these standards are within analytical uncertainties of the latter values.

2.3. Mass spectrometry

Basically we followed the $Cs_2BO_2^+$ graphite method reported in Leeman et al. (1991), and first described by Ramakumar et al. (1985). The B/Cs molar ratio was maintained near 2.5, slightly in excess of the stoichiometric value for $Cs_2B_4O_7$; small deviations from this ratio result in no significant mass fractionation. A VG Isomass 54E thermal ionization, single collector mass spectrometer was used for all analyses. Samples (ca. 0.4–0.8 μg B) were loaded onto single outgassed tantalum filaments (0.025 × 0.76 mm) following the procedure of Xiao et al. (1988) with slight modification. The dried boron sample, containing mannitol (Leeman et al., 1991), was dissolved in Cs_2CO_3 solution, then loaded onto a graphite layer (before complete dryness of graphite) to make a sample–graphite mixture. The filament was heated at 1.0 A for 5 min and then at 1.4 A for 1 min.

The mass spectrometer analytical protocol is almost the same as described by Leeman et al. (1991) and Nakamura et al. (1992). The ratio of $Cs_2^{11}BO_2^+$ ($m/e = 309$) to $Cs_2^{10}BO_2^+$ ($m/e = 308$) was measured when the ion current of $Cs_2^{10}BO_2^+$ reached $2–5 \times 10^{-12}$ A on the Faraday cup collector (10^{11} Ω); the base line is taken at $m/e = 306.5$. An individual analysis typically comprises 15–20 blocks of 10–20 individual ratios; in-run statistics are based on the block averages. The acquisition program used is ANALYST (Ludwig, 1991).

Measured ratios were corrected for the contribution of ^{17}O (as the species $Cs_2^{10}B^{16}O^{17}O^+$) to the 309 peak by subtracting 0.00079 (cf. Spivack and Edmond, 1986). For convenience the oxygen-corrected isotopic composition of boron ($^{11}B/^{10}B = R$) in a sample (Sa) is reported as per mil (‰) deviation from a standard (Std; SRM-951 boric acid) as follows: $\delta^{11}B = 1000 * ([R_{Sa}/R_{Std}] - 1)$.

3. Results

3.1. Analytical precision and accuracy for SRM-951 standard

The SRM-951 standard was repeatedly analyzed to determine precision and reproducibility of our method; measured $^{11}B/^{10}B$ ratios are given in Table 2. Eleven analyses of separate aliquots (0.2–0.6 μg boron) of our shelf solution during a 4-month period gave a mean of 4.0506 ± 0.0007 (2σ, external uncertainty); in-run precision of individual analyses generally is better. The average $^{11}B/^{10}B$ ratio (R_{meas}) is significantly higher than the certified value of 4.04362 (R_{cert}; Catanzaro et al., 1970). A fractionation correction (fc) factor is calculated as ($[R_{cert} + 0.00079]/R_{meas}$); this value (0.99882) is close to that obtained by Xiao et al. (1988; 0.99853), Nakamura et al. (1992; 0.99832), and Gaillardet and Allègre (1995; 0.99836) for PTIMS analyses of SRM-951 as $Cs_2BO_2^+$.

To evaluate potential isotopic fractionation during the ion-exchange procedure we also repeatedly processed aliquots of SRM-951 through the full chemistry procedure. Separate analyses of these aliquots are reported in Table 2; the average value of $^{11}B/^{10}B$ (4.0492 ± 0.0017, 2σ external uncertainty) is about

Table 2
Boron isotopic analyses of NBS SRM 951 standard

Sample	$^{11}B/^{10}B$ (measured)	$\pm 2\sigma_m$ s.e.	$^{11}B/^{10}B$ (corrected)
Standards without chemistry			
1	4.05004	0.00036	4.0445
2	4.05093	0.00030	4.0454
3	4.05115	0.00025	4.0456
4	4.05079	0.00032	4.0453
5	4.05039	0.00023	4.0449
6	4.04992	0.00027	4.0444
7	4.05100	0.00034	4.0455
8	4.05082	0.00056	4.0453
9	4.05070	0.00030	4.0452
10	4.05043	0.00020	4.0449
11	4.05050	0.00090	4.0450
Average	4.0506		4.0451
$\pm 2\sigma$	0.0007		
External uncertainty	(0.18‰)		

Sample size (μg B)	$^{11}B/^{10}B$ (measured)	$\pm 2\sigma_m$ s.e.	$^{11}B/^{10}B$ (corrected)
Standards through full chemistry			
20	4.0490	0.0004	4.0435
10	4.0486	0.0003	4.0431
2	4.0496	0.0013	4.0441
2	4.0495	0.0008	4.0440
5	4.0484	0.0009	4.0429
2	4.0488	0.0015	4.0433
5	4.0503	0.0008	4.0448
2	4.0491	0.0005	4.0436
2	4.0490	0.0005	4.0435
4	4.0482	0.0018	4.0427
5	4.0509	0.0010	4.0454
3	4.0489	0.0020	4.0434
3	4.0481	0.0003	4.0426
4	4.0500	0.0003	4.0445
3	4.0483	0.0023	4.0428
2	4.0499	0.0010	4.0444
2	4.0478	0.0010	4.0423
2	4.0493	0.0003	4.0438
1	4.0506	0.0010	4.0451
Average	4.04917		4.04362
$\pm 2\sigma$	0.0017		
External uncertainty	(0.42‰)		

0.4‰ lower than the unprocessed standard. This discrepancy is consistent for both large and small size samples and is unlikely to reflect contamination effects. Rather, a small systematic partial loss of ^{11}B during column elution is indicated. This conclusion is supported by the observed retention of small

amounts of sample boron on the Amberlite ion-exchange resin. With respect to data for the chemically untreated standard, both 2σ and the errors on individual runs are double. This difference likely reflects the effects of residual organic impurities on ion beam stability for samples put through the chemical separation. The fc value (0.99882) for SRM-951 through full chemistry was used to make fractionation corrections to all boron isotopic data presented in Tables 2 and 3.

3.2. Analytical reproducibility for a natural volcanic rock sample

Nakamura et al. (1992) reported four separate determinations of boron isotopic composition of the standard rock JB-2 (island arc tholeiitic basalt, Geological Survey of Japan) obtained using their acid dissolution and ion-exchange chromatography procedure. Their average corrected $^{11}B/^{10}B$ ratio is 4.0723 ± 0.0006 (2σ external uncertainty), corresponding to $\delta^{11}B = +7.09 \pm 0.16\%o$.

In our study, variable amounts of powdered JB-2 standard were analyzed following the fusion and ion-exchange procedure described above (Table 3; Fig. 3). The average corrected $^{11}B/^{10}B$ ratio obtained is 4.0729 ± 0.0019 (2σ external uncertainty), corresponding to $\delta^{11}B = +7.23 \pm 0.47\%o$. The in-
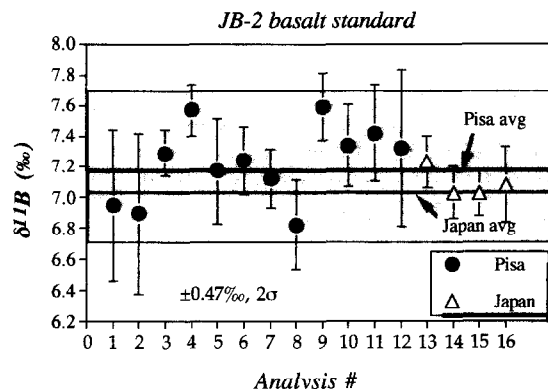

Fig. 3. Record of corrected boron isotopic ratios measured in the JB-2 standard rock over a period of 4 months. Each analysis represents complete fusion and chemical purification of a different aliquot of the standard. Long-term precision for twelve measurements (2σ external uncertainty $= \pm 0.47\%o$) is similar to precision of individual analyses. Note that all data lie within in this conservative error limit. Comparable results from Nakamura et al. (1992) are shown for convenience.

run analytical precision for individual analyses ranges from ± 0.2 to $\pm 0.5\%o$, two to three times higher than that (0.1–0.2‰) quoted by Nakamura et al. (1992), but similar to that obtained for SRM-951 standard put through our full chemistry treatment. All of our measurements lie within conservative uncertainty limits ($\pm 0.5\%o$) estimated for single analyses. Impurities in the boron extracted from natural silicate samples may contribute to poorer in-run precision; such effects are most notable in the earliest analyses which were conducted during development of our separation procedure. However, because we see a similar effect in the pure SRM-951 standard, the causative impurity is likely organic material derived from the ion-exchange resins. Nevertheless, our mean $\delta^{11}B$ for the JB-2 standard is statistically indistinguishable from the average of Nakamura et al. (1992), and it appears that isotopic fractionation is effectively eliminated by normalization to the average of concurrent SRM-951 analyses; most significantly, there is no significant bias between these two laboratories.

Some authors (Hemming and Hanson, 1994; Gaillardet and Allègre, 1995) report negligible boron losses during evaporation of acidic solutions of the SRM-951 standard, perhaps because they remove the

Table 3
Boron isotopic analyses of JB-2 standard (tholeiitic basalt)

Sample size (μg B)	$^{11}B/^{10}B$	$\pm 2\sigma_m$ s.e.	$^{11}B/^{10}B$ (corrected)	$\delta^{11}B$
2.0	4.0773	0.0020	4.0718	6.96
4.0	4.0771	0.0021	4.0716	6.91
2.0	4.0787	0.0006	4.0731	7.30
3.0	4.0798	0.0007	4.0743	7.58
2.0	4.0782	0.0014	4.0727	7.18
1.5	4.0785	0.0009	4.0730	7.26
2.0	4.0780	0.0008	4.0724	7.13
2.0	4.0768	0.0012	4.0713	6.83
3.0	4.0799	0.0009	4.0743	7.60
2.0	4.0789	0.0011	4.0734	7.35
2.0	4.0792	0.0013	4.0736	7.42
2.0	4.0788	0.0021	4.0732	7.32
Average	4.07843		4.07285	7.23
$\pm 2\sigma$	0.00192			
External uncertainty	(0.47‰)			

residues from heat at the moment of dryness. Such meticulous observation of the residues is impractical and unnecessary in the presence of mannitol. The utility of mannitol to repress boron volatilization is confirmed by the strong reduction of blank level in 6.6 N HCl when purified by two-bottle sub-boiling distillation in its presence.

Furthermore, in our experience boron volatilization from HF solutions is not completely suppressed by mannitol. For example, we have observed cross-contamination of such solutions when concurrent evaporations were carried out in the same fume hood. It is partly for this reason, and partly for time efficiency, that we developed an alternative method of boron extraction to replace the HF-based method of Nakamura et al. (1992).

4. Conclusion

Extraction and purification of boron via rapid fusion with purified K_2CO_3 and a simple three-step ion-exchange procedure greatly facilitates sample preparation for boron isotopic (and concentration) determination. Combined with PTIMS analysis, this relatively simple method produces precise boron isotopic analyses of silicate rocks and good agreement with data obtained via other high precision methods – as evidenced by the interlaboratory comparison for the JB-2 standard ($\delta^{11}B = 7.09 \pm 0.16\%o$, Nakamura et al., 1992; and $7.23 \pm 0.47\%o$, this study).

Owing to considerable analytical difficulties in measuring the isotopic composition of boron in silicate rocks, high precision data are scarce and interlaboratory comparisons of boron isotopic composition are based mainly on analyses of SRM-951 boric acid. Because this standard is also used to correct for isotopic fractionation in most laboratories, it is not an appropriate indicator of analytical accuracy. Moreover, considering all potential sources of isotopic fractionation during the extraction and purification of boron, the availability of an international rock standard is highly desirable to check actual reproducibility and accuracy of rock analyses. Given the close agreement obtained for JB-2 by different techniques, we recommend that this sample be analyzed routinely in the course of future boron isotopic studies to facilitate assessment of analytical uncertainties.

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