

TECHNICAL NOTE

Measurement on high-precision boron isotope of silicate materials by a single column purification method and MC-ICP-MS

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A method with simplified chemical treatment has developed to determine high-precision $\delta^{11}\text{B}$ in silicate rocks by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using sample-standard-bracketing (SSB) mode. Boron in silicate rocks was extracted by digesting with HF, and purified by a single ion-exchange chromatographic step through a column filled with AG MP anion resin. Only one dryness process was involved in the entire chemical treatment procedure. This simplified procedure diminishes the risk of boron contamination and losses during chemical treatment. An introduction system with a PFA spray chamber and a sapphire injector was adopted to decrease boron memory during the measurement on MC-ICP-MS, which provides high-precision $\delta^{11}\text{B}$ results. The internal precision for $\delta^{11}\text{B}$ was better than $\pm 0.05\%$ (2σ standard error), and the external precision for $\delta^{11}\text{B}$ was better than $\pm 0.30\%$ (2σ standard error) estimated by the long-term results of SRM 951. The $\delta^{11}\text{B}$ of a series of international rock standard references were measured by this method. Some of the samples have $\delta^{11}\text{B}$ reference values, and our results agree well with them within analytical errors. This indicates that our method is feasible for high-precision $\delta^{11}\text{B}$ measurement in various silicate rocks, and our results may provide $\delta^{11}\text{B}$ reference values for these rock standards.

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Introduction

Boron isotope is a very powerful tracer for various geological processes. For example, boron isotope in marine carbonates is a good proxy for seawater pH,^{1,2} which can be used in tracing the ocean acidification associated with anthropogenic CO₂ emissions in modern time.^{3,4} Meanwhile, boron isotope in silicate rocks and minerals shows a very large variation range.⁵ Consequently it is very useful in tracing fluid–rock interaction processes,⁶ and has now become one of the key tracers in active geological processes, such as subduction zone processes and arc volcanism.^{7,8} Because the chemical extraction and purification of boron from silicates is much more complicated than that of other materials, such as carbonate and aqueous samples, the analysis of boron isotope on silicate materials has to date been a difficult affair.

There are basically two methods to extract boron from silicates. The first is to digest the silicates by using hydrofluoric and hydrochloric acids (HF + HCl) with some mannitol to

suppress the volatilization of boron.⁹ The second is to fuse the silicates by using K₂CO₃ and then to dissolve in pure water.¹⁰ After these steps, several ion-exchange chromatography processes are employed to purify and collect boron for mass spectrometry measurement.^{9,10} Chemical treatment is very important for the accuracy of the boron isotopes, and poor recovery and contamination are the two most serious problems that may significantly bias the boron isotopes during chemical treatment. Poor recovery of boron is generally caused by precipitation loss during digestion, volatilization loss during drying processes and loss during ion-exchange chromatography processes, while boron contamination generally comes from reagents used during chemical treatment.^{9–11} Additionally, air contamination is another serious problem, and shorter exposure time for the samples to contact the air may help to diminish boron contamination.¹¹ It is therefore a chemical treatment process with less drying and ion-exchange chromatography steps and less reagents used may be helpful to obtain good boron isotope results.

Measurement of high-precision boron isotope on mass spectrometry can generally be carried out by positive thermal ionization mass spectrometry (PTIMS) measuring on Cs₂BO₂⁺,¹² negative thermal ionization mass spectrometry (NTIMS) on BO₂[−],¹³ and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) on B⁺.¹⁴ The mass bias of the PTIMS

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method is the least, and to date most of boron isotope measurements for silicates were carried out by this method.^{9–11} The PTIMS method, however, is time-consuming,^{15,16} and is generally subject to isobaric interference of Cs_2CNO^+ on Cs_2BO_2^+ , in which some additional processes should be employed^{17,18} or careful monitoring⁴ is necessary to diminish isobaric interference and to achieve good precision for boron isotope. In contrast, the MC-ICP-MS method is less time-consuming and free from isobaric interference from organic matters.¹⁴ The mass bias of the MC-ICP-MS method can be externally corrected by using a standard bracket measuring mode and will achieve good precision comparable to that of PTIMS.¹⁴

We herein report an approach for high precision boron isotope of silicate rocks by using HF digestion, one column ion-exchange chromatographic purification, and MC-ICP-MS measurement. Only HF, a small amount of HCl and trace amount of mannitol and H_2O_2 were used in the whole chemical treatment to diminish the risk of reagent contamination. Meanwhile, one column ion-exchange chromatographic purification process, with only one evaporation process involved, not only simplifies the chemical treatment but also diminishes the risk of boron loss and contamination. Finally, MC-ICP-MS measurement provides high precision $\delta^{11}\text{B}$ results comparable to those by PTIMS. This approach can be used for high precision boron isotope analysis for various kinds of silicate rocks with high efficiency.

Experimental

Rock samples

Some of the geological standard rock references were selected for boron isotope analysis. These samples cover a wide range of rock styles, from basic rocks such as basalt to acid rocks such as

granite and rhyolite, and some of them have reported boron isotopic compositions. Details of the samples are summarized in Table 1.

Reagents

Water. The water was purified by deionized water by a Millipore system coupled with Q-Gard® Boron that can effectively remove boron. The purified water (Milli-Q water) yields a resistivity of 18.2 Ω cm. The boron blank of the Milli-Q water was tested by isotope dilution spiked with the ^{10}B of SRM 952, and was measured using NTIMS.⁴ The results indicate that the boron blank of the purified water is less than 0.02 ng mL^{-1} .

Hydrofluoric acid. BVIII grade (for electronic production) 49% HF, in which ~ 0.25 g L^{-1} mannitol was added, was sub-boiled using a Savillex DST-1000 system at temperature of <60 °C. The concentration of the distilled HF was generally >30 M, and it was further diluted by Milli-Q water to appropriate concentrations, for example ~ 24 M for sample digestion. The boron blank of the distilled HF is about 2 ng mL^{-1} tested by isotope dilution method spiked with SRM 952.

Hydrochloric acid. Ultrapure grade concentrated HCl was purified using the method similar to that for HF. The distilled HCl was diluted to 0.1 M for chemical treatment. The boron blank of the 0.1 M HCl is about 0.01 \sim 0.02 ng mL^{-1} .

Mannitol and H_2O_2 . The mannitol and H_2O_2 used are in analytical grade form. The mannitol was dissolved in Milli-Q water to make a concentration of about 1%, and the H_2O_2 was diluted with Milli-Q water in a proportion of 1 : 1. The boron blanks of the mannitol and H_2O_2 are all less than 10 ng mL^{-1} tested by isotope dilution method.

Boric acid. The boron isotope standard reference, SRM 951 boric acid, was dissolved in Milli-Q water to obtain appropriate boron concentrations, for example, 100 $\mu\text{g mL}^{-1}$ for chemical

Table 1 Summary of the samples analyzed in this study

Sample ID	Rock type	Source	B ($\mu\text{g g}^{-1}$) ^f	$\delta^{11}\text{B}$ (‰) ^g	Reference
AGV-2	Andesite	USGS ^a	7.0		
B5	Basalt	IAEA ^b	8	−4.22 to −3.52 (−3.95)	20
B6	Obsidian	IAEA	210	−1.83 to −1.23 (−1.61)	20
B8	Clay	IAEA	100	−5.14 to −4.67 (−4.75)	20
BCR-2	Basalt	USGS	4.2		
BHVO-2	Basalt	USGS	2.5		
GSR-1	Granite	NRCCRM ^c	24		22
GSR-3	Basalt	NRCCRM	3.5		22
JA-2	Andesite	GSJ ^d	20.7		22
JB-2	Basalt	GSJ	30.2	6.7–7.7 (7.2)	9,10,20,21
JB-3	Basalt	GSJ	18	5.38–6.39 (5.85)	21
JR-1	Rhyolite	GSJ	117		22
JR-2	Rhyolite	GSJ	145	2.28–3.52 (2.9)	11,21
SDC-1	Schist	USGS	12.8		22
W-2	Diabase	USGS	12		22
UB-N	Serpentine	ANRT ^e	140		22

^a USGS: United States Geological Survey. ^b IAEA: International Atomic Energy Agency. ^c NRCCRM: National Research Center for Certified Reference Materials (China). ^d GSJ: Geological Survey of Japan. ^e ANRT: Association Nationale de la Recherche Technique (France). ^f The boron concentrations of AGV-2, BCR-2 and BHVO-2 are the measured values by ICP-AES. ^g $\delta^{11}\text{B} = 1000 \times ({}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}/{}^{11}\text{B}/{}^{10}\text{B}_{\text{SRM 951}} - 1)$, datum in the bracket indicates the average.

treatment test, and $\sim 100 \text{ ng mL}^{-1}$ as monitoring standards for MC-ICP-MS measurement.

Sample digestion

About 100 mg of rock powder was weighed and poured into a pre-cleaned 7 mL PFA beaker, then 100 μL mannitol, 100 μL H_2O_2 and 1 mL 24 M HF were added. The beaker was tightly capped and put on a hot plate at a temperature of 60 $^\circ\text{C}$ for 3 days. Generally the rock powder was dissolved after 3 days, but there exists some white deposits in the beaker, which may possibly be fluorite.⁹ 2 mL Milli-Q water was added into the beaker, and then both the solution and deposit were transferred into a pre-cleaned polypropylene (PP) tube, and centrifuged. The supernatant was collected, and another 2 mL Milli-Q water was added into the tube to wash the deposit. This was centrifuged again and the supernatant was collected and collected together with the previously collected supernatant. The collected supernatant was then diluted by Milli-Q water to make the HF concentration of 3 M for ion-exchange purification.

As suggested by Nakamura *et al.* (1992), such fluorite does not contain boron.⁹ This was further checked by the following tests. After the rock powders were digested and the supernatant was collected, the deposit was dissolved by 8 M HCl, and the residue was further dissolved by 4 M HNO_3 . No visible deposit was retained after being dissolved by HCl and HNO_3 . The boron concentrations in both the supernatants and the solutions dissolved from fluorite deposits by HCl and HNO_3 were measured using a Varian Vista Pro inductively coupled plasma atomic emission spectrometry (ICP-AES). All the measured rock types have been tested, and JR-2, rhyolite with high boron concentration, and GRS-3, basalt with low boron concentration were repeatedly tested along with the measurement of the sample to monitor the extraction efficiency. The results indicated that the boron in the supernatants accounts for over 98% of the boron in the rock powder; boron in the solution dissolved from fluorite deposits was under the detection limit of the ICP-AES ($<1 \text{ ng mL}^{-1}$). This again supports the finding of Nakamura *et al.* (1992) that all the boron in rock can be extracted into the supernatant by HF digestion.

In the order to diminish the influence of blank on the boron isotope of the sample, at least 1 μg B were needed for each measurement in the following procedure. The boron concentrations in these samples vary over a wide range, from 2.5 $\mu\text{g g}^{-1}$ to 210 $\mu\text{g g}^{-1}$, and one digestion of 0.1 g sample yields 0.25–21 μg boron. As for the samples with boron concentration $<10 \mu\text{g g}^{-1}$, 2–4 digestions of 0.1 g sample powder were carried out in a separate beaker.

Ion-exchange chromatography

The AG MP-1strong anion exchange resin of the Bio-Rad company was selected for ion-exchange chromatographic purification. Each new 0.6 g AG MP-1 resin with 100–200 mesh in size was loaded into an Eichrom 20 mL polypropylene column. The ion-exchange chromatography procedure was summarized in Table 2. The whole procedure from loading new resin to

Table 2 Ion-exchange chromatography procedure

Step	Operation
Step 1	Resin washing and condition Milli-Q water 10 mL \times 3 24 M BVIII HF 4 mL \times 3 24 M purified HF 2 mL \times 2 Milli-Q water 5 mL \times 3
Step 2	Sample loading In 3 M HF 1 mL each time
Step 3	Matrix rinsing Milli-Q water 3 mL \times 3 0.1 M HCl 10 mL \times 7
Step 4	Boron eluting 24 M purified HF 2 mL \times 4

putting the eluted boron on hot plate for dryness generally takes about 7–8 hours.

In the order to diminish the influence of blank on the boron isotope of the sample, we generally input $>1 \mu\text{g}$ boron for each sample to be treated through the ion-exchange chromatographic process and in the on-going analysis processes. For the samples with boron concentration $>10 \mu\text{g g}^{-1}$, loading with 1 digestion of 0.1 g sample powder is enough. However, as for the samples with boron concentration $<10 \mu\text{g g}^{-1}$, the supernatants of 2–4 digestions of the sample were loaded onto a column to make at least 1 μg boron being loaded onto each column.

The elution curves of this ion-exchange chromatographic procedure for boron and the main matrices were calibrated by using both rock sample and chemically treated SRM 951. All the elutions, including sample loading, rinse and boron elutions were collected, and the concentrations of boron and the main matrices in each elution were measured using a Varian Vista Pro ICP-AES equipped with a Teflon spray chamber and a sapphire injector. The proportion of each element relative to its total amount in each elution was then calculated from the measured concentrations, and shown in Fig. 1. The elution curves for all the measured rock types have been calibrated, and the efficiency to remove the matrix and to collect boron is similar. Here, we show the curves of GSR-3 and JR-2 as examples.

It can be shown in Fig. 1 that both rock samples and SRM 951 have the same boron elution curve. The collected boron eluted by 8 mL (2 mL \times 4) 24 M HF generally accounts for $>99\%$ of the total boron loaded on the column. The matrix of the collected elution of rock sample was further checked by an entire mass scan (from m/z 6 to m/z 300) on the MC-ICP-MS, the instrument for boron isotope measurement. No significant peak of the matrixes could be found except for boron (m/z 10 and 11), argon and argon's interference masses. Therefore this ion-exchange chromatographic process can efficiently purify boron from rock matrix and yield a recovery of $>99\%$ for boron.

Dryness of the elution

Because of the high HF concentration, 24 M, the elution could not be measured directly on the instrument. It should be dried to remove most of the HF before measurement. The eluted

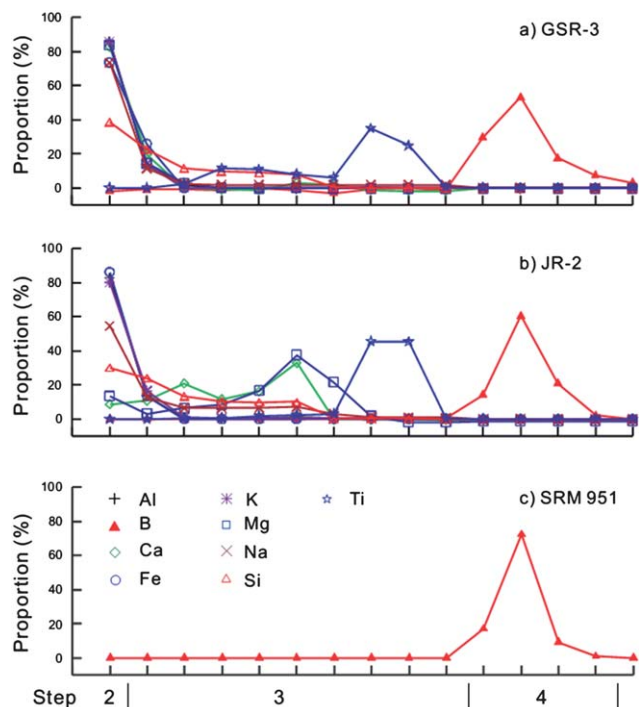


Fig. 1 Elution curves for boron and the main matrix elements on AG MP column. Rock samples represented by (a) GSR-3 and (b) JR-2; and (c) SRM 952. The proportion for each element is expressed as the percentage of the amount in each elution relative to the total amount loaded on column.

boron was collected in a pre-cleaned 15 mL PFA beaker. 100 μL mannitol was added into the beaker to reduce volatilization losses of boron during drying. The 15 mL PFA beaker was then put on a hot plate at temperature of 55 ± 2 $^{\circ}\text{C}$. The dryness generally took 2–3 days depending on the climate (humidity). Even though the dryness was handled in a clean hood with clean room class of 100 established in ultra-clean lab, such a long period for the elution to be exposed to air may also cause serious boron contamination.¹¹ Here we adopt two steps to diminish the boron contamination during dryness.

The first step is similar to that by Rosner and Meixner (2004).¹¹ The generally used boron-bearing materials, such as paper and glass fiber in the air filters of clean bench were replaced with boron free materials, such as polypropylene (PP). The second step is to cover a pre-cleaned PP beaker above each of the beakers containing the elution with only a narrow gap for the vapor to exit. Boron contamination during the dryness process was significantly diminished.

The effect of such modification can be shown from the procedure blanks. Spiked by the ^{10}B of SRM 952, the boron blank of the whole procedure, including digestion, ion-exchange chromatography and dryness, was repeatedly measured along with the samples. Given the same digestion and ion-exchange chromatography process, the boron blank dried on an un-modified clean bench without cover on the beaker was 100–150 ng, and the boron blank was decreased to about 20 ng when dried on the modified clean bench. It was further decreased to about 10 ng when covered with beaker.

The dried samples were re-dissolved by 1.5 mL Milli-Q water. They were further diluted to ~ 100 ng mL^{-1} of boron concentration, which was similar to that of the SRM 951 for measurement, yielding ~ 1 V of ^{11}B signal on the MC-ICP-MS.

In the order to evaluate the influence of chemical treatment to boron isotope, each 10 μL 100 $\mu\text{g mL}^{-1}$ SRM 951 solution was repeatedly used as a sample, and chemically treated in the same manner as the rock standards.

Instrumentation

A Thermo Fisher Scientific Neptune plus MC-ICP-MS in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS) was employed for boron isotope measurement. This instrument is a double focusing magnetic sector field mass spectrometry equipped with 9 Faraday cups and 4 ion counters, which enables a static measurement of m/z 10 and m/z 11 on Faraday cups.

Because boron memory on the introduction system is one of the most serious problems for boron isotope measurement on MC-ICP-MS,^{14,19} a low-flow PFA Microflow nebulizer, a PFA spray chamber, a sapphire injector and a Ni sampler cone and a Pt skimmer cone were used to minimize sample carry-over and memory effects. The details are given in Table 3. Such an introduced system can significantly decrease boron memory, enabling low machine background and low contamination risk between samples. The ^{11}B intensity could rapidly drop from ~ 1 V to ~ 5 mV by washing for 15–20 minutes. This can decrease the washing time between samples, and enable high efficient measurement.

Measuring strategies

The typical operating conditions for boron measurement are summarized in Table 3. ^{10}B and ^{11}B were assigned to L3 and H3 Faraday cup, respectively. The working concentrations of boron for both SRM 951 standards and samples were adjusted to ~ 100 ng mL^{-1} , which yielded an ^{11}B intensity of ~ 1 V. There is an isobaric interference on the ^{10}B isotope from the $^{40}\text{Ar}^{4+}$ species at low resolution (400) of MC-ICP-MS. The influence of this isobaric interference can be estimated by measuring the Milli-Q water. The intensity of m/z 11 and 10 is generally of ~ 5 mV and ~ 2 mV, respectively. Giving that the abundance of ^{11}B is about 4 times of ^{10}B , the contribution on ^{10}B of this isobaric interference is less than 1 mV. This may not influence the boron isotope result measured in a standard-sample bracketing mode because both the samples and the standards had the same intensity of ~ 1 V, and were corrected by on-peak blank subtraction.

The measuring sequence was similar to that of Guerrot *et al.* (2011)¹⁹ and is as follows: background – SRM 951 – background – sample – background – SRM 951, sample was chemical treated SRM 951, procedure blanks and rock samples. The washing process after each measurement of SRM 951 standard or sample was handled by the following steps: 0.3 M HCl + trace HF for 2 minutes; 0.3 M HCl + 0.15 M HF for 10 minutes; 0.1 M HCl for 5 minutes; and finally Milli-Q water for 3 minutes. The ^{11}B intensity

Table 3 Typical operating parameters for B isotopes measurement on Neptune

Parameter	Value
RF forward power	1310 W
Ar cooling gas flow	16 L min ⁻¹
Ar auxiliary gas flow	1.0 L min ⁻¹
Ar sample gas flow	1.0 L min ⁻¹
Extraction voltage	-2000 V
Acceleration voltage	10 kV
Detection system	L3, H3 Faraday cups
Nebulizer	MicroFlow PFA-50 (50 μL min ⁻¹)
Spray chamber	47 mm PFA spray chamber
Injector	Sapphire injector
Sample cone	TF1001-Ni/Cu nickel
Skimmer cone	TF1008-Pt High Performance Skimmer Cone, Platinum
Instrument resolution	400 (low)
Integration time	4.194 s
Idle time	3 s

after this washing process was generally at the level of ~5 mV, which was less than 1% of that of the SRM 951 standards and samples. We did not use NH₄OH solution in washing²⁴ because of its poor efficiency to reduce real boron memory on our machine. When washing with NH₄OH solution, the boron intensity is significantly reduced, but when Milli-Q water is introduced after NH₄OH solution washing, the boron intensity gradually increases to the level before NH₄OH solution washing. Thus, NH₄OH solution appears not to remove real boron memory but instead suppresses the boron signal on our machine.

The background in the measuring sequence was measured on the Milli-Q water, with each acquisition containing 1 block, and each block containing 30 cycles. As for the SRM 951 standards and samples, each data acquisition contains 10 blocks with each block containing 10 cycles. The integration time for each cycle is 4.194 s, and the total 100 scan takes about 12 minutes, yielding an internal precision of ¹¹B/¹⁰B better than 0.002% (RSD: relative standard deviation). Peak blank correction was handled for each SRM 951 standard and sample by subtracting the corresponding intensity of the anterior measured background as follows:

$$\left(\frac{{}^{11}\text{B}}{{}^{10}\text{B}}\right)_C = \frac{({}^{11}\text{B}_{\text{sample}} - {}^{11}\text{B}_{\text{blank}})}{({}^{10}\text{B}_{\text{sample}} - {}^{10}\text{B}_{\text{blank}})}$$

Consequently, the $\delta^{11}\text{B}$ of a sample could be calculated as follows:¹⁹

$$\delta^{11}\text{B} = \left(\frac{2 \times {}^{11}\text{B}/{}^{10}\text{B}_{\text{Sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{SRM 951B}} + {}^{11}\text{B}/{}^{10}\text{B}_{\text{SRM 951A}}} - 1 \right) \times 1000$$

where SRM 951B and SRM 951A indicate the standard measured before and after the sample, respectively, and all the ¹¹B/¹⁰B ratios are the results after on peak blank correction. The internal precision for $\delta^{11}\text{B}$ was estimated by Gaussian error transport equation with both the measured errors of the sample and the bracketed SRM 951 standards being considered. The <0.002% (RSD) internal precision of ¹¹B/¹⁰B ratio for each data

acquisition corresponds to an uncertainty of better than $\pm 0.05\%$ (2σ : standard error) for $\delta^{11}\text{B}$.

The measurements were generally carried out for about 5 hours after the ignition of the plasma to maintain stable mass fractionation of ¹¹B/¹⁰B.¹⁹ Fig. 2a shows the typical drift of the ¹¹B/¹⁰B of SRM 951 standard within a measuring sequence. The measured ¹¹B/¹⁰B ratios drifted from 4.635 to 4.650, with mass bias of about 14.7–14.9% compared to the certified ¹¹B/¹⁰B value of SRM 951, 4.04362.²³ The measured ¹¹B/¹⁰B ratios of SRM 951 were slightly different in different measuring sequence due to the difference of the instrumental status, but the variations of mass bias within a measuring sequence were generally less than $\pm 0.3\%$. If these measured ¹¹B/¹⁰B were transferred into $\delta^{11}\text{B}$ by calculating with the above equation using the results of the adjacent SRM 951 standards, the $\delta^{11}\text{B}$ of SRM 951 within a measuring sequence changed from -0.29% to 0.32% (Fig. 2b), with an average of $0.01 \pm 0.14\%$ (1 s: standard deviation). This can be an estimate for the reproducibility of SRM 951 within a measuring sequence. The long term reproducibility was estimated by the average of the calculated $\delta^{11}\text{B}$ of SRM 951 during the past several months, of $0.00 \pm 0.35\%$ (2 s: standard deviation) ($n = 400$).

The $\delta^{11}\text{B}$ values of the chemically treated SRM 951 were from -0.3% to -0.5% . Such gaps from those of the SRM 951 without chemical treatment may be attributed to contamination of procedure blank and matrix difference. As boron in the chemically treated SRM 951 may be in the form of boron–mannitol complex,⁹ while boron in the SRM 951 without chemical treatment may be in the form of B(OH)₃. In order to estimate the influence of matrix difference, SRM 951 was mixed with some mannitol and HF, dried and measured as samples. The $\delta^{11}\text{B}$ values of were from 0 to -0.1% , indicating that the matrix difference may not be the main cause for such gaps. It is therefore boron contamination during chemical treatment that may account for this even though the exact contribution of the procedure blank could not be identified. These gaps may represent the bias of $\delta^{11}\text{B}$ from the whole chemical treatment process. At least 2–3 chemically treated SRM 951 were measured within a measuring sequence, a further correction by subtracting the average of these $\delta^{11}\text{B}$ values was performed for the measured $\delta^{11}\text{B}$ of each sample, and then the final $\delta^{11}\text{B}$ results for the samples were obtained.

Results and discussion

The $\delta^{11}\text{B}$ results of the rock samples are summarized in Table 4. Each $\delta^{11}\text{B}$ measurement was measured from an individual sample with full chemical treatment. The external precision of the $\delta^{11}\text{B}$ of these samples was generally better than $\pm 0.4\%$ (2σ standard error), which is similar to that of previous works.^{9,10,20,21} Some of these rocks, such as B5, B6, B8, JB-2, JB-3 and JR-2, have $\delta^{11}\text{B}$ reference values reported in previous studies, and they have also been included in Table 4. Our measured $\delta^{11}\text{B}$ results of these rock samples agree well with the previous results, all of the $\delta^{11}\text{B}$ measurements vary within the ranges of the reference values with the averages being identical to that of the reference values within analytical error.

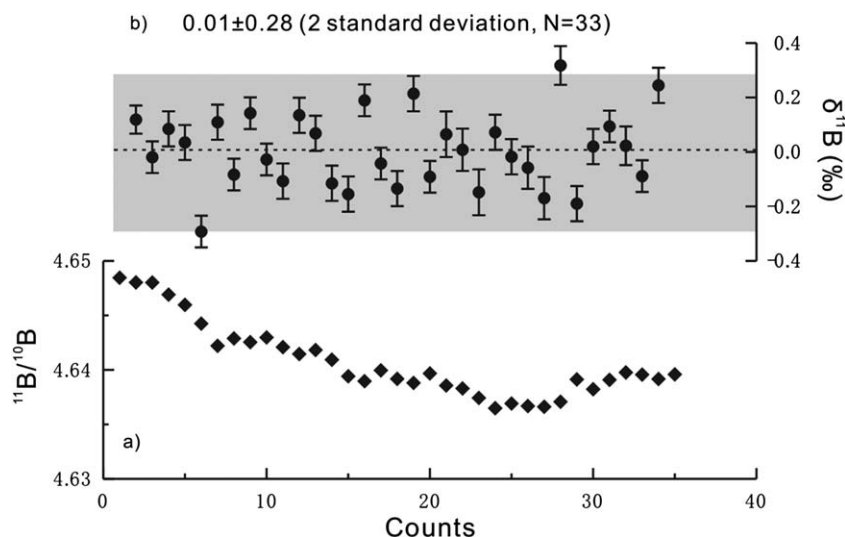


Fig. 2 Drifting of $^{11}\text{B}/^{10}\text{B}$ and their $\delta^{11}\text{B}$ values of SRM 951 within a measuring session. The $\delta^{11}\text{B}$ was calculated by using the equation exhibited in the text.

Table 4 The $\delta^{11}\text{B}$ results of the rock samples

Sample ID	$\delta^{11}\text{B}$ (‰) ^a	Number	Reference value ^b
AGV-2	-3.0 ± 0.4	3	
B-5	-3.6 ± 0.4	3	-4.22 to -3.52 (-3.95)
B-6	-1.6 ± 0.3	4	-1.83 to -1.23 (-1.61)
B-8	-4.8 ± 0.2	5	-5.14 to -4.67 (-4.75)
BCR-2	-5.9 ± 0.2	4	
BHVO-2	-0.7 ± 0.1	5	
GSR-1	-13.3 ± 0.4	6	
GSR-3	-1.4 ± 0.3	3	
JA-2	-9.3 ± 0.4	5	
JB-2	7.2 ± 0.2	7	6.7 – 7.7 (7.2)
JB-3	5.6 ± 0.1	4	5.38 – 6.39 (5.85)
JR-1	2.8 ± 0.2	6	
JR-2	2.7 ± 0.2	8	2.28 – 3.52 (2.9)
SDC-1	-5.5 ± 0.4	3	
W-2	12.2 ± 0.4	3	
UB-N	13.1 ± 0.3	2	

^a Errors of the mean is 2σ ($2s/\sqrt{n}$). ^b Reference values are previously reported results with details listed in Table 1.

Conclusion

These standard rock samples show a large variation range for $\delta^{11}\text{B}$. Among the measured samples, GSR-1, a granite from China has the most negative $\delta^{11}\text{B}$, $-13.3 \pm 0.4\text{‰}$. Giving that GSR-1 is originated from re-melting of continental crust, this is a reasonable value.⁵ Meanwhile, the serpentinite, UB-N, has the most positive $\delta^{11}\text{B}$ value, $13.1 \pm 0.3\text{‰}$. Giving that serpentinite comprises altered oceanic crust, which tends to combine boron with more positive $\delta^{11}\text{B}$ from seawater,⁵ such a positive value is also reasonable for UB-N. Therefore our simplified method containing only one column purification and one evaporation process, respectively, and measured by high efficient MC-ICP-MS can provide high precision determination of $\delta^{11}\text{B}$ for silicate rocks, and is applicable for boron isotope trace studies in various geological fields.

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