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A robust methodology for high precision isotopic analysis of boron by thermal ionization mass spectrometry using $Na_2BO_2^+$ ion

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ABSTRACT

A detailed study to develop a robust methodology for determining $^{11}B/^{10}B$ isotope ratio using sodium metaborate ($Na_2BO_2^+$) in positive thermal ionisation mass spectrometry (P-TIMS) was performed. Different parameters of sample preparation and sample loading procedure, using single tantalum filament assembly, were optimized and their effects on ion intensity and precision in isotope ratio were evaluated. A comparative evaluation of precision achievable using Na_2CO_3 and NaCl to adjust the B/Na mole ratio in the sample was also carried out. This was done to confirm the robustness of the approach for analysing different kinds of sample matrices e.g., solids and solutions which require chemical purification and pre-concentration prior to TIMS analysis. NIST isotopic reference material SRM-951 with $^{11}B/^{10}B$ isotope ratio of 4.044 ± 0.003 was used for various experiments. Loading of boron in the form of boromannitol complex along with sodium carbonate (for solid samples) and with NaCl (for solutions) on the graphite coated single tantalum filament assembly was found to give high precision (better than 1‰) in the isotope ratios using 500 ng to 1 μg of boron. The results were not influenced by variations in the B/Na mole ratio, which is an important aspect of using this methodology for analyzing unknown samples. Robustness of the developed methodology is demonstrated by analyzing solid samples as well as solutions for boron isotopic composition.

1. Introduction

Precise and accurate data on $^{11}B/^{10}B$ isotope ratio, in a wide variety of samples, are required in many areas of research. These include isotope hydrology, marine biochemistry, geochemistry, cosmochemistry, environmental sciences, health sciences, nuclear technology etc. One of the well known reasons for this is that the $^{11}B/^{10}B$ amount ratio depends upon pH of the solution; with ^{10}B enriched in $B(OH)_4^-$ (tetrahedral) species and ^{11}B preferentially in $B(OH)_3$ (trigonal) species in pH between 7 and 11 [1]. A number of studies have demonstrated the potential of boron as a proxy to study sea water pH variation and atmospheric CO_2 concentrations [2,3]. Isotopic composition of B in coals has shown that the coals are ^{10}B enriched (negative $\delta^{11}B$ values) compared to terrestrial waters and thus is useful in tracing fluids derived from organic sources [4]. Boron is also an essential element for the growth of plant materials as well as for human life. In addition, the high thermal neutron absorption cross-section of ^{10}B (about 4000 barns) makes it an attractive nuclide for the nuclear reactor technology. As an example, B_2O_3 dissolved in D_2O, with an overall boron concentration of a few ppm, is used as a liquid poison in the moderator system of pressurized heavy water reactors (PHWRs). B_4C enriched in ^{10}B (60%–90%) is used as a control rod material in fast nuclear reactors [5].

The above mentioned applications require robust methodologies to determine isotopic composition of boron from bulk as well as in situ micro-scale samples. The different methodologies which have been used include thermal ionization mass spectrometry (TIMS) in the positive ($M_2BO_2^+$) [6–15] and negative ion mode (BO_2^-) [16–20], quadrupole and high resolution magnetic sector based multi-collector inductively coupled plasma mass spectrometry (ICP-QMS and MC-ICPMS) [21–25], secondary ion mass spectrometry (SIMS) [4], resonant laser-sputtered neutral mass spectrometry (SNMS) [26,27], laser mass spectrometry [28] etc. Boron amounts ranging from 0.1 ng to 500 ng are routinely analysed with precision values ranging from 0.1‰ to 10‰, i.e., a variation of two orders of magnitude [29,30]. In fact, inter-laboratory inter-comparison experiments are conducted from time to time to evaluate the status of precision in B isotope ratio measurements, with new developments in the instrumentation and experimental methodologies [31,32]. It is recognized that no technique is a panacea and each methodology has some limitations and can be suitable for solving specific problems. An evaluation of different analytical techniques was also published by Aggarwal and Palmer [33].

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B isotope ratio determination by P-TIMS or N-TIMS has an inherent problem of isotope fractionation in thermal ionization source, with the latter giving quite large isotope fractionation [34]. The P-TIMS has been used for more than four decades using $Na_2BO_2^+$ [6,15] and more recently by using $Cs_2BO_2^+$ ion, with a few hundred nanograms of boron (typically 500 ng) [10,12]. The use of $Cs_2BO_2^+$ ion reduces mass fractionation considerably due to high mass of the species being monitored (m/z 308 and 309) compared to $Na_2BO_2^+$ ion (m/z 88 and 89). However, in P-TIMS, there can be problems of isobaric interferences from Cs_2CNO^+ at m/z 308, particularly if the B solution contains HNO_3 and from ^{88}Sr, in case of $Na_2BO_2^+$ ion. The generation of $M_2BO_2^+$ (M = alkali metal) ions in P-TIMS requires a careful control of M/B mole ratio as well as special sample loading procedure on high purity single Ta filament assembly, using colloidal graphite and mannitol to enhance the formation of $M_2BO_2^+$ ion compared to M^+ ion. The range of M/B mole ratio in the sample needs be controlled more strictly when using $Cs_2BO_2^+$ ion in comparison to $Na_2BO_2^+$ ion, due to low ionization potential of Cs versus that of Na. At times, this can be a limiting factor when samples containing unknown amounts of boron have to be analysed. Isotopic analysis of B using BO_2^- provides very high sensitivity with a possibility to perform analysis with a few nanogram amounts (<10 ng) of boron. However, this also requires activators like boron free sea water or $Ba(OH)_2 + MgCl_2$ to enhance the formation of BO_2^- ion. One has to monitor the isobaric interference from CNO^- during N-TIMS analysis of boron. There is large mass fractionation in the ion source of the mass spectrometer due to low mass of the species (m/z 42 and 43) being used for analysis. Recently, total evaporation was reported [17] in N-TIMS, but this would necessitate loading sub-ng amount of boron which demands a very strict control of the laboratory/reagents blank. Using 400 pg loading, a total analysis time of about 2 h was required for carrying out total evaporation in N-TIMS. In fact, natural boron contamination is very common and can be checked by running an enriched B isotope solution through the complete procedure. Generally, meticulous loading and mass spectrometric analyses protocols are necessary to achieve high precision by P-TIMS and N-TIMS.

ICP-QMS and MC-ICPMS are quite popular techniques for $^{11}B/^{10}B$ isotope ratio determinations in variety of samples including biological fluids (serum, plasma, urine etc.), environmental samples (ground water, river water etc.), marine carbonates (foraminiferas, corals etc.). ICP-QMS systems provide relative precision values of about 1% and are used for biological samples or enrichment plants where high precision and accuracy are not mandatory. However, MC-ICPMS systems are quite popular these days, due to the possibility of achieving high precision (0.01% or better) in isotope ratios. Mass fractionation is also encountered in ICPMS due to space charge effects leading to preferential transmission of heavier isotope through skimmer cone. This is usually accounted for by using standard-sample-standard bracketing approach. Generally NIST-SRM-951 with $^{11}B/^{10}B$ certified isotope ratio close to natural, is used in the bracketing procedure. When analyzing samples with widely different ^{10}B contents, there is a problem of memory effect which is one of the main limitations of ICPMS systems. Several attempts are reported in literature to understand and minimize the memory effects, but the challenge still remains. Different kinds of wash solutions have been employed including NaF [21], Triton-X-100 [22], NH_3 [23], mannitol [24], but with a limited success. Direct injection nebulization (DIN) [25] avoids contact of the aerosol with plasma torch and spray chambers and overcomes the memory effect. Nevertheless, the carry-over effect is negligibly small when dealing with environmental samples e.g., marine carbonates, where one is interested in determining a few per mil (‰) changes in the $^{11}B/^{10}B$ isotope ratios. Further, solution based-ICPMS cannot provide distribution of boron in histological preparations required in boron neutron capture therapy (BNCT) [35].

Resonant laser-SNMS using electron impact gun for sputtering, Ga^+ primary ion source and a gridless reflectron ToF mass analyzer was employed for determining B isotope ratios in a single foraminifera calcite shell. Three-step ionization scheme accomplished with two tunable dye lasers and the fundamental wavelength of Nd-YAG laser was used. However, limited accuracy was reported [27] and the authors suggested an improvement by increasing the repetition rate of the measurements cycles and/or by using primary ion guns with very high ion currents. Marine carbonates have been analysed recently using a single collector Cameca ims 4f SIMS instrument (primary ion beam of $^{16}O^-$, 15 keV energy, beam current 10–40 nA, resolving power 1600) as well as with a multicollector Cameca ims 1270 SIMS machine (5 nA, 22 keV $^{16}O^-$ primary ion beam and resolving power of 2400). These kind of in situ isotopic analysis of biogenic carbonates are still in its infancy [2]. Laser ionization mass spectrometry using a reflectron-time of flight mass spectrometer (R-TOFMS) was reported [5] for the routine isotopic analysis of boron using graphite as a matrix and Q-switched Nd-YAG (532 nm) laser. A negative bias of about 4% was obtained for $^{11}B/^{10}B$ isotope ratios with atom% of ^{10}B values agreeing within 1% of the expected data.

Thus, despites advances in different mass spectrometric instrumentations and methodologies, P-TIMS is the method of choice to achieve high precision in the B isotope ratios, when dealing with samples of widely different $^{11}B/^{10}B$ ratios, as required in nuclear science and technology. The $M_2BO_2^+$ ion used in P-TIMS for B isotopic analysis is generated by converting boron to an alkali tetraborate where the alkali metal (in the form of carbonate, hydroxide or chloride) can be lithium, sodium, potassium, rubidium or cesium. Among these Li, Rb and K are multi-isotopic elements resulting in the distribution of ion current over a wide mass range and this reduces the intensity of the monitoring ions. In addition, the peaks to be used for calculating the $^{11}B/^{10}B$ isotope ratio from the observed intensities need be selected judiciously and this depends upon the relative proportions of ^{11}B and ^{10}B in the given sample. Mono-isotopic alkali metals viz. Na and Cs are preferred since the mass spectra are simple and the $^{11}B/^{10}B$ isotope ratio can be directly obtained from the intensities of the two consecutive peaks corresponding to $M_2{}^{10}B^{16}O_2^+$ and $M_2{}^{11}B^{16}O_2^+$, after subtracting a small contribution of ^{17}O at the latter peak. Though $Cs_2BO_2^+$ (m/z 308,309) has high mass, but simultaneous multi-collection of both the ions is not possible in many of the old versions of TIMS machines (e.g., MAT-261) existing in various laboratories, due to the physical limitation of adjusting the Faraday cups. Therefore, the use of $Na_2BO_2^+$ ion continues to be one of the approaches for the isotopic analysis of boron. A comparison of the $^{11}B/^{10}B$ isotope ratios obtained for NIST-SRM-951 isotopic standard in literature reveals that the sample loading conditions followed such as pH of the loading solution, addition of mannitol in the boron solution, pre-coating the single Ta filament with graphite, the B/alkali mole ratio are important parameters to obtain high precision in the isotopic analysis of boron. As a matter of fact, inter-laboratory inter-comparison experiments conducted [31,32] demonstrate the need to carry out further investigations for making the different mass spectrometric approaches quite robust so that these do not remain restricted to a few specialized laboratories and can be adopted by various laboratories around the globe. The work presented in the present manuscript is an attempt, towards this aim, using the decades old method of $Na_2BO_2^+$ ion for B isotopic analysis. The TIMS analysis using $Na_2BO_2^+$ ion can be done by loading the sample on a single Ta filament with or without coating the filament with graphite as well as with or without the addition of mannitol to boron solution. Further, there is no consensus on the B/Na mole ratio necessary under different loading conditions as well as the sodium compound to be used for achieving optimum B/Na mole ratio. Recently, we reported a method for precise determination of $^{11}B/^{10}B$ isotope ratio inde-

pendent of B/Na mole ratio (range 5–0.05) using mannitol and NaCl with boron for loading on graphite coated Ta filament [15]. However, there are instances where either the pH of the boron solution is controlled prior to loading [8] or the loaded solution is acidified on the filament [14] to obtain precise $^{11}B/^{10}B$ isotope ratio.

Since boric acid is a weak acid, the formation of the borate compound for mass spectrometric analysis involves a complicated set of parameters such as the extent of neutralization leading to the formation of different borates, with different physical properties like melting point, boiling point, decomposition temperature of the borates etc. Also for determination of boron isotopic composition in geological or in nuclear samples, the separation methods followed such as methyl borate distillation, pyrohydrolysis, extraction with 2-ethyl 1,3 hexane-diol (EHD), chromatographic technique using Amberlite IRA 743 have different extraction efficiencies with the purified boron available in neutral, acidic or alkaline medium after separation. Therefore, detailed studies on the sample preparation as well as loading procedure are necessary to make the P-TIMS approach more robust. The present investigations were, therefore, aimed at understanding the individual effects of the various reagents used such as Na_2CO_3, NaCl, Mannitol and pre-coating of filament with graphite on the precision achievable in determining $^{11}B/^{10}B$ isotopic ratio.

The present manuscript gives the results obtained by studying these parameters individually for B isotope ratio measurements using $Na_2BO_2^+$ ion. We believe that these investigations would allow different laboratories to obtain precision values equal to or better than those achievable by using $Cs_2BO_2^+$ ion in P-TIMS.

2. Experimental

A single focusing TIMS (Isoprobe-T, Micromass U.K) with 9 Faraday cups for multi-collection was employed in the present work. High purity Tantalum single filament assemblies with dimensions (10 mm × 1 mm × 0.04 mm) were used for loading the samples. Boron solution of isotopic reference material NIST-SRM 951 was used for preparing different samples. Various mixtures of boron and sodium with B/Na mole ratios ranging from 0.05 to 5 were prepared separately using sodium carbonate and sodium chloride. The amount of mannitol, whenever used, was 40 times that of boron to form a 1:2 complex of boron with mannitol. All the samples were evaporated to near dryness before use. Bare Ta filaments as well as graphite coated Ta filaments were used in the present studies. The graphite slurry was prepared by mixing 40 mg of graphite in 1 mL of 50% ethanol. 2–3 μL of the slurry was used for coating the Ta filament on which the boron solution was loaded. About 1 μg of boron per filament was used for loading in each experiment. Heating of the filament in the ion source was programmed to heat upto 1.6 A in 10 min, followed by a waiting period of 10 min. Finally, the temperature of the filament was increased further, in steps, to obtain a steady signal for data acquisition. Different sample preparation and loading conditions were studied. These were (i) use of bare and graphite pre-coated filaments for boric acid with sodium carbonate, (ii) sodium carbonate + mannitol versus NaCl + mannitol with boric acid on graphite coated filament. In each case, the intensity of the major ion beam as well as the $^{11}B/^{10}B$ isotope ratios were obtained by recording the data for a number of blocks, each block consisting of 12 scans. Static mode of multi-collection was employed for data acquisition.

3. Results and discussion

Fig. 1 shows the different $^{11}B/^{10}B$ isotope ratios reported for NIST SRM 951 by different laboratories using sodium borate and cesium borate. It is obvious that despite the fact that P-TIMS has been used for quite some, still a significant scatter in the isotope ratio is observed among values determined by different laboratory, even in a well characterized sample like NIST standard.

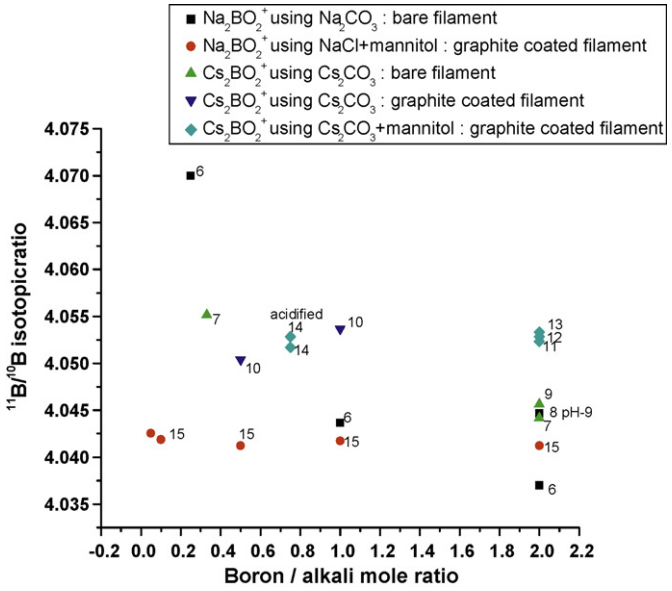

Fig. 1. $^{11}B/^{10}B$ isotope ratios in NIST-SRM-951 determined by different laboratories using $Na_2BO_2^+$ and $Cs_2BO_2^+$. The numbers in parentheses are the literature references.

Tables 1a and 1b give the $^{11}B/^{10}B$ isotope ratios obtained during the present investigations for NIST SRM-951 under different loading conditions as well as using different B/Na mole ratios, by mixing boric acid with Na_2CO_3. Data given in Table 1a compares the results obtained using bare filament as well as graphite coated filament. In both the cases, the $^{11}B/^{10}B$ isotope ratio obtained varies with B/Na mole ratio used for sample preparation. The graphite coated filament analyses show less variation in the data (0.42%) compared to that in the bare filament (1.25%) for an overall variation in the B/Na mole ratio of 5 to 0.05 (i.e., two orders of magnitude). For isotope ratio determination of boron from bare filament, best results are obtained when B/Na ratio is between 2 and 5. It is clear that graphite coated filament is superior to bare filament for improving precision in the measurement of boron isotope ratios. Therefore, all further studies were done using graphite coated filaments.

Table 1b gives a comparison of data obtained using Na_2CO_3 versus NaCl along with boromannitol complex as well as the effect of different B/Na mole ratios in each case. It may be noted that pH of the solution was constant (about 5) for all the experiments with NaCl, whereas the pH values changed from 5 to 10 with different

Table 1a
A comparison of uncoated (bare) and graphite coated Ta filament for $^{11}B/^{10}B$ isotope ratios in NIST-SRM-951 (mixing boric acid with Na_2CO_3).

B/Na mole ratio	Bare (uncoated) Ta filament		Graphite coated filament
	$^{11}B/^{10}B$ ratio	pH of solution	$^{10}B/^{11}B$ ratio
5	4.0331 (0.05)*	~6.5	4.0339 (0.02)*
2	4.0381 (0.04)	~9	4.0404 (0.04)
1	4.0453 (0.10)	~10	4.0464 (0.10)
0.50	4.0469 (0.04)	~11	4.0464 (0.06)
0.25	4.0763 (0.18)	~11	4.0481 (0.11)
0.10	4.0841 (0.14)	~11	4.0507 (0.06)
0.05	Insufficient signal	~11	4.0508 (0.15)
Average $^{11}B/^{10}B$ ratio	4.0534 (0.55)		4.0452 (0.15) 4.0485 (0.05)**
Range of $^{11}B/^{10}B$ ratio obtained (%)***	1.25%		0.42%

Table 1b
A comparison of $^{11}B/^{10}B$ isotope ratio determined in NIST-SRM-951 using Na_2CO_3 and NaCl for adjusting B/Na mole ratio (boromannitol complex and graphite coated filaments).

B/Na mole ratio	Using Na_2CO_3		Using NaCl (pH ~5)
	$^{11}B/^{10}B$ ratio	pH of solution	$^{11}B/^{10}B$ ratio
5	4.0401 (0.05)*	~5.3	4.0419 (0.03)*
2	4.0426 (0.06)	~6	4.0422 (0.03)
1	4.0473 (0.07)	~7	4.0417 (0.04)
0.50	4.0506 (0.03)	~8	4.0420 (0.03)
0.25	4.0462 (0.06)	~8.5	4.0419 (0.03)
0.10	4.0502 (0.04)	~10	4.0409 (0.04)
0.05	4.0486 (0.10)	~10	4.0412 (0.04)
Average $^{11}B/^{10}B$ ratio	4.0465 (0.10) 4.0486 (0.05)**		4.0417 (0.03) 4.0415 (0.02)**
Range of $^{11}B/^{10}B$ ratio obtained (%)***	0.26%		0.04%

* Relative standard deviation, in percentage, obtained for 4 independent filament loadings.
** Average for the B/Na mole ratios from 1 to 0.05.
*** Difference between the lowest and the highest value for different B/Na mole ratios.

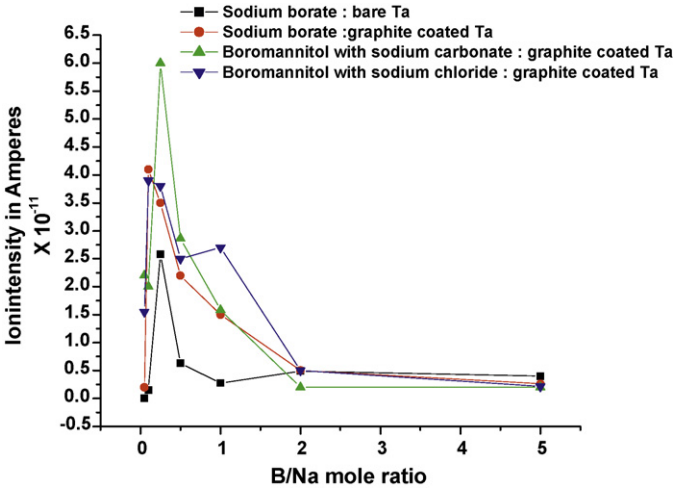

Fig. 2. Dependence of ion intensity of ^{11}B monitored at m/z 89 for NIST-SRM-951 with B/Na mole ratio using different procedures of sample preparation and sample loading.

B/Na mole ratios in case of Na_2CO_3. It is seen that the variation in the isotope ratio of boron with change in the B/Na mole ratio narrows down in the presence of mannitol. This is attributed to the fact that mannitol prevents formation of different species of boron, converting the entire amount of boric acid to tetrahedral species. This is in contrast to pure aqueous solutions where conversion to tetrahedral species depends on the basicity of the solution. Boric acid has a weak dissociation constant, ($K_a = 6.4 \times 10^{-10}$) but becomes a much stronger acid ($K_a = 1.5 \times 10^{-4}$) in presence of mannitol, and this enhances the progress of neutralization reaction of boric acid. As can be seen from the data in Table 1b with NaCl, the pH and the $^{11}B/^{10}B$ isotopic ratio is constant for the entire range of B/Na ratio studied with the isotope fractionation factor 1.0005. With Na_2CO_3 at higher pH corresponding to B/Na mole ratio 1 to 0.05, a higher but nearly constant $^{11}B/^{10}B$ ratio was observed with a fractionation factor of 0.9988. This is comparable to the $^{11}B/^{10}B$ ratio obtained when precoated graphite filament is used. Similar observations have been reported for the cesium borate method [10–14]. It is observed that use of NaCl significantly reduces the dependence of precision on B/Na mole ratio, giving an overall variation of (0.04%) compared to a variation of 0.26% with Na_2CO_3 for sample preparation. These studies demonstrate that use of graphite coated filament and boromannitol complex with NaCl is the best option to achieve high precision in the B isotope ratio determination using $Na_2BO_2^+$ ion. However, the precision values obtained during different mass spectrometric analyses are not significantly different when using NaCl or Na_2CO_3. This observation gives us confidence in the data obtained using different methods of purification e.g., using Amberlite 743 resin (for natural water) or separations using methyl borate distillation (for metals). In the former, loading procedure is based on NaCl + mannitol, whereas for the latter, sodium carbonate (B/Na in the range of 1 to 0.1) with mannitol is helpful in retaining boron during evaporation. Also solutions received directly from ^{10}B enrichment plants (using anion exchange based isotopic separation) are acidic emulating the NaCl based procedure. Again the above observations are important since some times, when solid samples of boric acid or boron carbide are to be analyzed, fusion of the mixture (paste) of sample with sodium carbonate can be done directly on the filament obviating the need of dissolving the solid sample.

Figs. 2 and 3 show the variation of ion intensity of ^{11}B (calculated as average intensity obtained during 3 blocks, each block consisting of 12 scans) and $^{11}B/^{10}B$ atom ratio, respectively, as a function of B/Na mole ratio using different procedures of sample preparation and sample loading. It is clearly seen from Fig. 2 that filament precoated with graphite is superior to bare filament for getting higher intensity. The ion intensity of ^{11}B decreases with increasing B/Na mole ratio and the $^{11}B/^{10}B$ isotope ratio values are quite consistant for B/Na mole ratios of 2 and 5. It is also noticed that with graphite coated filament and employing Na_2CO_3 and NaCl for adjusting the B/Na mole ratio, highest intensity is obtained for B/Na mole ratio of 0.25 for both Na_2CO_3 and NaCl. However, as can be seen from Fig. 3, the $^{11}B/^{10}B$ isotope ratio showed increased fractionation at low B/Na mole ratios which is significant for loadings on bare filament. This was attributed to the existence of different boron species on the filament. As shown in Table 2, a variety of sodium borates can be formed depending upon the ratio of $Na_2O:B_2O_3:xH_2O$. For example, polyborates are essentially formed at intermediate pH when the B/Na mole ratio is more than 1 and monomeric species are formed at higher pH [36]. It is well known that the fractionation in TIMS is affected by the molecular weight as well as volatility of the species evaporating from the filament.

100 fold increase in $Cs_2BO_2^+$ ion yield was also reported by Xiao et al. [10] by using graphite coated filament and this was explained on the basis of increase in the work function of filament. We observed two benefits when using graphite coated filament. First, it acts as an activator for the $Na_2BO_2^+$ ion formation with average ion intensity for three blocks increasing steadily from 5×10^{-12}

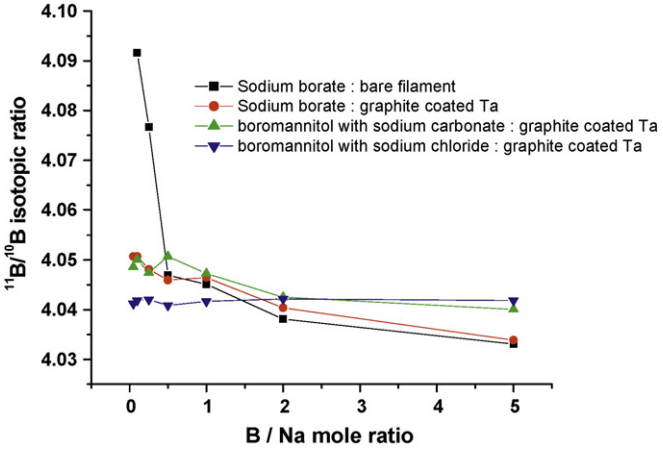

Fig. 3. Variation in $^{11}B/^{10}B$ isotope ratio of NIST-SRM-951 with B/Na mole ratio using different procedures of sample preparation and sample loading.

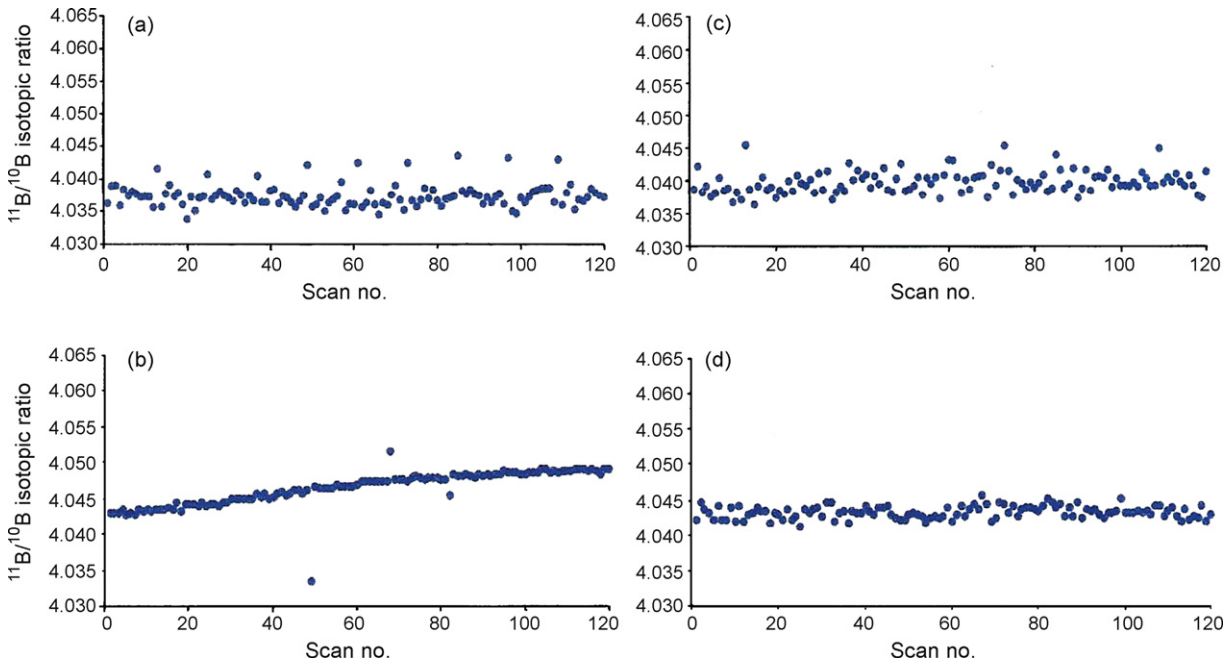

Fig. 4. (a) $^{11}B/^{10}B$ isotopic ratio in different scans for NIST-SRM-951 on graphite coated filament (Using Na_2CO_3 + mannitol, B/Na mole ratio = 5); (b). $^{11}B/^{10}B$ isotopic ratio in different scans for NIST-SRM-951 on graphite coated filament (Using Na_2CO_3 + mannitol, B/Na mole ratio = 0.25); (c). $^{11}B/^{10}B$ isotopic ratio in different scans for NIST-SRM-951 on graphite coated filament (Using NaCl + mannitol, B/Na mole ratio = 5); (d). $^{11}B/^{10}B$ isotopic ratio in different scans for NIST-SRM-951 on graphite coated filament (Using NaCl + mannitol, B/Na mole ratio = 0.25).

Table 2
Some known sodium borates reported in literature [36,38].

$Na_2O:B_2O_3:xH_2O$	Formula	Name
2:1:1,5	$Na_4B_2O_5{\cdot}xH_2O$	Disodium borate
1:1:0.5,2,4,6,8,12	$NaBO_2{\cdot}xH_2O$	Sodium metaborates
1:2:1,2,4,5,10	$Na_2B_4O_7{\cdot}xH_2O$	Sodium tetraborates
2:5.1:3.5	$Na_4B_{10.2}O_{17.3}{\cdot}7H_2O$	Ezcurrite
2:5:1,3,4,5,7	$Na_4B_{10}O_{17}{\cdot}xH_2O$	5Nasinite
3:8:10	$Na_6B_{16}O_{27}{\cdot}10H_2O$	–
1:3:2	$NaB_3O_5{\cdot}2H_2O$	Sodium triborate
2:9:11	$Na_4B_{18}O_{29}{\cdot}11H_2O$	–
1:5:0.5,1,2,4,10	$NaB_5O_8{\cdot}xH_2O$	Sodium pentaborates

A (for B/Na mole ratio of 5) to 4×10^{-11} A (for B/Na mole ratio of 0.1), for about 1 μg of boron on filament. Good ion intensity (nearly 10^{-11} A) was observed even at very low B/Na mole ratio of 0.05. Second, the dependence of $^{11}B/^{10}B$ isotope ratio on B/Na mole ratio (range 1–0.1) was also found to reduce. This can be attributed to the reducing properties which leads to reduction of excess of sodium carbonate or sodium oxide when the filament is heated to a temperature of about 900 °C [37]. The $^{11}B/^{10}B$ isotope ratio for NIST-SRM-951 standard was calculated to be 4.0485 ± 0.0020 (Table 1a) with a small isotope fractionation factor (K = true ratio/observed ratio) of 0.9988. The benefit of high sensitivity with good precision is best observed when boron is loaded as sodium salt of the boron mannitol complex on graphite.

Fig. 4(a) and (b) show the variation of isotopic ratios in the samples for B/Na mole ratios of 5 and 0.25 using Na_2CO_3. Results obtained using NaCl under the exactly same conditions are shown in Fig. 4(c) and (d). It is obvious that the data obtained using NaCl are more precise compared to those with Na_2CO_3 and the former shows negligibly small dependence of the observed $^{11}B/^{10}B$ isotope ratio on the B/Na mole ratio.

3.1. TIMS analysis of different unknown boron samples

Different kinds of samples are received in our Department for the determination of isotope ratios of boron. These include boric acid powder, D_2O moderator water samples, samples enriched and depleted in ^{10}B (compared to natural boron) from enrichment plant, ground water samples for isotope hydrology etc. The extraction, pre-concentration and sample preparation procedure depends on the type of sample. For boric acid powder or concentrated boric acid samples in water (mg of boron/mL of solution), a few μg of boron is used for loading and B/Na mole ratio is adjusted to about 2 with sodium carbonate, prior to loading directly on graphite coated Ta filament. However, for ground water and moderator samples, prior separation of boron from matrix or a preconcentration step is essential. In these case, mannitol is added to avoid boron loss during heating. The results shown in Tables 3a and 3b are for the analyses of sea water samples as well as for depleted and enriched ^{10}B samples from an enrichment plant. The Table also gives δ ^{11}B values for each sample w.r.t. NIST standard. It is seen that δ ^{11}B values remain unaffected when similar loading procedures are followed for the sample and the standard. For example, in case of ground

Table 3a
$^{11}B/^{10}B$ obtained for sea water samples using different loading procedures.

Experiment no.	pH of loading solution	$^{11}B/^{10}B$ atom ratio		$\delta^{11}B^{**}$ (‰)
		NIST-SRM-951	Sea water	
1	Acidic (~6)	4.0409 (0.02)*	4.2052 (0.02)	40.7
2	Basic (~8)	4.0463 (0.02)	4.2128 (0.01)	41.1

* % Relative standard deviation obtained from 5 blocks, each block consisting of 12 scans.
** Calculated with respect to experimentally determined isotope ratio in NIST-SRM-951 by same procedure.

Table 3b
$^{11}B/^{10}B$ isotope ratio determination in boron samples enriched and depleted in ^{10}B.

Loading conditions	NIST-SRM-951	Enriched B-sample-1		Enriched B-sample-2		Depleted B-sample-3	
	$^{11}B/^{10}B$ ratio	$^{11}B/^{10}B$ ratio	$\delta\ ^{11}B^{**}$ (‰)	$^{11}B/^{10}B$ ratio	$\delta\ ^{11}B^{**}$ (‰)	$^{11}B/^{10}B$ ratio	$\delta\ ^{11}B^{**}$ (‰)
B/Na ~0.5 (NaCl)	4.0417 (0.02)*	2.7401 (0.01)	−322	1.4227 (0.01)	−648	6.555 (0.03)	622
B/Na ~2 (Na_2CO_3)	4.0380 (0.02)	2.7395 (0.01)	−322	1.4192 (0.01)	−648	6.547 (0.03)	621

* % Relative standard deviation obtained from 5 blocks, each block consisting of 12 scans.
** Calculated with reference to experimentally determined isotope ratio in NIST-SRM-951.

water or sea water samples, a separation procedure using boron specific resin Amberlite IRA- 743, was followed and subsequently, mannitol was added during preconcentration of the acidic solution to prevent loss of boron. For experiment 1, the eluted boron solution (10 mL of 1 M HCl) was pre-concentrated after addition of sodium carbonate so that B/Na mole ratio was ~0.25. The addition of sodium carbonate in presence of acid and subsequent heating would result in removal of carbonate and conversion to sodium chloride. Repeated washings gave a solution of pH nearly 6 when tested on a graded pH paper. However, for experiment 2, the eluted solution was pre-concentrated in presence of mannitol alone, without addition of sodium carbonate and the solution was basic (pH 8). Similar $\delta\ ^{11}B$ values, within the experimental uncertainties, are obtained in the two cases. Thus when analyzing seawater or other geological samples, it is advisable to follow the same treatment procedure for sample and standard. Table 3b gives data for samples analysed by using two different loading procedures. The comparable $\delta^{11}B$ values suggest that the above observations are valid for a wide range of isotopic ratios.

4. Conclusions

The studies demonstrate that high precision in determining $^{11}B/^{10}B$ isotope ratio can be obtained using $Na_2BO_2^+$ ion in TIMS. The precision values obtained are in the order: boromannitol complex with NaCl on graphite coated filament > boromannitol complex with Na_2CO_3 on graphite coated filament > sodium borate on graphite coated filament > sodium borate on bare Ta filament. The formation of $Na_2BO_2^+$ from the reaction of boromannitol complex with NaCl or Na_2CO_3 is advantageous since B/Na mole ratio need not be strictly controlled. It is a desirable feature when analyzing different types of samples containing unknown amounts of boron and also requiring different sample pretreatment procedures. Thus a robust methodology for the determination of B isotope ratios, with precision better than 1 ‰, in different kinds of samples, is demonstrated in the present studies. It would be interesting to employ total evaporation and ion current integration in P-TIMS for $Na_2BO_2^+$ ion and evaluate the precision and accuracy by employing certified reference materials prepared by mixing enriched isotopes on weight basis, over a broad range of $^{11}B/^{10}B$ isotope ratios.

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