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An improved procedure for separation/purification of boron from complex matrices and high-precision measurement of boron isotopes by positive thermal ionization and multicollector inductively coupled plasma mass spectrometry

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ABSTRACT

In order to eliminate boron loss and potential isotopic fractionation during chemical pretreatment of natural samples with complex matrices, a three-column ion-exchange separation/purification procedure has been modified, which ensures more than 98% recovery of boron from each step for a wide range of sample matrices, and is applicable for boron isotope analysis by both TIMS and MC-ICP-MS. The PTIMS-$Cs_2BO_2^+$-static double collection method was developed, ensuring simultaneous collection of $^{133}Cs_2{}^{11}B^{16}O_2^+$ (m/z 309) and $^{133}Cs_2{}^{10}B^{16}O_2^+$ (m/z 308) ions in adjacent H3–H4 Faraday cups with typical zoom optics parameters (Focus Quad: 15 V, Dispersion Quad: −85 V). The external reproducibilities of the measured $^{11}B/^{10}B$ ratios of the NIST 951 boron standard solutions of 1000 ng, 100 ng and 10 ng of boron by PTIMS method are ±0.06‰, ±0.16‰ and ±0.25‰, respectively, which indicates excellent precision can be achieved for boron isotope measurement at nanogram level boron in natural samples. An on-peak zero blank correction procedure was employed to correct the residual boron signals effect in MC-ICP-MS, which gives consistent $\delta^{11}B$ values with a mean of 39.66±0.35‰ for seawater in the whole range of boron content from 5 ppb to 200 ppb, ensuring accurate boron isotope analysis in few ppb boron. With the improved protocol, consistent results between TIMS and MC-ICP-MS data were obtained in typical geological materials within a wide span of $\delta^{11}B$ values ranging from −25‰ to +40‰.

1. Introduction

Because of the large range in boron isotopic composition in nature ($\delta^{11}B$, about 100‰) [1], applications of boron isotopic variation have advanced rapidly in a wide range of research fields, including high-temperature and low-temperature geochemical processes, natural anthropogenic pollution sources, wastewater recharge monitoring, paleo-oceanic pH reconstruction, and global biogeochemical cycles [2–16]. For instance, the joint use of nitrogen and boron isotopes in groundwater constrained the origin of nitrite ions and provided semi-quantification of their contribution to pollution sources [17]. Boron isotopic fractionation in weathering and hydrothermal processes provides new constraints on the origin and evolution of the geothermal fluids that were involved in the formation of altered minerals at the Ries crater (Germany) [18]. The contribution by Vogl and Rosner et al. provided analytically validated methods to determine the boron isotopic composition in plant tissues and water samples, extending the application of boron isotopes to provenance studies of foods [19,20].

General summaries on the detection limits and the major advantages/disadvantages of various techniques (positive thermal ionization mass spectrometry (PTIMS), negative thermal ionization mass spectrometry (NTIMS), secondary ion mass spectrometry (SIMS), and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) etc.) have been published by various authors [16,21–23]. Among these techniques, PTIMS and MC-ICP-MS are evaluated as the most precise and accurate techniques for

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boron isotope determination [24], and NTIMS gives the highest sensitivity to analyze isotopic composition in few nano-grams of boron [25–26]. Initially, $M_2BO_2^+$ ions (M represents alkali metals, e.g. Na, K, Rb, Cs) were observed with PTIMS, and $Na_2BO_2^+$ and $Cs_2BO_2^+$ were employed for boron isotopic composition measurements since 1948 [27–29]. The $Cs_2BO_2^+$ PTIMS method was greatly improved by Xiao et al. who found the intensity of $Cs_2BO_2^+$ emitted from $Cs_2B_4O_7$ can be increased by two orders of magnitude when coating the filament with graphite slurry at low temperatures (<700 °C) [30], resulting in an analytical reproducibility of 0.1‰ (2σ) for samples with more than 1000 ng of B for the international boron standard NIST 951. Later on, the sample loading procedure for determining the $^{11}B/^{10}B$ ratio using sodium metaborate ($Na_2BO_2^+$) was optimized by Rao et al. [31]. To enhance the capacity of high precision isotope measurement in nanogram amounts of boron and eliminate the signal drift correction for the decay of the ion beam, static multicollection techniques have been developed by Nakano et al. [32] and Deyhle [33] on modified mass spectrometers (Finnigan-MAT 261, Germany) where $Cs_2BO_2^+$ ions at *m/z* 308 and 309 were collected by a specially fixed double collector package after reducing the accelerating voltage from 10 kV to 8 kV. The mass spectrometer modification is necessary in order to separate the two heavy molecular species, with which the external reproducibility of 0.24‰ for 100 ng B of NIST 951 is superior to the dynamic peak jumping method. The mass spectrometer-induced isotopic fractionation during measurement remains one of the major problems preventing widespread use of the BO_2^--NTIMS method. In the interest of solving this problem, an approach to normalize $^{11}B^{16}O^{18}O/^{11}B^{16}O^{16}O$ to a fixed $^{18}O/^{16}O$ has been reported by Shen and You [34], but this method has not been widely used because of the difficulty in measuring the small $^{45}BO_2/^{43}BO_2$ ratios and the fact that the $^{18}O/^{16}O$ ratios may vary considerably for different loading conditions [35]. Recently, an internal normalization approach was found to obtain consistent fractionation-corrected $^{11}B/^{10}B$ ratios based on oxygen isotopes determined using ReO_4^- ions measured on the same filament as the sample, and a precision of 0.6‰ for NIST 951 was achieved regardless of sample size, solution pH, and loading temperature [35]. Ishikawa and Nagaishi showed that the new pretreatment protocol on sample loading increased the ionization efficiency of $Cs_2BO_2^+$ ions, achieving an external reproducibility better than ±0.1‰ for 50–100 ng B and ±0.2‰ for 10 ng B [36]. With regard to the isobaric ion interference induced by organic matter on the boron isotope determination by either BO_2^--NTIMS or $Cs_2BO_2^+$-PTIMS methods, an optimized procedure with a micro-sublimation technique was established to extract boron from organic matter, which ensures a precise determination of the boron isotopic composition in river water samples containing a few ppb of boron [14,37]. In recent years, MC-ICP-MS is becoming the dominant method for precise boron isotopic analysis with an external reproducibility of ±0.25‰ [38–41]. Wang et al. corrected the mass bias effect for boron isotopic analysis by MC-ICP-MS using the pseudo internal normalization of lithium isotopic reference (LSVEC), which could achieve an accurate boron isotope analysis for natural waters and marine biogenic carbonates by means of the modified micro-sublimation purification method associated with the high performance and throughput of MC-ICP-MS [42].

Even though various procedures for boron isotope analysis have been advanced significantly as discussed above, the need for improved methods for boron extraction from complex matrices has been emphasized by Gonfiantini et al. on the basis of the intercomparison of boron isotope and concentration measurement [43], especially for minerals, rocks and clays with high silica and rich metal oxide components. With the boron separation procedure using Amberlite IRA 743 boron-specific resin, acidic sample solutions have to be adjusted to a pH of ~7–8 by adding a proper amount of base (e.g. NaOH) before being loaded into the ion-exchange column because the resin mostly adsorbs boron from neutral or weak basic solution. However, strong adsorption of boron by hydroxide precipitates (such as amorphous $Al(OH)_3$, amorphous $Fe(OH)_3$) has been observed [44], and the associated boron isotopic fractionation has been studied in detail by Lemarchand et al. [45]. Therefore, possible boron loss and potential isotopic fractionation cannot be neglected when adjusting acidic sample solutions that contain large amounts of Al, Fe and Mg ions (e.g. geological samples like clay, tourmaline) by adding OH^- directly.

Therefore, more precise and accurate measurement of boron isotopic ratios in natural samples with trace boron contents and complex matrices remains a great challenge because of the following reasons: (i) the purification of natural geological samples with complex matrices (especially for rocks and minerals) is complicated with the potential loss of boron by volatilization or by adsorption; (ii) the potential for mass spectrometer-induced isotopic fractionation, and the potential for isobaric interference. The main objective of this study is to achieve high precision and high accuracy measurements of boron isotopic compositions in natural geological samples, improving in the separation/purification process of boron from complex matrices, establishing of static double-collection PTIMS-$Cs_2BO_2^+$ method without special requirements on instrumental hardware, and evaluating of the dominant effects that cause deviation on $\delta^{11}B$ measurement by the two leading techniques of TIMS and MC-ICP-MS.

2. Experimental section

2.1. Materials

Milli-Q water (Resistivity, 18.2 MΩ cm) was used throughout the experiments. Concentrated HCl and HNO_3 were purified twice by sub-boiling distillation. Solutions of NIST 951 boric acid, K_2CO_3, $NaHCO_3$ (Sigma-Aldrich, SP), EDTA (Sinopharm Chemical Reagents Limited Company, AR), and Cs_2CO_3 (Sinopharm Chemical Reagents Limited Company, SP) have been prepared using Milli-Q water.

2.2. Dissolution of solid geological samples

To ensure the full extraction of boron from solid samples, different chemical manipulation procedures are employed: (1) Solid carbonate samples were soaked in 30% H_2O_2 to remove any organic matter or residues on sample surfaces before being ground to a powder of approximately 100 mesh. Then, 6.0 mol L^{-1} HCl was added to dissolve the sample, followed with a continuous addition of 0.5 mol L^{-1} HCl (several milliliters) until the solution becomes slightly acidic. The insoluble residue in solution was removed by centrifugation, and a weak acidic and transparent solution was obtained for the first ion exchange separation column; (2) Fine tourmaline (a boron-rich alumosilicate mineral) powder was prepared followed by boron extraction with alkali fusion (tourmaline: $K_2CO_3=1{:}25$(wt/wt)) at 950 °C and the sintered materials were totally dissolved by adding 2.5 mol L^{-1} HCl after being cooled down immediately at room temperature, and the transparent solution that was obtained was ready for the ion-exchange column. The boron blank from the alkali fusion step is 21 ng, and does not significantly contribute to the analytical uncertainty of boron isotopes in tourmaline samples that contain 60 μg g^{-1} of boron on average.

2.3. Boron separation/purification procedure

2.3.1. Setup of peristaltic pump coupled with mini exchange-column

The use of a peristaltic pump coupled with an ion exchange micro-column for extraction of boron using a boron-specific resin, Amberlite IRA 743, has been modified on the basis of the procedure reported by Hemming and Hanson [25]. It consists of a multi-channel peristaltic pump (205U Watson Marlow, 16 channels), an 0.12 mm diameter peristaltic pump tubing and Teflon resin columns (250 μL in volume). The pump speed is tunable from 0.5 to 50 rpm, allowing optimization of the flow through the column for each step of the procedure. A schematic diagram of the setup is shown in Scheme S1.

2.3.2. Preparation of ion exchange resin column

On the basis of the investigation from this study, a three-column procedure was established for the boron separation–purification, consisting of a 2.5 mL of mixed cation–anion resin column, a ~25 μL of boron-specific resin Amberlite IRA 743 column and a second 0.5 mL of mixed resin column. The mixed resin consists of a strongly acidic 200–400 mesh cation resin (Dowex 50W × 8, H-Form, USA) and a weak alkaline 60–100 mesh anion resin (Ion Exchanger II, HCO_3^--Form, Germany). Initially, ~5 mL of cation and anion resins were conditioned with 10 mL of 1.0 M HCl and 10 mL of saturated $NaHCO_3$ solutions to convert them into the H^+ and HCO_3^- forms individually, and subsequently equal volumes were mixed (v/v=1:1). Due to the difference in size, Ion Exchanger II and Dowex 50W × 8 can be separated from each other by sieving through 100 meshes for a next regeneration. The boron-specific resin Amberlite IRA 743 was conditioned through 0.1 M HCl, milli-Q water and 0.3 M $NH_3 \cdot H_2O$ and washed to neutral pH prior to use. The detailed procedure for boron separation/purification by three-column ion exchange will be discussed in Section 3.1.2. The total procedural blanks from the ion-exchange procedure is in the range of 0.50 ± 0.04 ng (2 RSD) as determined by ID-MS, which can be neglected compared to the sample size used in these experiments.

2.4. Instruments

2.4.1. Boron isotope analysis

A Triton TI (Thermo Fisher Scientific, Finnigan, Germany) thermal ionization mass spectrometer (TIMS) was used for boron isotope analyses by collecting $^{133}Cs_2{}^{11}B^{16}O_2^+$ (m/z 309) and $^{133}Cs_2{}^{10}B^{16}O_2^+$ (m/z 308) ions. Single tantalum filaments (0.75 cm × 0.076 cm × 0.0025 cm) from NIST were degassed under vacuum for 1 h at a current of 3.0 A and then allowed to oxidize at ambient atmosphere (protected from contamination in closed boxes) for at least 24 h prior to use. Graphite (John-Matthew Company, 99.9999% pure) slurry was prepared by mixing the graphite with 80% ethanol/20% water (v/v). A drop of graphite slurry with a volume of ca. 1.0 μL was first loaded onto the filament. After vaporizing the slurry drop at room temperature for 30 seconds, the sample solution is added on top of the graphite. Both samples and the NIST SRM 951 standard solutions with the molar ratio of B/Cs 2:1 were loaded as described above. A static double-collector method for boron isotope measurements was established [46], where the mass 308 and 309 peaks were collected by the adjacent H3 and H4 cups, and then the parameters in the zoom optics were adjusted to allow perfect alignment of the two peaks, while maintaining excellent peak shape with flat tops (discussed in detail in Section 3.2 below). $^{11}B/^{10}B$ ratios were obtained from measured 309/308 ratios with a correction for oxygen isotopes (^{17}O): $^{11}B/^{10}B = R_{309/308} - 0.00079$ [47,48]. Boron isotopic composition is reported as $\delta^{11}B$ in per mil (‰) deviation from the standard (NIST SRM 951) as follows: $\delta^{11}B\ ‰ = 1000[(^{11}B/^{10}B_{sample}/^{11}B/^{10}B_{standard}) - 1]$. Stable runs (n ≥ 3, 100 cycles in each run) were obtained with loading the standard NIST SRM 951 and natural samples containing ~0.5 μg of boron on the filament when the filament current is at ~1.2 A (less than ~650 °C). The average ($n=10$) internal analytical precision and the external precision of the measured $^{11}B/^{10}B$ ratios of NIST 951 are ±0.05‰ and 0.09‰, respectively.

A Neptune Plus (Thermo Fisher Finnigan, Germany) MC-ICP-MS with an ESI PFA 50 μL/min nebulizer in a quartz spray chamber were used for parallel measurement of boron isotopic composition in various natural samples by following the procedure described by Foster et al. [37]. The ions of $^{11}B^+$ and $^{10}B^+$ are detected using Faraday cups H3 and L3. The mass bias is corrected by a sample-standard bracketing procedure (SSB)[49,50]. $(^{11}B/^{10}B)_{true} = (^{11}B/^{10}B)_{measured} \times (M^{11}/M^{10})^{\beta}$, and β is a correction factor where $\beta = \ln[(^{11}B/^{10}B)_{standard\ NIST\ 951}/(^{11}B/^{10}B)_{measured\ NIST\ 951}]/\ln(M^{11}/M^{10})$. The β value from repeated measurement of NIST 951 is constant for a single analytical session and the $(^{11}B/^{10}B)_{standard\ NIST\ 951} = 4.04362 \pm 0.00137$, certified value by NIST [51]. The boron content in both sample solution and NIST 951 solution was kept close to 200 ng m L^{-1} to obtain ~1.2 V of $^{11}B^+$ signal with the conventional H-skimmer cones and 5.0 V of signal with X-skimmer cones. The memory effect was reduced to around ~3–9 mV with continuous washing with 3% HNO_3 and 1% HNO_3 and boron-free Milli-Q water in sequence for ~25 min. All reproducibilities described in this work are quoted from replicated measurements ($n \geq 3$, 2 S.D., 95% confidence limits). The average internal analytical precision ($n=100$) and the external precision of the measured $^{11}B/^{10}B$ ratios of 200 ng mL^{-1} NIST 951 are ±0.02‰ and 0.11‰, respectively.

2.4.2. Elemental content analysis

The concentrations of Ca, Mg, Fe, Al ions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY38S) with the instrumental parameters (Wavelength: 165–800 nm, RF power: 900 W, Frequency: 40.68 MHz, Resolution: 0.005 nm) and an analytical reproducibility (2RSD) of ≤2%. The boron concentration was analyzed by the quadrupole ICP-MS (aurora M90, Bruker) with an analytical reproducibility of ±3% in our laboratory.

3. Results and discussion

3.1. Improvement in separation/purification procedures for natural samples with various matrices

3.1.1. Effects of major cations on boron extraction by Amberlite IRA 743 ion exchange

As described in Section 1, significant hydroxide precipitates (such as amorphous $Al(OH)_3$, $Fe(OH)_3$ etc) would have been produced when adjusting solution pH into neutral for geological samples with rich metal oxide components (e.g. minerals, rocks and clays). Previous study employed a first step of AG 50 × 8 resin to remove cations before rising the pH of the solution to 8 for introduction on the Amberlite resin by Paris et al. [38]. In order to avoid the boron loss and the possible isotopic fractionation when adjusting the acidic sample solution into neutral, four options were tested to neutralize acidic dissolved tourmaline solutions containing large amount of Al^{3+}, Fe^{3+} and Mg^{2+} ions. The first three options are not practicable as compared in Table 1. It is worth of noting that, with adding EDTA the determined $^{11}B/^{10}B$ ratios of NIST 951 and natural samples (e.g. seawater, tourmaline) by the PTIMS-$Cs_2BO_2^+$-graphite method are significantly lower than the true values (Table 2), and the negative-shift extent of

Table 1
Comparison on possible options to convert acidic sample solution into neutral prior to Amberlite IRA 743 boron-specific resin ion exchange.

Options	Description	Advantages	Disadvantages
A	Adjusting pH by adding NaOH	Simple, rapid adjustment, and suitable to samples with simple matrices	Obvious boron loss caused by specific adsorption by large amount of amorphous hydroxide precipitate formed
B	Neutralizing H^+ ions through weak basic resin ion exchange	No precipitate formed	Amberlite IRA 743 boron-specific resin column is easily blocked by amorphous hydroxide precipitate formed during ion-exchange process
C	Screening major cations by adding EDTA and adjusting pH by adding NaOH	No precipitate formed and avoid possible boron loss	Serious isobaric ion interference on determination of boron isotopic composition by TIMS
D	Removing major cations and neutralizing H^+ ions through the mixed resin	Most cations are removed and no precipitate formed	

Table 2
Isobaric ion interference induced by EDTA on the determination of boron isotopic composition by TIMS.

Sample type	Single run $^{11}B/^{10}B$ ratios (2SE)	
	With EDTA	Without EDTA
NIST SRM 951	3.97172 (0.00280) 3.92 ~ 3.97 ~ 4.04	4.05160 (0.00006)
Seawater (South China Sea)	4.17919 (0.00077)	4.21052 (0.00006)
Tourmaline	3.93774 (0.00091)	3.97524 (0.00008)

determined 309/308 ratios depends on the amount of EDTA left in the final eluted solution. The isobaric ion interference induced from the groups of $-C{=}O-NH_2$ and $COOH^-$ in EDTA has been discussed in detail in previous works [52,53]. In this work, the mixed resin consisting of the strongly acidic cation resin (Dowex 50W × 8, USA) and the weak alkaline anion resin (Ion Exchanger II, Germany) was selected to remove major cations and neutralize H^+ ions in parent solutions. With this procedure, a neutral eluted solution is obtained and no colloidal precipitate appears in the next boron extraction column by Amberlite IRA 743 boron-specific resin.

3.1.2. Optimum condition for boron separation using peristaltic pump coupled with ion-exchange columns

To establish the optimum procedure for boron extraction by using the peristaltic pump coupled with ion-exchange columns, the operating parameters have been optimized in this study, including washing volume, elution volume, pump speed etc. (Table 3). In view of the complex matrices in tourmaline samples that contain large amount of Fe, Mg and Al cations, the elution curves of major cations during the washing step by water have been monitored to achieve full separation of boron from the matrices (Fig. 1). The concentration of major cations decreases with increased washing volume and gradually reaches to blank levels, indicating that sufficient washing ensures the full cleanup of major cations without boron loss. Therefore, a washing volume of ~8 mL was established for this step.

Four natural samples were selected to evaluate the boron recovery from the Amberlite IRA 743 ion-exchange procedure. After adding 200 μL of sample solutions containing ~1 μg boron, 200 μL of each eluted solution was collected in individual vials and the boron content was determined. As shown in Fig. 2, 1 mL of the total elution ensures the full extraction of boron with a mean recovery of 100.6%.

The isobaric ion interference induced by NO_3^- or organic matter on the boron isotope determination by either BO_2^--NTIMS or $Cs_2BO_2^+$–PTIMS has been observed and widely investigated [25,54–61]. Therefore, HNO_3 medium must be strictly avoided in the chemical procedure for TIMS measurements. According to the general procedure, boron adsorbed in Amberlite IRA 743 boron-specific resin can be eluted either by dilute HCl for TIMS measurement or by dilute HNO_3 for MC-ICP-MS measurement as presented in Scheme S2(a). To satisfy the different solution medium requirements for boron isotope analysis by both these methods simultaneously and avoid possible contamination of HNO_3 on resin and columns, a third ion exchange column was added to convert the acidic eluted solution into neutral. The final elution is divided into two parts, with one portion prepared for TIMS measurement after CsOH addition, while another portion of solution is prepared for MC-ICP-MS measurement by adding high-purity HNO_3 (Scheme S2(b)). The recovery experiment indicates that ion exchange using the mixed resin column is able to convert the acidic medium into neutral with 97.98% recovery of boron.

As described above, a three-step ion exchange procedure for boron separation/purification from various natural geological samples has been established, and this protocol can be adjusted according to the sample type as shown in Scheme 1, in which only the second and the third column could be employed for samples with simple matrices (e.g. ground water, biocarbonates etc.) and the first one would be added to deal with complex samples (e.g. clay, minerals and rocks, *etc*). The third column is optional, only using for comparison study between MC-ICP-MS and TIMS.

3.2. Establishment of static double-collection method for high precision boron isotope analysis by TIMS

3.2.1. Selection of parallel faraday cups and setting of parameters in zoom optics

Deyhle measured the 309 and 308 masses using a double Faraday cup collector with fixed spacing after reducing the accelerating voltage from 10 to 8 kV in a modified Finnigan-MAT 262 (Finnigan, Bremen, Germany) mass spectrometer [33]. Considering that the very small relative mass difference (i.e. $\Delta m/m = 1/309$) between $^{133}Cs_2{}^{11}B^{16}O_2^+$ ion (m/z 309) and $^{133}Cs_2{}^{10}B^{16}O_2^+$ (m/z 308) ions requires the use of adjacent cups at their closest possible position, three Faraday cup groups were selected to achieve the static collection, including Axial-L1, Axial-H1, and H3–H4. As shown in Figs. S1, S2, the adjacent peaks do not fully overlap without adjusting two parameters in the zoom optics. However, with adjusting parameters in the zoom optics available on the Triton TI mass spectrometer, two peaks change accordingly but full overlap could still not be achieved in the whole range of Focus Quad and Dispersion Quad parameters for the cup groups C-L1 and C-H1. It was observed that the two peaks of 308 and 309 are mostly superposed when the H3–H4 cups with the largest

Table 3
Boron separation/purification procedure by the three-step ion exchange column.

First column-2.5 mL of mixed resin consisting of 50% Dowex 50W × 8 cation resin and 50% ion exchange II anion resin (v/v)

Step	Procedure	Reagent	Dosage (μL)	Collect/Discard	Notes
1	Load column	Mixed resin	1500	Discard	
2	Clean	Water	4000	Discard	
3	Load sample	Sample solution	200	Collect	
4	Elute boron	Water	5000	Collect	Neutral solution

Second column-25 μL of Amberlite IRA 743 boron specific resin

Step	Procedure	Reagent	Dosage (μL)	Pump speed	Collect/Discard
1	Load column	IRA-743 B-specific resin	20	20	Discard
2	Clean	Water	4000	20	Discard
3	Clean	0.1 M HCl	400	10	Discard
4	Clean	Mill-Q water	2000	10	Discard
5	Equilibrate	0.3 M NH_3H_2O	400	10	Discard
6	Rinse	Mill-Q water	2000	10	Discard
7	Load	Sample at pH ~ 8		0.5	Discard
8	Elute cations	Mill-Q water	8000	10	Discard
9	Elute boron	0.1 M HCl	2000	2	Collect
10	Evaporate	at 60 °C			

Third column-0.5 mL of mixed resin consisiting of 50% Dowex 50W × 8 cation resin and 50% Ion Exchange II anion resin (v/v)

Step	Procedure	Reagent	Dosage (μL)	Collect/Discard	Notes
1	Load column	Mixed resin	500	Discard	
2	Clean	Water	8000	Discard	
3	Load sample	Sample solution	200	Collect	
4	Elute boron	Water	8000	Collect	
5	Divide	Divide the solution into two aliquots for TIMS and MC-ICP-MS measurement respectively			
6	(a) Adding CsOH	B:Cs = 1:2 and heat at 60 °C			TIMS analysis
	(b) Adding HNO_3	3% HNO_3 medium			MC-ICP-MS analysis

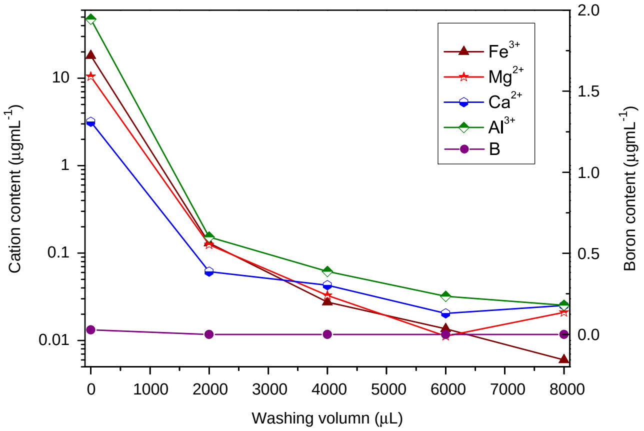


Fig. 1. Removal of typical cations by the washing step in Amberlite IRA 743 boron-specific resin column. Boron content from each elution (Solid circles with wine color) refers to Right-*Y* axis (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

deflection radius was selected. Numerous trials in setting various zoom optics parameters have been performed, and finally the optimum peak overlap was achieved at a specific condition (Fig. 3). Under this condition, both ions collected by the two parallel Faraday Cups have well-defined flat peaks without tailing peaks and prepeaks as shown by the green curves in Fig. 3, where the mass number of the central cup ranges from 287 to 289, depending on the peak scan graph in each analysis session. It indicates that both selection of parallel cups with larger deflection radii and setting optimal parameters in zoom optics are the two essential steps in the establishment of the static double collection method. Therefore, the static method established in this work has the superior advantages of simultaneous collection without special requirement on instrumental hardware.

3.2.2. *Comparison of measurement of boron isotopic composition by static double collection and dynamic single collection methods*

A comparable study on the PTIMS-$Cs_2BO_2^+$-static double-collection method and the dynamic single jumping collection method has been undertaken as shown in Table 4. Clearly, the analysis efficiency is greatly improved by the PTIMS-$Cs_2BO_2^+$-Static method, with which the data acquisition of 100 cycles only takes ~7 min compared to ~60 min for the PTIMS-$Cs_2BO_2^+$-Dynamic method. There is no correction needed for signal variations occurring during data acquisition, which ensures high internal precision for individual runs even for small amounts of boron in samples with obviously decaying signals.

The internal precision of individual run and the external reproducibility from duplicate measurement with the static double-collection method and the dynamic single-collection method ($n > 4$) have been compared [46]. Briefly, a stable signal of $Cs_2BO_2^+$ ions will last for several hours for a loading of 1000 ng boron, and the external reproducibility of PTIMS-$Cs_2BO_2^+$-Dynamic parallels that of the PTIMS-$Cs_2BO_2^+$-Static method without any obvious discrepancy. The mean values for the static method (4.05092 ± 0.00023, $n = 6$, 2σ) and dynamic method (4.05043 ± 0.00020, $n = 6$, 2σ) are similar to the value of 4.05037 ± 0.00023 given by Xiao et al. [30]. The internal precision of each single run by the static method is better than the dynamic method because the analysis errors caused by random signal variations were eliminated with the static method. When reducing the loaded amount of boron, both the intensity and the stable emission time of $Cs_2BO_2^+$ ion decrease accordingly, and the $^{11}B/^{10}B$ values determined from a single run (100 cycles) varied greatly for the dynamic single collection mode and worse internal/external precision was produced as a result. By contrast, the static

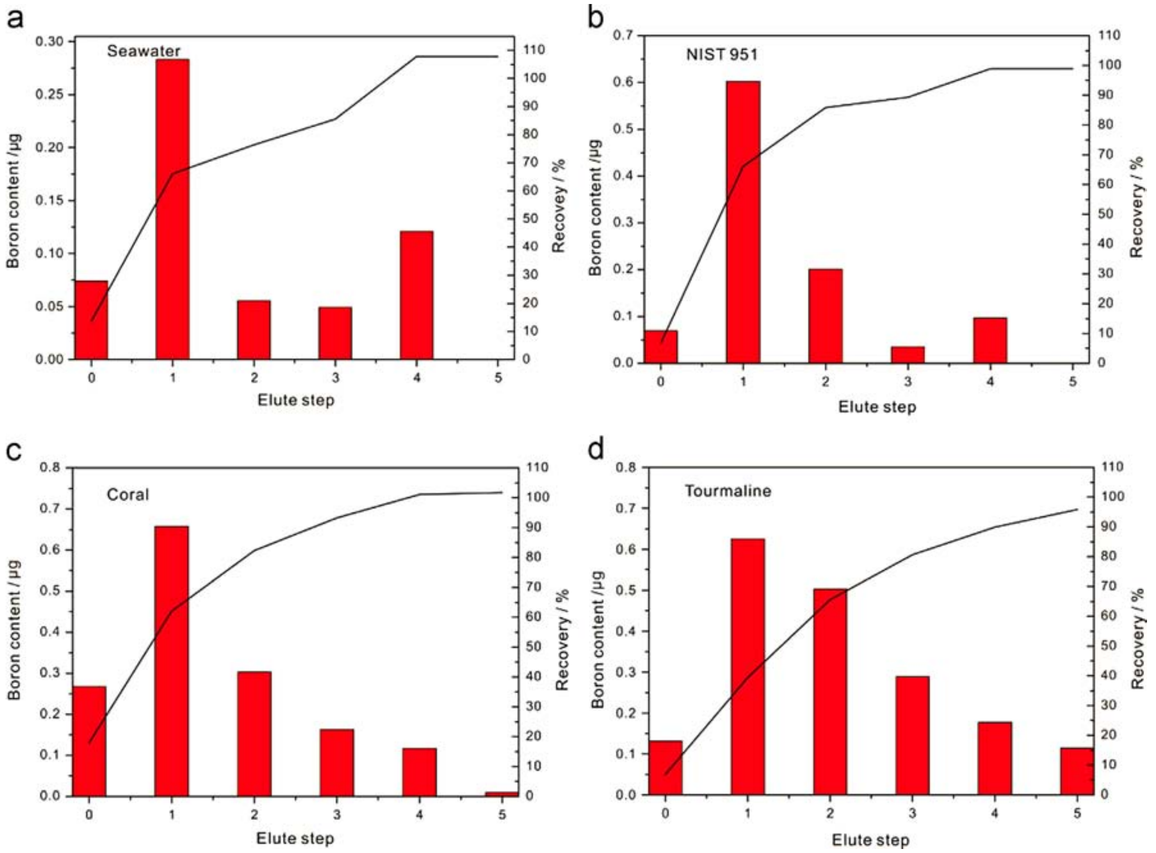
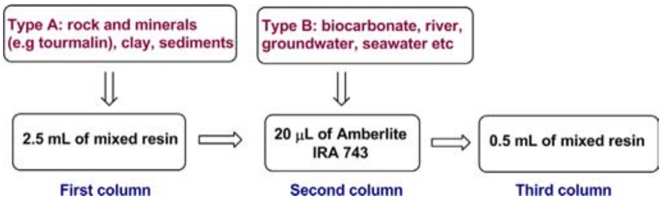


Fig. 2. Elution curves of ~1 μg boron from natural samples and NIST 951 with 20 μL column of Amberlite IRA 743 resin using the setup of peristaltic pump coupled with exchange-column. Shaded areas indicate the cumulative recovery of boron.



Scheme 1. Schematic illustration for the potential adjustment of the three-step ion-exchange protocol according to the sample type.

double-collection method overcomes the problems mentioned above, and the external reproducibility (2RSD) of measured $^{11}B/^{10}B$ ratios of NIST 951 are as high as ±0.06‰, ±0.16‰ and ±0.25‰ for 1000 ng, 100 ng and 10 ng boron, respectively (as shown in Fig. 4).

The $^{11}B/^{10}B$ ratios for NIST 951 with various sample sizes from this study and previous contributions are compared in Fig. 5. When the loading amount of boron is higher than 100 ng, the $^{11}B/^{10}B$ ratios are consistent with the mean value of 4.05172 ± 0.00099 among different laboratories, and the external reproducibilities are parallel regardless of different data acquisition modes and sample loading conditions. More significant differences in measured $^{11}B/^{10}B$ ratios and external reproducibilities are observed with reduced boron loadings in the range from 10 to 100 ng, which could be due to the discrepancy in emission capacity of the graphite promoter used in different laboratories, according to our previous investigation [52]. For NIST 951 sample containing 10 ng of boron, the external reproducibility of ±0.25‰ obtained from this work is equivalent to that of ±0.2‰ given by Ishikawa and Nagaishi [36]. The $^{11}B/^{10}B$ ratio of 4.02972 ± 0.00101 (2SD) in this work is lower than that of 4.05259 ± 0.00090 (2SD) obtained with a special filament preheating procedure [36]. Considering the diversity in the sample loading procedure, possible influence of boron–mannitol complexes or the environmental blank on the determined $^{11}B/^{10}B$ ratios will be investigated in future work. Therefore, the continuous improvements in the PTIMS method of boron isotope measurements with higher internal/external precision for the minute size of samples usually available would greatly benefit the high precision measurement of boron isotopic compositions in natural samples with low boron contents (e.g. rainwater, foraminifer).

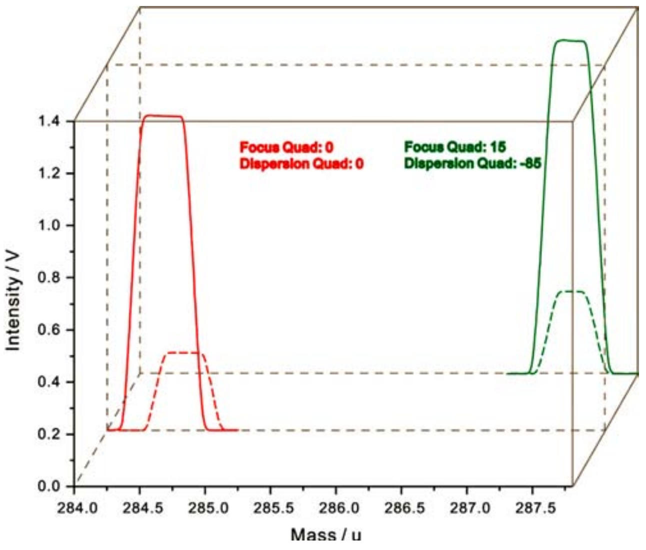


Fig. 3. Mass scan graphs of $^{133}Cs_2{}^{11}B^{16}O_2^+$ (*m/z* 309) and $^{133}Cs_2{}^{10}B^{16}O_2^+$ (*m/z* 308) as collected by H4 (solid line) and H3 cups (dash line) under different conditions in zoom optics.

Table 4
Comparison between PTIMS-$Cs_2BO_2^+$-static double-collection method and dynamic single-collection method for determination of boron isotopic composition.

Main Parameter		**PTIMS-$Cs_2BO_2^+$-Static**	**PTIMS-$Cs_2BO_2^+$-Dynamic**
Faraday collector parameters	Selection of Faraday cups	Cup H3 and Cup H4	Cup C (Central Cup)
	Positions of the target cups	H3-F (308): 89.236 H4-F (309): 99.000	
Mass number of cup C		~289.9	309.0
Data acquisition method		Static double collection	Dynamic jumping single collection
Zoom optics parameters	Focus Quad/V	15	0
	Dispersion Quad/V	−85	0
100 Cycles data acquisition time/min		7	60

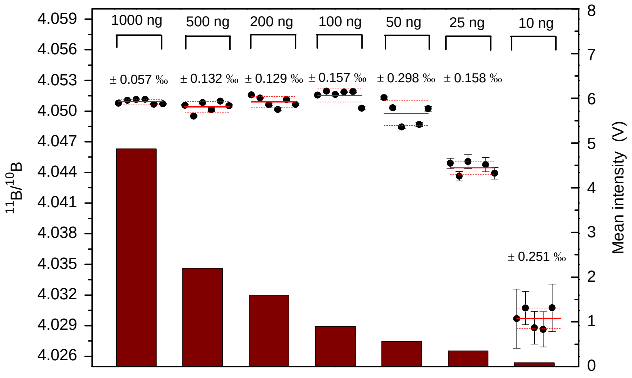


Fig. 4. The determined $^{11}B/^{10}B$ values for NIST 951 and the intensity of $Cs_2BO_2^+$ ion with loading different amount of boron from 1000 ng to 10 ng with PTIMS-$Cs_2BO_2^+$-Static method. The mean intensity of $Cs_2{}^{11}BO_2^+$ ion (*m/z* 309) in histogram refers to Right-*Y* axis. Vertical error bars represent the internal precision (2SE) for each run with 100 cycles.

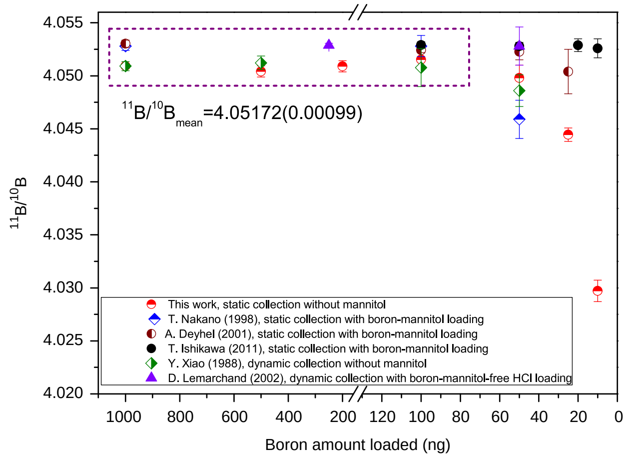


Fig. 5. Comparison of the $^{11}B/^{10}B$ ratios for NIST 951 measured by PTIMS-$Cs_2BO_2^+$ method with different sample sizes. Vertical error bars are the external reproducibility (2SD).

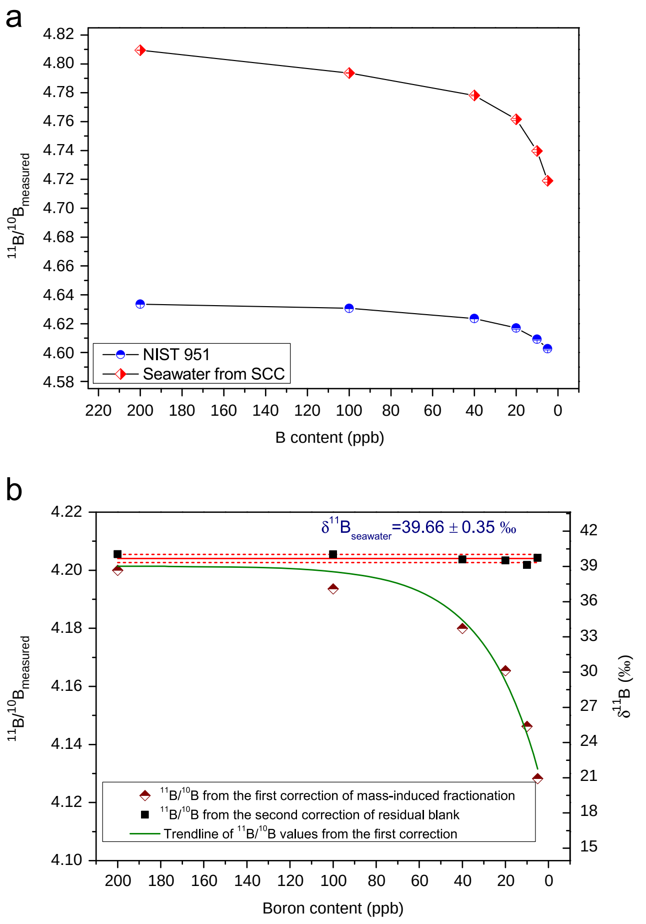


Fig. 6. (a) Measured $^{11}B/^{10}B$ values of NIST 951 and seawater sample solutions with different boron concentration (200 ppb, 100 ppb, 40 ppb, 20 ppb, 10 ppb, 5 ppb) in one analysis session; (b) comparison on the corrected $^{11}B/^{10}B$ values by the first correction on mass-induced fractionation and the second correction on residual boron blank.

3.3. A comparison study of boron isotope analysis by TIMS and MC-ICP-MS

3.3.1. Memory effect on the boron isotope analysis by MC-ICP-MS

The wash-out problem of boron by ICP-MS (or MC-ICP-MS) has been well demonstrated [40,60]. In order to quantify potential inaccuracies from residual boron signals, the boron isotope ratios in NIST 951 and in one internal-laboratory standard seawater sample were determined when decreasing the boron concentration from 200 ppb to 5 ppb under the same measurement conditions in one analysis session. As shown in Fig. 6(a), the measured $^{11}B/^{10}B$ values in both NIST 951 and the seawater sample decreased with a reduction of the boron content. After the first correction for mass-induced fractionation with the SSB procedure, most $^{11}B/^{10}B$ values of seawater were lower than their true value, especially for samples with lower boron content (Fig. 6(b)), indicating a significant contribution from the residual boron blank. After following the on-peak zero blank correction (i.e. $(^{11}B/^{10}B)_{sample} = ((^{11}B_{measured} - {}^{11}B_{blank})/(^{10}B_{measured} - {}^{10}B_{blank}))$, consistent $^{11}B/^{10}B$ ratios of seawater with a mean $\delta^{11}B$ value of 39.66 ± 0.35‰ were obtained in the whole range of boron content from 5 ppb to 200 ppb.

Therefore, cautious attention must be paid to the correction on the residual boron blank for natural samples with trace boron contents, because the relative contribution of the residual blank becomes increasingly larger for small boron concentrations, such as foraminifer, fossils etc.

3.3.2. *Isobaric ion interference on the determination of boron isotopic composition by TIMS*

The isobaric ion interference from very small amounts of organic compounds present in the final eluted solution on the measurement of boron isotopic composition by P-TIMS has been discussed in our previous work [53]. Because of the very low $R_{309/308}$ ratio (i.e. 0.01517) from the interference ions (Cs_2CNO^+) due to the isotopic abundance of N, C and O in nature,[61] the drift in measured $^{11}B/^{10}B$ values by P-TIMS for small samples could be significant. When measuring natural samples with low boron content, it cannot wait for the total evaporation of the interfering species because the signal is vanishing to zero rapidly in a short time. The MC-ICP-MS technique provides reliable results with high accuracy/precision for such kinds of natural samples.

3.3.3. *Matrix effects on the determination of boron isotopic composition by MC-ICP-MS*

For PTIMS-$Cs_2BO_2^+$ method, stable emission of $Cs_2BO_2^+$ cannot be maintained if major impurities still exist in the final loading solution. The intensity and stability of $Cs_2BO_2^+$ ions could be employed as a good sign to judge the reliability of $^{11}B/^{10}B$ ratios determined. By comparison, the internal precision of individual runs on $^{11}B/^{10}B$ ratios determined by MC-ICP-MS always has a standard deviation of ~0.06%, no matter whether the sample solution passes a purification procedure or not. In this work, the $^{11}B/^{10}B$ ratios of two typical samples (i.e. tourmaline, seawater) with/without a pretreatment procedure have been compared. As shown in Fig. 7(a) and (b), the internal precision of single runs for samples with pretreatment parallels to that without pretreatment, but the external precision from duplicative measurement ($n=6$–7) for samples with pretreatment is generally better than without pretreatment. After following the pretreatment procedure, the mean $\delta^{11}B$ value of 39.60 ± 0.19‰ in seawater (South China Sea), is identical to the value of the average value (39.61 ± 0.04‰) for global open-ocean seawater recently reported [62,63]. However, the mean $\delta^{11}B$ value of 30.69 ± 0.73‰ obtained without pretreatment procedure is ~9‰ lower than the true values and there still is ~2‰ negative deviation when ~10% EDTA (v/v) was added into the final eluted solution. A similar observation was made for a tourmaline sample, where the determined $\delta^{11}B$ value without a pretreatment procedure is ~10‰ lower than that with a pretreatment procedure. The replicate measurements on samples without pretreatment seem to show a drift with time, which could indicate high amount of matrix makes the mass bias more unstable and susceptible. A similar negative shift in the $\delta^{11}B$ values with a seawater matrix was observed, and the underlying principles for the instrumental mass bias from higher matrix loads were discussed in more detail by Vogl et al. [19]. These consistent results prove that solution matrices induce negative deviations of $\delta^{11}B$ values dramatically. Therefore, complete separation of boron from matrices is a key step in order to achieve accurate and precise measurement of boron isotopes.

3.3.4. *Intercomparison of boron isotopic compositions in natural samples by TIMS and MC-ICP-MS after pretreatment*

In order to check the reproducibility and comparability of boron isotope determination by both TIMS and MC-ICP-MS, different typical geological materials with a wide span of $\delta^{11}B$ from −25‰ to +40‰, have been prepared and tested for this purpose, including NIST 951, a seawater sample from South China Sea, IAEA-B1, IAEA-B2, IAEA-B3, and other natural samples from various sources (Table S1). After being subjected to the modified ion-exchange procedure discussed above, the final eluted solutions were divided into two portions for TIMS and MC-ICP-MS measurement, respectively. In general the $^{11}B/^{10}B$ ratios obtained by the PTIMS-static method are in a good agreement with the corrected $^{11}B/^{10}B$ values from MC-ICP-MS as shown in Fig. 8, and the consistent results from the comparison demonstrate that no isotopic fractionation occurs during the extraction procedure and the minor discrepancy in $\delta^{11}B$ values was probably due to analytical uncertainties. An certification campaign on the $^{11}B/^{10}B$ ratios of IRMM-011 and NIST SRM 951 was performed using TIMS technique by Vogl et al. [64], in which the difference of the K-factor (i.e. the correction factor of mass fractionation) for IRMM-011 and NIST SRM 951 is the sum of the difference of the observed isotope ratio and the certified isotope ratio. Besides, the

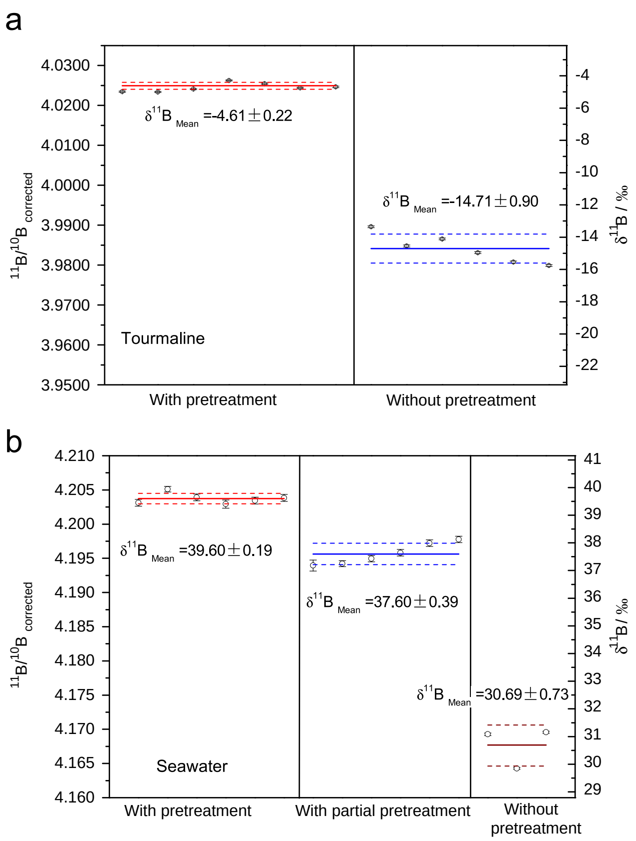
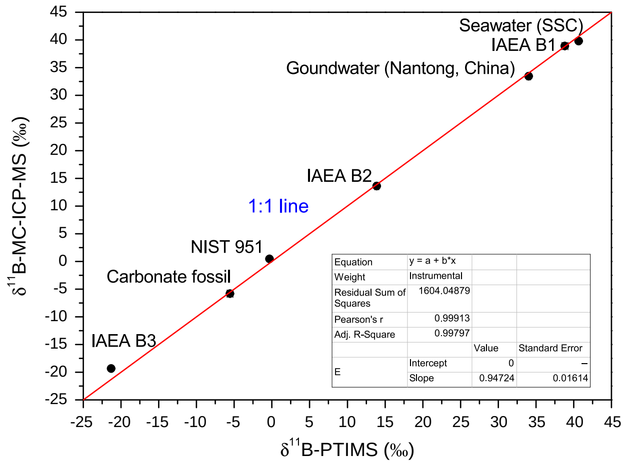


Fig. 7. Solution matrix effect on measurements of boron isotopic composition by MC-ICP-MS: (a) tourmaline sample; (b) seawater sample from South China Sea. Data with pretreatment refers to samples that passed through the ion-exchange separation/purification procedure, and that without pretreatment are original liquid samples prior to the separation/purification procedure.



Equation	y = a + b*x		
Weight	Instrumental		
Residual Sum of Squares	1604.04879		
Pearson's r	0.99913		
Adj. R-Square	0.99797		
		Value	Standard Error
E	Intercept	0	–
	Slope	0.94724	0.01614

Fig. 8. Intercomparison of boron isotopic compositions in various natural samples determined by TIMS and MC-ICP-MS expressed as $\delta^{11}B$ values. Solid wine circles are data obtained from this study and the uncertainty bar (2σ) is within the symbol size.

potential difference among different units of NIST SRM 951 was cross-checked and the measurement revealed no heterogeneity was observed with less than 0.08‰ of difference and the analysis difference is fully covered by the stated uncertainties within the certificate [64]. Therefore, it could be concluded that consistent and accurate determination of boron isotopic composition by TIMS and MC-ICP-MS can be achieved when the dominant effects (e.g. residual matrix effect, isobaric ion interference) are well controlled as reached by Louvat et al. [16].

4. Conclusions

Improvements on separation/purification procedures for natural samples with various matrices, the establishment of a static double-collection method for boron isotopic analysis by PTIMS and comparison on measurement of boron isotopic composition by TIMS and MC-ICP-MS have been investigated in detail in this study.

(1) In order to separate/purify boron from natural geological samples with complex matrices (e.g. tourmalines, sediments), a three-column ion-exchange procedure has been developed in this work, which ensures more than 98% recovery of boron from each step and satisfies the different requirement on the solution medium for boron isotope analysis by both TIMS and MC-ICP-MS without any contamination by nitrate acid in the boron-specific resin column. It is adjustable according to sample type and analysis techniques.

(2) A PTIMS-$Cs_2BO_2^+$-static double-collection method has been developed in a Triton TI mass spectrometer, which can simultaneously collect the polyatomic ions $^{133}Cs_2^{11}B^{16}O_2^+$ (m/z 309) and $^{133}Cs_2^{10}B^{16}O_2^+$ (m/z 308) in adjacent H3–H4 Faraday cups with typical zoom optics parameters (Focus Quad: 15 V, Dispersion Quad: −85 V) without special requirement on instrumental hardware. This method has the following superior advantages: (i) greatly improves the analysis efficiency; (ii) ensures a high internal precision for individual runs even for small amounts of boron in samples with obviously decaying signals; (iii) achieves an external reproducibility of ±0.25‰ for NIST 951 containing only 10 ng of boron, allowing high precision measurements of boron isotopes in natural samples with low boron contents at nanogram level (e.g. rainwater, foraminifer).

(3) A comparable investigation of boron isotope analysis on natural geological samples that were subjected to the same separation/purification procedure has been performed. For boron isotope measurement by MC-ICP-MS, potential inaccuracies from residual boron signals can be corrected by the on-peak zero blank correction procedure, which ensures accurate measurements of boron isotopic ratios at boron content of a few ppb levels. The isobaric ion interference caused by trace organic matter or nitrate and the potential residual matrix effect can induce remarkable negative deviations in $^{11}B/^{10}B$ ratios (or $\delta^{11}B$ values) for TIMS and MC-ICP-MS methods respectively. A consistent comparison between TIMS and MC-ICP-MS was obtained in different typical geological materials with a wide span of $\delta^{11}B$ values ranging from −25‰ to +40‰. The results further confirm that no boron isotopic fractionation occurred in the modified procedure and a good agreement could be achieved when the dominant effects that cause deviations in measurements of $\delta^{11}B$ values by the two leading techniques were well controlled.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.02.009.

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