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International Journal of Mass Spectrometry 235 (2004) 187–195

www.elsevier.com/locate/ijms

Effective elimination of isobaric ions interference and precise thermal ionization mass spectrometer analysis for boron isotope

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Received 5 January 2004; accepted 21 April 2004

Abstract

An ionization depressor, 1% H_3PO_4 was used to eliminate the isobaric interference that has been of a great concern during the procedure of boron isotopic ratio analysis by thermal ionization mass spectrometer (TIMS). Our experiments have shown that it appears to be an effective method to completely restrain the formation of isobaric ions of CNO^- and Cs_2CNO^+ in the ionization source of mass spectrometer. We have also discussed the optimum proportion of depressor to nitrite for precise analysis of boron isotopes in natural samples based on a conditional experiment. In this case, the pretreatment of boron extraction from natural samples is greatly simplified since it is not necessary to remove nitrite and organic matter completely. In virtue of the method, we determined boron isotope in different types of natural samples, and our results are consistent with previous reports.

Keywords: Boron isotopes; Isobaric ions interference; Ionization depressor; Thermal ionization mass spectrometer

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1. Introduction

Boron isotope, due to its broader δ^{11}B-scale and remarkable indicative significance for the change of environment, has attracted a considerable attention in recent decades. Correspondingly, the analytical methods for boron isotope have been significantly developed and improved in order to deal with various types of samples, equipment limitations and high precision requirements. Currently, majority of studies focus on the boron isotopic ratio determination in natural materials with rich organic matter and trace amount of boron. It is a great challenge to measure isotopic ratios precisely due to some inherent disadvantages related to different measurement techniques [1,2], such as, relatively large quantity of boron required for the positive thermal ionization mass spectrometry (PTIMS), and larger measurement uncertainty for negative thermal ionization mass spectrometry (NTIMS), higher random errors for inductively coupled plasma-mass spectrometry (ICP-MS), poor internal precision and crucial dependence on sample matrix for secondary ion mass spectrometry (SIMS), and so on.

When compared with other techniques for boron isotopic analysis, PTIMS is considered as the most precise method [1] currently available for natural samples, while NTIMS is well suited for biogenic carbonates due to its high sensitivity allowing isotopic analyses of boron quantities in the nano-gram range. But both PTIMS and NTIMS face the problem of isobaric ion interference during the determination of boron isotopic ratios [3–9]. The intensity ratios of isobaric ions CNO^- ($R_{43/42}$) and Cs_2CNO^+ ($R_{309/308}$) (here, $R_{43/42}$ or $R_{309/308} = {}^{15}N/{}^{14}N + {}^{13}C/{}^{12}C + {}^{17}O/{}^{16}O = 0.003673 + 0.01112 + 0.00038 = 0.01517$ [3]) is significantly lower than that of $BO_2{}^-$ ($R_{43/42}$) and $Cs_2BO_2{}^+$ ($R_{309/308}$). Thus, the presence of trace nitrate and organic matter in a sample solution would bring evident negative shifts for $^{11}B/^{10}B$ ratios and δ^{11}B value.

Currently, most studies focus on removing $NO_3{}^-$ ion and organic matter, which could induce the formation of isobaric ions of CNO^- and Cs_2CNO^+ in the ionization source of thermal ionization mass spectrometer (TIMS) during the pretreatment of samples. Many trials are not very satisfactory, the use of organic matter specific resins, activated carbon

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doi:10.1016/j.ijms.2004.04.010

and hydrogen peroxide. Lemarchand et al. [5] developed a procedure for the extraction and purification of boron with a micro-sublimation set based on the ability of boron to sublimate at low temperatures, and the procedure has been efficiently applied to analyze river water samples. An interesting observation reported in the literature [7,10–21] is that there are larger discrepancies in $^{11}B/^{10}B$ values measured by PTIMS and NTIMS for NIST SRM 951 boric acid in different laboratories in the world, ranging from 3.9989 to 4.0104 for NTIMS, and from 4.0506 to 4.05595 for PTIMS. The detailed data is shown in Table 1. In general, the observed difference is attributed to the intrinsic systematic error of equipment or method. In fact, during the procedure of isotopic ratios measurement by NTIMS, different ionization prompters, such as $La(NO_3)_3$, $Ca(NO_3)_2$, boron-free seawater as well, have been used to improve the determination sensitivity. No doubt, the introduction of NO_3^- ions and the unspecified amount of promoter added must result in an evident negative bias of $^{11}B/^{10}B$ value and a different degree of the shift.

Unfortunately, it is very difficult to completely remove organic matter and nitrate during the pretreatment procedure due to the wide use of scour containing nitrate and nitric acid media. Also, in NTIMS, there is a larger uncertainty in the estimation of the presence of CNO^- and its interferential degree by monitoring CN^- ion [22].

The main objective of this study is to effectively eliminate the interference of isobaric ions in thermal ionization mass spectrometry technique by: (i) searching for an effective depressor that would restrain the formation of isobaric ions in the ionization source of TIMS; (ii) establishing the optimum condition for precise analysis of boron isotopes in natural samples in virtue of a conditional experiment and chemometric calculation; (iii) simplifying the pretreatment procedure of boron extraction.

2. Experimental

2.1. Reagents

High purity graphite (JMC 99.9999%) has been mixed with 80% ethanol/20% water (v/v) to form slurry as a promoter for PTIMS. Sub-boiling water has been used through out the experiments. Concentrated HCl has been re-purified in laboratory by sub-boiled distillation. Solutions of NIST SRM 951 boric acid (0.5, 1.0, and 2.0 μg/μl), H_3PO_4 (1%), Cs_2CO_3 (12.3 μg/μl), $CsNO_3$ and aqueous mannitol (1.82%), $La(NO_3)_3$, $Ca(NO_3)_2$, $MgCl_2$, NaOH have been prepared using the sub-boiling water. CsCNO (5.0 μg/μl CNO^-) has been transferred from KCNO (Fluka, GR) using Cs^+-resin.

2.2. Chemical procedure and boron extraction procedure from natural materials

2.2.1. Preparation of ion exchange resin column

The Amberlite IRA 743 resin crushed 100–120 mesh, a mixed resin consisted of a strongly acidic resin (Dowex 50 W × 8, USA) of 200–400 mesh and a weak alkaline anion resin (Ion Exchanger II, Germany) of 60–100 mesh, have been used during the boron chemical purification. The individual resins have been conditioned using HCl and $NaHCO_3$ to convert into H^+ and HCO_3^--forms. Due to the difference in size, Ion Exchanger II and Dowex 50 W × 8 can be separated each other by a sieving sifter of 100 meshes for further regeneration and use.

2.2.2. Extraction procedure of boron in samples with rich organic matter

The procedure used for the extraction of boron has been based on the modified Wang method [23]. Solid samples, shell and coral, have been dipped in 30% H_2O_2 to clean their surfaces before they have been ground to powder of

Table 1
Partial results reported of $^{11}B/^{10}B$ for NIST SRM 951 boric acid

Author	$^{11}B/^{10}B$ (2σ)		References
	NTIMS (promoter)	PTIMS (promoter)	
J.K. Aggarwal	4.0003 ± 0.005	4.0528 ± 0.005 (graphite)	[10]
S. Barth	4.00125 ± 0.00264 (B-free sea water)		[11]
A. Deyhle		4.05226 ± 0.003 (graphite)	[12]
D. Lemarchand		4.0529 ± 0.0002 (graphite)	[13]
N.G. Hemming	4.0014 ± 0.0027 (B-free sea water)		[14]
S. Tonarini		4.0506 ± 0.0007 (graphite)	[15]
H.J. Brumsack	4.0104 ± 0.0036 (Seawater)		[16]
U.S. Klotzli	3.9989 ± 0.0125 ($La(NO_3)_3$)		[7]
T. Ishikawa		4.0513 ± 0.004 (graphite)	[17]
M.R. Palmer		4.0529 ± 0.001 (graphite)	[18]
G.H. Swihart		4.05595 ± 0.0007 (graphite)	[19]
S. Eisenhut	4.0069 ± 0.0049 ($Ba(OH)_2$)		[20]
M. Zhai		4.0533 ± 0.0004	[21]

approximately 100 mesh. Then 5.0 mol/l HCl has been added to dissolve a carbonate component which is rich in boron, followed with a continuous addition of refined 0.5 mol/l HCl (several milliliters) until the solution has become slightly acidic. After being filtrated to remove unsolvable residue, the solution has been passed through a weak alkaline anion resin (Ion Exchanger II) to remove partial anions and obtain a neutral eluent used in the next step of ion exchange.

The sample solution has been first loaded into the conditioned Amerlite IRA 743 resin at a flow rate of 2.5 ml/min. After being rinsed with 3 mol/l $NH_3 \cdot H_2O$ and high purity water, the column has been eluted using 10 ml of 0.1 mol/l HCl at 75 °C. Then the eluent has been sequentially passed through a mixed ion exchange resin column quickly, and after that, the column has been eluted by 15 ml of high purity water. The final eluent has been collected in a clean Teflon beaker, and a proper amount of Cs_2CO_3 has been added into the final eluent (B/Cs molar ratio of 1:2). After being evaporated to about 0.5 ml in an oven under 60 °C and clean air stream, the solution has been transferred to a clean jar and condensed to approximate concentration of 1 mg B per ml. The jar has then been tapped tightly and stored for mass spectrometric analysis.

2.3. Instrument

A VG 354 positive thermal ionization mass spectrometer (Micromass, UK Ltd, Wynthenshawe, Manchester, UK) and an improved MAT 261 negative thermal ionization mass spectrometer mass (Finnigan MAT) have been used for the measurement of boron isotopic composition. Single tantalum and rhenium filament (0.75 cm × 0.076 cm × 0.0025 cm), degassed in vacuum for 1 h at current 3.0 A, has been firstly treated with the graphite slurry of 2.5 μl and the sample solution has then been successively loaded when the slurry became close to dry. An analytical method for the boron isotopic ratios determination has followed the procedure reported by Xiao et al. [24] for PTIMS method and Liu et al. [6] for NTIMS method.

3. Results and discussion

3.1. Formation of isobaric ion $Cs_2(CNO)^+$ in ionization source

Previous studies [3–9] assume that the isobaric ion of $Cs_2(CNO)^+$ or CNO^- is induced from nitrate or organic matter. To test what causes the formation of isobaric ion, we have recorded mass spectra for different reagents containing NO_3^- and CNO^-.

3.1.1. Effect of NO_3^-

Fig. 1 shows, the scan recorded in the range from *m*/*e* 308 to 332, displays two strong peaks at masses of 312 and 328 when $CsNO_3$ solution is loaded with graphite slurry. Under the conditions applied, isobaric ion Cs_2CNO^+ with masses of 308 and 309 has not been recorded, which indicates that NO_3^- ion could not transfer to CNO^- ion in ionization source without another activator.

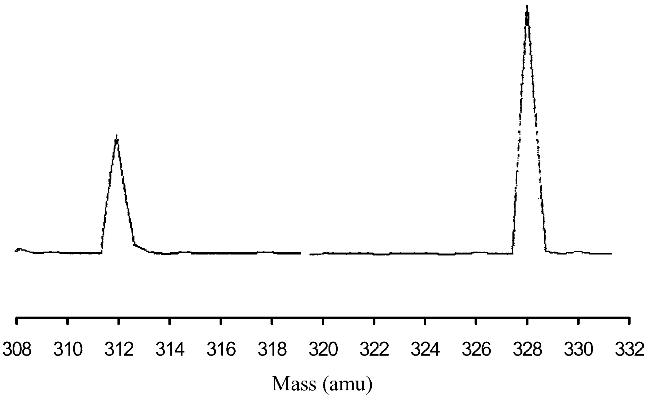


Fig. 1. Mass spectrum for $CsNO_3$ reagent in the presence of graphite at current 1.20 A. Scanning ranges are from *m*/*e* 308 to 332. Two well-defined ion peaks are ${}^{133}Cs_2{}^{14}N^{16}O_2{}^+ (m/e\,312)$ and ${}^{133}Cs_2{}^{14}N^{16}O_3{}^+ (m/e\,328)$, respectively.

However, the situation changes greatly when small amount so of boron are present. From *m*/*e* 306 to 330, there are four well defined peaks at mass of 308, 309, 312, and 328. With the increase of heating current and time, the intensity of 308 and 309 peaks gradually raises, while that of 312 and 328 obviously decays, and approaches close to 0 (see Fig. 2). From the experiments presented it can be seen that the polyatomic ions of $Cs_2(NO_2)^+$ and $Cs_2(NO_3)^+$ are not only easier to generate prior to $Cs_2BO_2{}^+$ ion at a lower ionization temperature, but also quicker to decline

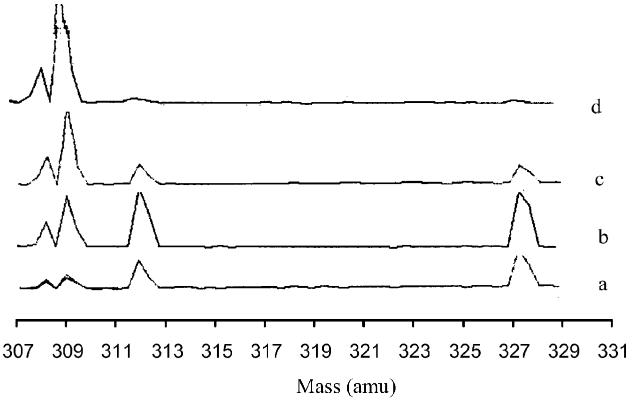


Fig. 2. Mass spectrum for mixture of $CsNO_3$ and NIST SRM 951 boric acid in the presence of graphite. The intensity of each ion changes with time and heating current. Scanning ranges are from *m*/*e* 307 to 331. Four ion peaks at *m*/*e* 308, 309, 312, and 328 are ${}^{133}Cs_2{}^{10}B^{16}O_2{}^+$ and ${}^{133}Cs_2({}^{12}C^{14}N^{16}O)^+$, ${}^{133}Cs_2{}^{11}B^{16}O_2{}^+$, and ${}^{133}Cs_2({}^{12}C^{15}N^{16}O)^+$, ${}^{133}Cs_2{}^{14}N^{16}O_2{}^+$, ${}^{133}Cs_2{}^{14}N^{16}O_3{}^+$, respectively. Each curve has been scanned with 5 min intervals. Curve (a): Heating current is 1.24 A, the ratio of 309/308 is around 1:1. Curve (b): Heating current is 1.30 A, the ratio of 309/308 is around 2:1. Curve (c): Heating current is 1.38 A, the ratio of 309/308 is around 3:1. Curve (d): Heating current is 1.40 A, the ratio of 309/308 is around 4:1.

due to the thermal instability of nitrate and nitrite. Here, $^{133}Cs_2{}^{10}B^{16}O_2{}^+$ and $^{133}Cs_2(^{12}C^{14}N^{16}O)^+$ ions contribute to the peak at *m*/*e* 308 while $^{133}Cs_2{}^{11}B^{16}O_2{}^+$, $^{133}Cs_2(^{12}C^{15}N^{16}O)^+$ ion to the peak at *m*/*e* 309. Similar conclusions have also been reported by Xiao et al. [3], where in the presence of $NO_3{}^-$, the measured 309/308 ratios have been shown to be initially low, but then increase toward the accepted value of NIST SRM 951 boric acid.

By comparing Fig. 1 with Fig. 2, we deduce that it is the boron, as an effective activator that could induce the generation of Cs_2CNO^+ ion from $CsNO_3$ in thermal ionization source.

3.1.2. Effect of CNO^-

When CsCNO solution containing about 5 μg of CNO^- has been loaded alone with graphite slurry, no ion peak has been recorded, except a strong $^{133}Cs^+$ peak, until the heating current rose to 2.2 A. On the contrary, after traces of NIST SRM 951 boric acid solution about 0.5 μg boron has been added, two well-defined peaks at the masses of 308 and 309 have been recorded. The results demonstrate that the intensity ratio of the two peaks (309/308) changes with time. As shown in Fig. 3, the dynamic change of 309/308 ratio proves that ion of Cs_2CNO^+ has appeared mainly at the initial stage of ionization, and then decayed quickly, but $Cs_2BO_2{}^+$ ion could last for a long time under a higher heating current.

Similarly to the phenomena described in the previous section, the isobaric interference $Cs_2(CNO)^+$ ion could not be generated directly from CsCNO, but the reaction might be induced in the presence of boron. What is the role of boron element in this thermal reaction is something that needs to be to investigate further.

3.2. Elimination of isobaric ions interference in the thermal ionization mass spectrometry

3.2.1. Choice of a suitable ionization depressor

Taking into account that it is difficult to remove $NO_3{}^-$ completely from the sample preparation, we have searched for a suitable ionization depressor that may restrain the formation of Cs_2CNO^+ in ionization source without affecting the boron isotopic measurement. None of attempts, the adding of hydrochloride acid, hydrofluoric acid, and sulfuric acid, has been shown to be satisfactory. Fortunately the addition of H_3PO_4 seems to be a useful method to resolve the problem from our primary experiment.

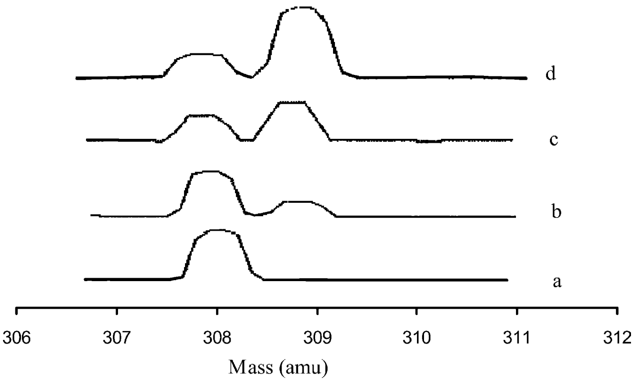


Fig. 3. Mass spectrum for the mixture of CsCNO and NIST SRM 951 boric acid in the presence of graphite. Scanning ranges are from *m*/*e* 306 to 311. Two peaks are *m*/*e* 308($^{133}Cs_2{}^{10}B^{16}O_2{}^+$ and $^{133}Cs_2{}^{12}C^{14}N^{16}O^+$) and *m*/*e* 309 ($^{133}Cs_2{}^{11}B^{16}O_2{}^+$ and $^{133}Cs_2{}^{12}C^{15}N^{16}O^+$). With the increase in heating current and time, the ratios of 309/308 increases from 0.015 to 4.043. Each curve is scanned at 10 min intervals. Heating current for Curve (a), Curve (b), Curve (c), and Curve (d) is 1.28 A, 1.50 A, 1.60 A, and 1.60 A, respectively.

3.2.2. Effective elimination of interference of isobaric ions

3.2.2.1. Affect of the depressor on the boron isotopic measurement of NIST SRM 951. In a practical view, to test whether the depressor solution induce a positive or negative shift in the isotopic measurement of boron, we have added the depressor solution of different volumes on the ionization filament when the drop of the sample solution (NIST SRM 951 boric acid) became close to dry, and then determined the ratios of $^{11}B/^{10}B$, respectively.

The results (Table 2) show that the ratios of $^{11}B/^{10}B$ for SRM 951 containing depressor of different volume are consistent with that of pure NIST SRM 951. That means the presence of depressor in the sample solution could not bring any shift of the ratios of $^{11}B/^{10}B$.

3.2.2.2. Effective elimination of isobaric interference induced from $NO_3{}^-$ and CNO^- ions after adding the depressor.

$Cs_2BO_2{}^+$-graphite-PTIMS method. By recording the mass spectrum for two mixtures of $CsNO_3$ and NIST SRM 951, CsCNO, and SRM 951 with the depressor H_3PO_4 (see Figs. 4 and 5), we have observed that just two ion peaks at mass 308 and 309 have emerged out when the heating current exceeded 2.0 A. However, their initial ratios of 309/308 are

Table 2
Ratios of $^{11}B/^{10}B$ for pure NIST 951 after adding depressor solution H_3PO_4

No.	Volume of 1% H_3PO_4 added (μl)	Single ratios of $^{11}B/^{10}B$ determined			Average $^{11}B/^{10}B$ (2σ)
1	0	4.048680	4.052046	4.054198	4.05164 ± 0.0028
2	1	4.050205	4.050052	4.046858	4.04904 ± 0.0019
3	3	4.051833	4.053342	4.046562	4.05058 ± 0.0036

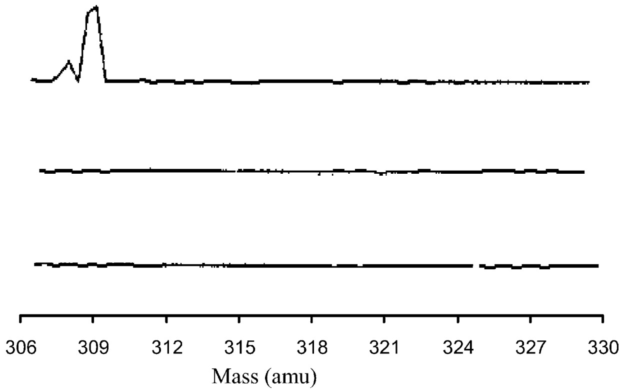


Fig. 4. Mass spectrum for the mixture of $CsNO_3$ and NIST SRM 951 boric acid in the presence of graphite, after adding the depressor of H_3PO_4. Scanning ranges are from *m*/*e* 306 to 330. Two ion peaks, at *m*/*e* 308 and 309 appear on the screen till the heating current rises to 2.0 A, and the ratio of 309 to 308 is 4.0438.

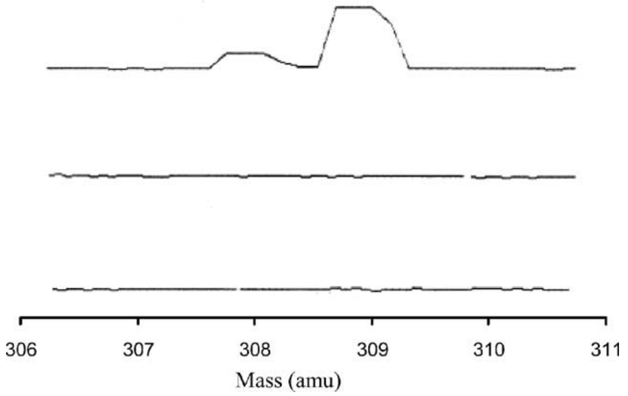


Fig. 5. Mass spectrum for the mixture of CsCNO and NIST SRM 951 boric acid at the presence of graphite, after adding the depressor of H_3PO_4. Scanning ranges are from *m*/*e* 306 to 311, and the ratio of 309 to 308 is 4.0493.

all higher than 4.04, which approach to the standard value of NIST SRM 951. Deduced from the ratios of 309/308, two peaks at masses of 309 308 are not $^{133}Cs_2{}^{12}C^{15}N^{16}O^+$ ion and $^{133}Cs_2{}^{12}C^{14}N^{16}O^+$ ion, but $^{133}Cs_2{}^{11}B^{16}O_2{}^+$ ion and $^{133}Cs_2{}^{10}B^{16}O_2{}^+$ ion, respectively.

Figs. 4 and 5 illustrate, the generation of Cs_2CNO^+ ion from $CsNO_3$ and CsCNO could be restrained effectively using the depressor. In addition, we have determined the mass ratios 309/308 for SRM 951 solution containing 5.7 μg $NO_3{}^-$ and 5.0 μg CNO^- ion with different volume of 1% H_3PO_4.

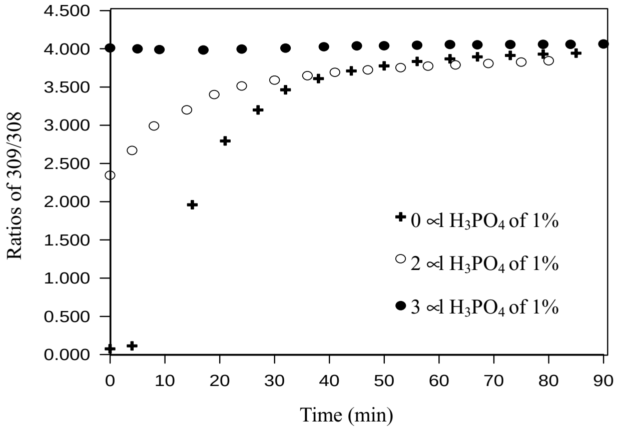


Fig. 6. Time variation of $R_{309/308}$ for NIST SRM 951 containing 5.7 μg of $NO_3{}^-$ in the presence of different volumes of the depressor.

For the sample of SRM 951 solution containing $NO_3{}^-$ ion (Table 3 and Fig. 6), it can been seen that with the increase in the volume of depressor the mass ratio 309/308 also increases and gradually approaches the normal isotopic ratio of NIST SRM 951(4.052). Moreover, the external precision is also improving accordingly. The initial mass ratio 309/308 is nearly equal to 4.052 when 3 μl H_3PO_4 is added. In this case, the isobaric interference of $Cs_2(CNO)^+$ ion is completely restrained after adding enough depressor solution.

Similarly, Table 4 shows that in the presence of CNO^-, the initial 309/308 ratios measured are around the value of 0.015, which is close to the calculated value according to the absolute isotope ratios of $^{15}N/^{14}N$, $^{13}C/^{12}C$, $^{17}O/^{16}O$ in nature [3]. After adding H_3PO_4 depressor, we can see that the initial 309/308 ratios approach the normal value of NIST SRM 951, which confirms that Cs_2CNO^+ ion has not been formed during the whole ionization procedure.

$BO_2{}^-$-NTIMS method. Choosing boron free seawater, $MgCl_2$ and NaOH, $La(NO_3)_3$ as promoters, we preliminarily measured the ratios of $R_{43/42}$ for pure NIST SRM 951 solution and SRM 951 containing $NO_3{}^-$ and H_3PO_4. Results are presented in Table 5.

In agreement with the data previously reported (Table 1), the mass ratios 43/42 of pure SRM 951 sample changes with the change of promoters used, $R_{43/42}$ ($MgCl_2 + NaOH$) > $R_{43/42}$ (boron free seawater) > $R_{43/42}$ ($La(NO_3)_3$). This confirms our conclusions outlined above, i.e., that the use of promoter in NTIMS, would introduce $NO_3{}^-$ ion into sample and subsequently result in the isobaric

Table 3
Boron isotopic composition of NIST SRM 951 containing 2.0 μg of boron and 5.7 μg of $NO_3{}^-$ after adding different volume of H_3PO_4

No.	Volume of 1% H_3PO_4 (μl)	Average current (A)	Average intensity (pA)	Single $R_{309/308}$		Average $R_{309/308}$ (2σ)
1	0	1.408	1.38	3.813486	3.852145	3.83282 ± 0.0273
2	2	1.586	1.30	3.911480	3.916969	3.91422 ± 0.0039
3	3	1.633	1.35	4.052894	4.050641	4.05177 ± 0.0016

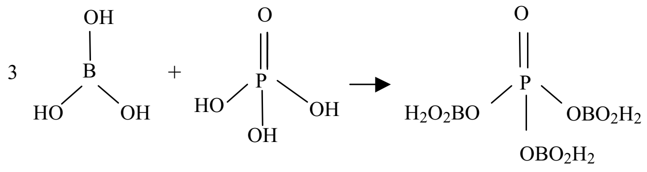
Table 4
Comparison of measured 309/308 ratios for SRM 951 containing 5.0 µg CNO^- in the presence and absence of H_3PO_4

Loaded	Heating current (A)	Ion intensity (10^{-12} A)	Measured 309/308 ratios		
			Initial	Single run	Average
2 µg B, 5.0 µg CNO^-	1.496	3.9	0.01553	3.67813	3.76485
	1.560	4.1	0.01681	3.85159	
2 µg B, 5.0 µg CNO^-, 1 µl 1% H_3PO_4	2.073	3.7	4.05892	4.04932	4.05135
	1.664	4.2	4.05823	4.05338	

interference. However, after adding H_3PO_4, it is obvious that the initial ratio of 43/42 raises and an average value approaches to that of ratio determined by PTIMS, 4.05037. From the preliminary experiment on NTIMS, the data are not ideal except for giving us a general trend, and we need search for the detailed experimental conditions later.

In addition, the results also show the discrepancy between the determined values for boron isotopic composition using PTIMS and NTIMS methods, which cannot only be ascribed to the intrinsic discrepancy of the instruments used and the isotopic fractionation due to the lighter mass of $BO_2{}^-$ ion, but also to the use of promoter containing $NO_3{}^-$.

Note that, after adding phosphoric acid, there is an evident increase of heating current (about 0.2–0.3 A) both in PTIMS and NTIMS mode. It would be due to the formation of a phosphate-ligand, in which the addition of phosphoric acid changes the morphological properties of boron (see Scheme 1).



Scheme 1.

3.3. Establishment of optimum condition for boron isotopic composition analysis and its application in natural samples

3.3.1. Conditional experiment and chemometric calculation

3.3.1.1. Conditional experiment. Orthogonal design and uniform design have been applied in chemical engineering and chemical research to establish the optimum technical and determination conditions. Here, we chose a mixed-level uniform design ($U_{12}(4^4) \rightarrow U_{12}(3\times4^3)$) in the design of an

Table 5
Boron isotopic composition of NIST SRM 951 obtained using different promoters

No.	Sample loaded	Filament	$V_{H_3PO_4}$ (µl)	Current (A)	I_{43} (mV)	Average $R_{43/42}$ measured (2σ)
$La(NO_3)_3$ as promoter						
1–1	0.2 µg B	Re	3	1.650	483	4.04175 ± 0.0011
1–2	0.2 µg B	Re	0	1.601	1950	3.98970 ± 0.0012
1–3	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	0	1.679	745	3.99489 ± 0.0019
1–4	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	3	1.655	1393	4.05112 ± 0.0082
1–5	0.5 µg B, 5.7 µg $NO_3{}^-$	Re	3	1.705	884	4.04732 ± 0.0199
Boron-free seawater as promoter						
2–1	0.2 µg B	Re	3	–	–	N.D.
2–2	0.2 µg B	Re	0	1.735	2575	4.00535 ± 0.0014
2–3	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	0	1.386	440	4.00202 ± 0.0007
2–4	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	3	1.430	13	4.05855 ± 0.0231
2–5	0.5 µg B, 5.7 µg $NO_3{}^-$	Re	3	1.535	10	4.05497 ± 0.1106
$MgCl_2$ and NaOH as promoter						
3–1	0.2 µg B	Re	3	1.900	24	4.01655 ± 0.1070
3–2	0.2 µg B	Re	0	1.799	2003	4.03422 ± 0.0088
3–3	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	0	1.800	340	4.01217 ± 0.0012
3–4	0.5 µg B, 1.0 µg $NO_3{}^-$	Re	3	–	–	N.D.
3–5	0.5 µg B, 5.7 µg $NO_3{}^-$	Re	3	–	–	N.D.

N.D.: not determined; –: unstable ion and quick decay.

Table 6
Corresponding value of each factor

Levers factors	1	2	3	4
A. SRM 951 boron content (μg)	0.5	1.0	2.0	
B. Mannitol content (μg)	0	1.0	2.0	4.0
C. Volume of 1% H_3PO_4 (μl)	0	1.0	2.0	3.0
D. NO_3^- content (μg)	0	0.1	1.0	5.7

experiment with the purpose to measure boron isotopic ratios (see Tables 6 and 7). $\delta^{11}B$ (‰) value reflects the $^{11}B/^{10}B$ ratio shifts between pure NIST SRM 951 and SRM 951 mixed with other reagents.

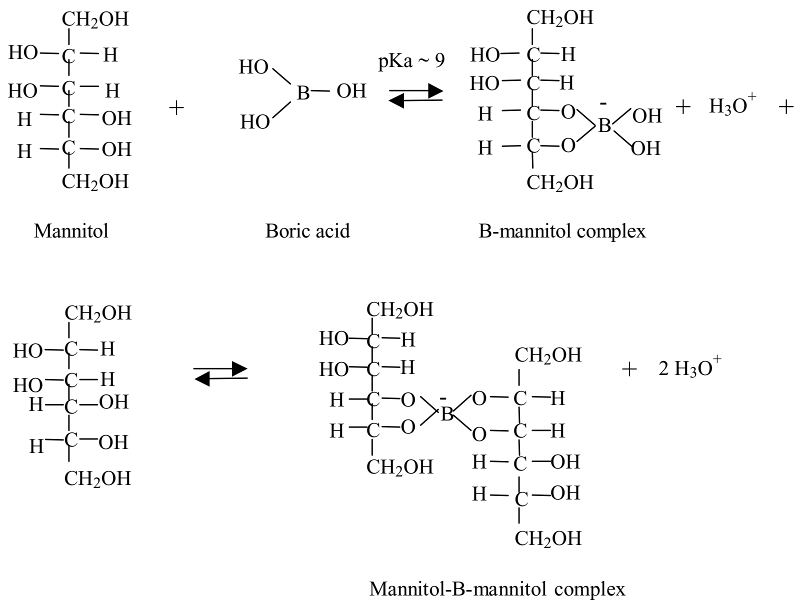
3.3.1.2. Interaction among different factors. To estimate the interaction among different factors, we calculated the alternant coefficient β_{ij} using a central quadratic polynomial model [25] (Eq. (1)) based on the results listed in Table 7. The value of β_{ij} indicates the degree of influence between factor i and factor j. The higher the value of β_{ij} is, the stronger the interaction between two factors. In Eq. (1) x_i represents each variable, x_1 boron content, x_2 mannitol content, x_3 volume of 1% H_3PO_4 added, x_4 NO_3^- content and y is response value of $\delta^{11}B$ (‰), viz. shift of $^{11}B/^{10}B$ determined.

$$\begin{aligned} y = {} & \beta_0 + \beta_1(x_1 - \bar{x}_1) + \beta_2(x_2 - \bar{x}_2) + \beta_3(x_3 - \bar{x}_3) \\ & + \beta_4(x_4 - \bar{x}_4) + \beta_{12}(x_1 - \bar{x}_1)(x_2 - \bar{x}_2) \\ & + \beta_{13}(x_1 - \bar{x}_1)(x_3 - \bar{x}_3) \\ & + \beta_{23}(x_2 - \bar{x}_2)(x_3 - \bar{x}_3) + \beta_{24}(x_2 - \bar{x}_2)(x_4 - \bar{x}_4) \\ & + \beta_{34}(x_3 - \bar{x}_3)(x_4 - \bar{x}_4) \end{aligned} \tag{1}$$

Using MATLAB, we calculated each alternant coefficient β_{ij}: −549.7, −129.6, −303.5, −181.9, −91.4, −91.2, 14.3, −114.5, −24.2, −23.7, respectively. As it is obvious, $\beta_{13} = 14.3$, $\beta_{24} = -24.2$, $\beta_{34} = -23.7$ are higher than other coefficients, which indicates that there is a stronger interaction between factor 1 (boron content) and factor 3 (volume of H_3PO_4), factor 2 (mannitol content) and factor 4 (NO_3^- content), factor 3 (volume of H_3PO_4) and factor 4 (NO_3^- content). This outcome basically agrees well with our experimental results and with the literatures.

(i) The interaction between boron content and volume of H_3PO_4 showed that the existence of H_3PO_4 would change the morphological properties of boron (as in Scheme 1), and restrain the further thermal reaction between boron and nitrate.

(ii) Generally, boric acid and borate are known to form stable esters with carbohydrate compounds in aqueous solution. So mannitol is widely used to prevent boron loss during the chemical manipulations and loading of boron. Much research has been done on the study of boron volatilization and its isotope fraction. Ishikawa [17] reported, the degree of volatilization and mass fractionation of boron decreases with increasing of mannitol/boron mole ratio, and the boron volatilization is completely suppressed when the ratio is more than unity. So the formation of this complex in the acids solutions allows us to make use of hydrofluoric and hydrochloric acids in the boron separation from natural samples. And as Xiao's [26] results, in the absence of mannitol, a significant negative shift of boron isotopic composition was observed in neutral solution and alkaline solution, but no evident isotopic fractionation of boron in acid solution. Whereas in the present of mannitol, the isotopic fractionation of boron is negligible in a neutral solution, but small negative isotopic shifts occurs in dilute HCl and alkaline solution. As



Scheme 2.

Table 7
The table of uniform design ($U_{12}(4^4) \rightarrow U_{12}(3 \times 4^3)$)

No	A	B	C	D	Average $R_{309/308}$	$\delta^{11}B$ (‰)
1	3(2.0)	3(2.0)	3(2.0)	3(1.0)	4.06099	2.11
2	1(0.5)	4(4.0)	4(3.0)	2(0.1)	4.04832	−1.01
3	2(1.0)	4(4.0)	1(0)	1(0)	4.05242	0
4	2(1.0)	3(2.0)	1(0)	4(5.7)	3.88324	−41.75
5	2(1.0)	1(0)	4(3.0)	4(5.7)	4.04873	−0.91
6	3(2.0)	2(1.0)	3(2.0)	2(0.1)	4.03765	−3.64
7	3(2.0)	2(1.0)	2(1.0)	3(1.0)	3.89901	−37.86
8	3(2.0)	1(0)	2(1.0)	1(0)	4.04982	−0.64
9	1(0.5)	4(4.0)	3(2.0)	4(5.7)	3.93457	−29.08
10	2(1.0)	3(2.0)	2(1.0)	2(0.1)	4.05426	0.45
11	1(0.5)	2(1.0)	4(3.0)	1(0)	4.05136	−0.26
12	1(0.5)	1(0)	1(0)	3(1.0)	3.65543	−97.96

Normalized to standard mean value $^{11}B/^{10}B = 309/308_{measured} - 0.00078 = 4.05164$.

Hu et al. [27] and van den Berg et al. [28], and Duggan et al. [29] reported, a full complex was presented as the mannitol–B-mannitol complex at pH 7, and the association constant log K (B-sugar) is 0.60–3.30.

The possible equilibrium between boric acid and the borate esters is exemplified in Scheme 2. It is clear that B-mannitol or mannitol–B-mannitol complex is favored in neutral or alkaline media, and higher pH can shift the equilibrium towards the formation of complex. According to the equilibrium constant K_a value, we calculated the percent of B-mannitol complex under different pH value (see Fig. 7). The percent of complex is less than 50% when the pH of solution equals 7, so boron cannot be well retained from volatilization and mass fractionation in an acidic solution even in the presence of mannitol, which is out of our original thought that prevents boron loss or isotopic fractionation occurred during evaporation of acidic solution using the formation of boron–mannitol complex.

Here, our theoretical calculations confirmed what Xiao et al. [3] has reported, i.e., that the interference of NO_3^- on boron isotopic measurement can be enhanced by the presence of mannitol. So, the addition of mannitol cannot prevent the loss of boron in acid medium, but worsen the interference of isobaric ion for boron isotope analysis by TIMS. Thus, to our knowledge, mannitol should be avoided during the pretreatment of natural samples with rich organic matter.

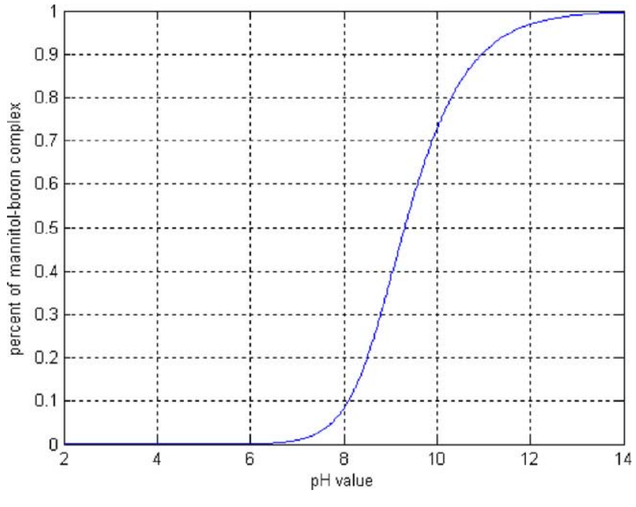


Fig. 7. Variation of percent of B-manntiol complex under different pH value.

(iii) The relationship between the volume of H_3PO_4 added and NO_3^- content further testified that H_3PO_4 could effectively prevent NO_3^- from translating into CNO^- with the presence of boron in ionization source of TIMS. The mechanism is unknown, but it is a very interesting topic to discuss sooner.

3.3.1.3. Establishment of optimum experimental condition. By using a multivariable linear regression technique, we got a regress equation:

$$y = -59.8 - 30.4x_1 + 6.9x_2 - 2.6x_3 - 51.3x_4 + 4.2x_3^2 + 8.1x_4^2 + 1.4x_3x_4 \qquad r^2 = 0.9275 \qquad (2)$$

Based on Eq. (2), the Nelder–Mead simplex method has been use to search for the optimal experimental condition. In theory, boron content could not affect boron isotopic, and mannitol is avoided using in case of severer interferences of isobaric ions according to our primary study. Providing x_1 is constant and x_2 equals to 0, then the best ratio of x_3 to x_4 is 0.56 if y value approaches 0. It means that the shift of $^{11}B/^{10}B$ caused by NO_3^- could be eliminated when a sufficient amount of H_3PO_4 is added. Commonly, the volume of 1% H_3PO_4 (μl) is 0.56-times to the mass of NO_3^- (μg).

3.3.2. Application in natural samples with trace nitrate and organic matter

The extraction and purification of boron from natural samples have been carried out following Section 2.2.2. In this case, the pretreatment of natural samples is simplified, without a procedure to remove organic matter and nitrate ion

Table 8
Boron isotopic composition of natural samples

No.	Sample type	Average $^{11}B/^{10}B$ measured (2σ)		$^{11}B/^{10}B$ reported
		Without H_3PO_4 loading	Loading H_3PO_4	
1	Coral 8#	4.15023 ± 0.0021	4.14694 ± 0.0041	4.14238 ± 0.0063[a]
2	Coral 11#	4.15058 ± 0.0069	4.14414 ± 0.0124	4.15244 ± 0.0016[a]
3	Coral 1#	4.14936 ± 0.0030	4.15444 ± 0.0026	
4	Coral 2#	4.14668 ± 0.0004	4.14684 ± 0.0077	
5	Coral 3#	4.14491 ± 0.0052	4.14657 ± 0.0015	
6	Seawater-SY	4.20898 ± 0.0043	4.20690 ± 0.0075	4.19829 ± 0.0015[a]
7	Seawater-1#	4.23475 ± 0.0017	4.22589 ± 0.0030	
8	Seawater-2#	4.20558 ± 0.0020	4.20592 ± 0.0146	
9	Seawater-3#	4.21214 ± 0.0016	4.21098 ± 0.0032	
10	Boric acid	3.94992 ± 0.0030	4.03111 ± 0.0087	

N.D.: no determination.
[a] See reference [30].

carefully by UV irradiation and hydrogen peroxide washing. Adding depressor during the measurement of boron isotopes can eliminate the isobaric interference from trace CNO^-.

To test analytical precision and accuracy of the method, we measured boron isotopic composition in different natural samples and contrasted our data with previous report.

It shows (Table 8) that our results are consistent with Zhang's report that employed UV irradiation and hydrogen peroxide washing during the pretreatment of natural samples. Obviously, the depressor H_3PO_4 eliminates isobaric interference when traces of organic matter exist in a sample solution, but do not induce any shift for boron isotopic analysis by thermal ionization mass spectrometer.

4. Conclusions

Our experimental results have shown that it is possible to eliminate isobaric interference in the analysis of boron isotope in natural samples with rich nitrate and organic matter, by using an ionization depressor and a simple pretreatment procedure. Compared with previous methods (UV irradiation, hydrogen peroxide washing, micro-sublimation), the technique is less time-consuming, more practical and simpler. Currently, the pathway and mechanism of the thermal reaction between CNO^- (or $NO_3{}^-$) ion and the depressor H_3PO_4 is unknown and needs to be further investigated.

Acknowledgements

We thank the National Natural Sciences Foundation of China for the support this research project through grant no. 40373006. We are very grateful to Professor Sasha Omanovic for English revision and Professor Zha Jinrong for very helpful suggestions on the conditional experiment design and data analysis.

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