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Micro-sublimation separation of boron in rock samples for isotopic measurement by MC-ICPMS

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Abstract

The technique of the micro-sublimation for boron (B) separation in silicates has been evaluated carefully. Nine international standards (rock powder) comprising eight felsic to mafic igneous rocks and one clay were dissolved in acids using the HF + mannitol method. These rock solutions were then doped with concentrated NaCl solution and subjected to the B micro-sublimation processes. Isolated drops of micro-sublimation were examined for matrix elements, B recovery, and used for high precision isotopic measurements by MC-ICPMS.

These experimental results confirm that the micro-sublimation technique can be used to isolate B in digested silicate solutions efficiently with very low blank and excellent recovery. These new isotopic values in rock standards are in good agreement with literature reports. The unseparable matrix after micro-sublimation suggests a small difference of 0% to -0.8‰ for most silicates on B isotopic measurement using multi-collector inductively coupled plasma mass spectrometry. This NaCl doping + micro-sublimation technique is readily applicable for B isotopic measurements of silicate rocks containing medium to high B levels (e.g., > 5 ppm).

This study presents a novel NaCl doping modified micro-sublimation procedure for B isolation in digested silicates. This protocol enjoys low B blank, and is a less labor intensive and simple procedure compared with traditional ion exchange purification. It can be used to facilitate B isotopic measurements in silicates and promote - geochemical applications in environmental aqueous solutions and rocks.

Keywords: Boron isotopes, Micro-sublimation, MC-ICP-MS
Introduction

Boron (B) is an excellent geochemical tracer for studying crust-mantle recycling processes, mainly because of its large discrepancy in both concentration and isotopic ratio between continental and the oceanic crust \(^1\)\(^-\)\(^3\), but also because of its superior sensitivity to fluid activity during metamorphic devolatilization and arc magmatic partial melting \(^4\)\(^-\)\(^7\). However, B isotope measurements in rocks have encountered difficulties due to potential contamination and vapor loss during chemical digestion, as well as from problems associated with ion exchange purification. These challenges have hindered the routine analysis of B and B isotopic compositions in silicates, resulting in limited knowledge of the B isotopic compositions in rock specimens.

Several rock digestion methods have been applied for extracting B from silicates, including pyrohydrolysis, fusion, and acid dissolution. Among them, acid dissolution is one of the most reliable and popular techniques \(^8\). Boron is rather volatile under acidic conditions, especially in hydrofluoric (HF) and hydrochloric (HCl) acids \(^9\), but HF is the most efficient decomposition reagent for felsic rocks \(^10\). It has been suggested that the addition of proper mannitol in HF causes no B loss during decomposition of natural rocks \(^11\) and it has been proven applicable for B isotopic analysis and confirmed as practicable in natural rocks (e.g., Makishima et al., (1997)\(^12\); Rosner and Meixner (2004)\(^13\); Ciaglo et al. (2007)\(^14\)).

However, proper purification is required for separating B from its matrix prior to any mass spectrometry isotopic measurement. Usually, this is performed through various steps of cation/anion exchanges in which potential B loss and isotopic deviation also need to be evaluated carefully \(^11,13,15,16\).
Wei et al.\textsuperscript{17} reported a single step ion-exchange chromatographic purification technique to reduce possible contamination. However, a large quantity of potentially rather hazardous chemicals was involved and it was rather labor intensive in preparation processes. Gaillardet et al.\textsuperscript{18} proposed a micro-sublimation method to separate B from acid solutions rich in organic media. Their experiments demonstrated that B is lost readily in sublimation if the dry residue were heated further. This isolates B from the matrix and obtains close to 100% B recovery with no isotopic fractionation. Wang et al.\textsuperscript{19} modified the micro-sublimation procedures and implemented them successfully for samples of Na- and Ca-rich matrices for high precision isotopic analysis, where it shows that the micro-sublimation strategy has low blank contribution of B than conventional column procedures, and circumvents interference from organic matter during mass spectrometry. These evaluations demonstrate the potential of micro-sublimation as a powerful tool for B purification in other natural samples.

During the last two decades, MC-ICP-MS has been proven an excellent tool for precise isotopic analyses; it has precision comparable with P-TIMS and is fast\textsuperscript{15,20-22}, although its potential memory and matrix artifacts must be eliminated carefully\textsuperscript{23}. In this study, we examine the efficiency of micro-sublimation on B separation in complex rock matrices, and demonstrate the great potential of the applicability of micro-sublimation for efficient B purification in rock samples. Nine international rock standards were selected in this experiment, including felsic to mafic igneous and clay samples, to test the robustness of this analytical procedure. The B concentrations and B isotopic values obtained show good consistency with literature reports. This protocol combines acid digestion and micro-sublimation for
high precision B isotopic measurement using MC-ICP-MS, which is a simple, robust and efficient method for silicates. This developed method improves greatly the experimental cost and blank contamination; thus, it can facilitate further research in the studies of crustal-mantle geochemical evolution.

**Experimental Procedures**

**Samples and reagents**

This study examined nine international rock standards in powder form, including eight felsic to mafic igneous rocks and one clay: RGM-1 (rhyolite), STM-1 (nepheline syenite), AGV-2 (andesite), and W-2 (diabase) purchased from the USGS; JB-2 (island arc tholeiitic basalt), JB-3 (basalt), and JA-1 (andesite) obtained from GSJ; and B-5 (basalt) and B-8 (Pliocene clay) received from the IAEA. All these standards have analyzed B concentrations and seven have published $\delta^{11}$B values.

A certified boric acid reference material, NIST SRM 951, was dissolved in Milli-Q water (1000 ppm B) and served as a stock solution for monitoring instrumental sensitivity and drift in this study. A 20-ppb B solution was prepared from the stock solution in 0.02M HNO$_3$ and used as a bracketing standard during the MC-ICP-MS procedures.

Ultrapure HF (J. T. Baker, 47-51% w/w, B≤100 ppt) and ultrapure HNO$_3$ (J. T. Baker, 67-69% w/w, B≤20 ppt) were used for silicate digestion. Other diluted nitric acids: 20% and 0.02M HNO$_3$ were made from ultrapure HNO$_3$ diluted by Milli-Q water and another 0.3M HNO$_3$ was made from diluting home-
made sub-boiling HNO\textsubscript{3} with de-ionized water. The NaCl solution was made from dissolving superpure solid NaCl (Merck) into Milli-Q water to ca. 175000 ppm. The 2\% mannitol solution is made from mannitol powder dissolved in Milli-Q water.

To reduce possible contamination from the surroundings, all wet chemical operations except for adding HF, were conducted in a Class-10 positive pressure hood coupled with a B-free ventilation system. The hot plate used to evaporate the samples was also contained within a hood equipped with the same influx air filter and a venting system.

Sample dissolution

The HF + mannitol acid digestion method\textsuperscript{11} was modified for rock sample dissolution in this study. Sample aliquots of 50–200 mg, which contain 1.2~5 µg B, were weighed in a 15-mL PFA beaker and soaked with 0.1 mL 2\% mannitol. Then, 0.1 mL ultrapure HNO\textsubscript{3} and 2–3 mL ultrapure HF were added. These sample-containing beakers were closed tightly and placed on a Teflon coated metal rack on a hot plate at 80 °C for three days. The addition of HNO\textsubscript{3} was assist in achieving complete dissolution without the aid of ultrasonics.

Complete dissolution is defined by visual inspection\textsuperscript{11}. The samples in the beakers had become nearly colorless, even though some contained white fluoride deposits, except for B-8 (clay), which contained black carbonaceous residues. After the samples were cooled, the caps were unscrewed and the beakers were placed on a hot plate at 65 °C to dryness to remove most Si and HF as gases. Then, 2 mL
5M HNO\textsubscript{3} was added and dried on 65 °C hot plate (this step was repeated with 1 ml 5M HNO\textsubscript{3}). Finally, 2~4 mL 0.1M HNO\textsubscript{3} were added and the lid closed to re-dissolve all the dried material at 80 °C for 4 hours. Then, the samples were cooled and centrifuged to collect just the supernatant.

When evaporating to dryness, the beakers and hot plates were installed within the hood equipped with the filtered air influx and ventilation system to reduce the potential blank contribution. All operations were conducted in a class-10000 clean room.

**Boron concentration measurements**

For rock analysis, the most commonly used instruments include an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)\textsuperscript{5,6} and an Inductively Coupled Plasma Mass Spectrometry (ICP-MS)\textsuperscript{12,24,25}. Because the high matrix in rock solutions may affect the calibration of concentration during analysis\textsuperscript{26,27}, the samples either have to be diluted with proper acid, purified through complex ion-exchange processes or correct the bias after evaluation. To evaluate the bias caused by the matrix, standard addition\textsuperscript{25,28} or internal standards addition of similar mass\textsuperscript{29} are usually performed.

In this study, ICP-OES was used for concentration analysis, and the standard addition method was employed for the matrix evaluation and correction. Rock solution samples were directly diluted to 10~50 times for B concentration measurement at the line at 208.9 nm, where no interference from iron was presented. Typical standard addition techniques were conducted to correct for the matrix effect. The ICP-OES detection limit is about 10 ppb for B and the internal precision is better than 2% (RSD).
integrated total uncertainty is ca. 5% for B concentration measurements.

**Micro-sublimation for B isolation**

In our previous study, we discovered excellent B separation from a matrix with high salt content using the micro-sublimation process, where neither B loss nor B isotopic fractionation was observed in the presence of Na ranging from 100 to 5000 ppm and of Ca from 500 to 8000 ppm, and in tests on international standards like IAPSO seawater, IAEA-B-2 and IAEA-B-3 showed good recovery and consistent isotope values with previous certifications\(^9\). This concept was adopted in this study and the NaCl-doping + micro-sublimation procedures were applied for B separation in silicate rocks, instead of the conventional ion exchange column method of separation.

Owing to contained complex matrices in rock solutions, direct micro-sublimation did not achieve good B isolation, where experimental results showed large amounts of Si cannot be separated from B and the recovery of B was rather low. By doping NaCl into the rock solutions, the Si content in the vapor phase was reduced significantly and the recovery of B became excellent (Table 1). Combining the experimental results in Table 1, the best concentrations of NaCl for doping ranged from 17600 to 24000 ppm for excellent B recovery, and typically, a concentration of 20000 ppm NaCl was adopted. Except for Si, other major elements such as Al, Fe, Ca, Na, Mg, K, and Ti were also measured and found to be negligible in the vapor phases (Table 1).

The processes of our NaCl-doping modified micro-sublimation are shown in Figure 1 and
described in detail below. An aliquot of rock solution (e.g. 0.4 mL) was doped with NaCl solution (ca. 175000 ppm) in 8:1 proportion, and mixed completely by repeated sucking and dropping with the pipet tip. The processes that follow are similar to those of Wang et al.\textsuperscript{19}, modified from Gaillarde et al.\textsuperscript{18} Briefly, 50 µL of the doped rock solution was dropped on the center of the cap of a 5-mL conical vial (PFA, Savillex), then the vial was closed tightly and placed upside down in a Teflon-coated metal rack (each rack can host 15 vials, 2 racks for a regular hot plate) on a thermostatic hot plate set at 98 °C. This heating continued for 18~24 h before the vials were removed and cooled. The condensed droplets on top of the vials were collected and each specimen was diluted to ~20 ppb B in 0.02M HNO\textsubscript{3} for MC-ICP-MS measurement.

**B isotopic measurements**

The B isotopic measurements are conducted using multi-collector ICP-MS (Thermo Fisher Scientific, Neptune) in Isotope Geochemistry Laboratory, NCKU. The samples were measured following the standard-sample bracketing approaches\textsuperscript{15} in a sequence of blank – standard – sample – standard – sample – blank. To reduce the memory effects, samples and NBS951 boric acid standards were prepared in a low concentration of 20 ppb in 0.02M HNO\textsubscript{3}, which has typical \(^{11}\text{B}\) intensity of 400~500 mV. Then, 0.3M HNO\textsubscript{3} washing solutions were used between each measurement for 180 sec to lower the noise-to-signal ratio to below 2%. The \(^{11}\text{B}/^{10}\text{B}\) ratio was corrected further by subtracting the mean value of the two adjacent blanks. Prior to sample analysis, the gas flow was adjusted to gain a
flow-rate vs. $^{11}\text{B}/^{10}\text{B}$ ratio plot and the optimal gas flow was selected. Each isotopic measurement consisted of 60 runs in 10 blocks and baselines were measured before data collection. The external precision from long-term repeated analysis of 20 ppb NBS 951 is 0.3% (2SD, $N=8$) and the 20 ppb home standard is -5.4 ± 0.34‰ (2SD, $N=7$). For quality assessment, a second home standard of B was also measured for each analysis. Table 2 lists the detailed instrumental operation conditions of the MC-ICP-MS (Neptune) in our laboratory.

**Results**

Table 3 shows the B concentration and isotopic results in this study, as well as available reference values in literature. Our measured B concentrations of the nine standard rocks, ranging from 6 to 100 ppm, agree well with all reported data. The B concentration results confirm proper extraction of B by our modified acid digestion method.

Seven of the nine samples have measured B isotopic values with different methods. For the most frequently measured certified samples, such as B-5, JB-3, JA-1, JB-2, and B-8, our results show identical isotopic values within the range of literature values. AGV-2 and W-2 have isotopic values that deviated significantly (-1.78 and -4, respectively) from the only published data. However, the data available for the two samples are too few to clarify any systematic differences. There is no B isotopic data available for STM-1 (Nepheline Syenite) and RGM-1 (Rhyolite), but the measured B concentrations are rather close to the reported data. The measured $\delta^{11}\text{B}$ for STM-1 and RGM-1 is -0.61
and -5.15, respectively. All available B isotopic results from this study and in literature are plotted
in Figure 2 for comparison.

Discussion

Blank contributions

B contaminations can occur easily during any experimental procedure, biasing the natural isotopic
values and thus, it is important to evaluate carefully any blank contribution. In this study, potential blank
contributions were evaluated with respect to the dissolution and micro-sublimation processes.

In each dissolution process, at least one blank test was conducted as same as the other rock samples,
and finally 1mL 0.1M HNO₃ was added in the beaker of the blank test and heated to make sure all
dissolved before measurement. The B content of blank was estimated using MC-ICP-MS by comparing
the ¹¹B intensity to the known concentration bracketing standards. These intensities were corrected by
subtracting the mean value of the two adjacent blanks in the measurement sequence. The measured B
content and δ¹¹B of the blanks for two batch experiments were 22 ng/ 7.9‰ and 21 ng/ 1.9‰,
respectively. The amount of blank is similar to those of reported by Rosner and Meixner¹³ and Wei et al.
¹⁷. For our operation, the blank due to dissolution procedures was less than 2 % of the digested rock B
(1.2~5 µg B). Assuming the δ¹¹B difference between the samples and the blank, as large as 15‰, the
maximum biase caused by blank was less than 0.3‰, within the range of external deviation of
instrumental measurement. The blank during dissolution processes is almost negligible with regard to
causing notable isotopic deviation in the specimens.

The potential B blank contributed from the micro-sublimation procedure have been proved to be extremely low \(^{19}\). The measured isotopic values of NaCl-doped NBS 951 after microsublimation show insignificant deviation (-0.05±0.04‰, \(N=2\)) from the certified values. This confirms that the microsublimation procedures are rather clean and reliable for B separation.

**Modified acid dissolution and B concentrations measurement**

We modified the available HF + mannitol acid dissolution procedures by adding HNO\(_3\) and discarding the ultrasonic treatment \(^{11}\). The B concentrations obtained for the nine rock standards, eight igneous and one clay, are in good agreement with earlier research.

It has been argued that volatile B in acid needs the addition of mannitol to prevent any B loss during acid digestion. The issue on volatile loss of B during rock digestion can be traced back to 1990 and earlier. Mills \(^{33}\) decomposed rocks by HNO\(_3\) (35%) and HF (50–55%) (10:1.5) on a hot plate at 130 °C (±10 °C) for two hours for total dissolution without adding any mannitol and then examined the recovery of B for various degrees of dryness. The recovery was nearly 100% when the final volume was evaporated to > 1 mL, 98% at > 0.5mL, and 84% to 96% when completed dryness was reached. Hu \(^{34}\) used HNO\(_3\)-HF (40%) (2:1) with mannitol for digesting silica samples and found no significant loss of B at 110 °C (±5 °C) for seven hours evaporation when the quantity of the solution was reduced to ca. 0.1 ml, but 8% B loss occurred when evaporated to dryness. More recently, Gaillarde et al. \(^{18}\) concluded that
mannitol is unnecessary for preventing B loss during the evaporation of acidic solutions, because B loss
starts to occur only when the dried residues are heated further. Mannitol addition does help retain boron
for ca. 30 minutes after complete dryness, but fails to do so over longer periods or at higher
temperatures. In this study, long periods of evaporation following dryness were avoided and
consequently, the results showed no B loss.

There have been some studies that avoided the use of nitric acid to preclude mannitol
decomposition, e.g., Meredith et al. Under our experimental temperatures, however, nitric acids seem
not to either decompose mannitol or cause boron loss.

Efficiency of the NaCl-doping modified micro-sublimation for silicates

As discussed in the experimental section, micro-sublimation is rather efficient for the isolation of B
from NaCl-doped rock solutions. The recovery of B is excellent and most major elements are removed
except for rather minor Si content (see Table 1).

The Si content in the vapor phase, following the developed micro-sublimation procedure, was
examined further to evaluate its potential effect on B isotopic measurements using MC-ICP-MS. Table 4
shows the Si content in the fractions after micro-sublimated. To evaluate the Si matrix effect for the
measurement of B isotopes, various amounts of Si were doped into the NBS 951 20 ppb B standard
solutions to see whether ΔB deviated from its certified value. Figure 3 shows the combined results of
matrix artifacts from this study and Geurrot et al. The negative shift trend in the ΔB values are
consistent generally with Vogl et al.\textsuperscript{36}, where it goes parallel with a signal enhancement of the boron intensity, which was also found in our study from 2\% to 12\%. The cause of matrix effect for ICPMS is discussed in Vogl et al.\textsuperscript{36}

The matrix-effect test results imply that in our micro-sublimated fractions contain <0.1~7 ppm of Si, -0.2\% to < -1.3\% deviations in $\delta^{11}$B was detected (Figure 3). The Si content is generally reduced to below 2 ppm if it was expelled properly during sample digestion (see Table 4). The overall matrix caused deviation is typically less than -0.8\%.

### Conclusion

We have evaluated a new method for the efficient separation of B in silicate rock standards using a NaCl-doping modified micro-sublimation procedure. This protocol is an efficient, simple, and clean method for separating B from dissolved silicates.

This method can be used to isolate B efficiently from complex rock solutions if Si expelled properly. The Si remained in the micro-sublimated fractions was analyzed and the matrix artifacts were evaluated to cause 0 to -0.8\% deviation in $\delta^{11}$B. Combining with the uncertainty derived from MC-ICPMS measurements (reproducibility better than 0.3\%) and also from blank contribution (<0.3\%), the total uncertainties of $\delta^{11}$B measurement in this study is rather small and sensitive enough for many geochemical investigations. The combined micro-sublimation and rock NaCl doping procedures, in addition to the conventional complex ion-exchange methods, could become applicable in the precise
measurement of B isotope ratios in natural rocks.

This newly established protocol for B purification and high precision B isotopic measurement needs to be integrated with other criteria: low chemical blank, high yield, low degree of isotope fractionation, complete separation of potential interference compounds or elements, use of hazardous chemical solutions, manpower, and time efficiency. We have modified steps in acid digestion and have applied micro-sublimation procedures for the isolation of B from rock solutions and have achieved low blank separation for high-precision isotopic measurement using MC-ICP-MS.

Acknowledgements

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Reference


Figure Captions:

Fig. 1 Experimental protocol of the micro-sublimation technique for silicates

Fig. 2 Plot of $\delta^{11}$B results v.s. literature $\delta^{11}$B-values for the international rock standards analyzed in this study. Error bars represent 1 standard deviation from the mean value ($N=2$) and the analytical external precision is 0.3‰ (2SD).

Fig. 3 Matrix-artifacts may have occurred during the doping experiments on B isotopic measurements by MC-ICP-MS. The $\delta^{11}$B are biased generally towards negative values when increased the doped Si concentration. Doping Ca and Mg (Guerrot et al, 2011) also showed similar effects.
NaCl was doped into an aliquot of rock solutions to ~20000 ppm and mixed fully.

50 μL of the doped solution was dropped on the center of the cap of a 5-mL conical vial.

The vial was closed tightly and placed upside down in a Teflon-coated metal rack on 98 °C hot-plate for 18-24 h.

The condensed droplet was collected and diluted to ~20 ppb B for MC-ICP-MS measurement.
Table 1 No NaCl and NaCl-doping experiments for micro-sublimation procedures. NaCl-doping specimens appear to suppress the evaporation/sublimation of major elements and raise the recovery of B in the micro-sublimation.

<table>
<thead>
<tr>
<th>Sample name / doping</th>
<th>NaCl concentration</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
<th>Ti</th>
<th>[B ] recovery(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-5 no doping</td>
<td>ND</td>
<td>0.014</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>50.47</td>
<td>ND</td>
<td>93</td>
</tr>
<tr>
<td>NaCl 17600 ppm</td>
<td>ND</td>
<td>0.013</td>
<td>0.01</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.31</td>
<td>ND</td>
<td>104</td>
</tr>
<tr>
<td>NaCl 20000 ppm</td>
<td>ND</td>
<td>0.013</td>
<td>0.01</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.27</td>
<td>ND</td>
<td>102</td>
</tr>
<tr>
<td>JB3 no doping</td>
<td>ND</td>
<td>0.010</td>
<td>0.01</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>3.01</td>
<td>ND</td>
<td>62</td>
</tr>
<tr>
<td>NaCl 17600 ppm</td>
<td>ND</td>
<td>0.013</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.86</td>
<td>ND</td>
<td>96</td>
</tr>
<tr>
<td>NaCl 20000 ppm</td>
<td>ND</td>
<td>0.014</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.86</td>
<td>ND</td>
<td>102</td>
</tr>
<tr>
<td>B-8 no doping</td>
<td>0.24</td>
<td>0.017</td>
<td>2.18</td>
<td>0.08</td>
<td>0.46</td>
<td>0.13</td>
<td>ND</td>
<td>ND</td>
<td>0.19</td>
<td>ND</td>
<td>79</td>
</tr>
<tr>
<td>NaCl 17600 ppm</td>
<td>ND</td>
<td>0.018</td>
<td>0.01</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.14</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>NaCl 20000 ppm</td>
<td>ND</td>
<td>0.017</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.12</td>
<td>ND</td>
<td>94</td>
</tr>
</tbody>
</table>

Data were obtained by ICP-OES measurements (unit: ppm). ND: not detectable.

Table 2 Instrumental operating conditions for MC-ICP-MS analyses.

<table>
<thead>
<tr>
<th>Mass spectrometer</th>
<th>Neptune</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1200W</td>
</tr>
<tr>
<td>Ar cooling gas flow rate</td>
<td>15.0 L min⁻¹</td>
</tr>
<tr>
<td>Ar sample gas flow rate</td>
<td>1.05-1.10 L min⁻¹</td>
</tr>
<tr>
<td>Ar auxiliary gas flow rate</td>
<td>0.7 L min⁻¹</td>
</tr>
<tr>
<td>Interface cones</td>
<td>Nickel sampler and X-skimmer</td>
</tr>
<tr>
<td>Nebulizer type</td>
<td>PFA microflow, 100 µL min⁻¹</td>
</tr>
<tr>
<td>Spray Chamber</td>
<td>Quartz</td>
</tr>
<tr>
<td>Resolution</td>
<td>Low resolution</td>
</tr>
<tr>
<td>Faraday cup</td>
<td>H3(¹¹B) and L3(¹⁰B)</td>
</tr>
</tbody>
</table>
Table 3 Concentration and isotope results of B in nine rock standards analyzed in this study and the available corresponding literature values.

<table>
<thead>
<tr>
<th>Standard ID/ Rock Type</th>
<th>B [µg g⁻¹]ᵃ</th>
<th>Literature B [µg g⁻¹]ᵇ</th>
<th>δ¹¹B (‰)ᵃ</th>
<th>Literature δ¹¹B (‰)ᵇ</th>
<th>Numberᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>STM-1 Nepheline Syenite</td>
<td>6.55±0.25</td>
<td>6.4ᵇ</td>
<td>-0.61±0.20</td>
<td>-3.0±0.4ᵇ¹⁷</td>
<td>2</td>
</tr>
<tr>
<td>AGV-2 Andesite</td>
<td>6.21±0.10</td>
<td>6.34ᵇ²⁵</td>
<td>-4.78±0.40</td>
<td>-3.6±0.4ᵇ¹⁷</td>
<td>2</td>
</tr>
<tr>
<td>B-5 Basalt</td>
<td>9.27±0.14</td>
<td>10.09 (± 1.20)ᵇ¹⁸</td>
<td>-3.86±0.32</td>
<td>-4.1 (± 2.7)ᵇ¹⁸</td>
<td>2</td>
</tr>
<tr>
<td>W-2 Diabase</td>
<td>12.98±0.13</td>
<td>12.675, 12.952ᵇ²³</td>
<td>8.12±0.12</td>
<td>12.2±0.4ᵇ¹⁷</td>
<td>2</td>
</tr>
<tr>
<td>JB-3 Basalt</td>
<td>19.92±0.22</td>
<td>20.0±2.0ᵇ¹³</td>
<td>5.89±0.06</td>
<td>6.5 - 6.7 (± 0.4)ᵇ¹²</td>
<td>2</td>
</tr>
<tr>
<td>JA-1 Andesite</td>
<td>22.63</td>
<td>23.8ᵇ¹²</td>
<td>5.27</td>
<td>5.4 (± 0.4)ᵇ¹²</td>
<td>1</td>
</tr>
<tr>
<td>JB-2 Island Arc Tholeiitic Basalt</td>
<td>30.88±0.54</td>
<td>31.2ᵇ¹²</td>
<td>7.3ᵇ¹²</td>
<td>7.08 (± 0.08)ᵇ¹¹</td>
<td>2</td>
</tr>
<tr>
<td>RGM-1 Rhyolite</td>
<td>28.28±0.72</td>
<td>28ᵇ</td>
<td>-5.15±0.47</td>
<td>7.2±0.2ᵇ¹⁷</td>
<td>2</td>
</tr>
<tr>
<td>B-8 Pliocene Clay</td>
<td>98.8±1.65</td>
<td>101.6 (± 5.3)ᵇ¹⁰</td>
<td>-5.47±0.32</td>
<td>-4.8±0.2ᵇ¹⁷</td>
<td>2</td>
</tr>
</tbody>
</table>

ᵃ The error of the mean is 1 SD. The total uncertainty for B concentration is ca. 5% and the external precision of δ¹¹B is 0.3‰. ᵇ STM-1, RGM-1 data from GeoReM website database, which was referenced as K. Govindaraju in Geostandards Newsletter 1994, 18, 1-158. ᶜ The number means the repeated times of the whole procedure, which is from sample digestion for MC-ICP-MS measurement.
Table 4 Si and B content of the fractions after micro-sublimation for $\delta^{11}$B MC-ICP-MS measurements. The Si matrix reduced significantly to $<0.1 \sim 2.5$ ppm in the second batch experiments, where Si was driven off more properly during the evaporation stage of the rock digestion.

<table>
<thead>
<tr>
<th>sample name / rock type</th>
<th>First batch of experiment</th>
<th>Second batch of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Si] ppm $^a$</td>
<td>[Si] ppm $^a$</td>
</tr>
<tr>
<td>STM-1 Nepheline Syenite</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>AGV-2 Andesite</td>
<td>7.3</td>
<td>1.7</td>
</tr>
<tr>
<td>B-5 Basalt</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>W-2 Diabase</td>
<td>3.9</td>
<td>1.1</td>
</tr>
<tr>
<td>JB-3 Basalt</td>
<td>2.7</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>JA-1 Andesite</td>
<td>2.2</td>
<td>22.9</td>
</tr>
<tr>
<td>JB-2 Island Arc Tholeiitic Basalt</td>
<td>&lt;0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>RGM-1 Rhyolite</td>
<td>4.5</td>
<td>1.1</td>
</tr>
<tr>
<td>B-8 Pliocene Clay</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$^a$ Si concentration was measured by ICP-OES with detection limit ca. 0.1 ppm.

$^b$ B concentration was determined by comparing the $^{11}$B intensities with the bracketing standards during MC-ICP-MS measurement.