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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 unseperable 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 de-volatilization 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 pyro-hydrolysis, 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. [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. [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. [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 [15,20-22], although its potential memory and

matrix artifacts must be eliminated carefully [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_3were 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_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 coupledwith 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 [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_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_3 was assist in achieving complete dissolution without

the aid of ultrasonics.

Complete dissolution is defined by visual inspection [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$_3$ was added and dried on 65 °C hot plate(this step was repeated with 1 ml 5M HNO$_3$). Finally,

2~ 4 mL 0.1M HNO$_3$ 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) [5,6] and an Inductively Coupled Plasma Mass Spectrometry

(ICP-MS) [12,24,25]. Because the high matrix in rock solutions may affect the calibration of concentration

during analysis [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 [25,28] or internal standards addition of similar mass [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). The

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 [19]. 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. [19], modified from Gaillarde et al. [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_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 [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 HNO3, which has typical ^{11}B intensity of

400~500 mV. Then, 0.3M HNO_3 washing solutions were used between each measurement for 180 sec to

lower the noise-to-signal ratio to below 2%. The $^{11}B/^{10}B$ 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. $^{11}B/^{10}B$ ratio plot and the optimal gas flow was selected [19]. 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 method. 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 $\delta^{11}B$ 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 HNO_3 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 ^{11}B 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 $\delta^{11}B$ 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 Meixner [13] 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 $\delta^{11}B$ 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 micro-sublimation 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 [18]. 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. [35] 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 $\delta^{11}B$ deviated from its certified value. Figure 3 shows the combined results of

matrix artifacts from this study and Geurrot et al. [22] The negative shift trend in the $\delta^{11}B$ values are

consistent generally with Vogl et al.[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.[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 sillicate 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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Figure Captions:

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

Fig. 2 Plot of δ^{11}B results *v.s.* literature δ^{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 δ^{11}B are biased generally towards negative values when increased the doped Si concentration. Doping Ca and Mg (Guerrot et al, 2011) [22] also showed similar effects.

NaCl was doped into an aliquot of rock solutions to ~20000 ppm and mixed fully

↓

50μL 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

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Doped matrix in mg-Kg^{-1}

δ11B v.s. NIST SRM951 in ‰

the unbiased value

♦ Si, 20 ppb B (run1, this study)
■ Si, 20 ppb B (run2, this study)
△ Ca, 50 ppb B (Guerrot et al.,2011)[22]
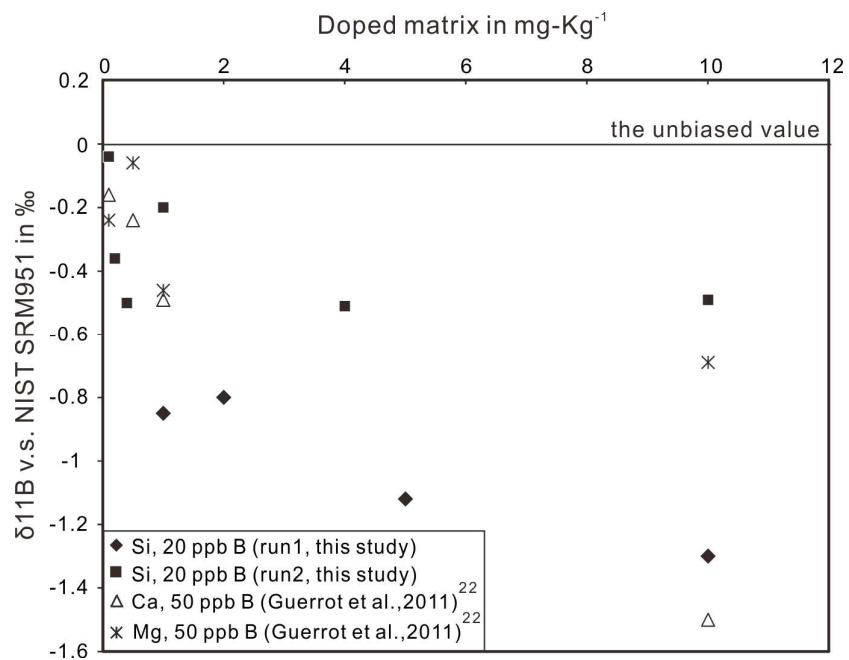✳ Mg, 50 ppb B (Guerrot et al.,2011)[22]
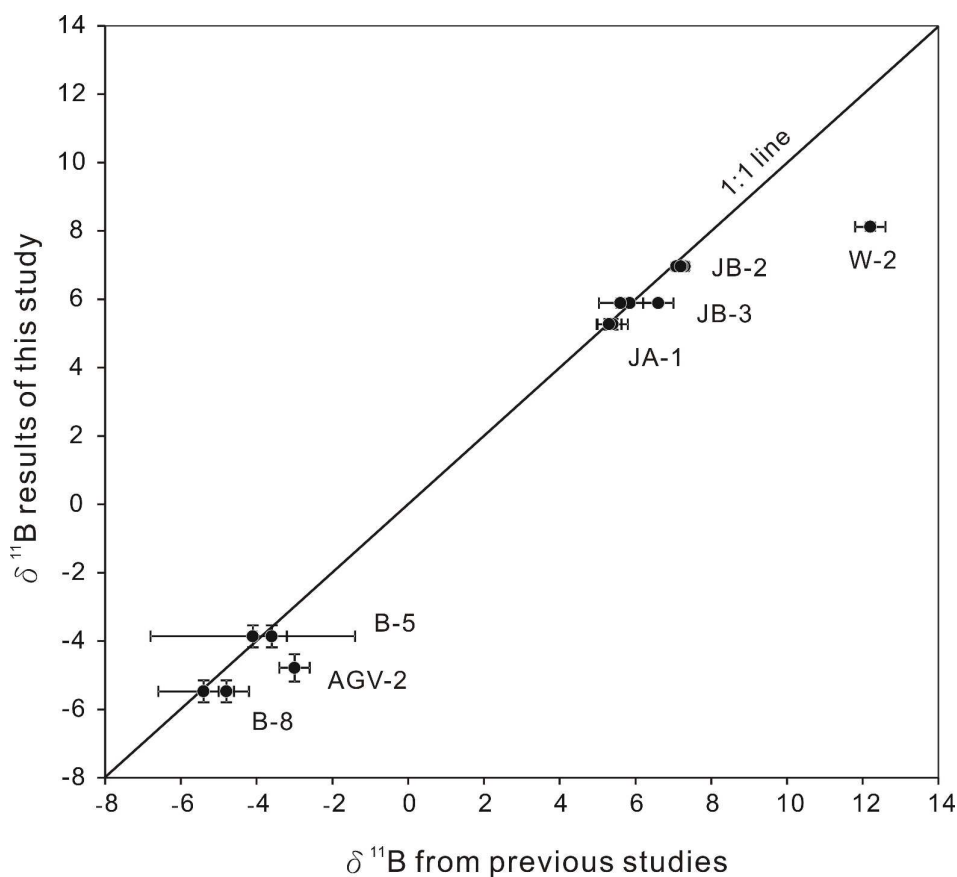
Table 1 No NaCl and NaCl-doping experiments for micro-sublimation procedures. NaCl-doping specimens appear to suppress the evaporation/sublimation of major elements and raise the recovery of B in the micro-sublimation.

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

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

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

Mass spectrometer	Neptune
RF power	1200W
Ar cooling gas flow rate	15.0 L min^{-1}
Ar sample gas flow rate	1.05-1.10 L min^{-1}
Ar auxiliary gas flow rate	0.7 L min^{-1}
Interface cones	Nickel sampler and X-skimmer
Nebulizer type	PFA microflow, 100 μL min^{-1}
Spray Chamber	Quartz
Resolution	Low resolution
Faraday cup	H3(^{11}B) and L3(^{10}B)

Table 3 Concentration and isotope results of B in nine rock standards analyzed in this study and the available corresponding literature values.

Standard ID/ Rock Type	B [µg g-1] [a]	Literature B [µg g-1]	δ^{11}B (‰) [a]	Literature δ^{11}B (‰)	Number [c]
STM-1 Nepheline Syenite	6.55±0.25	6.4 [b] 5.5±0.09[32]	-0.61±0.20		2
AGV-2 Andesite	6.21±0.10	6.534[25]	-4.78±0.40	- 3.0 ± 0.4 [17]	2
B-5 Basalt	9.27±0.14	10.09 (± 1.20) [30]	-3.86±0.32	-4.1 (± 2.7) [30] -3.6 ± 0.4 [17]	2
W-2 Diabase	12.98±0.13	12.675, 12.952[25] 11.8±0.2[32]	8.12±0.12	12.2 ± 0.4 [17]	2
JB-3 Basalt	19.92±0.22	20.0 ± 2.0 [13] 20.3 [2] 20.7 ± 0.3 [29]	5.89±0.06	6.5 - 6.7 (± 0.40) [2] 5.85 (± 0.81) [13] 5.6 ± 0.1 [17]	2
JA-1 Andesite	22.63	23.8 [2] 23.0 [29]	5.27	5.4 (± 0.40) [2] 5.3 (± 0.33) [13]	1
JB-2 Island Arc Tholeiitic Basalt	30.88±0.54	31.2 [2] 27~33 [31]	6.96±0.11	7.3 [2] 7.08 (± 0.08) [11] 7.23 [16] 7.2 ± 0.2 [17]	2
RGM-1 Rhyolite	28.28±0.72	28 [b] 26.1±0.4[32]	-5.15±0.47		2
B-8 Pliocene Clay	98.8±1.65	101.6 (± 5.3) [30]	-5.47±0.32	-5.4 (± 1.2) [30] -4.8 ± 0.2 [17]	2

[a] The error of the mean is 1 SD. The total uncertainty for B concentration is *ca.* 5% and the external precision of δ^{11}B 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 δ^{11}B MC-ICP-MS measurements. The Si matrix reduced significantly to <0.1 ~ 2.5 ppm in the second batch experiments, where Si was driven off more properly during the evaporation stage of the rock digestion.

sample name / rock type	First batch of experiment		Second batch of experiment	
	[Si] ppm [a]	[B] ppb [b]	[Si] ppm [a]	[B] ppb [b]
STM-1 Nepheline Syenite	2.2	27.1	2.5	22.5
AGV-2 Andesite	7.3	27.1	1.7	22.8
B-5 Basalt	2.4	37.2	0.8	22.0
W-2 Diabase	3.9	30.9	1.1	28.9
JB-3 Basalt	2.7	39.9	<0.1	24.0
JA-1 Andesite	2.2	22.9	--	--
JB-2 Island Arc Tholeiitic Basalt	<0.1	27.9	0.8	23.5
RGM-1 Rhyolite	4.5	26.1	1.1	25.1
B-8 Pliocene Clay	0.3	46.6	0.2	42.2

[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.