NOTE

Boron determinations of silicate reference rocks by the isotope dilution method in a high-background environment

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Boron concentrations in silicate reference rocks were determined using an inductively coupled plasma mass spectrometer (ICP-MS) installed in a laboratory with a high background noise level of boron. The feasibility of three methods of internal standard, standard addition, and isotope dilution were examined. Application of the internal standard analysis is difficult in the absence of an appropriate internal standard element. Repeated analyses of the reference rocks showed that the isotope dilution analysis yielded more reproducible concentrations than the standard addition analysis in the high background environment. Results of boron determinations of 12 standard silicate rocks using the isotope dilution method were mostly consistent with values reported earlier from wet chemical analysis and from prompt gamma ray neutron activation analysis. The isotope dilution method can be recommended for boron determination.

Keywords: background, boron, ICP-MS, isotope dilution, reference rock

INTRODUCTION

Altered oceanic crust and sea floor sediments are rich in boron. It is transferred with fluid phase squeezed by dehydration processes of a subducting slab. Subduction-related volcanic rocks are rich in boron compared with Mid-Ocean-Ridge basalts and volcanic rocks related to intra-plate volcanism. Consequently, boron is used as a tracer to assess contributions of subduction fluids in arc environments (Sano *et al.*, 2001; and references therein). Although boron has been determined using inductively coupled plasma-atomic emission spectrometry (Ryan and Langmuir, 1993), inductively coupled plasma mass spectrometry (Makishima *et al.*, 1997; Nagaishi and Ishikawa, 2009), thermal ionization mass spectrometry combined with isotope dilution analysis (Ishikawa and Nakamura, 1992), and secondary ionization mass spectrometry (Chaussidon and Jambon, 1994), the loss of volatile boron and contamination from the laboratory environment have persisted as obstacles that hinder determination of boron concentrations through wet chemical analyses. Prompt gamma ray neutron activation analysis (PGNAA) has been used for boron determination since the 1990s. This method can avoid the two difficulties explained above because it requires no chemical handling

of rock samples (Yonezawa *et al.*, 1999; Sano *et al.*, 1998, 1999, 2001; Miyoshi *et al.*, 2010; Shinjoe *et al.*, 2013). Sano *et al.* (1998, 1999) reported that relative standard deviations (% RSD) of replicate analyses of standard rocks were better than 5% for the wide range of boron concentrations of 8–160 ppm. After the nuclear power plant accident in 2011, neutron radiation experiments were halted in Japan.

Boron determination was attempted in a high background environment in this study. An ICP-MS used for boron determinations was installed in a laboratory where laser ablation ICP mass spectrometry analyses on glass bead samples fused with LiBO₄ was conducted with another ICP-MS. The author investigated effective methods to reduce the influence of a high background on boron peaks.

Three analytical methods were compared to improve the accuracy of boron determination. When the concentration of an element is measured using a sensitivity method that compares a signal intensity of an element in a sample solution with that in a standard solution, an internal standard element is often doped to the sample solution to correct the influence of the sample-derived matrix. The internal standard element is selected from elements that are not included in the sample solution and which have a similar mass number to that of the element to be analyzed. Finding a suitable internal standard element is difficult when light elements such as Li, Be, and B in silicate rock samples are determined. Gotan *et al.*

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Table 1. ICP-MS operating conditions

<i>ICP Ion Source</i>	
RF power	1.4 kW, frequency 27.12 MHz
Torch	Fassel type, made of quartz glass
Plasma Ar flow rate	14 L/min
Auxiliary Ar flow rate	0.8 L/min
Nebulizer Ar flow rate	0.98 L/min (typical)
Collision gas He flow rate	6.0 mL/min
Nebulizer	Concentric type, Teflon
Spray chamber	Conical type, quartz glass (cooled to 3°C by a Peltier cooler)
Solution uptake rate	0.25 mL/min (auto-aspiration)
<i>Interface</i>	
Sample cone	Pt tip insert in a Ni base, 1.1 mm diameter orifice
Skimmer cone	Pt tip insert in a Ni base, 0.9 mm diameter orifice
<i>Data Acquisition</i>	
Acquisition mode	Peak jumping
Detection mode	Pulse counting mode points/peak 5
Dwell time	10 ms/isotope
Integration time	2200 ms/isotope
Replication	3 times

(2008) reported that the In internal standardization yielded more than 10% lower Be concentrations than that determined using the standard addition method and the column separation method. Nagaishi and Ishikawa (2009) used Be as an internal standard element for B analyses, taking advantage of the low sensitivity for Be of the ICP-MS used in their study. Mori *et al.* (2007) used a mixture of internal standard elements composed of Ge, In, Tm, and Bi for B determinations. Liu *et al.* (2019) used Rh as an internal standard element. The feasibility of Be internal standardization was examined for the ICP-MS used for this study. The author also examined methods of standard addition and isotope dilution to test the accuracy and reproducibility of boron concentration determinations. Application of isotope dilution inductively coupled plasma mass spectrometry to boron determination was first reported by Makishima *et al.* (1997). This method can reduce difficulties of volatile boron loss. Results of boron determination obtained when using the three methods are compared: the author analyzed 12 standard rocks and compared the results with earlier reported values obtained using wet chemical analyses and PGNAA analysis.

ANALYTICAL TECHNIQUES

Instrumentation and reagents

The ICP-MS used for this study (X-series 2; ThermoFischer Scientific, USA) was installed at the Earthquake Research Institute, The University of Tokyo, Japan. This instrument is equipped with a collision cell. Operating conditions are presented in Table 1. Typical

sensitivity for ^{11}B in this study was 1400 cps/ppb.

All solutions used for this study were prepared using purified 18 M Ω ·cm H₂O produced using a Milli-Q Element system (Millipore Corp., USA). The Milli-Q water was purified with resin of AmberSepTM IRA743 (Rohm and Haas Co., USA), which removes boron from water. Commercially supplied high-purity reagents of HF, HCl, and HNO₃ (TAMAPURE AA-100; Tama Chemicals Co. Ltd, Japan) were used for this study. A 1% mannitol solution was prepared by dissolving mannitol powder (Merck and Co. Inc., Germany) in 0.015 M HF. The 0.015 M HF/0.15 M HNO₃ acid mixture was used for diluting sample solutions and also as a sample washing-out solution during ICP-MS analyses.

A boron atomic absorption standard (Kanto Chemical Co. Inc., Japan) was used as a concentration standard. Also, SRM 981 (NIST, USA) was used as an isotope ratio standard. ISOT-B10 (Spex Industries Inc., USA) enriched in ^{10}B was used as a spike for isotope dilution analysis. Isotope abundances of ^{10}B and ^{11}B were measured as 0.9709 ± 0.0002 and 0.0291 ± 0.0002 , respectively, which is close to the ICP-MS measured values of 0.973 and 0.0271 reported by Spex Industries Inc. ISOT-B10 was diluted to around 0.5 ppm using a 0.015 M HF/0.15 M HNO₃ acid solution. The spike solution concentration was calibrated by the inverse isotope dilution with the boron atomic absorption standard.

Sample preparations

For isotope dilution analyses, 20–40 mg of rock powder was weighed in a 25-mL screw-top PFA vial (Saville Corp., USA). Samples were spiked with appropriate

Fig. 1. Mass spectra from $m/z = 9.5$ to $m/z = 11.4$, obtained for a 20 ppb boron solution (solid line) and a blank solution (dotted line) without (a) and with (b) addition of He collision gas. It is noteworthy that tailing of the $^{12}\text{C}^+$ peak on the ^{11}B peak was avoided.

amounts of Spex B-10 solution so that the spike-sample mixture had $^{10}\text{B}/^{11}\text{B}$ ratio close to the optimum ratio of 3. 0.2 mL 1% mannitol solution, 0.1 mL 6 M HCl and 0.5 mL 21 M HF were added. After the vial was tightly capped, the sample was decomposed at 70°C for 24 h on a hot plate. After it cooled to room temperature, the sample was evaporated to dryness at 60°C for more than 17 h in a closed system (EvapoClean; Meinhard, USA). Subsequently, after 5 mL of 0.015 M HF/0.15 M HNO_3 acid mixture was added to the dried sample, the vial was capped tightly again. The vial was heated at 70°C for a few hours to extract boron into the solution. After it cooled to room temperature, a 1 mL aliquot of the supernatant was transferred into an 8-mL low density polyethylene bottles. Then 4 mL of the 0.015 M HF/0.15 M HNO_3 acid mixture was added to the supernatant aliquot.

For standard addition analyses, rock powder was weighed in 25-mL PFA vials. The mannitol solution, 6 M HCl, and 21 M HF were added similarly to the manner described for isotope dilution analyses. After decomposition, drying with EvapoClean and boron extraction steps were conducted in the same way as the method used for isotope dilution analyses; 1 mL of supernatant was transferred into three PE bottles. A boron standard solution was added to two of the bottles so that their respective added boron concentrations became 30 ppb and 60 ppb. The 0.015 M HF/0.15 M HNO_3 acid mixture was added to each bottle to make the total liquid amount 5 mL. Abundances of boron were calculated following the method described by Gotan *et al.* (2008). To minimize contamination of boron by the experimental environment, all chemical operations were conducted in a clean room.

ICP-MS

During this study, a 0.015 M HF/0.15 M HNO_3 acid

mixture was used as a washing out solution. It usually took around 10 min before the background became stable. The X series-2 quadrupole ICP-MS used for this study was installed in a room where LA-ICP-MS analyses of glass bead samples were conducted. Although the X series-2 was not used for glass bead analyses, backgrounds on m/z 10 and 11 are high. Scanning diagrams of a 20 ppb boron standard solution and a blank solution with and without He collision gas are presented in Fig. 1. Without the He collision gas (Fig. 1(a)), background on $m/z = 11$ was more than 10,000 cps. Replacements of cones and torch did not reduce the background level. Addition of He collision gas with a flow rate at 6.0 mL/min reduced the boron sensitivity from 12000 cps/ppb (Fig. 1(a)) to 1400 cps/ppb (Fig. 1(b)). The background on $m/z = 11$ decreased to less than 4000 cps (Fig. 1(b)). The addition of the He collision gas did not greatly improve the signal-to-noise ratio. The addition of the He collision gas apparently accelerated the decay rate of background. Therefore, the He collision gas was used for this study. Irrespective of the collision gas use, the tailing of $^{12}\text{C}^+$ on the ^{11}B peak was avoided.

Although a glass nebulizer gave lower backgrounds on boron isotopes and high sensitivity compared with the Teflon nebulizer, background accumulations during analyses were recognized for the glass nebulizer. Consequently, a Teflon concentric nebulizer was used for this study.

The addition of He collision gas reduced a transmission of low mass isotopes. Measured $^{10}\text{B}/^{11}\text{B}$ of SRM951, for which the $^{10}\text{B}/^{11}\text{B}$ is certified as 0.2473, dropped from around 0.2 without He collision gas to around 0.1 when the He collision gas was added. The stability of $^{10}\text{B}/^{11}\text{B}$ of SRM951 in a day was around 1%.

The influence of matrix elements on $^{10}\text{B}/^{11}\text{B}$ ratio was investigated using BIR-1a. Around 30 mg of the BIR-1a was decomposed and evaporated using the method described in the preceding section. The residue was diluted with the 0.015 M HF/0.15 M HNO_3 acid mixture so that 1 mL of the solution contain around 1.2 mg of initial amount of the rock, which is typical dilution factor used for the rocks with boron concentrations of more than a few ppm. The solution gave ^{11}B signals less than 100 cps. A solution of NIST SRM951 was added to the BIR-1a solution to make the boron concentration 20 ppb. The $^{10}\text{B}/^{11}\text{B}$ of SRM951 in the BIR-1a matrix agrees with matrix-free SRM951. The results indicated that matrix levels in this study did not modify $^{10}\text{B}/^{11}\text{B}$ ratios. Then, it was concluded that matrix-free SRM951 solution is useful to correct the instrumental mass bias during the boron isotopic analysis of a spike-doped sample solution.

Beryllium sensitivity under the settings described in Table 1 was about one-third of that of boron. The signal intensities of ^9Be in rock solutions of basalts, andesite, and granites were more than a few thousands. Conse-

Table 2. Boron concentrations (ppm) of silicate reference rocks

	This study isotope dilution mean $\pm$ 1s (n)	This study standard addition mean $\pm$ 1s (n)	ID-ICPMS	ICP-MS (Internal standard)	Compilation	PGNAA ^(j)
BCR-2	4.14 $\pm$ 0.11 (6)	3.97 $\pm$ 0.38 (3)	4.61 $\pm$ 0.02 (3) ^b	4.1 $\pm$ 0.6 (10) ^c ; 4.10 $\pm$ 0.06 (3) ^f ; 3.42 $\pm$ 0.31 ^g	4.4 ⁱ	
BHVO-2	2.51 $\pm$ 0.08 (6)	2.85 $\pm$ 0.30 (3)	2.81 $\pm$ 0.09 (7) ^b	2.8 $\pm$ 0.3 (11) ^c ; 2.44 $\pm$ 0.09 (3) ^f ; 2.41 $\pm$ 0.16 ^g	2.95 ⁱ	
BIR-1a [*]	0.114 $\pm$ 0.005 (5)		0.34 $\pm$ 0.01 (2) ^b	0.147 $\pm$ 0.012 (5) ^f ; 0.211 $\pm$ 0.182 ^g	0.25 ⁱ	
JB-1	8.02 $\pm$ 0.18 (3)		5.38 $\pm$ 0.19 (3) ^b ; 8.45 $\pm$ 0.25 (10) ^c ; 8.43 $\pm$ 0.15 (3) ^d	8.18 $\pm$ 0.19 (3) ^f	9.35 ^h , 7.6 ⁱ	8.93 ^k
JB-1a	7.12 $\pm$ 0.25 (3)		6.40 $\pm$ 0.06 (3) ^a	7.75 $\pm$ 0.20 (6) ^f	7.88 ^h , 7.6 ⁱ	7.31 ⁱ , 7.75 ^k
JB-2	30.0 $\pm$ 0.4 (3)	35.3 $\pm$ 4.3 (3)	28.4 $\pm$ 0.6 (10) ^a ; 31.2 $\pm$ 0.3 (5) ^c ; 31.3 $\pm$ 0.4 (4) ^d	29.7 $\pm$ 0.5 (9) ^c ; 30.5 $\pm$ 0.4 (3) ^f	30.2 ^h , 29.98 ⁱ	30.4 ⁱ , 31.7 ^k
JB-3	20.2 $\pm$ 0.5 (3)		18.1 $\pm$ 0.8 (4) ^a ; 20.7 $\pm$ 0.2 (10) ^c ; 20.9 $\pm$ 0.3 (4) ^d	20.7 $\pm$ 0.3 (7) ^f	18.0 ^h	20.4 ⁱ , 20.4 ^k
JA-1	23.1 $\pm$ 0.3 (3)		28.9 $\pm$ 0.4 (2) ^b ; 23.7 $\pm$ 0.2 (10) ^c ; 23.9 $\pm$ 0.2 (4) ^d	24.1 $\pm$ 0.5 (4) ^f	21.0 ^h , 25 ⁱ	23.1 ⁱ , 24.0 ^k
JA-2	22.7 $\pm$ 0.2 (3)		20.5 $\pm$ 0.6 (4) ^a ; 22.7 $\pm$ 0.2 (10) ^c ; 31.3 $\pm$ 0.4 (4) ^d	21.6 $\pm$ 1.0 (3) ^f	20.7 ^h , 21.1 ⁱ	21.0 ⁱ , 22.3 ^k
JA-3	25.7 $\pm$ 0.1 (3)		23.2 $\pm$ 0.3 (3) ^a ; 26.1 $\pm$ 0.3 (10) ^c ; 26.4 $\pm$ 0.2 (4) ^d	26.5 $\pm$ 0.6 (4) ^f	24.8 ^h	25.9 ⁱ , 26.5 ^k
JG-3	1.90 $\pm$ 0.03 (3)				2.15 ^h	1.95 ⁱ
JR-2	165 $\pm$ 3 (3)			158 $\pm$ 6 (4) ^f	145 ^h	151 ⁱ , 156 ^k

*: (f) Nagaiishi and Ishikawa (2009) and (b) Menard et al. (2013) analyzed BIR-1, whereas this study and Liu et al. (2019) analyzed BIR-1a.

References: (a) D'Orazio (1998), (b) Menard et al. (2013), (c) Lu et al. (2007), (d) Makishima et al. (1997), (e) Mori et al. (2007), (f) Nagaiishi and Ishikawa (2009), (g) Liu et al. (2019), (h) Imai et al. (1995), (i) Jochum et al. (2016), (j) Yonezawa et al. (1999), and (k) Sano et al. (1999).

Fig. 2. Boron concentrations of geochemical reference materials analyzed using isotope dilution in this study and values from the literature. A logarithmic scale is used to clarify differences for results of BIR-1a.

Fig. 3. Boron concentrations of geochemical reference materials analyzed using isotope dilution in this study and values by PGNAA (Sano et al., 1999; Yonezawa et al., 1999): linear scale.

quently, applying the internal standard method described by Nagaishi and Ishikawa (2009) is difficult.

RESULTS AND DISCUSSION

Boron blank and detection limit

The boron procedural blanks operated in a closed evaporation system measured during this study varied: 0.3–7 ng (0.01–0.2 ppm for a 30 mg sample).

Three times the standard deviation of replicate measurements of a blank solution is usually reported as the detection limit. In this study, because of the high and changeable backgrounds, three times the standard deviation of the difference shown by a blank solution measured before and after a sample in a day is used as a detection limit of boron. The detection limit varied from 0.05 ppb to 0.1 ppb depending on the concentrations of samples analyzed in the day.

Standard addition and isotope dilution methods

Results of boron determinations obtained using isotope dilution and standard addition methods are presented in Table 2 for three reference rocks: BCR-2, BHVO-2, and JB-2. Although the two methods yielded consistent average values, the percent one sigma relative standard deviations obtained using the standard addition method were around 10: they were 3–10 times larger than those obtained using the isotope dilution method. Gotan *et al.* (2008) reported results of Be determination obtained using the standard addition method. Results of repeated Be abundances of JB-2 and JA-2 yielded the percent one sigma relative standard deviations of 4.6 ($n = 6$) and 2.2 ($n = 4$) %, reproducibility. It was likely that high and variable backgrounds on boron isotopes deteriorated the repeatability in the standard addition analyses. Results show that the isotope dilution method yielded more reproducible results in a high-background environment.

Analysis of silicate reference rocks

Table 2 presents results of boron determination by the isotope dilution in this study along with data reported earlier. Results of prompt gamma ray neutron activation analysis are shown. Reference values of Imai *et al.* (1995) and Jochum *et al.* (2016) based on data compilations are also shown. Figure 2 presents a comparison of our results with earlier data obtained using wet chemistry analyses. D'Orazio (1998), Menard *et al.* (2013), and Lu *et al.* (2007) used isotope dilution method by ICP-MS. Our results showed deviation from those reported by D'Orazio (1998) and Menard *et al.* (2013). However, the deviations were around 10% for most samples. Our results agree with those reported by Lu *et al.* (2007). Makishima *et al.* (1997) analyzed boron concentrations of JB-1, JB-2, JB-3, JA-1, JA-2, and JA-3 by isotope dilution with an ICP-MS.

Except for JA-2, their results agree with those reported by Lu *et al.* (2007). Nagaishi and Ishikawa (2009) and Mori *et al.* (2007) determined boron concentrations using ICP-MS internal standard method. Most of our results agreed with data presented in the two earlier reports.

The interpretation of the results of BIR-1 is not straightforward. Nagaishi and Ishikawa (2009) and Menard *et al.* (2013) analyzed BIR-1, whereas the present study and that of Liu *et al.* (2019) analyzed BIR-1a. The certificates of the two reference materials show that the two reference materials have identical chemical compositions. Our result obtained for BIR-1a showed deviation from that of Menard *et al.* (2013): it was close to that of Nagaishi and Ishikawa (2009), although some difference exists. Liu *et al.* (2019) reported a higher mean value than that reported by Nagaishi and Ishikawa (2009), although it includes rather large error.

During analyses of BIR-1a, high matrix solutions (10 mg of initial sample in 1 mL of analyzed solution) were used to compensate for the low concentration of boron in BIR-1a. Drops of background levels were found when sample solutions were aspirated, probably because of high viscosity resulting from high matrix concentration. The instability of background values might have hampered accurate analysis for the sample with low boron concentration of less than 1 ppm. Further studies must be conducted to elucidate differences of the boron concentration in this reference material. Figure 3 presents a comparison of our results with PGNAA results reported by Yonezawa *et al.* (1999) and by Sano *et al.* (1999). Differences between our results and data of PGNAA analyses were less than 10% for a wide range of boron concentrations.

CONCLUDING REMARKS

Results of this study indicate that the isotope dilution method yielded more precise data than the standard addition method in a high background environment. Considering the difficulty of the selection of an internal standard element for boron determination, the isotope dilution method can be recommended irrespective of the background level.

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