Rapid boron isotope and concentration measurements of silicate geological reference materials dissolved through sodium peroxide sintering

Journal:	*Journal of Analytical Atomic Spectrometry*
Manuscript ID	JA-ART-06-2021-000195.R1
Article Type:	Paper
Date Submitted by the Author:	15-Jul-2021
Complete List of Authors:	Cai, Yue; Lamont-Doherty Earth Observatory, Rasbury, Troy; Stony Brook University Wooton, Kathleen; Stony Brook University Jiang, Xin; China University of Geosciences Wang, Di; Nanjing University

Rapid boron isotope and concentration measurements of silicate geological reference materials dissolved through sodium peroxide sintering

Yue Cai[1*], Troy Rasbury[2], Kathleen M. Wooton[2], Xin Jiang[3], Di Wang[4*]

[1]Lamont-Doherty Earth Observatory of Columbia University, 61 Rt. 9W, Palisades, NY 10964, USA

[2] Department of Geosciences, 255 Earth and Space Sciences Building, Stony Brook University, Stony Brook, NY 11794-2100, USA

[3] China University of Geosciences, Wuhan, China

[4] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, 168 Xianlin Avenue, Qixia District, Nanjing 210046, China

*Corresponding authors cai@ldeo.columbia.edu, diwang@nju.edu.cn

ABSTRACT

Understanding the movement of fluids in the solid Earth system is crucial for answering a wide range of important questions in Earth Science. Boron (B) is a perfect tracer for geofluids because of its high solubility and large isotopic fractionation that depends on both temperature and alkalinity. However, high volatility of boron in acidic solutions at moderate temperatures presents a significant challenge for accurate measurements of boron concentration and boron isotopic ratios for silicate rock samples. To circumvent this problem, most laboratories use low-temperature dissolution methods that involve concentrated hydrofluoric acid with or without mannitol. However, hydrofluoric acid is highly hazardous and the controlled temperature condition may be difficult to monitor. As a result, relatively few silicate samples have been analyzed for high precision B concentration and isotopic compositions, which hinders our understanding of the behavior of B in the solid earth system and the utility of this powerful tracer. Here we report B concentrations and isotopic compositions of the most commonly used geological reference standards dissolved through sodium peroxide sintering and purified using a rapid single-column exchange chromatographic procedure. This streamlined method effectively removes Na and Si from the sample matrix and generates accurate B concentration and isotopic data in as little as a day without the need for expensive lab equipment and reagents. Sintering is already routinely used to dissolve zircon-bearing silicate samples as it ensures complete dissolution. Besides boron, other elemental and isotopic analyses can be performed using aliquots of the same dissolution, which greatly speeds up chemical processing time and reduces uncertainties associated with sample heterogeneity. Using this method, large amounts of material can be processed for chemistry without the need of splitting each sample into separate beakers for dissolution as is often required for the HF + mannitol dissolution method. This new method can rapidly expand the available dataset of boron concentration and boron isotopes of silicate materials which will certainly advance our understanding of many geologic problems involving fluids.

Keywords:

Boron isotopes, boron concentration, isotope dilution, sodium peroxide sintering, mass spectrometry, exchange chromatography

1. Introduction

Boron (B) is a fluid-mobile element with two naturally occurring stable isotopes, ^{10}B and ^{11}B with relative abundances of 19.8% and 80.2%, respectively[1]. In aqueous environments, boron mainly exits as two species: trigonal boric acid $B(OH)_3$, and tetragonal borate $B(OH)_4^-$. The trigonal species is isotopically heavy relative to the tetrahedrally coordinated species by ~ 27.2 ± 0.6‰[2-3]. Following tradition, we will use [B] to represent boron concentration and $\delta^{11}B$ in per mil (‰) unit to represent B isotopic composition which equals to 1000 times the difference of $^{11}B/^{10}B$ ratios between the sample and the NIST SRM 951 standard. The large variations of [B] and $\delta^{11}B$ (0.1-30000 ppm, and >90‰, respectively) in the terrestrial environment make them powerful tracers in geochemistry[4-5]. They are particularly useful in studying subduction zone processes, continental crust evolution, and mantle dynamics as boron is very depleted in the primitive mantle (~ 0.26 ppm[6]), but strongly enriched in the continental crust (~ 17 ppm[7]), seawater (~4.5 ppm[8-9]), and sediments (up to 132 ppm[10]). Key endmembers in the subduction system also have very different isotopic signatures (for a review[11]). Furthermore, slab dehydration preferentially volatilizes ^{11}B, which generates arc magmas with much higher [B] and δ^{11}B at the arc front than the back-arc[12-15]. Despite their usefulness, rapid and accurate measurements of [B] and δ^{11}B in silicate materials remain challenging[16]. Recent improvements in analytical precision for in situ measurements using SIMS and LA-ICP-MS have greatly expanded the available dataset of B isotopes in silicate materials[17-21]. However, in situ methods have relatively large errors and they are best suited for volcanic glass or minerals and generally not suitable for bulk rock samples unless the sample powders are fused into homogeneous glass beads[22].

Sample dissolution is a big hurdle in obtaining precise and accurate B isotopes measurements in silicate materials because trigonal boron is more volatile than tetragonal boron during evaporation, which leads to progressively lower [B] and δ^{11}B in the residue[23-24]. Even though some studies have come up with smart ways to circumvent this problem by using heat lamp for evaporation[25] or stopping the evaporation before the liquid fully evaporates[26], the necessary conditions are often difficult to control and monitor as most hotplates and heat lamps heat unevenly. Mannitol can be added to acids during silicate digestion to suppress B volatilization[27]. However, this method still requires controlled temperature conditions (<60°C), and the addition of an organic compound in the run solution matrix may incur additional mass fractionation for ICP-MS measurements. For example, Wei et al.[28] reported 0.3-0.5 per mil lower δ^{11}B for 951 standards treated with HF + mannitol dissolution. While this systematic error could be corrected by normalizing the unknowns to chemically treated 951 standards, this added complexity significantly decreases sample processing efficiency.

Alkaline fusion is an alternative method sample dissolution method for silicate materials. The obvious advantage of alkaline fusion for boron isotope is that all the boron would be present as borate in the resulting alkaline solution, which eliminates the risk of boron isotope fractionation due to evaporation. Early studies using NaOH and Na_2CO_3 required high-temperature (900-1500°C) and high flux to sample ratios (8:1) (for a review[29]). Tonarini et al.[30] successfully reproduced boron isotope and concentration of 951 standards and international rock standards using a K_2CO_3 fusion technique. This method also requires high temperature (900 - 1000°C) and as a result, expensive lab equipment (Pt crucibles).

In this study, we report [B] and $\delta^{11}B$ data of geological standards dissolved using sodium peroxide (Na_2O_2) sintering and purified through a rapid single-column exchange chromatographic procedure adapted from Hemming and Hanson[25]. Sodium peroxide sintering is already routinely used for high-field-strength element (HFSE) and rare-earth element (REE) measurements of zircon-bearing rocks to ensure complete sample dissolution[31-33]. The application of this dissolution method for [B] and $\delta^{11}B$ analyses of silicate materials has yet to be explored in the literature. We demonstrate that sodium peroxide sintering is suitable for [B] and $\delta^{11}B$ measurements of silicate samples because of the relatively low flux to sample ratio (3-5) and the relatively homogenous [B] and $\delta^{11}B$ compositions of the reagent (< 60 ppb and ~ -5‰, respectively) (Table 1), which allows for accurate blank correction. Additionally, this method uses a moderate temperature (490°C), which is achievable in most laboratories with inexpensive glassy carbon crucibles and a muffle furnace. We present a streamlined sample dissolution and single-column chromatographic procedure which is very effective in removing salt and sample matrix. We demonstrate that the small amounts of residual Na and Si in the eluent do not generate any observable difference in boron isotopic ratios or boron signal intensities as measured by the Nu instrument Plasma II MC-ICP-MS (Multicollector Inductively Coupled Plasma Mass Spectrometer).

Finally, this method can be easily scaled up for low-concentration samples without the need for separate dissolutions of the same sample, which is often required for HF + mannitol dissolution. Normally, a batch of 10 silicate samples can be processed and measured for boron concentration and isotope compositions on the ICP-MS within 24-hours. We believe that this new method will greatly expand our ability to use boron isotope and boron concentration measurements in solid earth research.

2. Experimental

2.1 Reagents and equipment for sample dissolution

Sodium Peroxide. Sigma-Aldrich (223417) granular +140 mesh reagent grade 97% Na_2O_2 is routinely used for this procedure. We also used ACROS organics ACS grade sodium peroxide 95% for some of our concentration measurements. Sodium peroxide absorbs water from air and as a result loses effectiveness over time. Newly purchased peroxide is generally factory sealed in a bottle that had been flushed with nitrogen. After opening the bottles, they should be used within 2 months. Storing unused peroxide in airtight containers with desiccant helps to prolong its effectiveness. Sodium peroxide comes in beads that should be powdered right before sintering and mixed thoroughly with the sample powder to ensure complete dissolution, especially for concentration measurements. Generally, extra sodium peroxide is powdered for each sintering session which permits precise measurements of [B] and $\delta^{11}B$ of the reagent (Table 1). The B compositions of each batch of reagents have been fairly homogeneous and the blank contribution is generally less than 5% (Table 4). Blank corrections are made for each sample based on the weight and composition of the sodium peroxide powder used for each sample.

Water. Deionized water purified using the Millipore system with resistance of 18.2 Ω was used for chemistry and the dilution of nitric acid.

Nitric acid. Reagent grade nitric acid was mixed with water to generate a 2% (v/v) solution for all aspects of boron measurements, including chemistry and ICP-MS measurements.

Ammonia. Optima grade Aristar® Ultra ammonia is used to adjust the solutions to pH > 9 for boron column chemistry reported in this paper. The B concentration for the ammonia is 0.003 ug/g, which contributes negligible amount of boron blank to silicate samples and standards reported in this study and therefore no blank correction was made for the ammonia. However, it is safe to assume that each bottle of ammonia is homogeneous in its boron composition and therefore additional cleaning and/or blank quantification is possible.

Glassy carbon crucibles. Sigradur® GAK3 glassy carbon crucibles were preferred because of its added thickness (3 mm) and the small bottom area which prevents the sample and reagent powder mixture from spreading out too much. We recommend covering the crucibles with the matching GAD2 glassy carbon lids during sintering in the muffle furnace to prevent dust accumulation and covering the crucibles with clean 5-6 cm diameter watch glass for the water addition afterward to avoid losing sample solutions during the reaction.

Boric acid standard reference material (NBS SRM 951). Standards are first dissolved in Milli-Q water to make a concentrated solution (100 ppm). Aliquots are then made to match the sample concentration using the same 2% nitric acid used for sample elution and blank measurements on the ICP-MS.

Resin. Amberlite® IRA-743 free base resin from Aldrich® is used for boron ion-exchange chromatography. Amerlite ® IRA-743 has high affinity for boron, especially when the beads are powdered[34]. Smaller resin size corresponds to more free sites available for B adsorption. Therefore, resin beads are powdered with an alumina mortar and pestle and a few milliliters of water. After powdering, the resin is wet-sieved and the **63-125** um size fraction is used for boron column chromatography. This size fraction seems to work well in terms of both the flow rate and B adsorption.

Purchase date	Brand	Lot #	Product #	[B]	$\delta^{11}B$	2SE	Description
April, 2021	Acros Chemicals	A0410290	315761000	0.042	-5.53	0.23	ACS reagent, 95%
March, 2021	Sigma-Aldrich	MKCL8750	223417-100G	0.053	-4.74	0.97	ACS reagent, granular, +140 mesh, 97%
July, 2020	Acros Chemicals	A0404530	207701000	0.060			96%
July, 2019	Acros Chemicals	A0387690	315760250	0.044			ACS reagent, 93%
March, 2018	Sigma-Aldrich	MKCD6833	223417-100G	0.020			ACS reagent, granular, +140 mesh, 97%
December, 2017	Sigma-Aldrich	BCBR2416V	71883-250G	0.021			ACS reagent beads (small) >= 95%

Table 1. B composition of different batches of sodium peroxide reagents. We note that the sodium peroxide available from these vendors were all made in France. It might be interesting to compare the B composition between French sodium peroxide and those made in other countries.

2.2 Sample digestion

We adapted the sintering dissolution methods used by Kleinhanns[32] and Meisel et al.[31]. These authors mixed 100 mg of sample powder with 400 mg of Na_2O_2 beads in glassy carbon crucibles and placed them in preheated muffle furnace at 490°C for 30 minutes for sintering. After the crucibles cooled to room temperature, water is added dropwise to the sintered cake to dissolve the samples. We've made two modifications to this method: 1) we powdered the sodium peroxide beads as this greatly increases the efficiency of sintering; 2) we tested preheating vs. not preheating the furnace and found that in both cases the samples were completely dissolved. Therefore, to prevent accidental spillage of powdered sample and peroxide inside the muffle furnace, which is difficult to clean and can create future contaminations, we recommend placing the crucibles with the samples and peroxide powder mixtures inside the muffle furnace first by hand before the furnace is turned on. After all the crucibles have been positioned inside the furnace, the furnace door is shut and the temperature is set to 490°C for 30 minutes. After 30 minutes, the furnace is turned off and the crucibles can be taken out with a metal tong and placed on heat-resistant surfaces to cool to room temperature. The sintered cake is generally stuck to the bottom of the crucibles after sintering which presents minimal risks of sample spillage. Regardless, it is generally a good idea to place an additional layer of heat-resistant material inside the furnace just in case.

We calculated the minimum amount of sodium peroxide needed for each sample based on stoichiometry and found that generally a 2:1 flux to sample ratio is more than enough for the reaction, provided that the sample powder is thoroughly mixed with the sintering reagent. Based on this knowledge, we tested different flux to sample ratios and found that a ratio of 3:1 is sufficient for most samples, especially when the Na_2O_2 beads are powdered on the same day of the sintering experiment. We found that powdering the Na_2O_2 greatly increases the efficiency of sintering. However, as the boron composition is fairly homogeneous in the flux reagent and the weights of the sample and the flux reagents can be accurately obtained, the flux to sample ratio should not matter as long as the sample is fully dissolved. Therefore, to demonstrate the accuracy of the method, we've used flux to sample ratios of 5 or higher for the data collected in this paper.

After the crucibles are cooled to room temperature, they can be taken to the clean lab for dissolution and chemistry. In the clean lab, water is slowly added to the sintered cake in drop-wise fashion and a vigorous reaction occurs. It is important to place the glass coverslip on the crucible as soon as the water is added and throughout this process to prevent sample spillage and cross contamination. Most of the sample should be fully released from the bottom of the crucible as an alkaline suspension after the addition of 3 ml of water. Most of the B, Li, K and Na are in the supernatant while most other cations form hydroxide precipitates.

Concentrated HCl is added to the crucibles after most of the alkaline suspension has been transferred into pre-weighed 50 ml centrifuge tubes. The glass covers can be rinsed using drops of water and the rinse can easily be collected into the crucibles and combined with the rest of the solution. Finally, the crucible is rinsed with 1 ml of concentrated HCl three times, which should dissolve all the material from the bottom of the crucibles and neutralize most of the hydroxides in the alkaline suspension to form a clear solution. Additional HCl can be added to this solution until all the hydroxide is dissolved in solution.

Colloidal silica gel could form in the solution if it is too concentrated, which is easily resolved by dilution with water. We also found that more diluted solutions generate eluents with lower Si/B ratios (Table 3).

After thorough mixing, the tubes with the solutions are weighed and aliquots are taken for boron isotope dilution or other trace element analyses. For high-precision boron concentration measurements, small aliquots of the sample solution are taken from homogenized solutions and mixed with a small amount of ^{10}B enriched SRM 952[35]. The spike + sample mixture is vortexed and adjusted for pH using ammonia before column chemistry. An excel spreadsheet used for boron concentration calculation and blank correction is provided in the Supplementary Material.

To achieve accurate results for concentration measurements using isotope dilution (ID), besides accurate weighing and aliquoting of the solutions, one has to make sure the following: 1) complete sample dissolution; 2) complete equilibration between the sample aliquot and the spike. The sodium peroxide sintering method ensures total sample dissolution when performed correctly, i.e., with enough reagent and thorough mixing between the sample and the powdered reagent. To ensure complete equilibration between the sample aliquot and the spike, it is important to dilute the solution sufficiently so that colloidal silica gel does not form in the solution. It is also recommended that the sample solution be vortexed prior to aliquoting for boron concentration measurements. Additionally, after the spike is added to the ID aliquot, the mixture should be vortexed prior to pH adjustment for chemistry.

After taking aliquots for B ID, the remaining solutions are used for B isotope composition (IC) measurements. They are adjusted for pH using ultrapure ammonia until abundant iron hydroxide precipitates form (i.e., pH~10). The supernatant that contains boron can be separated from the hydroxide precipitates, diluted further, and mixed directly with clean Amberlite resin. Boron in the solution can adsorb onto the resin within an hour[34]. We recommend leaving the resin and supernatant mixture on a shaker to ensure thorough equilibration. Afterward, the resin can be loaded directly onto acid cleaned columns for expedited B purification. Large amounts of sample can be processed this way without prolonging the sample loading process.

2.3 Column chemistry

Purification of boron through ion-exchange chromatographic columns, or column chemistry, is necessary for both ID and IC measurements on the ICP-MS. We adopted the column chemistry method of Hemming and Hanson[25] using 63-125 um Amberlite 473 resin and a peristaltic pump. There are a number of advantages of using a peristaltic pump for boron chemistry: 1) it controls the flow speed, which is important both for sample loading and for elution; 2) it minimizes environmental blank because the final eluent containing purified boron is not collected right underneath the columns where samples are loaded; 3) it circumvents the bubble-in-the-resin problem that often occurs due to the change in pH, which could stop a gravity driven column from dripping.

The boron columns are made using 1 ml LDPE pipette tips fitted with a 2mm thick porous Millipore-sigma® Supelco® polyethylene frit (Manufacturer Part #57184) (Figure 2). Liquids are pumped out using a Watson-Marlow® peristaltic pump and PVC tubing with 1.02 mm ID (accu-rated) 16” length with two clips. The pump speed is set to 5 rpm for sample loading and 1 rpm for sample elution. Low pump speed is utilized to ensure sample-resin equilibration. The eluents are collected into 2 ml centrifuge tubes using a set up with two stacked Eppendorf ® 24-place 1.5-2 ml vessel autoclavable clear non-slip tube storage racks (Manufacturer Part #22364227) (Figure 2). The PVC tubing should be visually examined prior to column chemistry to ensure that there are no precipitates inside the tubing. In one occasion, we did find unusual boron isotopic fractionation due to carbonate precipitates present in the tubing after solution was left in the tubing overnight. As a preventative measure, we recommend always finishing the chemistry with water and air, similar to a normal cleaning procedure of ICP-MS tubing after measurements.

We recommend changing the tubing whenever the inside of the tubing appear cloudy, which could indicate degradation of the tubing material. Typically, we change the PVC tubing after 5-10 rounds of chemistry. Making sure that the tubing is dry at the end of a batch of chemistry can significantly extend the life of the tubing.

Prior to chemistry, pH adjusted solution are centrifuged and the supernatants are loaded onto acid cleaned and pH adjusted columns with resin for boron column chemistry. In the boron isotope literature, it is generally recommended that the pH of the solution used for chemistry is maintained at 10 or lower to avoid hydroxide precipitates[30, 36]. The excellent agreement in our [B] and $\delta^{11}B$ results of geological standards loaded onto Amberlite resin as high pH solutions demonstrate that while some of the boron in the solution is adsorbed to the hydroxide precipitates, the boron of the supernatant have the same isotopic composition as the boron in the precipitate. Therefore, it is advantageous to keep the pH higher rather than lower for boron purification using Amberlite resin.

Amberlite resin contains a hydrophobic polystyrene backbone and a tertiary amine group with two hydroxyls that will only complex with boron in alkaline conditions[37]. Darwish et al.[34] found that finely fractionized Amerlite IRA743 resin is much more effective for boron removal than larger resin beads regardless of reaction time. They also found the highest percentage of boron adsorption from dilute solutions at high pH and the concentration of side salt ions (e.g., Na+) does not appear to negatively impact boron adsorption onto the resin. These findings are consistent with earlier findings by Lemarchand et al.[26]. Lemarchand et al.[26] found that at pH of 8, ungrounded Amberlite IRA743 resin has an exchange capacity of about 1.5 mg/ml or 1.5 ug/ul, which is lower than earlier estimates of around 10 mg/ml[38-39]. It is evident from these earlier results and our own tests that the amount of acid needed to elute 100% of boron from the resin is proportional to the amount of resin used, which is probably related to the amount of acid required to change the pH of the resin before the majority of boron is eluted (Figure 2). Therefore, a minimum amount of resin is used to avoid overdiluting the final eluent which is measured directly on the ICP-MS without the need for further evaporation. The column chemistry and elution curve presented in Table 2 and Figure 1 is for 50-70 ul of ground and sieved resin with particle sizes between 63 um and 125 um, which is sufficient for 75-100 ug of boron.

Kakihana et al.[40] found that ^{10}B preferentially adsorbs on certain anion resins but not on cation resins. This effect is confirmed experimentally by Lemarchand et al.[26] who found higher δ11B in the first 50% of the eluent and lower $\delta^{11}B$ in the last 25% of the eluent. They suggested that the loss of 1% boron at the end of the elution should cause a shift of 0.2‰ for the recovered solution. We found that 99.97% of boron is collected in the first 1200 ul of eluent with our method and both the first 700 ul of the eluent and the first 1200 ul of the eluent yielded accurate $\delta^{11}B$ values for seawater as very little boron is eluted after 700 ul of 2% nitric wash (Table 3).

Finally, we note that nitric acid had traditionally been avoided in boron purification chemistry as it causes an isobaric interference for PTIMS measurements of boron isotope as CsC_2NO^+. However, this problem does not exist for plasma mass spectrometers that measure boron isotopes directly. A recent study also found that nitric generated less mass fractionation effect than HCl and HF[41]. Additionally, nitric acid is routinely diluted in large quantities for various measurements in our labs. This ensures that the same acid is used for sample dilution and blank correction. Therefore, we chose to use nitric acid to elute boron in our chemistry.

Pump speed	Reagent
5 rpm	Clean resin and columns with full reservoirs of 2% nitric acid x2
5 rpm	Condition the columns with 500 ul pH adjusted water x2
5 rpm	Load the alkaline supernatant of centrifuged sample solutions
5 rpm	Elute Na, K, Li with full reservoirs of pH adjusted water x3
1 rpm	Elute B with 0.4 ml of 2% nitric acid x3 (making 1.2 ml total elution)

Table 2. Step by step column chromatography for 50-70 ul of 63-125 um Amberlite® IRA743 boron specific resin. The pump speeds correspond to flow rates of 1 ml/min at 10 rpm and 0.1 ml/min at 1 rpm.

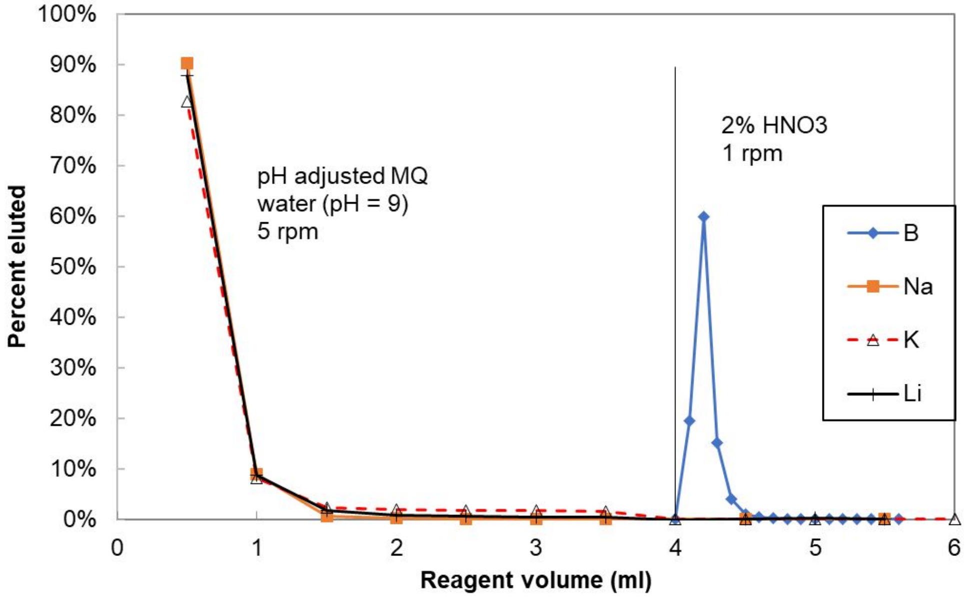


Figure 1. Elution curve for boron column chemistry. The reagent volumes are in milliliters. The chemistry is calibrated for roughly 70ul of 63-125um Amberlite® IRA743 *boron specific resin.*

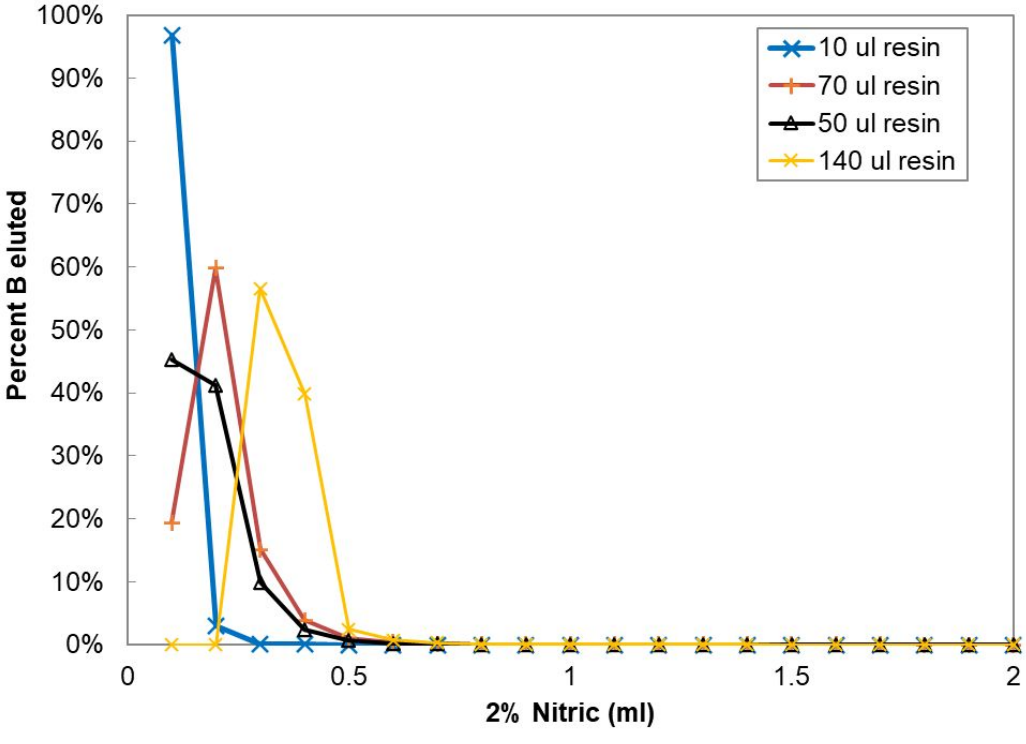


Figure 2. Elution of boron with different resin volumes showing that 50-70ul of resin is optimal and 1.2 ml of 2% nitric is sufficient to wash out 99.9% of B from the column.

	Intensity	B% eluted	$^{11}B/^{10}B$	$\delta^{11}B$
B1	153.20	45.35%	4.713	40.86
B2	139.20	41.21%	4.705	39.09
B3	33.60	9.95%	4.702	38.43
B4	8.00	2.37%	4.693	36.44
B5	2.36	0.70%	4.692	36.22
B6	0.61	0.18%	4.683	34.23
B7	0.40	0.12%	4.702	38.43
B8	0.14	0.04%	4.674	32.24
B9	0.06	0.02%	4.679	33.35
B10	0.04	0.01%	4.658	28.71
B11	0.04	0.01%	4.632	22.97
B12	0.04	0.01%	4.603	16.56
B13	0.03	0.01%	4.617	19.66
B14	0.03	0.01%	4.58	11.48
B15	0.02	0.00%	4.584	12.37
B16	0.02	0.00%	4.576	10.60
Sum	337.79	100%		
First 700 ul		99.88%		39.68
First 1200 ul		99.97%		39.72

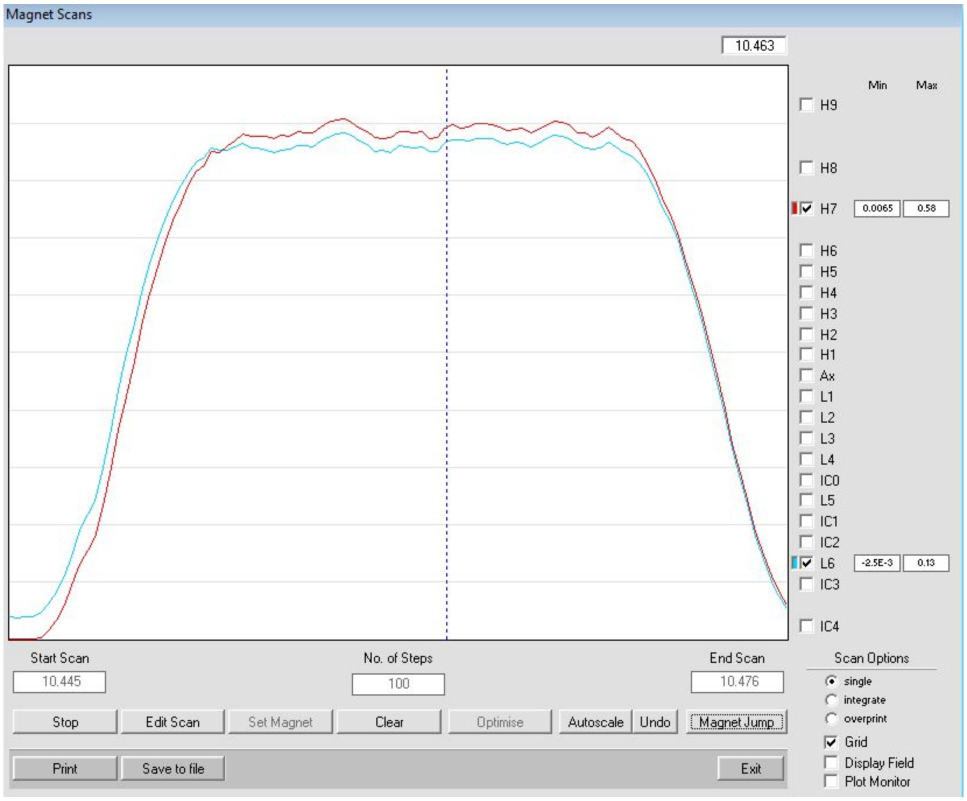
Table 3. Measured ^{11}B intensities and $^{11}B/^{10}B$ ratios of 100 ul eluents of a column with 50 ul of Amberlite resin and 1 ml of seawater. B1 to B15 corresponds to the lab ID of each 100 ul eluent. The $\delta^{11}B$ value of the first 700 ul and the first 1200 ul of the eluent are calculated and both agree with published values for seawater.

3. Instrumentation and measurement strategy

Both isotope dilution and isotopic compositions were measured at the Facility for Isotope Research and Student Training (FIRST) laboratory at SUNY Stony Brook University on a Nu Plasma II MC-ICPMS equipped with 16 Faraday cups and 5 Ion counters. ^{11}B is measured on Faraday cup H7 while ^{10}B is measured on Faraday cup L6. Each measurement begins with a peak center on B11 and 30 seconds of zero measured by ion deflection. Each analysis contains 25 cycles and takes about 2 minutes. The internal precision is generally better than 0.1‰ (1SE) and the external precision monitored by repeated 951 analysis is generally better than 0.5‰ (2SD). A detailed list of the instrument parameters used is provided in Table 4 and a typical peak alignment is shown for 50 ppb of 951 standard (Figure 3). A Cetac® auto sampler was used for the measurements reported in this study.

Parameter	Value
RF forward power	1300
Ar cooling gas flow	13 L/min
Ar auxiliary gas flow	1 L/min
Nebulizer pressure	38.8 Psi
Cup setting	H7 and L6 Faraday cups
Spray chamber	Peltier cooled Twister® spray chamber with Helix®
Injector	Quartz glass
Nebulizer	ARG-1-UM01Q MicroMist quartz glass
Sample cone	Ni 1.15 mm hole
Skimmer cone	Ni WA7 Skimmer cone
Instrument resolution	400 (low)
Integration time	5 s
Source V1	59
Source H1	-13
Source H2	65
Source V2	-48
Transfer H1	32
Transfer V2	1
Transfer V2	27
HV 1	5998
HV 2	4120
HV 3	3689
HV 4	1800
HV 5	2350
HV 6	2274
Quad 1	44.2
Quad 2	-142
ESA plates	334.7
ESA V Dell	75
Rotation	-2
Suppressor	-100
MOP	-15
IC0 Deflector 2	549
IC0 Quad	-61
IC0 Quad Dell	80
IC2 Deflector 2	-610
IC3 Deflector 2	-574

Table 4. Instrument parameters used for boron isotope measurements using the Nu instrument Plasma II MC-ICP-MS.



Magnet Scans

10.463

	Min	Max
☐ H9		
☐ H8		
☑ H7	0.0065	0.58
☐ H6		
☐ H5		
☐ H4		
☐ H3		
☐ H2		
☐ H1		
☐ Ax		
☐ L1		
☐ L2		
☐ L3		
☐ L4		
☐ IC0		
☐ L5		
☐ IC1		
☐ IC2		
☑ L6	-2.5E-3	0.13
☐ IC3		
☐ IC4		

Start Scan: 10.445

No. of Steps: 100

End Scan: 10.476

Scan Options

● single
○ integrate
○ overprint

☑ Grid
☐ Display Field
☐ Plot Monitor

Figure 3. Example B isotope peaks acquired using the PII Nu instrument MC-ICP-MS at Stony Brook University (SBU).

Boron is volatile and can condense on the spray chamber, especially when water droplets are present, which makes it difficult to rinse. As a result, people have tried to dissociate boron from the sample introduction system by altering the pH environment of the spray chamber with the introduction of ammonia gas. However, we and others have noticed that this method only temporarily reduces the apparent boron blank in the system, while as soon as acids are introduced, the high boron background returns[28]. Alternatively, some people use long HCl and/or HF acid washes in between samples and standards[28]. In this study, we use the method of blank subtraction. Instead of bracketing samples directly with SRM 951, we bracket both SRM 951 runs and sample runs with full measurements of the same 2% nitric acid that was used to dilute the standards and the samples. The boron isotope intensities measured on the bracketing nitric acid is subtracted from the standards and the samples first, then $^{11}B/^{10}B$ values of the samples are normalized to the $^{11}B/^{10}B$ values of the SRM 951 standards run before and after the samples to correct for mass fractionation. We find the best stability and reproducibility runs can be achieved with keeping the acid matrix constant throughout the measurements. Therefore, it is important to use the same 2% nitric acid throughout the entire process, including the wash, sample matrix, standard matrix, and the acid for blank subtraction. This method also avoids the need for expensive parts such as sapphire injectors and platinum cones. Instead, we found that routine cleaning of the glass spray chamber with warm tap water and thorough drying of the spray chamber and the glass injector help to improve both sensitivity and stability of boron measurements. Figure 4 demonstrates that 60 seconds of washing using clean water is sufficient to reduce the boron background between samples. This is followed by 60 seconds of nitric or sample uptake which further reduces the boron background and ensures the accuracy of the sample measurements (Figure 4). A full run sequence is: 60s wash - nitric - 60s wash – 951 - 60s wash – nitric - 60s wash – sample - 60s wash – nitric - 60s wash – 951 - 60s wash – nitric - 60s wash. The concentration of the 951 and the sample should be matched for their ^{11}B intensities to within 10%. This blank subtraction method should also correct out any residual isobaric interferences from $^{40}Ar^{4+}$ on ^{10}B even though this isobaric interference should be sufficiently avoided by aligning the right shoulder of the ^{11}B peak with the right shoulder of the ^{10}B peak (Figure 3), and by peak centering on ^{11}B.

To monitor the external reproducibility of the unknowns, we propose that purified seawater be run as unknowns repeated throughout the run session. Seawater has high B concentrations and well-constrained B isotopic ratio which is very different from silicate materials and 951. Accurate measurements of purified seawater validate both the chromatography and the mass spectrometry. A seawater is included in every batch of column chemistry as an unknown. Repeated measurements of seawater within each session generally yields better than 0.5‰ 2SD external reproducibility.

A typical ICPMS measurement session begins with thorough cleaning of the sample and skimmer cones, rinsing and drying of the nebulizer and the injector assembly. After tuning for optimal intensity, stability, and peak shape, the machine is left to wash in water while it warms up for about 1 hour. After the warm up and further tuning, 20 measurements of 951 is carried out to assess machine stability, which takes about 1.5 hours. Seawater samples that have been purified for B using the same ion-exchange chromatography are run first after this warm up period and an agreement with long-term seawater average within 95% confidence interval needs to be achieved before samples are run. Further tuning and trouble-shooting is performed until these criteria are met before measuring unknowns.

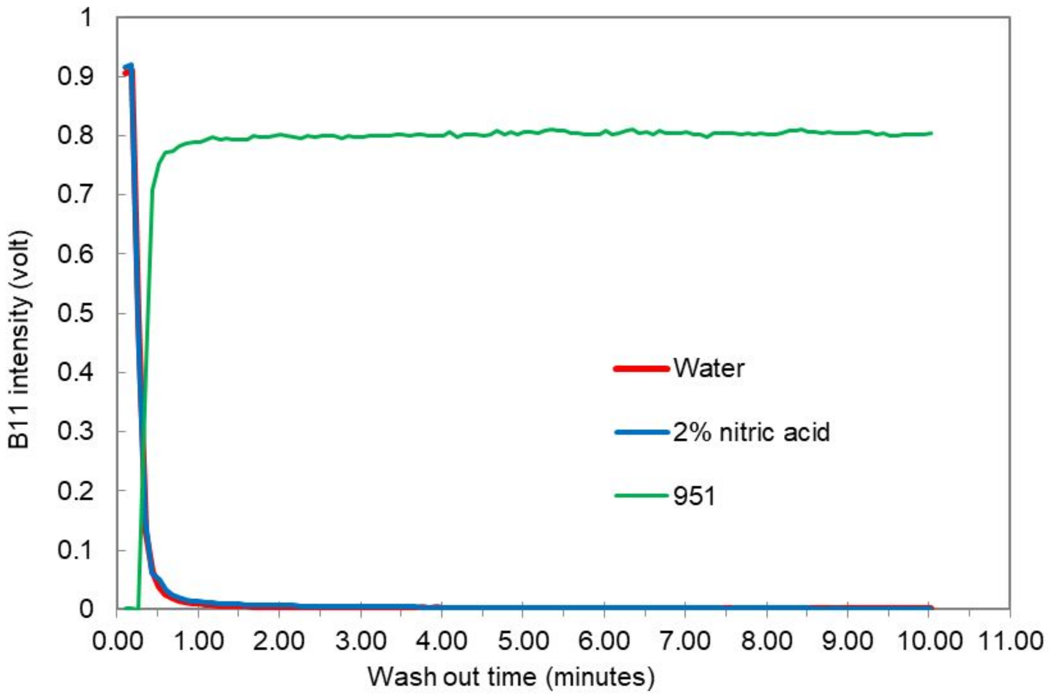


Figure 4. Boron washout using water and 2% nitric, respectively, directly after running a 60 ppb of 951 solution showing that 60 seconds of water wash followed by 60 seconds of nitric wash should be sufficient to effectively wash out the residual boron. Also shown is the sample uptake curve of the 951 solutions.

4. Results and discussion

4.1 Isotopic compositions of international standards

We analyzed geologic reference materials with vastly different compositions ranging from felsic clay and rhyolite to mafic basalts and ultramafic serpentinite and present the data in Table 2 along with published values. The excellent accuracy and reproducibility of both [B] and δ^{11}B of these vastly different silicate standards demonstrates the validity of this method (Figures 5, 6). The small deviations between measured and published δ^{11}B between some of the standard materials may reflect inherent heterogeneity of boron isotopic composition in these standards (e.g., W-2a and UBN), which were not prepared specifically for boron isotopes. Finally, we find that the recommended B concentrations from the USGS are generally 20-30% lower than high precision B ID measurements carried out using alkaline fusion method, which is consistent with boron loss during traditional acid dissolution.

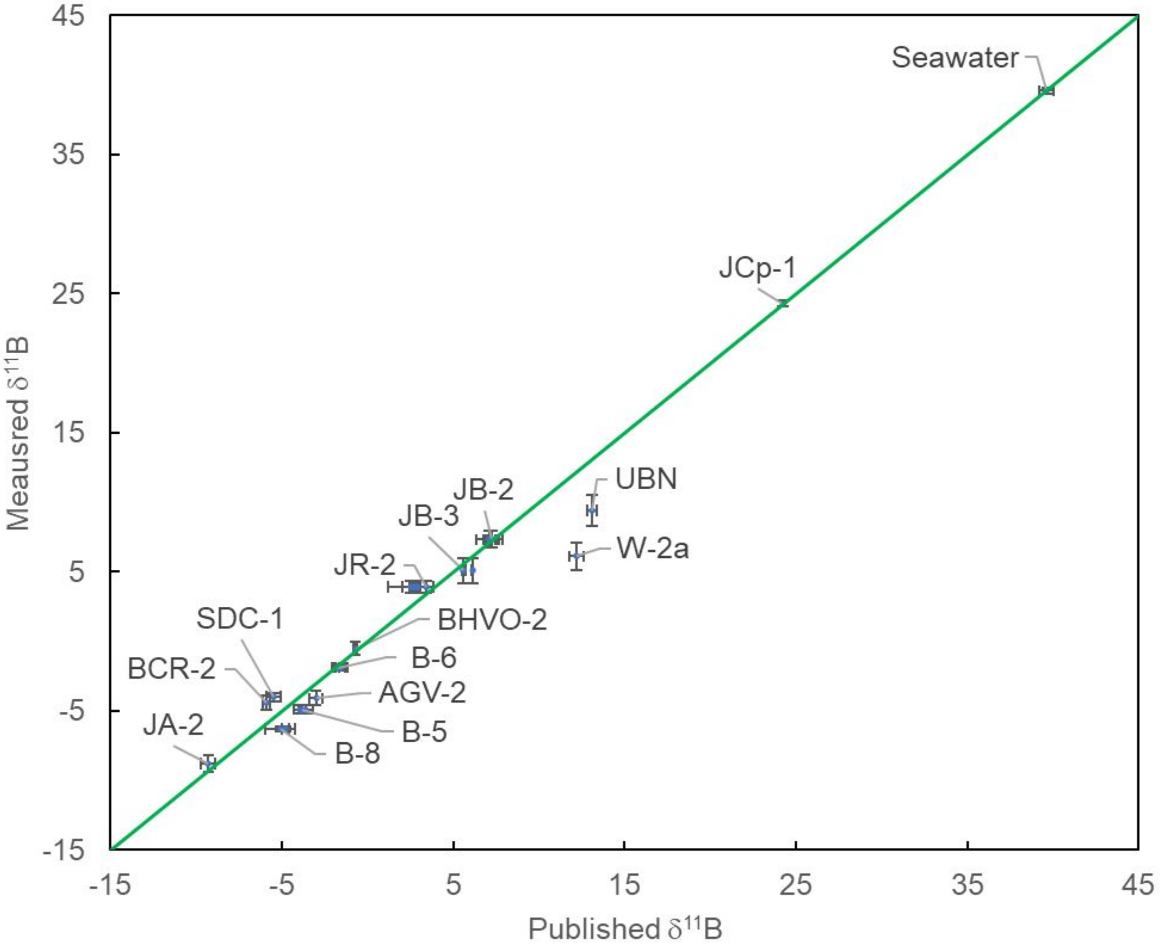


Figure 5. Comparison between measured and published boron isotope values for international standards. The green line is the 1:1 line. Error bars shown represent 2σ combined standard errors of the mean.

		Measured values							Published values						
		δ^{11}B	2SE	N	[B] ppm	2SE	N	% B blank	δ11B	2SE	[B] ppm	2SE	Reference	Dissolution method	Analytical method
IAEA-B-5	basalt	-4.90	0.3	15	9.45	0.3	1	3.05%	-4.0	0.3	8.42	0.3	Tonarini et al., 2003	K_2CO_3	PTIMS
IAEA-B-5	basalt								-3.8	0.2			Brand et al., 2014		
IAEA-B-5	basalt								-3.6	0.4			Wei et al., 2013	HF+mannitol+H_2O_2	MC-ICP-MS
IAEA-B-6	obsidian	-1.90	0.2	19	206.69	3.28	3	0.13%	-1.6	0.4	205.8	15	Tonarini et al., 2003	K_2CO_3	PTIMS
IAEA-B-6	obsidian								-1.8	0.2			Brand et al., 2014		
IAEA-B-6	obsidian								-1.6	0.3			Wei et al., 2013	HF+mannitol+H_2O_2	MC-ICP-MS
IAEA-B-8	clay	-6.30	0.2	19	99.94	0.69	3	0.26%	-4.8	0.3	99.7	3	Tonarini et al., 2003	K_2CO_3	PTIMS
IAEA-B-8	clay								-5.1	0.9			Brand et al., 2014		
IAEA-B-8	clay								-4.8	0.2			Wei et al., 2013	HF+mannitol+H_2O_2	MC-ICP-MS
JR-1	Rhyolite								2.8	0.2			Wei et al., 2013	HF+mannitol+H_2O_2	MC-ICP-MS
JR-2	Rhyolite	3.90	0.4	8	159.30	2.85	3	0.17%	2.8		158	5.7	Rosner and Meixner, 2004	K2CO3	PTIMS
JR-2	Rhyolite								3.4				Rosner and Meixner, 2004	HF+mannitol	PTIMS
JR-2	Rhyolite								2.9				Rosner and Meixner, 2004	HF+mannitol	PTIMS
JR-2	Rhyolite								2.7	0.2			Wei et al., 2013	HF+mannitol+H_2O_2	MC-ICP-MS
JR-2	Rhyolite								2.5	1.3			Kaseman et al., 2001	K_2CO_3	NTIMS
JR-2	Rhyolite								2.9	0.5			Kaseman et al., 2001	K_2CO_3	PTIMS
JR-2G	Rhyolite								2.6	0.5			Kaseman et al., 2001	K_2CO_3	PTIMS
JB-2	Basalt	7.30	0.6	9	26.61	0.31	1	0.86%	7.1	0.8	30.4	3.2	Kaseman et al., 2001	K_2CO_3	PTIMS
JB-2	Basalt								7.2	0.5	27.5	1.5	Tonarini et al., 1997	K_2CO_3	PTIMS
JB-2	Basalt								7.2	0.3			Brand et al., 2014		
JB-2	Basalt								7.1	0.3			Kaseman et al., 2001	K_2CO_3	NTIMS
JB-2	Basalt								7.1	0.1			Nakamura et al., 1992	HF+mannitol	PTIMS
JB-3	Basalt	5.10	0.9	4	20.54	0.15	1	1.31%	6.1	0.0	20	2	Rosner and Meixner, 2004	K_2CO_3	PTIMS
JB-3	Basalt								5.6	0.1	18		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
JB-3	Basalt								5.6	0.0			Rosner and Meixner, 2004	HF	PTIMS
JA-1	Andesite								5.3	0.0			Rosner and Meixner, 2004	HF	PTIMS
JA-2	Andesite	-8.80	0.6	8	27.57	0.39	3	0.95%	-9.3	0.4	20.7		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
JA-3	Andesite	-11.29	0.6	1	28.38	0.85	1	0.93%			26.8	1	Rosner and Meixner, 2004	K_2CO_3	PTIMS
JCp-1	Coral	24.30	0.2	22					24.2				Brand et al., 2014		
Seawater		39.60	0.2	37					39.6	0.4			Brand et al., 2014		
AGV-2	Andesite	-4.10	0.5	3	8.98	0.02	3	2.87%	-3.0	0.4	7		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
BCR-2	Basalt	-4.43	0.5	4	10.40	0.20	1	5.94%	-5.9	0.2	4.2		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
BHVO-2	Basalt	-0.53	0.5	11	4.30	0.15	1	9.58%	-0.7	0.1	2.5		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
SDC-1	Schist	-4.00	0.3	8	23.40	0.22	2	2.03%	-5.5	0.4	12.8		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
UBN	Serpentinite	9.40	1.1	4	181.20	8.20	2	0.19%	13.1	0.3	140		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS
W-2a	Diabase	6.10	1.0	8	18.62	0.31	1	2.16%	12.2	0.4	12		Wei et al., 2013; USGS	HF+mannitol+H_2O_2	MC-ICP-MS

Table 5. Measured and published boron concentration and isotopic compositions of silicate geological standards, seawater and coral. USGS standards for United States Geological Survey. IAEA stands for International Atomic Energy Agency. PTIMS and NTIMS stand for positive-ion and negative-ion Thermal Ionization Mass Spectrometer, respectively. The IC uncertainties reported in this table are the square root of the sum of the internal errors (2SE of the 25 cycles of analysis) and the external error (2SD of the 951 analyses from the run session). For ID measurements, relative weighing errors are added to the combined error of IC measurements to generate the combined ID error with methods similar to those reported by Miller and Miller[42] (equation 8). The equations used for these calculations are provided in the Supplementary Material. The relative weighing errors are estimated from repeated pipetting and weighing measurements carried out by the operator.

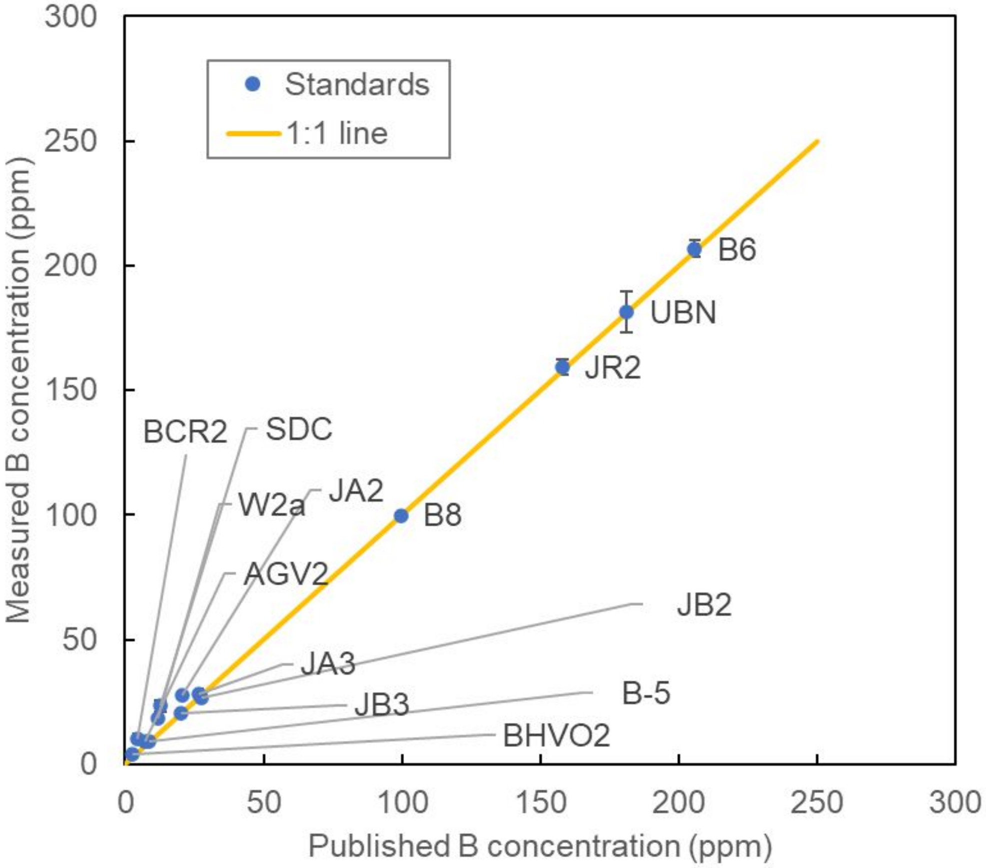


Figure 6. Measured vs. published boron concentration of silicate geological reference standards. Error bars shown represent 2σ combined standard errors of the mean.

4.2 Potential Matrix effects

Matrix effect is an important factor to consider for plasma mass spectrometer measurements. The presence of excessive amounts of salt matrix in the analyte can reduce signal intensity, clog up tubing and cones of the ICPMS. Some matrix elements may also change the mass fractionation behavior of different isotopes, which reduces the effectiveness of the standard-sample bracketing method for mass fractionation correction. The Amberlite resin is very effective in separating B from Na and other salts (Figure 1). However, trace amounts of Na and Si are still present in the final eluent (Table 5). Therefore, doping tests were carried out to assess the effect of sample matrices. Generally, the Na/B ratio is less than 5 in the eluent after chemistry, which means for a 50 ppb B solution, there is up to 0.25 ppm of Na. This level of Na does not appear to affect the measure boron isotopic ratios or cause any noticeable salt deposit.

We found no statistical difference in measure seawater B isotopic ratios with the addition of up to 480 ppm of Na[43]. These findings are consistent with observations from various earlier studies[44-46].

Similar to B, but to a much lesser extent, metasilicates can adsorb to the Amberlite resin and elute with acids[47]. These authors suggested that the presence of metasilicates in the eluent could generate elevated δ^{11}B in high Si/B samples due to matrix effects, which could limit the application of alkaline fusion for boron isotope analyses using ICP-MS. We find that the eluents have lower Si/B ratios when the sintered supernatants are more diluted (Table 6). Without additional dilution, the eluents of geologic reference materials ranging from rhyolite (JR-2) to clay (B-8) yielded Si/B ratios of up to 12, which means up to 0.6 ppm Si in 50 ppb B. We observed no deviation in measured B isotopic ratios for 951 standards doped with 4 ppm of Si compared with pure 951 standards (Figure 7), which means that samples purified using alkaline fusion can be accurately measured for boron isotopes on the ICP-MS, at least for the Nu Plasma II MC-ICPMS.

Sample	**Si/B**	**Na/B**
SW	0.02	0.01
JR-2	11.56	0.45
JR-2 (diluted)	0.39	0.22
BHVO-2	6.46	0.02
BCR-2	6.57	0.04
AGV-2	6.39	0.51
JB-3	0.93	2.16
JA-2 (diluted)	1.32	0.73
B-5 (diluted)	1.47	4.74
B-4 (diluted)	0.03	0.23
B-6 (diluted)	0.05	0.02
B-8 (diluted)	0.77	0.29

Table 6. Si/B and Na/B ratios of purified boron for studied reference materials. For 50 ppb solution, the highest Si concentration in the eluent is 0.6 ppm, and the highest Na concentration is 0.25 ppm.

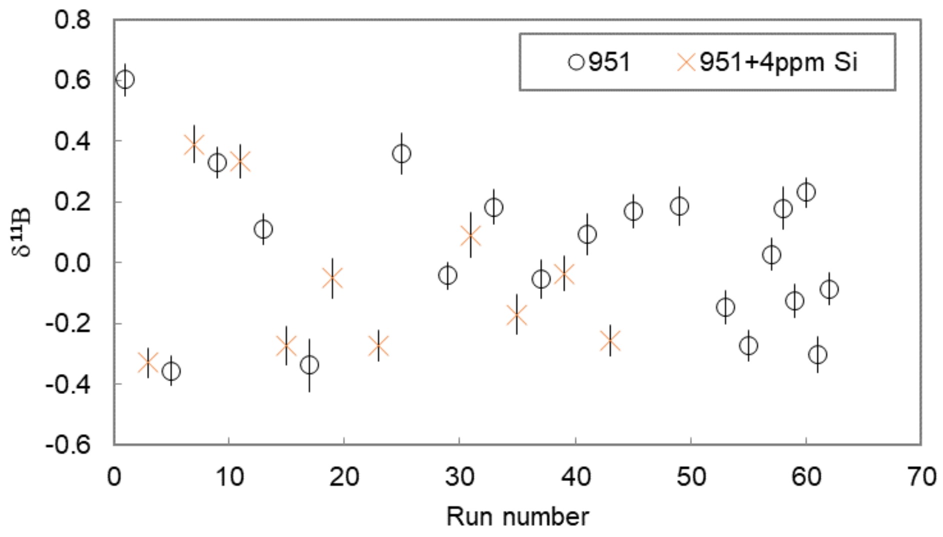


Figure 7. δ^{11}B values of 50 ppb 951 standards and bracketed 951 standards doped with 4 ppm of Si. Error bars shown represent 1σ internal errors of each measurement.

5. Conclusion

In this study, we report the first set of boron concentration and boron isotope data on a large set of silicate geological reference materials dissolved through sodium peroxide sintering. We demonstrate that the boron blank level in the sintering reagent has been relatively low and homogenous which permits accurate blank subtraction. We also demonstrate that the single-column exchange chromatographic procedure using peristaltic pump is highly effective in removal sample matrix and the small amounts of residual Na and Si in our samples do not affect the accuracy and precision of our measurements. Our measured [B] and δ^{11}B values of international rock standards agree very well with published values. This method does not require expensive equipment (e.g., platinum crucibles or cones and sapphire injectors) or dangerous reagents (e.g., HF). It is also extremely efficient and easy to scale up. We believe that this method will help to greatly expand our knowledge of boron in the terrestrial system and beyond.

6. Author contributions

YC conceived the study and wrote the manuscript. TR perfected the column chemistry, steered the development of the methodology, and edited the manuscript. KMW especially, along with XJ and DW, contributed to the method development and data collection. All authors reviewed the manuscript.

7. Acknowledgements

YC would like to thank Gary Hemming for his friendship and the numerous inspiring conversations about boron, geochemistry, and life in general, no matter when the conversation strikes, be it at a conference or on the subway where the idea for this paper first formed. We thank Sidney Hemming for years of support and encouragement. We would also like to thank Steven Goldstein and Louise Bolge for providing the crucibles and some of the rock standards. This study was supported by EAR-GeoPRISIMS 1457293 and EAR-1714892 to YC, NSF grants EAR-1324725 to TR, and two seed grants from the Lamont Climate Center to YC. TR would also like to acknowledge NSF grant 1324725. The FIRST lab instrumentation was funded through the NSF Major Research Instrumentation grant EAR0959524.

8. References

1 E. J. Catanzaro, *Boric acid: isotopic and assay standard reference materials*, National Bureau of Standards, Institute for Materials Research, 1970.

2 K. Klochko, A. J. Kaufman, W. Yao, R. H. Byrne and J. A. Tossell, *Earth and Planetary Science Letters*, 2006, **248**, 276-285.

3 O. Nir, A. Vengosh, J. S. Harkness, G. S. Dwyer and O. Lahav, *Earth and Planetary Science Letters*, 2015, **414**, 1-5.

4 T. B. Coplen, *Compilation of minimum and maximum isotope ratios of selected elements in naturally occurring terrestrial materials and reagents*, US Department of the Interior, US Geological Survey, 2002.

5 H. R. Marschall, in *Boron Isotopes*, eds. H. Marschall and G. Foster, Springer International Publishing, Cham, 2018, pp. 189-215.

6 H. Palme and H. S. C. O'Neill, *The mantle and core*, 2005, 1.

7 R. Rudnick, S. Gao, H. Holland and K. Turekian, *The crust*, 2003, **3**, 1-64.

8 H. Schwarcz, E. Agyei and C. McMullen, *Earth and Planetary Science Letters*, 1969, **6**, 1-5.

9 A. Spivack and J. Edmond, *Geochimica et Cosmochimica Acta*, 1987, **51**, 1033-1043.

10 T. Ishikawa and E. Nakamura, *Earth and Planetary Science Letters*, 1993, **117**, 567-580.

11 J. C. M. De Hoog and I. P. Savov, in *Boron Isotopes*, eds. H. Marschall and G. Foster, Springer International Publishing, Cham, 2018, pp. 217-247.

12 T. Moriguti, T. Shibata and E. Nakamura, *Chemical Geology*, 2004, **212**, 81-100.

13 T. Ishikawa and F. Tera, *Oceanographic Literature Review*, 1998, **4**, 664.

14 T. Ishikawa, F. Tera and T. Nakazawa, *Geochimica et Cosmochimica Acta*, 2001, **65**, 4523-4537.

15 W. P. Leeman, S. Tonarini and S. Turner, *Geochemistry, Geophysics, Geosystems*, 2017, **18**, 1126-1162.

16 R. Gonfiantini, S. Tonarini, M. Gröning, A. Adorni-Braccesi, A. S. Al-Ammar, M. Astner, S. Bächler, R. M. Barnes, R. L. Bassett, A. Cocherie, A. Deyhle, A. Dini, G. Ferrara, J. Gaillardet, J. Grimm, C. Guerrot, U. Krähenbühl, G. Layne, D. Lemarchand, A. Meixner, D. J. Northington, M. Pennisi, E. Reitznerová, I. Rodushkin, N. Sugiura, R. Surberg, S. Tonn, M. Wiedenbeck, S. Wunderli, Y. Xiao and T. Zack, *Geostandards and Geoanalytical Research*, 2003, **27**, 41-57.

17 C. Martin, E. Ponzevera and G. Harlow, *Chemical Geology*, 2015, **412**, 107-116.

18 C. Martin, K. E. Flores and G. E. Harlow, *Geology*, 2016, **44**, 899-902.

19 C. Martin, K. E. Flores, A. Vitale-Brovarone, S. Angiboust and G. E. Harlow, *Chemical Geology*, 2020, **545**, 119637.

20 H. R. Marschall and B. D. Monteleone, *Geostandards and Geoanalytical Research*, 2015, **39**, 31-46.

21 H. R. Marschall, V. D. Wanless, N. Shimizu, P. A. E. Pogge von Strandmann, T. Elliott and B. D. Monteleone, *Geochimica et Cosmochimica Acta*, 2017, **207**, 102-138.

22 I. P. Savov, W. P. Leeman, C.-T. A. Lee and S. B. Shirey, *Journal of Volcanology and Geothermal Research*, 2009, **188**, 162-172.

23 B. Chetelat, J. Gaillardet, R. Freydier and P. Negrel, *Earth and Planetary Science Letters*, 2005, **235**, 16-30.

24 R. E. Zeebe and J. W. B. Rae, *Chemical Geology*, 2020, **550**, 119693.

25 N. G. Hemming and G. N. Hanson, *Chemical Geology*, 1994, **114**, 147-156.

26 D. Lemarchand, J. Gaillardet, C. Göpel and G. Manhès, *Chemical Geology*, 2002, **182**, 323-334.

27 E. Nakamura, T. Ishikawa, J.-L. Birck and C. J. Allègre, *Chemical Geology*, 1992, **94**, 193-204.

28 G. Wei, J. Wei, Y. Liu, T. Ke, Z. Ren, J. Ma and Y. Xu, *Journal of Analytical Atomic Spectrometry*, 2013, **28**, 606.

29 J. K. Aggarwal and M. R. Palmer, *Analyst*, 1995, **120**, 1301-1307.

30 S. Tonarini, M. Pennisi and W. P. Leeman, *Chemical Geology*, 1997, **142**, 129-137.

31 T. Meisel, N. Schoner, V. Paliulionyte and E. Kahr, *Geostandards Newsletter-the Journal of Geostandards and Geoanalysis*, 2002, **26**, 53-61.

32 I. C. Kleinhanns, K. Kreissig, B. S. Kamber, T. Meisel, T. F. Nagler and J. D. Kramers, *Analytical Chemistry*, 2002, **74**, 67-73.

33 Y. Cai, M. Rioux, P. B. Kelemen, S. L. Goldstein, L. Bolge and A. R. Kylander-Clark, *Earth and Planetary Science Letters*, 2015, **431**, 119-126.

34 N. B. Darwish, V. Kochkodan and N. Hilal, *Desalination*, 2015, **370**, 1-6.

35 NIST, *Certificate of analysis: Standard reference material(R) 952.* http://www.nist.gov/. 1999.

36 X. Y. Chen, F. Z. Teng and D. C. Catling, *Rapid Communications in Mass Spectrometry*, 2019, **33**, 1169-1178.

37 C. Jacob, *Desalination*, 2007, **205**, 47-52.

38 E. Kiss, *Analytica Chimica Acta*, 1988, **211**, 243-256.

39 W. P. Leeman, R. D. Vocke Jr, E. S. Beary and P. J. Paulsen, *Geochimica et Cosmochimica Acta*, 1991, **55**, 3901-3907.

40 H. Kakihana, M. Kotaka, S. Satoh, M. Nomura and M. Okamoto, *Bulletin of the Chemical Society of Japan*, 1977, **50**, 158-163.

41 X. Chen, L. Zhang, G. Wei and J. Ma, *Journal of Analytical Atomic Spectrometry*, 2016, **31**, 2410-2417.

42 J. C. Miller and J. N. Miller, *Analyst*, 1988, **113**, 1351-1356.

43 M. A. Smit, A. Scherstén, T. Næraa, R. B. Emo, E. E. Scherer, P. Sprung, W. Bleeker, K. Mezger, A. Maltese, Y. Cai, E. T. Rasbury and M. J. Whitehouse, *Geochemical Perspectives Letters*, 2019, DOI: 10.7185/geochemlet.1930, 23-26.

44 J. K. Aggarwal, D. Sheppard, K. Mezger and E. Pernicka, *Chemical Geology*, 2003, **199**, 331-342.

45 P. Louvat, J. Bouchez and G. Paris, *Geostandards and Geoanalytical Research*, 2011, **35**, 75-88.

46 M. Y. He, L. Deng, H. Lu and Z. D. Jin, *Journal of Analytical Atomic Spectrometry*, 2019, **34**, 1026-1032.

47 H. Z. Wei, S. Jiang, T. L. Yang, J. H. Yang, T. Yang, X. Yan, B. P. Ling, Q. Liu and H. P. Wu, *J. Anal. At. Spectrom.*, 2014, **29**, 2104-2107.