

# A REVIEW ON THE DETERMINATION OF ISOTOPE RATIOS OF BORON WITH MASS SPECTROMETRY

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The present review discusses different mass spectrometric techniques—viz, thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICPMS), and secondary ion mass spectrometry (SIMS)—used to determine  $^{11}\text{B}/^{10}\text{B}$  isotope ratio, and concentration of boron required for various applications in earth sciences, marine geochemistry, nuclear technology, environmental, and agriculture sciences, etc. The details of the techniques—P-TIMS, which uses  $\text{Cs}_2\text{BO}_2^+$ , N-TIMS, which uses  $\text{BO}_2^-$ , and MC-ICPMS, which uses  $\text{B}^+$  ions for bulk analysis or  $\text{B}^-$  and  $\text{B}^+$  ions for in situ micro-analysis with SIMS—are highlighted. The capabilities, advantages, limitations, and problems in each mass spectrometric technique are summarized. The results of international interlaboratory comparison experiments conducted at different times are summarized. The certified isotopic reference materials available for boron are also listed. Recent developments in laser ablation (LA) ICPMS and QQQ-ICPMS for solids analysis and MS/MS analysis, respectively, are included. The different aspects of sample preparation and analytical chemistry of boron are summarized. Finally, the future requirements of boron isotope ratios for future applications are also given. Presently, MC-ICPMS provides the best precision and accuracy (0.2–0.4‰) on isotope ratio measurements, whereas N-TIMS holds the potential to analyze smallest amount of boron, but has the issue of bias (+2‰ to 4‰) which needs further investigations. © 2016 Wiley Periodicals, Inc. Mass Spec Rev 9999: 1–21, 2016.

**Keywords:** boron; mass spectrometry; thermal ionization mass spectrometry; inductively coupled plasma mass spectrometry; secondary ion mass spectrometry; laser ablation; isotopic reference materials; nuclear technology; marine science; geo- and earth sciences; B/Ca ratio

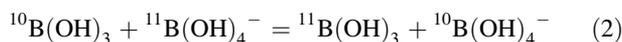
## I. INTRODUCTION

Boron (B) is a light element that has two isotopes  $^{10}\text{B}$  and  $^{11}\text{B}$  with 19.9 atom% and 80.1 atom% abundances, respectively. Boron exists in solution in two forms—viz, trigonal boric acid  $\text{B}(\text{OH})_3$  and tetrahedral borate anion  $\text{B}(\text{OH})_4^-$ . These two forms equilibrate in solution, and their relative proportions depend

upon the pH of the solution, as given below



Trigonal  $\text{B}(\text{OH})_3$  is predominant in acidic solutions whereas the tetrahedral anionic form is predominant in basic solutions.  $\text{B}(\text{OH})_3$  is more enriched in  $^{11}\text{B}$ , whereas  $\text{B}(\text{OH})_4^-$  is more enriched in  $^{10}\text{B}$  as given below. This is because of differences in the vibrational frequencies of the two boron isotopes and the molecular coordination between boron species in solution.



The anionic form gets incorporated into marine organisms (i.e., the corals or foraminifera shells) during their growth in the sea from calcium carbonates and thus  $^{11}\text{B}/^{10}\text{B}$  isotope ratio in marine carbonates is a useful proxy for paleo-pH and thus paleo- $\text{CO}_2$  (Vengosh et al., 1991; Hemming & Hanson, 1992). The dissociation constant ( $\text{pK}_\text{B}$ ) between these two forms of boron is 8.8 at 281.7 K and at 35.7 practical salinity unit. This dissociation constant depends upon salinity, ionic strength, temperature, pressure (Dickson, 1990; Millero, 1995), and major ion chemistry (Hain et al., 2015). Further, boron is geochemically incompatible and has high volatility, which leads to its migration and enrichment in Earth's upper continental crust compared to primitive mantle (Tonarini, Pennisi, & Gonfiantini, 2009). A large isotope fractionation exists in solution with borate anion depleted in  $^{11}\text{B}$ . Experimentally, a value of  $1.0272 \pm 0.0006$  was obtained for boron isotopic equilibrium constant at 25°C, salinity of 35 and ionic strength of 0.70 mol.  $\text{kg}^{-1}$  water (Klochko et al., 2006). Recently, an isotope fractionation factor of  $26.0 \pm 1.0\%$  at 25°C was determined (Nir et al., 2015) for boron in sea water. These data are corroborated by the *ab initio* molecular orbital calculations (1.0207–1.0360 by Oi (2000); 1.027 by Liu & Tossell (2005); 1.020–1.050 by Zeebe (2005); 1.026–1.028 by Rustad et al. (2010)). The residence time of boron in sea water is about 14 Myr (Lemarchand et al., 2000) with  $\delta^{11}\text{B}$  value of  $+39.61 \pm 0.04\%$  (Lemarchand et al., 2002a; Simon et al., 2006). Because the B residence time is much greater than the mixing time of the oceans (about 1,000 years), the isotopic composition of boron is uniform in sea water. It was also shown experimentally that sea water is isotopically homogeneous with respect to boron with a mean concentration of about  $416 \mu\text{mol. kg}^{-1}$  (Foster, Pogge von Strandmann, & Rae, 2010). In view of the isotopic homogeneity, boron isotopes find

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increasing interest to understand environmental processes. A precision of better than 1‰ (2 SD) is needed in boron isotope ratio data for pH reconstruction with a resolution of about 0.1 pH (Foster et al., 2006). The high precision of 0.2–0.4‰ in boron isotope ratio data is required at low pH, because the slope of  $\delta^{11}\text{B}$  curve gets shallower at low pH.

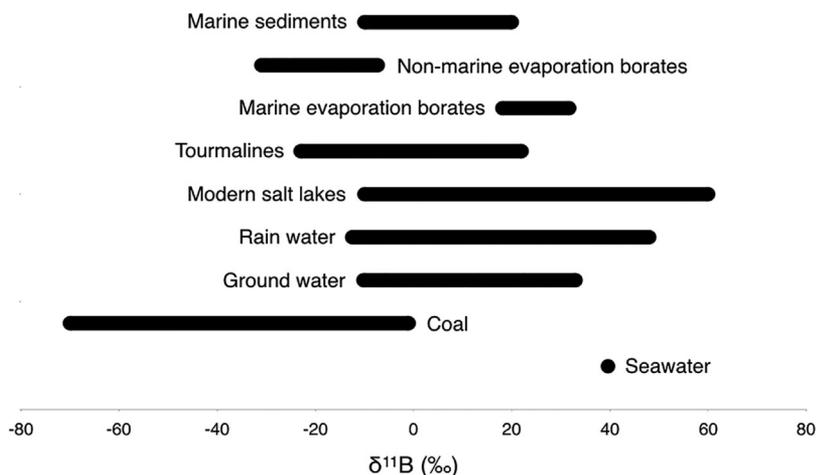
The isotope ratios of boron show large variations in nature (Fig. 1), and are of great interest to geo-, environmental, and marine scientists (Spivack, & Palmer, Edmond, 1987; Spivack, You, & Smith, 1993; Spivack & You, 1997; Lemarchand et al., 2002b; Kubota et al., 2015). These include studies in hydrology for ground water contamination by sea water (Barth, 1997); to assess the impact of artificial recharge on water sources; to identify mechanisms of adsorption/desorption on clay minerals; and in the environment as potential tracers of contamination of ground water with coal combustion residues, etc. (Davidson & Bassett, 1993; Vengosh et al., 1994; Ruhl et al., 2014; Warner et al., 2014). B isotope ratios are also used for provenance studies in archaeology (Devulder, Degryse, & Vanhaecke, 2013; Devulder et al., 2014, 2015) and hold potential in agriculture for crop plants (Wieser et al., 2001; Rosner et al., 2011; Geilert et al., 2015).

One of the isotopes of B ( $^{10}\text{B}$ ), has a high thermal neutron absorption cross-section (about 3,800 barns) and is, therefore, a useful nuclide in nuclear technology (IAEA Report, 1995; Subramanian, Suri, & Murthy, 2010).  $\text{B}_2\text{O}_3$  dissolved in heavy water ( $\text{D}_2\text{O}$ ) is used as a liquid poison in the moderator system of pressurized heavy-water reactors (PHWRs) to control the reactivity.  $\text{B}_4\text{C}$  enriched in  $^{10}\text{B}$  is used in control rods in nuclear reactors. Boric acid is also used in the primary cooling circuit of pressurized water reactors (PWRs), which require regular determination of isotopic composition and concentration of boron. Boron-alloyed steels are used as shielding materials for storage containers of irradiated nuclear fuel, reactor shielding, and in instruments used to detect neutrons. The nuclear reaction of  $^{10}\text{B}$  with thermal neutrons produces alpha particles. This property of B is exploited for boron neutron capture therapy (BNCT) to destroy cancerous cells in cancer treatment (Probst et al., 1997). In contrast, in other circumstances B may be less helpful, with the presence of B in aluminum, zirconium alloy, and stainless steel—clad materials or in nuclear fuel materials detrimental to neutron economy in nuclear reactors.

The utilization of B for palaeo-proxies, geology, archaeology, agriculture, nuclear technology, and medicine requires B isotopic composition data, which can be determined by various mass spectrometric techniques. The various mass spectrometric techniques used are thermal ionization mass spectrometry, inductively coupled plasma source mass spectrometry and secondary ion mass spectrometry. Because boron has a high first ionization potential (8.3 eV), generation of  $\text{B}^+$  ions is not possible in TIMS. For the same reason, the yield of  $\text{B}^+$  ions in an inductively coupled plasma (ICP) source is relatively low (about 50–60%), which necessitates solutions containing about 20 ppb of boron. Further, a difference of about 10% in the atomic masses of the two boron isotopes (i.e., 1 in 10) contributes to isotope fractionation or mass discrimination during their mass spectrometric analysis. In addition, the sticky nature of boron to various parts of the mass spectrometer causes memory effect or carry over in mass spectrometric analysis with ICPMS. This memory effect poses a severe problem when samples with widely varying boron isotopic ratios are analyzed, with an inductively coupled plasma source mass spectrometer.

The analytical chemistry of boron is challenging due to the propensity for contamination of boron from apparatus (e.g., borosilicate glass), chemicals, personnel, and laboratory environment during wet chemistry (Downing et al., 1998). At the same time, boron can be lost during separation and purification steps due to its volatile nature, which leads to incomplete recoveries. There can be fractionation between the two boron isotopes during chemical separations (Lemarchand et al., 2002a) and volatilization due to relative large mass difference between the two isotopes. Mass spectrometric techniques like P-TIMS and ICP-MS demand boron to be free from matrix and major abundant elements in the sample to achieve high sensitivity and high precision and accuracy to determine B isotope ratios. The small changes in  $^{11}\text{B}/^{10}\text{B}$  isotope ratio are expressed in delta ( $\delta$ ) notation (per mil), which is defined as

$$\delta(^{11}\text{B})\text{in}\text{‰} = \left[ \frac{\{^{11}\text{B}/^{10}\text{B}\}_{\text{sample}}}{\{^{11}\text{B}/^{10}\text{B}\}_{\text{standard}}} - 1 \right] \times 1,000 \quad (3)$$



**FIGURE 1.** A comparison of  $\delta^{11}\text{B}$  (‰) values in various materials (Adapted from Xiao et al., 2014).

Precise and accurate determination of  $\delta^{11}\text{B}$  in various samples (geological, biological, environmental etc.) demands the sample to be completely dissolved followed by separation and purification of boron. Great care has to be taken to prevent B contamination even when working in an ultra-clean laboratory (Rosner, Romer, & Meixner, 2005). It was shown that boron-rich fibrous silicate glass filters should not be used in laboratories where samples with small amounts of boron are handled, and the glass filters should be replaced with synthetic poly-carbon filters made of polyethylene/polystyrene, which reduce the boron blank by an order of magnitude (Rosner, Romer, & Meixner, 2005). Also the laboratory ware to be used should be of Teflon, PFA, and properly leached prior to use (Downing et al., 1998). All chemicals should be of ultra-high purity, and acids used should be sub-boiling distilled.

In addition to great interest to obtain precise and accurate data on  $\delta^{11}\text{B}$ , B/Ca ratio is important because this ratio in foraminifera samples is dependent on the partition coefficient of boron between sea water and calcium carbonate (calcite or aragonite). B/Ca ratio can, therefore, provide direct information on the  $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$  ratio of the sea water, because the amount of boron precipitated in the biological/inorganic carbonate is known to increase with increasing pH (Yu & Elderfield, 2007; Yu et al., 2010). Recent reports, however, show that B/Ca amount ratio is not a robust proxy and extensive careful studies are needed to evaluate its usefulness for the past ocean carbonate system (Allen & Hönisch, 2012; Babila et al., 2014; Henehan et al., 2015; Uchikawa et al., 2015).

The present review is written with the objective to summarize and highlight the scientific and technological advances that have taken place in the last two decades for the mass spectrometric analysis of boron (Hemming & Hanson, 1994; Al-Ammar, Reitznerova, & Barnes, 2000; Lemarchand et al., 2002a; Aggarwal et al., 2004; Albarede and Bear, 2004; Foster, 2008; Guerrot et al., 2010; Pennisi et al., 2011; Rae et al., 2011; McCulloch et al., 2014). The advancements are mainly because of two reasons: one is the availability of advanced fully automated multi-collector based high sensitivity thermal ionization and inductively coupled plasma mass spectrometers (MC-TIMS and MC-ICPMS) capable to provide high precision (better than 0.2‰) and secondly, an increasing interest in the bio-geochemistry of boron, particularly for marine carbonates, which serves as a proxy for paleo-pH and paleo- $\text{CO}_2$  levels. Further, extensive experience in different international laboratories to determine isotope ratios of boron has highlighted the advantages and limitations of various methodologies to determine accurate isotope ratios, that circumvent various problems like isotope fractionation in TIMS, memory effect in ICPMS, and validation of the methodologies with recently available certified isotopic reference materials. Also, techniques like laser ablation (LA) ICPMS and secondary ion mass spectrometry (SIMS) have added a new dimension to the *in situ* micro-analysis of boron in different geological and other solid materials. These aspects are also discussed in this review.

## II. ANALYTICAL METHODOLOGY FOR EXTRACTION AND PURIFICATION OF BORON

Mass spectrometric analysis of boron with TIMS and ICPMS requires boron to be in a relatively pure chemical form to minimize matrix effects, organic isobaric interferences and

suppression of ionization in the thermal ion source (Hemming & Hanson, 1994; Farhat, Ahmad, & Arafat, 2013). A number of approaches have been used to fulfil this requirement (Sah & Brown, 1997). The extraction and purification methods include solvent extraction, ion-exchange, micro-sublimation, etc. Among these methods, ion exchange procedure (Van Hoecke et al., 2014; He et al., 2015a) has been used more often. Micro-sublimation is also popular these days due to the advantages of efficient matrix removal, labor intensiveness, cost of consumables, procedural blank, and throughput (Van Hoecke et al., 2014). A brief description of these methods is given below.

The solid rock samples require extraction of boron that use fusion with NaOH,  $\text{Na}_2\text{CO}_3$ ; pyro-hydrolysis, or acid dissolution (Aggarwal & Palmer, 1995). For example, boron can be extracted from borates and tourmaline (a complex alumina-silicate material) with fusion or pyro-hydrolysis. Pyro-hydrolysis consists of passing steam over the sample kept in a crucible (Pt) heated to high temperature (more than 1,000°C) and collecting the condensate (Aggarwal & Palmer, 1995). This method provides a relatively pure fraction of boron unless the sample contains other volatile elements like sulfur, which require further purification. Fusion with  $\text{Na}_2\text{CO}_3$  (flux: rock 8:1) or NaOH (5:1) offers the advantage that a large amount of solids that contain small amounts of boron can be taken up for fusion (Aggarwal & Palmer, 1995). Solid samples can also be dissolved with different acids like HF, perchloric acid, and nitric acid (Sah & Brown, 1997; Robinson, Skelly Frame, & Frame, 2014). Care has to be exercised with HF in view of the fact that  $\text{BF}_3$  is volatile in nature. Addition of small amounts of mannitol during acid dissolution prevents the loss of boron (Chen, Lin, & Yang, 1991; Nakamura et al., 1992). Care should be taken to use high purity acids, and also Teflon ware is a must with HF (Robinson, Skelly Frame, & Frame, 2014).

Boron extracted with the above procedures is further purified either with methyl borate distillation or more commonly with B-specific or non-specific ion-exchange resin columns (Aggarwal & Palmer, 1995). Distillation is based on the fact that trimethyl borate is volatile. The distillate will also include other volatile elements like halogens, Na, etc., which can be removed by passing the solution through a mixed cation-anion exchange resin bed treated with HCl and NaOH to convert the resin into  $\text{H}^+$  and  $\text{OH}^-$  forms, respectively. Boron can be eluted from the column with high purity water with cations and anions retained on the resin bed.

In biogenic carbonates, boron is generally separated and purified from the matrix with ion-exchange procedures. The foraminiferal carbonate tests (1–3 mg) are first cracked open with gentle crushing of the moist samples, in between the two clean glass plates (Barker, Greaves, & Elderfield, 2003; Rae et al., 2011; Henehan et al., 2013). The crushed samples are cleaned ultrasonically with high purity water, methanol, high purity water (in sequence) to remove clay contamination. Oxidative cleaning is done for cultured and sediment samples, three to five times, with 1%  $\text{H}_2\text{O}_2$  in 0.1 M  $\text{NH}_4\text{OH}$  at 80°C. Organic material is removed by oxidation with sodium hypochlorite ( $\text{NaClO}$ ; 5%Cl), which is removed by repeated rinsing with high purity water. The cleaned samples are dissolved in dilute (0.1–0.5 M)  $\text{HNO}_3$  and Al/Ca ratio ( $<100 \mu\text{mol mol}^{-1}$ ) in the dissolved sample is monitored with high resolution ICPMS, to confirm effectiveness of the cleaning protocol. Al/Ca ratios of  $<50 \mu\text{mol mol}^{-1}$  were achieved with this protocol (Foster, 2008). Boron-specific anion exchange resin (Amberlite IRA 743) is conventionally used, either alone or preceded by a cation exchange resin column (Kiss, 1988; Leeman

et al., 1991; Lemarchand et al., 2002a). Amberlite 743 contains a hydrophobic styrene backbone and a tertiary amine group (N-methyl glucamine), which is a weak base with a pKa value of about 7. The resin, therefore, behaves like an anion exchanger at pH <7 and absorbs only  $B(OH)_4^-$ . For example, separation of boron from seawater is given here (Foster, Pogge von Strandmann, & Rae, 2010). Seawater aliquots are mixed with a sodium acetate-acetic acid buffer to pH of about 5. The sample solution is loaded onto a micro-column (25  $\mu$ L volume, 50 mesh resin). The matrix is washed with high-purity 18.2 M $\Omega$  MilliQ water, and B is eluted with 450  $\mu$ L of 0.5 M  $HNO_3$ . The B isotopic composition determined from different fractions collected with the IRA-743 ion exchange experiments showed that the first few fractions are enriched in  $^{11}B$  and the tail fractions are depleted in  $^{11}B$  (Lemarchand et al., 2002a). It is, therefore, important to achieve a high recovery to eliminate any isotope fractionation during ion-exchange purification. This is done by passing the sample slowly through the resin, which allows re-equilibration of the sample with resin in the column, after the initially absorbed borate is eluted slowly from the resin column. In addition, elution tails are checked for boron and the total procedural blanks are monitored for every column batch. Because B in the anionic form  $B(OH)_4^-$  is only absorbed onto the IRA 743 resin, some investigators propose that the B solution prior to loading on the resin column should have a pH of 10 (Rosner et al., 2011), which is achieved by adding alkali or ammonia, to eliminate isotope fractionation during boron purification. However, at this pH, Na, Mg, and Ca, if present in the sample, precipitate as hydroxide on the resin column and will elute along with boron (with  $HNO_3$  or HCl), and these ions have to be removed with another cation exchange step (Aggarwal & Palmer, 1995).

For foraminiferal shells, the amount of sample to be taken depends upon the species in view of different B concentrations in various foraminiferal species. For example, a few hundred  $\mu$ g (preferably 1–2 mg) of the benthic foraminiferal shells, with high B concentrations, are crushed, and rinsed and ultrasonicated with deionized water and methanol several times to remove clay materials (Yu et al., 2005). This step is generally followed by oxidative step to remove organic matter, in a clean laboratory. Oxidation with sodium hydroxide and hydrogen peroxide is done (Boyle & Keigwin, 1985; Rosenthal, Boyle, & Slowey, 1997; Barker, Greaves, & Elderfield, Yu & Elderfield, 2007; Foster et al., 2013; Holcomb et al., 2015). The cleaned shells are dissolved in 0.1 M  $HNO_3$  and the solution is taken up for isotopic analysis with MC-ICPMS. In another study, bleaching with sodium hypochlorite solution for 24 hr was done to oxidize the organic matter (Foster et al., 2006). These foraminiferal shells were again rinsed and ultrasonicated to remove NaClO and any dissolved salts. The cleaned foraminifer sample (calcite) was dissolved in 2 M HCl, by drop wise addition until complete carbonate dissolution (Foster et al., 2006). The purified solution was taken for N-TIMS analysis. In the case of coal-combustion residues (CCRs), effluents from leaching experiments on CCRs from a variety of coals were used to determine  $\delta^{11}B$  (Davidson & Bassett, 1993; Williams & Hervig, 2004; Ruhl et al., 2014). The samples of surface water, effluents, and leachates were processed with a cation exchange resin (AG 50W-X8) to remove cations. The eluate was oxidized with  $H_2O_2$  to remove organic matter and CNO complexes, prior to loading on the filament for N-TIMS analysis (Ruhl et al., 2014). Detailed studies are reported recently (Holcomb et al., 2015) for cleaning and pre-treatment procedures

for biogenic and synthetic calcium carbonates formed in marine environments. Cleaning protocols that cause partial dissolution are troublesome for compositionally heterogeneous samples, and boron isotopes are always robust to sample pre-treatment cleaning procedures (Holcomb et al., 2015).

Studies were reported for evaporation and sublimation of boric acid to purify boron from organic-rich solutions (Gaillardet et al., 2001). It was shown that slow evaporation of boron solution in dil. HCl medium, over a period of 10–12 hr, at 60–65°C gave complete B recovery without any isotope fractionation and boron loss. On heating the dried residue for more than 1 hr, loss of boron was observed. The recovery of boron in micro-sublimation experiments was confirmed with isotope dilution experiments, and the absence of any isotopic fractionation was confirmed with NIST certified B isotopic reference material (Gaillardet et al., 2001). It was also proved that mannitol addition is not necessary with this procedure of micro-sublimation. Boron loss was observed if the dried residue was heated beyond 1 hr, or a higher temperature was used for boron solution evaporation and sublimation. For these experiments with high temperature sublimation or heating of dried residue for longer durations, addition of mannitol was necessary to form a solid matrix of non-volatile boron ester to avoid the boron loss (Ishikawa & Nakamura, 1990). The micro-sublimation procedure was also found useful to separate boron from organic rich media, in contrast to other methods like the use of activated carbon,  $H_2O_2$ , organic matter specific resin or UV irradiation (Lemarchand et al., 2002a). Recently, this micro-sublimation was used (Wang et al., 2010; Liu et al., 2013; Pi et al., 2014) for rock samples, marine carbonate, sea water, and *Porites* coral samples with an aim to avoid introduction of organic residue to the purified sample through the ion-exchange procedure. The quantitative recovery of boron from sea water and coral sample (Liu et al., 2013) was confirmed by the standard addition method (Foster et al., 2006). The procedure involved the addition of a known amount of SRM 951a standard to a sample before micro-sublimation and to another set of the same sample after sublimation, followed by the measurement of  $^{11}B/^{10}B$  isotopic ratios in the two mixtures to calculate the boron concentration. For the natural rock samples, doping with NaCl was necessary, prior to micro-sublimation, to recover boron from the digested silicates of the rock samples (Pi et al., 2014). The procedure is based on the fact that boron sublimates at a relatively low temperature (about 70°C) to leave the organic and alkaline matrices in solution or solid form. Further separation with resins and additional  $H_2O_2$  treatment is not required, and elimination of this separation step leads to low blanks in the separation procedure. The procedure involves taking a small volume of the boron-containing solution into the 5-mL conic bottom PFA vial, and setting it upside down so that the cap can be heated (about 70°C for 12 hr) and the top conical end can be cooled for condensation of the evaporated boron. The benefits of low-blank, high-throughput, and quantitative recovery can be realized with the micro-sublimation method (Van Hoecke et al., 2014). A comparison of the micro-sublimation and anion exchange procedure for four different matrices, that is, Ca aqueous solution (20 g L $^{-1}$ ), seawater, digests of spinach (100 g L $^{-1}$ ) and silicate glass (10 g L $^{-1}$ ), spiked with B standards showed good agreement in the chemical recoveries with the two methods, without any isotopic fractionation, except in spinach digests (Van Hoecke et al., 2014). Poor yield and isotopic

fractionation observed in the spinach digests was attributed to the preferential adsorption of  $^{10}\text{B}$ , present as tetrahedral anion, to the organics present in undissolved portion of the sample.

For nuclear samples (e.g., titanium borides), a small amount of the sample is crushed and disintegrated with concentrated  $\text{HNO}_3$ . The slurry is taken up in 0.5 M  $\text{HNO}_3$ , and a small portion is loaded onto the filament and fused with rubidium carbonate on the filament, at alkaline pH, for boron isotope analysis with positive ions MC-TIMS (Rao et al., 2014). For the periodic analysis of heavy water from PHWRs to determine the concentration of boron, the solution is spiked with a known amount of pre-calibrated  $^{10}\text{B}$  enriched spike (Heumann, 1992) and pre-concentrated by heating under an infra-red lamp in a fumehood, prior to boron isotope analysis with P-TIMS. The solution is not allowed to dry-up, in the pre-concentration step, to eliminate the isotope fractionation effects. Solid boric acid or  $\text{B}_2\text{O}_3$  samples for B isotope analysis are taken directly and fused with alkali carbonate on the filament. Solid samples like uranium oxide and aluminum, are first dissolved in suitable acids—for example,  $\text{HNO}_3$  for uranium and  $\text{HCl}$  for Al. Boron can be separated from different matrices in a 1 M  $\text{HCl}$  medium, by using solvent extraction with 0.65 M solution of 2-ethyl-hexane 1,3 diol (EHD) in 10% chloroform (Rao & Aggarwal, 2008). In the nuclear samples (except in case of nuclear fuels and clad materials [aluminum, zircaloy, stainless steel], where boron is undesirable), the amount of boron present is generally not a limitation, but the blank and laboratory contamination need to be controlled and monitored carefully.

For crop plant samples, dry ashing at  $600^\circ\text{C}$  in a microwave oven was used (Rosner et al., 2011). The ash was dissolved in 0.5 M  $\text{HCl}$ , and the solution was used to separate and purify boron with a 3-step ion chromatography procedure. The first step was to remove most of the cations with AG 50Wx8 resin on a polypropylene column. A boron solution was loaded under low-pH conditions so that boron was present as neutral  $\text{B}(\text{OH})_3$  and is not adsorbed by the resin in contrast to all other cations. This step was proceeded by second and third steps of anion exchange purification with Amberlite IRA-743 boron-specific anion exchange resin. In this step, the pH of the boron-containing solution was adjusted to  $>11$  with aqueous  $\text{NaOH}$  so that B was present as  $\text{B}(\text{OH})_4^-$  and was loaded onto the resin column. The boron fraction was eluted with 0.5 M  $\text{HCl}$  and mixed with mannitol ( $40\ \mu\text{g}$  mannitol/ $1\ \mu\text{g}$  of boron), followed by slow evaporation to dryness. No loss of boron was observed during dry ashing of these biological materials. A similar observation was reported (Noda & Ito, 2008) in coal combustion, where no loss of boron was observed under reducing conditions.

Among all the analytical methods discussed above, boron separation and purification with boron specific anion exchange resin IRA-743 is the most commonly used approach (He et al., 2015b) at various laboratories.

### III. MASS SPECTROMETRIC TECHNIQUES USED TO ANALYZE BORON

#### A. Thermal Ionization Mass Spectrometry (TIMS)

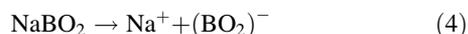
##### 1. Positive-TIMS

The high first- ionization potential of boron (about 8.3 eV) prevents the formation of  $\text{B}^+$  ions with surface ionization in

TIMS. Instead, alkali metal borate ions ( $\text{M}_2\text{BO}_2^+$ ) are conventionally used for P-TIMS analysis of boron isotopes (DeBievre & Debus, 1969; Xiao, Beary, & Fassett, 1988; Vengosh et al., 1991; Nakano & Nakamura, 1998; Xiao & Wang, 1998; Ishikawa & Nagaishi, 2010). Different alkali metals (Li, Na, K, Rb, and Cs) have been used to generate positive meta-borate ions (Ramakumar et al., 1985; Spivack & Edmond, 1986; Nakamura et al., 1992; Ding & Zhao, 1994; Sahoo & Masuda, 1995; Catanzaro et al., 1970; Deyhle, 2001; Rao et al., 2008, 2010a). To efficiently generate  $\text{M}_2\text{BO}_2^+$  ions and reduce the intensity of alkali metal ions, a special loading procedure (e.g., loading of graphite as a promoter and an optimum B/alkali metal mole ratio) needs to be employed. Among the different alkali metals, Na and Cs metal borates are employed quite often in view of the fact that both Na and Cs are mono-isotopic and do not complicate the mass spectra. The  $^{11}\text{B}/^{10}\text{B}$  isotope ratio can be conveniently calculated by measuring the ion intensities at 89/88 ( $\text{Na}_2\text{BO}_2^+$ ) and 309/308 ( $\text{Cs}_2\text{BO}_2^+$ ), with the exception to apply a small correction for an  $^{17}\text{O}$  contribution at masses 89 and 309. The correction of  $^{17}\text{O}$  contribution is straightforward and is accounted for by subtraction of  $2 \times (^{17}\text{O}/^{16}\text{O})$  isotope ratio value from the measured isotope ratio data. Between the two mono-isotopic alkali metals (Na and Cs), Cs is preferred in view of the high mass of the  $\text{Cs}_2\text{BO}_2^+$  ion, and this high mass minimizes the mass-dependent isotope fractionation, which is a source of variable systematic error in TIMS. This isotope fractionation is not a constant factor in TIMS, and depends on various parameters including the mass to charge ratio of the ions monitored in P-TIMS and N-TIMS. A high purity tantalum single-filament assembly is generally used for P-TIMS analysis. Because the use of  $\text{Cs}_2\text{BO}_2^+$  in a static mode of data collection was not possible with early models of TIMS, some laboratories continue to use  $\text{Na}_2\text{BO}_2^+$  ion in P-TIMS analysis. The continued use of  $\text{Na}_2\text{BO}_2^+$  ion is also partly due to the long experience of these laboratories in successful use of  $\text{Na}_2\text{BO}_2^+$  for isotope ratio measurements of boron (Rao et al., 2008, 2009; Rao, Parab, & Aggarwal, 2012).

For many years, the mechanism of formation of alkali metal borate ions remained elusive. During the past decade, a few interesting studies are reported by a few researchers (Lakshmi Narasimhan et al., 2013; Wei et al., 2011) that have shed light onto the mechanism of formation of  $\text{M}_2\text{BO}_2^+$  ions in TIMS. Studies were reported that used Raman spectroscopy and transmission electron spectroscopy (TEM) to compare the role of different carbon-based materials (e.g., graphite, carbon, fullerene, single-walled carbon nanotube SWNT; Wei et al., 2011). Based on the micro-structure properties of these four carbon-based materials, a surface-induced collision mechanism was proposed, and graphite gives the highest yield of polyatomic ions due to its perfect parallel and equidistant layers structure (only G-band observed with the lowest FWHM in Raman spectrum) and fullerene led to the lowest yield due to a block of their pathways (Wei et al., 2011). Studies performed on the reactions of B,  $\text{B}_2\text{O}_3$ , and  $\text{B}_4\text{C}$  with  $\text{Na}_2\text{CO}_3$  with transpiration thermogravimetry (TG), TIMS, and Knudsen effusion mass spectrometry (KEMS) showed that the formation of metaborate ion is a two-step phenomenon (Lakshmi Narasimhan et al., 2013). This two step process was concluded from the  $\text{NaBO}_2$  residue found in the TG experiments of all the three forms of boron (i.e., B,  $\text{B}_2\text{O}_3$  and  $\text{B}_4\text{C}$  with  $\text{Na}_2\text{CO}_3$ ) at a temperature much lower than that for  $\text{Na}_2\text{CO}_3$  alone, and also the high

intensity of  $\text{Na}_2\text{BO}_2^+$  ion observed in KEMS.



For TIMS analysis with  $\text{Na}_2\text{BO}_2^+$ , it is generally accepted that the B/Na mole ratio needs to be strictly controlled on the filament within a narrow range when mixing with  $\text{Na}_2\text{CO}_3$  or NaOH (Rao et al., 2008, 2009; Rao, Parab, & Aggarwal, 2012) to get good yield of  $\text{Na}_2\text{BO}_2^+$  ions. Studies (Rao et al., 2008) show that NaCl can also be used instead of  $\text{Na}_2\text{CO}_3$  or NaOH, and in this case, the B/Na mole ratio need not be strictly controlled and could vary from 1 to 0.1. However, addition of mannitol, which forms an anionic complex with boron (70  $\mu\text{g}$  of mannitol for about 1.7  $\mu\text{g}$  of B), was essential, apart from loading of graphite on the filament. This relaxation in the strict control of the B/Na mole ratio is an advantage to analyze samples with unknown amounts of boron; e.g., in the case of ground-water samples. A subsequent study (Rao et al., 2009) demonstrated the robustness of a boron-mannitol complex on graphite-coated tantalum filament with  $\text{Na}_2\text{CO}_3$  for solid samples and NaCl for solutions. With isotope dilution, P-TIMS was used to determine B at sub-ppm levels in uranium oxide samples (Rao et al., 2010b). For alloy samples of titanium boride, it was observed that graphite should be added onto the filament only after fusion of the slurry of the alloy with  $\text{Rb}_2\text{CO}_3$  (Rao et al., 2014) to get good intensity of  $\text{Rb}_2\text{BO}_2^+$  ions. Further, the possibility to perform internal normalization based on Rb isotope ratios was also demonstrated successfully (Rao et al., 2010a).

Isobaric interference limitation during TIMS analysis of boron with  $\text{Cs}_2\text{BO}_2^+$  is discussed in many papers (Hemming & Hanson, 1992; Aggarwal & Palmer, 1995). This isobaric interference is commonly encountered in organic samples—for example, marine carbonates, and lowers the  $\delta^{11}\text{B}$  values. One of the ways to minimize this organic-matter ( $\text{Cs}_2\text{CNO}^+$ ) interference is to digest the sample with  $\text{H}_2\text{O}_2$  (Grottoli et al., 2005) prior to loading on the filament. An experimental study (Wu et al., 2012) for Archaeo-cyatha fossil carbonates determined the exact nature of the organic matter with FT-IR, Raman, and TG-DSC-MS techniques. The results showed the presence of an acylamino ( $-\text{CO}-\text{NH}_2$ ) group in the carbonate samples, which would negatively bias the  $^{11}\text{B}/^{10}\text{B}$  isotope ratios and lower the  $\delta^{11}\text{B}$  values. It was also noted that, on external addition of acetamide ( $\text{CH}_3\text{CONH}_2$ ), the B isotope ratio gradually reaches the accurate value on heating the filament to 1.8 A in TIMS, when the organic compound is consumed on the heated filament.

Another way to circumvent the isobaric interference (Wei et al., 2004) is to add 1%  $\text{H}_3\text{PO}_4$  on the filament. The addition of  $\text{H}_3\text{PO}_4$  acts as an ion depressor and prevents the formation of  $\text{Cs}_2\text{CNO}^+$  in the presence of nitrate, probably by changing the morphology of boron compound. The temperature of TIMS analysis of B is also higher than that in the absence of ion depressor.

## 2. Negative-TIMS

Among different mass spectrometric techniques available, N-TIMS has the highest sensitivity for isotopic analysis of

boron, and can conveniently analyze samples that contain one ng or smaller amounts (150 pg) of boron (Duchateau & DeBievre, 1983; Zeininger & Heumann, 1983; Heumann & Zeininger 1985; Vengosh, Chivas, & McCulloch, 1989; Hemming & Hanson, 1992, 1994; Heumann et al., 1995; Sonoda et al., 2002; Shen & You, 2003; You, 2004). Samples like foraminifera with 1–2 ng of boron can be easily analyzed with this method. During N-TIMS, a single-filament assembly made of a zone-refined high-purity rhenium filament is used to load the sample solution. All efforts are made to minimize the isobaric interference of  $\text{CNO}^-$  at  $m/z$  42, which corresponds to  $^{10}\text{BO}_2^-$ . This minimization of isobaric interference is necessary, because even 0.1% of  $\text{CNO}^-$  in the ion beam will lower the  $^{11}\text{B}/^{10}\text{B}$  isotope ratio by 4.7‰ compared to the exact value (Tonarini, Pennisi, & Gonfiantini, 2009). Samples are treated with high-purity hydrogen peroxide to remove CNO complexes and any organic matter (Pelejero et al., 2005; Foster et al., 2006). In addition, signal is monitored at  $m/z$  26 ( $\text{CN}^-$ ) using secondary electron multiplier (due to its higher sensitivity compared to a Faraday cup) to confirm the absence of any signal at  $m/z$  26 and thus of no interference at  $\text{CNO}^-$ . All operations should be done in a laminar-flow clean hood equipped with boron-free PTFE HEPA filters to minimize boron contamination of the sample (Rosner, Romer, & Meixner, 2005). For N-TIMS, boron-free sea water is generally loaded on the filament to enhance ionization efficiency, because the electronic work function of the filament is lowered by salts present in sea water. The boron-free sea water is prepared with Amberlite IRA 743 ion-exchange resin (Barth, 1997), which introduces some organics from the resin. Another method with an alternative loading solution prepared by combining high-purity single element standard solutions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  in 5% HCl with proportions similar to those present in sea water was found to give encouraging results. This loading solution eliminates the risk of isobaric interference from  $\text{CNO}^-$  and provides the possibility to perform automatic data collection (Dwyer & Vengosh, 2008).

Owing to the low mass of  $\text{BO}_2^-$  ions, there is a problem of isotope fractionation in TIMS. This isotope fractionation is a serious problem in B because B has only two isotopes. Different methodologies are adopted to circumvent this drawback. The  $^{11}\text{B}/^{10}\text{B}$  isotope ratio is determined with any of the three approaches during TIMS data acquisition. These approaches are (i) follow a strict protocol developed previously with certified isotopic reference material like NIST-SRM-951; (ii) use total evaporation (TE) (Foster et al., 2006); and (iii) by internal normalization (IN) based on  $^{18}\text{O}/^{16}\text{O}$  ratios determined in-situ from  $\text{ReO}_4^-$  ions, from each filament loading, prior to mass spectrometry for boron (Aggarwal et al., 2009b). The total evaporation approach to take care of isotope fractionation in TIMS involves integration of the ion current until complete exhaustion of the sample on the filament and was proposed (Kanno, 1971) for elements with high ionization efficiencies and follow Rayleigh distillation as in the case of single-filament assembly. This total evaporation method requires less than 1 ng of boron to be loaded on the filament due to the very high sensitivity of N-TIMS of boron, and completion of the analysis within a reasonable time. This loading of about 1 ng of boron demands a strict control of boron blank during all stages of sample handling. Internal normalization is based on the invariant nature of one of the isotope amount ratios (e.g.,  $^{18}\text{O}/^{16}\text{O}$ ) present

in the sample on a given filament. The isotope fractionation factor is calculated from the  $^{18}\text{O}/^{16}\text{O}$  isotope ratio by using the  $^{187}\text{Re}/^{185}\text{Re}$  isotope ratio determined from  $\text{ReO}_4^-$  ions from the same filament. With the  $^{18}\text{O}/^{16}\text{O}$  isotope ratio from the  $\text{ReO}_4^-$  ion, the fractionation factor is calculated for the  $^{18}\text{O}/^{16}\text{O}$  ratio observed with the  $\text{BO}_2^-$  ion, and this factor is applied to account for isotope fractionation in the boron isotope ratio. The application of this internal normalization methodology was demonstrated on NIST-SRM-951 isotopic reference material, in sea water as well as in coral samples (Aggarwal et al., 2009b).

It has been reported that determination of  $\delta^{11}\text{B}$  in foraminifera samples with TE-NTIMS gives a bias with respect to the data obtained with MC-ICPMS. This bias is attributed to the incomplete decomposition of the organics that arise from foraminifera tests. This inference is supported by the observation that the same solution during repeated analysis with TE-NTIMS over a period of a few months gives a  $\delta^{11}\text{B}$  value lower by +6‰ probably due to the hydrolysis of organic matter by the acid present in the solution (Foster, 2008). In the studies performed previously with N-TIMS (Hönisch & Hemming, 2005; Pelejero et al., 2005; Hemming & Hönisch, 2007), each sample was analyzed with several independent filament loadings (at least three times), with strict protocol of filament heating and data acquisition, to confirm the absence of analytical artifacts such as excessive isotopic fractionation and isobaric interferences on mass 42 by the organic matter. The mass spectrometric analysis runs which showed fractionation and/or isobaric interference were discarded, until three acceptable runs data showing no fractionation (less than 0.1‰) in 20 min of acquisition were obtained and averaged. In the light of these discussions, further studies are necessary to make the N-TIMS method robust and rugged to achieve precision and accuracy of better than 0.2–0.4‰, to be useful for paleo-proxy studies.

## B. Inductively Coupled Plasma Mass Spectrometry (ICPMS)

ICPMS is a useful and quite convenient mass spectrometric method to determine the isotope ratios and concentrations of different elements in a variety of matrices. Solutions are analyzed with a pneumatic nebulizer (PN), whereas solids can directly be analyzed with laser ablation (LA). A number of commercial vendors—(e.g., Agilent [Japan], GBC Scientific [Australia], Nu Instruments [UK], Perkin Elmer [USA], Thermo Fisher [Germany]) supply a variety of ICPMS systems with different kinds of mass analyzers. These ICPMS instruments include quadrupole-based ICPMS with or without a collision or reaction cell, time-of-flight based ICPMS, high resolution double-focusing electrostatic and magnetic analyzers based ICPMS (Element 2 from Thermo and AttoM from Nu Instruments), and multiple collector magnetic sector based ICPMS (NuPlasma and Neptune).

Among the various types of ICPMS systems, Q-ICPMS and ToF ICPMS are employed to determine concentrations of different elements, and their isotope ratios in environmental and biological applications that do not demand high precision. These quadrupole- and ToF-based ICPMS systems are more cost-effective compared to MC-TIMS and MC-ICPMS, but provide lower precision and poor accuracy (Gregoire, 1987; Lu, 2014) in isotope ratio measurements due to Gaussian peak shapes. Therefore, these Q-ICPMS and ToF-ICPMS are not employed to

determine precise and accurate isotope ratios, but are used mostly for multi-elemental analysis to determine the trace and ultra-trace concentrations of different elements in various matrices. Most of the quadrupole-based ICPMS instruments are equipped with either a dynamic reaction cell (DRC) or a collision cell to overcome the isobaric interferences from the atomic isobars as well as to eliminate polyatomic interferences (Tanner & Baranov, 1999). This removal of isobaric interference is based on the preferential chemical reaction of the analyte ion or the interfering ion with a reactive reagent gas (e.g., oxygen, ammonia, etc.), which shifts the  $m/z$  ratio and thereby chemically resolves isobars. In addition, polyatomic molecular interfering ions are dissociated due to collisions with the reagent gas. Another approach is with kinetic energy discrimination with an inert gas. These systems provide an abundance sensitivity (contribution of high-abundant peak of mass  $M$  to adjacent peak at mass  $M \pm 1$ ) of  $10^7$ .

A novel QQ-ICPMS (from Agilent, 8800) with an octopole reaction cell is introduced recently in the market (Agilent, 2013). This triple-quad ICPMS eliminates the atomic and polyatomic isobaric interferences with the use of a collision or reaction gas in the second quadrupole, and in addition, gives a high abundance sensitivity of more than  $10^8$ . This instrument needs to be evaluated for its capability, in terms of precision and accuracy, to determine boron isotope ratios.

Single-collector magnetic sector based HR-ICPMS is quite popular to analyze samples for determination of concentrations of various trace constituents, because the use of double focusing electrostatic and magnetic analyzers allows to eliminate most of the polyatomic isobaric interferences commonly encountered at  $m/z$  below 80 in Q-ICPMS. MC-ICPMS systems from Thermo as well as Nu Instruments are available at different international laboratories, and are the best to perform isotopic analysis of various elements with the highest precision (0.01% or better) and accuracies. HR-ICPMS and MC-ICPMS both have the options to use these systems at low, medium, and high mass resolutions. Experience in different international laboratories over the past decade has demonstrated that samples with a lower chemical purity, compared to that required for MC-TIMS analysis, can be analyzed conveniently with MC-ICPMS to make the latter a more popular analytical tool compared to MC-TIMS (Yang, 2009). The MC-ICPMS-based techniques are also characterized by their fast analyses that lead to high throughput, subjected to optimization of different operating parameters of ICPMS and matching the matrices of sample and standard. Boron is analyzed as  $\text{B}^+$  ions, taking care of a tail contribution from  $^{12}\text{C}^+$ , memory or carry-over effect, and control of the laboratory and procedural blank values. The standard sample bracketing (SSB) approach is popularly used to take care of mass discrimination and signal drift during data collection. Among the various types of ICPMS instruments available commercially, only the MC-ICPMS allows the determination of  $^{11}\text{B}/^{10}\text{B}$  isotopic ratios with relative precision values of 0.2–0.4‰ required in paleo-proxy studies and is, therefore, the most popular with bio- and geo-scientists (Rehkamper, Schönbachler, & Stirling, 2003). However, to achieve such high precision in the isotopic ratio data, the non-spectroscopic matrix effects, for example, the effect of Na contamination and other matrix elements present in the sample have to be checked. Because B is a light element, and there is a difference of about 10% in the atomic masses of the two isotopes, the presence of Na (Na/B

molar ratio of 20,000 and Na concentration of 6,000 ppm in solution with 150 ppb of boron) was reported to give 12% suppression in the B count rate and 8% increase in the observed  $^{11}\text{B}/^{10}\text{B}$  isotopic ratio (Gregoire, 1987). Additionally, a comparison of the matrix effects with Na, Cs, and Pb showed that the presence of heavy element causes the highest suppression effect to the intensity of boron (Gregoire, 1987). Therefore, separation and purification of boron, from bulk of matrix elements or organic impurities is one of the important pre-requisites to the determination of boron isotopic ratios with high precision and accuracy.

### C. Mass-Bias Effect

The mass-bias effect (also known as isotope fractionation or mass discrimination) occurs in ICPMS due to space-charge effects or in the high vacuum region between sampler and skimmer cones. This effect leads to preferential extraction and transmission of the heavier isotope compared to the lighter one and, therefore, the isotope ratio data are positively biased with respect to the heavier isotope (Albarede et al., 2015). In case of boron, a mass-bias effect of 4–9% per atomic mass unit was reported with an MC-ICPMS (Thermo Axiom) system (Aggarwal et al., 2003). However, this mass discrimination is quite stable, and can be easily corrected for with the SSB approach (Foster, 2008). Sample solutions with 20–50 ppb of boron and NIST SRM-951 boron standard of similar concentration are analyzed. A typical sequence involves the analysis of blank, standard, sample, standard, blank. This is repeated two times for every sample and the average  $\delta$ - $^{11}\text{B}$  value is calculated. It is important that the sample and the standard are matrix-matched because the presence of large amounts of other elements (e.g., Na) and the acid strength used to introduce the sample will give rise to matrix effects affecting the B isotope mass fractionation

### D. Memory Problem

As stated previously, determination of B isotope ratios or B concentration is plagued by the carry-over effect or memory problem due to the adhering tendency of B to the instrumental components. This memory effect has been noticed by several researchers and a number of approaches have been used to minimize this effect. These approaches include a wash between analyses with ammonia solution, inject  $\text{NH}_3$  gas into the spray chamber during analysis (Al-Ammar, Gupta, & Barnes, 1999, 2000), wash with NaF, mannitol ( $\text{C}_6\text{H}_8(\text{OH})_6$ ), a wash with  $\text{H}_2\text{O}_2$  (10%), HF (0.3%),  $\text{HNO}_3$  (0.65 N), and finally  $\text{HNO}_3$  (0.05 N; Lecuyer et al., 2002). Nebulized ammonia reacts with boric acid to form ammonium borate, which is non-volatile, and is, therefore, washed out of the spray chamber without the production of  $\text{B}^+$  ions. Detailed studies were performed on the introduction of ammonia gas into the spray chamber to optimize the  $\text{NH}_3$  flow rate (Al-Ammar, Gupta, & Barnes, 2000). It was shown that a wash time of 2 min is sufficient to get rid of the boron memory. At the same time, an enhancement in the boron signal intensity was observed, which was attributed to an increase in the thermal conductivity due to hydrogen formation from ammonia or charge exchange reaction between the positively charged nitrogen species and boron atoms (Al-Ammar, Gupta, & Barnes, 2000). Also, no analyte loss, matrix precipitation, or nebulizer blockage was observed. Most

MC-ICPMS laboratories use dilute  $\text{HNO}_3$  (0.5 M) as the wash solution, for 2 min, in between the samples to minimize the memory effect in B isotope ratio measurements.

Several other approaches were tried in the past to circumvent the ubiquitous memory problem in B concentration determinations in various matrices. These methods cannot be used in B-isotope ratio measurements with MC-ICPMS, because of the matrix effects induced by the introduction of various chemicals. A rinse solution of 0.25% (w/v) mannitol in 0.1 M  $\text{NH}_3$  was used to eliminate the boron memory effect after a 5-min wash (Sun et al., 2000) to determine B in biological samples (e.g., serum, plasma, and urine). Mannitol has been used by several researchers in view of the tendency of boron to form complexes with alcohols and polysaccharides. A rinse solution of ammonia, EDTA, surfactant Triton X100, and  $\text{H}_2\text{O}_2$  was used (Wright et al., 2008) for standard sample introduction system during analysis of boron with Q-ICPMS in soil/plant samples. A mixture of 0.1 M  $\text{HNO}_3$  and 0.3M HF was used with a Teflon spray chamber (Misra et al., 2014). A demountable direct-injection high-efficiency nebulizer (d-DIHEN; Bellato, Mene-gario, & Gine, 2003) was also used to circumvent the memory effect. A comparison on the Meinhard pneumatic nebulizer with a Scott-type double-spray pass chamber and direct injection nebuliser (Smith et al., 1991) showed the advantages of DIN from the point of view of low sample consumption as well as quick wash with negligible memory. In the case of a pneumatic nebulizer, a signal of 2% of initial boron intensity, which decreased very slowly, was seen even after washing for eight minutes with a 2%  $\text{HNO}_3$  solution. With DIN, because liquid samples are transported inside a capillary by pumping at high pressure and by introducing its aerosol directly into the plasma, no spray chamber is required.

The best way to confirm the complete elimination of any memory effect is to make multiple injections of natural boron solution or NIST standard SRM-951, enriched  $^{10}\text{B}$  ( $\delta^{11}\text{B}$  value of at least  $-100$  or more) solution, and again natural B solution with similar concentrations of boron (Aggarwal et al., 2015, unpublished results).

In addition to extended washing with 2–3%  $\text{HNO}_3$ , it was suggested that an on-peak zero blank correction (Wei et al., 2014) should be applied to account for the memory effect, particularly when analyzing samples with widely varying  $\delta^{11}\text{B}$  values as well as for samples with extremely small amounts (ng or less) of boron. The corrected  $^{11}\text{B}/^{10}\text{B}$  isotope ratio of the sample is calculated as:

$$\left[ \frac{^{11}\text{B}}{^{10}\text{B}} \right]_{\text{sample}} = \left[ \frac{^{11}\text{B}_{\text{measured}} - ^{11}\text{B}_{\text{blank}}}{^{10}\text{B}_{\text{measured}} - ^{10}\text{B}_{\text{blank}}} \right] \quad (6)$$

### E. Laser Ablation ICPMS (LA-ICPMS)

Laser ablation ICPMS depends on the use of a laser to generate an aerosol of the material in an ablation cell. The generated vapors are transported with He, Ar, or  $\text{Ar}+\text{N}_2$  gas into the argon plasma of ICP, where they are atomized and ionized. Different kinds of lasers have been used (Table 1), and involved a 1,024 nm solid state Nd-YAG laser to start with, 532 nm (second harmonic), 266 nm (third harmonic), 213 nm (mixing of third

**TABLE 1.** Different types of lasers used in LA-ICPMS for boron

| Laser                       | Make/Company   | Some details   | Reference                            |
|-----------------------------|--|--|--------------------------------------|
| Ti-sapphire                 | Solstice<br>Newport/Spectra<br>Physics   | 194 nm, 200 fs, 0.085 mJ/pulse at 194 nm, 50 $\mu\text{m}$ spot, 2J $\text{cm}^{-2}$ | Kaczmarek et al., 2015               |
| Ti-sapphire                 | Legend, Coherent<br>Inc., Santa Clara,<br>USA                                    | About 150 fs, 795 nm   | Kurta et al., 2014                   |
| Ti-sapphire                 | CompexPro 102,<br>Coherent   | 193nm, 40-240 $\mu\text{m}$ spot size, 8 Hz, 2.5 J $\text{cm}^{-2}$                  | Devulder et al., 2013, 2014 and 2015 |
| UP-213, Nd:YAG              | New Wave Research,<br>Fremont, CA, USA   | ns laser, 213 nm   | Kurta et al., 2014                   |
| NWR Femto 200               | Electra Scientific<br>Industries, New Wave<br>Research Division<br>Portland, USA | 200 nm, fs, laser spot 10-55 $\mu\text{m}$ , 50 Hz, 0.8J $\text{cm}^{-2}$            | Jochum et al., 2014                  |
| Geolas 2005 ArF Excimer     | Lambda Physik,<br>Gottingen, Germany   | 193 nm, 8 Hz, spot 44 to 90 $\mu\text{m}$ , 200mJ, 5.3 J $\text{cm}^{-2}$            | Lin et al., 2014                     |
| UP-193 FX, Excimer          | ESI New Wave<br>Research   | 30 Hz, 2.5 J $\text{cm}^{-2}$ , spot analysis (500-900 shots), 100-150 $\mu\text{m}$ | Fietzke et al., 2010                 |
| LPF-202 (F/H <sub>2</sub> ) | Lambda Physik  | 157 nm, 10 Hz, 40 mJ, 9 ns, single shot  | Telouk et al., 2003                  |

and fourth harmonic), 193 nm ArF excimer nano-second (ns) laser, and about 800 nm (fundamental) Ti-sapphire femtosecond (fs) laser. Nowadays, most laboratories are equipped with either a ns UV excimer laser or a fs Ti-sapphire laser. Extensive studies (Diwakar et al., 2013, 2014; LaHaye et al., 2015; Zhang et al., 2016) have demonstrated the advantages of a fs laser to circumvent the problem of elemental fractionation, in contrast to the use of a ns laser, by reducing heating and thermal effects. In fs LA, the plasma plume is formed after the laser pulse compared to ns-LA, where plasma is formed during the laser pulse to lead to heat absorption. The mitigation of elemental fractionation effects is particularly important when determining the concentrations of different elements in a sample, and not absolutely necessary when determining isotope ratios of an element. A small isotope fractionation effect in the per mil range for Cu, probably due to preferential evaporation of the lighter isotope in view of thermal heating, has been reported (Jackson & Gunther, 2003; Horn & von Blanckenburg, 2007) with ns lasers for the isotopic analysis. Further, the use of fs lasers generates smaller particles with a more homogeneous particle size distribution, which leads to improved ionization of aerosols in the plasma and an increase in the sensitivity of ICP-MS analysis. A quadrupole-based and a multi-collector-based magnetic sector mass spectrometer are both used in LA-ICPMS.

LA-ICPMS is a convenient method because it does not require any elaborate sample preparation, and the sampling process is independent of physical or chemical properties of the material. It obviates the need to chemically dissolve the sample, and hence dilution of the element does not take place. Also, loss

of the volatile elements observed during dissolution of the sample is eliminated, and reagent blank problems are completely absent. This approach is less labor-intensive, and can be used routinely to analyze quickly a large number of samples. Determination of stoichiometry, spatial analysis, and depth profiling can be done along with micro-analysis. Further, there is a possibility to use non-matrix matched and non-isotope ratio matched calibration materials.

LA-ICPMS is an attractive non-invasive and fast-analysis alternative for samples that are either precious (e.g., archeological) and, therefore, not to be destroyed with wet chemistry, or for samples that contain small amounts of boron (e.g., foraminifera, corals). Solution-based ICP-MS definitely consumes a few mg (1–3 mg) of the sample, and is labor-intensive and time-consuming. In such cases, it is better to evaluate the precision and accuracy of LA-ICP-MS with samples with similar matrices, with solution-based ICP-MS.

## F. Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) is a well-recognized tool for *in situ* micro-analysis of boron in a variety of solid rock samples. The  $^{11}\text{B}/^{10}\text{B}$  isotope ratio was measured (Chaussidon et al., 1997) in terrestrial basaltic rocks and meteoritic chondrules with an IMS 3f SIMS that used an  $\text{O}^-$  primary ion beam of about 10 nA intensity. The isobaric interference of  $^{10}\text{BH}^+$  at  $^{11}\text{B}$  was eliminated with a mass resolution of about 1800. Accuracy values of 1.5 and 5% were obtained for samples that contained 5 ppm and 0.1–1 ppm of boron, respectively. An instrumental isotope fractionation of  $0.9538 \pm 0.0015$  was observed for the  $^{11}\text{B}/^{10}\text{B}$  isotope ratios.

In recent years, SIMS has been used to determine boron isotopic composition and concentration with the single collector Cameca IMS 4f as well as with the large-geometry Cameca IMS 1270 multicollector system. These large radius SIMS instruments provide high transmission, stability and sensitivity, and, therefore, allow the determination of B isotope ratios in low-B samples. Corals, bivalves, foraminifers, and reference glasses were analyzed with both the SIMS instruments (Kasemann et al., 2009). Pre-sputtering for about 1 min was done to remove surface contamination from samples. A primary ion beam of  $^{16}\text{O}^-$  ions was used to obtain  $^{10}\text{B}^+$  and  $^{11}\text{B}^+$  secondary ions in both the instruments. Primary beam currents and energies were 10–40 nA, 15 keV and 5 nA, 22 keV, respectively. Care was taken to check for isobaric interferences from  $^9\text{BeH}^+$ ,  $^{10}\text{BH}^+$ , and  $^{30}\text{Si}^{3+}$ , which were insignificant within the measurement uncertainties. The accuracy of the data obtained on  $\delta^{11}\text{B}$  for carbonate samples was sufficient for geochemical applications, and also demonstrated the applicability of *in situ* micro-analysis to improve current understanding of biological and environmental effects on boron-isotope fractionation.

Large radius ion-microprobe Cameca IMS 1270 and IMS 1280 were recently used (Blamart et al., 2007; Marschall & Monteleone, 2015) to determine boron isotope ratios in the deep-sea aragonitic corals and in silicate glasses, respectively. In the coral studies (Blamart et al., 2007), primary beam of  $^{16}\text{O}^-$  ions with an energy of 13 kV, intensity of 70 nA was focused to a spot of approximately 15-mm wide and 30-mm long to obtain homogeneous beam density. The data on B isotopes were acquired in mono-collection mode with the central electron multiplier. An overall difference of 10% in the B isotopic

composition was observed in different ultra-structural components in the deep-sea scleractinian *Lophelia pertusa*, and this difference could not be attributed to environmental parameters. For the silicate glasses (Marshall & Monteleone, 2015), a 40 nA  $^{16}\text{O}^-$  primary beam was used, and analyses were done with a spatial resolution of  $30 \times 30 \mu\text{m}^2$  within about 30 min. Precision values of 1.5 and 0.5‰, respectively, were achieved in basaltic glass at B concentrations of  $1 \mu\text{g g}^{-1}$  and in other samples that exceeded  $20 \mu\text{g g}^{-1}$ , respectively.

Resonant laser-sputtered neutral mass spectrometry (SNMS) with a  $\text{Ga}^+$  primary ion source and a gridless reflectron ToF mass analyzer was used to determine B isotope ratios in a single foraminifera calcite shell. A three-step ionization scheme that consisted of two tunable dye lasers and the fundamental wavelength of Nd-YAG laser was used. Precision of about 2%, limited only by counting statistics, was reported (Vering et al., 2006). Improvement was suggested by increasing the repetition rate of the measurement cycles and with primary-ion guns with very high ion currents to enhance the number of sputtered particles per shot.

At present, SIMS does not provide the precision and accuracy of 0.2–0.4‰ in B-isotope ratio measurements, required in paleo-proxy studies. However, precision and accuracy of 1–2‰ are possible with large geometry SIMS instruments, in solid rock samples like natural volcanic glasses, and these satisfy the requirement of geochemical analysis (Marshall and Monteleone, 2015).

### G. Gas-Source Mass Spectrometry (GSMS)

The isotopic composition of boron was initially determined with gas-source mass spectrometry with  $\text{BF}_3$ , and an electron-ionization source (Ingram, 1946; Thode et al., 1948; Gonfiantini et al., 1997a,b). The volatile nature of  $\text{BF}_3$  was exploited, and the  $^{11}\text{B}/^{10}\text{B}$  isotope ratio was obtained by monitoring  $\text{BF}_2^+$  ions. In spite of the high precision achievable with this procedure, it was abandoned, for boron, due to the memory problem associated with the adsorption of gas molecules in the inlet system of gas-source mass spectrometer and more so, due to the advent of techniques like ICPMS, which allow direct handling of the solution that contained boron to thereby eliminate the need to convert B into its fluoride. It is worth mentioning that GSMS has played an important role for Si isotopic analysis to reevaluate a new highly precise and accurate value of the Avogadro Number (DeBievre et al., 1995).

### H. Other Methods

In nuclear technology, it is necessary to provide chemical quality assurance of the B-containing finished products, for example,  $\text{B}_4\text{C}$  pellets, in a non-destructive way. For these verifications, precision and accuracies of 1–5% in B-isotope ratios are acceptable. An in house (India) laser-reflectron time-of-flight (RTOF) mass spectrometry system with a 532 nm Nd-YAG laser was used to determine boron isotopic ratios in boric acid and in  $\text{B}_4\text{C}$  pellets of control rods of a nuclear reactor with a precision of 50‰ ( $2\sigma$ ) (Manoravi et al., 2005; Manoravi, Joseph, & Sivakumar, 2008). A laser-based molecular isotopic spectrometry (LAMIS) method, with 1000 single shot accumulated spectra, was

also reported recently to determine  $^{11}\text{B}/^{10}\text{B}$  isotope ratios with a precision of 9‰ ( $2\sigma$ ; Sarkar, Mao, & Russo, 2014).

## IV. VARIOUS APPLICATIONS OF BORON ISOTOPE RATIOS

N-TIMS was used (Wieser et al., 2001) to study the  $\delta^{11}\text{B}$  variations in unroasted *Coffea arabica* beans from 14 different coffee-growing regions around the world. Significant differences observed in  $\delta^{11}\text{B}$  from –12 to +19‰ were attributed to the local changes in the isotopic composition of B, including soil, water, and fertilizer.

Three milligrams of enriched  $^{10}\text{B}$  (94.14 atom%) was fed to coffee plantlets by cultivating them in nutrient solutions for 3 months (Bellato, Menegario, & Gine, 2003) and by comparing the results with control samples. A Q-ICPMS system with direct-injection nebulizer was used for boron isotope measurements in leaves subjected to cell fractionation, stems, and roots.  $^{10}\text{B}/^{11}\text{B}$  isotope ratios that ranged from 1.02 to 1.326 showed a  $^{10}\text{B}$  enrichment of 29%, 27%, and 25% in the chloroplast, cell wall, and nucleus fractions, respectively. Boron isotopes were used as artificial tracers (Quast et al., 2006) in California, USA, where 3.6 kg of boron as boric acid, that contained 96% enriched  $^{10}\text{B}$ , was added to basin recharge water to estimate travel time and dilution during transport of the infiltrate from the reclaimed basin to nearby wells. The studies showed that boron is conserved during ground water transport, and is a useful tracer to understand dilution and transport, in addition to other conventional tracers; for example,  $^{124}\text{Xe}$ ,  $^{136}\text{Xe}$ ,  $\delta\text{D}$ , and  $\delta^{18}\text{O}$ .

Under the ISONITRATE project of the European water framework directive (WFD) program,  $\delta^{11}\text{B}$  was used to discriminate among the nitrate pollution sources—viz, organic fertilizer (animal manure), mineral fertilizer, and sewage water. Interesting screening results were obtained by determining  $\delta^{11}\text{B}$  in ground and surface water with single-collector TIMS (MAT 261, Finnigan) and single-collector ICPMS (ELEMENT II, ThermoFisher) instruments. These results should further promote the use of  $\delta^{11}\text{B}$  in future studies (Tirez et al., 2010).

Boron-isotopic characterization of coal combustion residues (CCR) was recently shown as a promising viable environmental tracer (Ruhl et al., 2014). The analysis of CCR effluents showed higher boron concentrations in flue gas discharge (FGD) effluents than those without FGD. These studies are very important in view of the world's largest CCR spill in 2008 at the Tennessee Valley Authority's Kingston Fossil Plant in USA. The  $\delta^{11}\text{B}$  values (–18 to +7‰), measured with N-TIMS of CCR leachates from different regions in USA, were found to be related to different coal sources. Previous SIMS studies showed heterogeneity of boron in organic sediments (kerogen, coal) with  $\delta^{11}\text{B}$  values much lighter (–1 to –70‰; Williams & Hervig, 2004).

$^{10}\text{B}/^{11}\text{B}$  isotope ratios determined with ICPMS (Perkin Elmer Nexion 300D) in the enamel of carious teeth and healthy teeth of males and females in the age groups of 7–79 years were shown to vary from 0.2007 to 0.2574. These preliminary results (He et al., 2015a) must be confirmed by other researchers on similar samples to arrive at definite conclusions.

Recently, LA-MC-ICP-MS (Neptune) was performed (Devulder, Degryse, & Vanhaecke, 2013; Devulder et al., 2014, 2015) on Roman glasses to elucidate the source of flux raw material used (i.e., natron flux or of plant origin) based on B

isotope ratios. A high-energy ArF excimer laser (193 nm) and 8 Hz repetition rate was used. The mass discrimination for  $^{11}\text{B}/^{10}\text{B}$  ratio was dependent upon the laser spot size (mass discrimination-corrected isotope ratio decreased with increasing spot size of 50–250  $\mu\text{m}$ ), and was standardized with NIST-610 glass standard. An expanded uncertainty of better than 2‰ was reported for different glass samples with B concentrations in the range of 10 to 1000  $\mu\text{g g}^{-1}$  and  $\delta^{11}\text{B}$  values ranged from –10 to +40‰. This methodology can be successfully adopted for provenance studies, subjected to the availability and spread of reference values for possible natron sources.

LA-MC-ICPMS was used (Fietzke et al., 2010) to determine  $\delta^{11}\text{B}$  in laboratory cultured aragonite corals at different pH values (7.8–8.3) of the solution. LA used a 193 nm ArF laser with 150  $\mu\text{m}$  spot size and repetition rate of 30 Hz. The SSB approach was used. No difference in the data was observed with different amounts of the ablated material with laser repetition rate of 5–40 Hz. An Axiom MC-ICPMS with Faraday cup for  $^{11}\text{B}$  and secondary electron multiplier for  $^{10}\text{B}$  was used for measurements. A reproducibility of 0.5‰ (1 SD) was observed for  $\delta^{11}\text{B}$ , and 0.2 ng of B was consumed during the laser ablation experiment. Further, no significant difference in the results, within the measurement uncertainty, was observed for three different matrices (i.e.,  $\text{CaCO}_3$ , Si-Na-Ca-Al glass, and NaCl). The authors confirmed the dependence of  $\delta^{11}\text{B}$  of coral aragonite with pH of the solution, and envisaged the use of NIST glass standards for SSB in future.  $\delta^{11}\text{B}$  values increased from 19.75 to 24.98‰, with a change in the pH of culturing water from 7.77 to 8.32.

Often, there is a need for a rapid non-destructive screening method for the finished product (e.g., in a metallurgical plant that prepares the boron-containing steel materials for nuclear technology). A comparison of ns and fs laser in LA-ICPMS demonstrated a precision poorer by a factor of 5 with ns-LA-ICPMS (Kurta et al., 2014). The precision of the B isotope ratios was 0.21–1.1‰ (1sd) and 0.04–0.51‰ (1sd) with ns-LA-Q-ICPMS and fs-LA-MC-ICPMS instruments, respectively. However, the lower cost of ns-LA-Q-ICPMS and its capability to meet the rapid screening requirements in the steel industry was projected as an incentive to use quadrupole-based ICPMS instruments.

LA-MC-ICPMS with a 193 nm excimer laser with Neptune Plus MC-ICPMS was used (Martin, Ponzevera, & Harlow, 2015) for *in situ* determination, with good spatial resolution, of B isotope ratios in mica, pyroxene, and serpentine. B and Li are known to preferentially partition into the liquid phase during fluid-rock and melt-rock interactions, and are, therefore, useful to track fluid-related processes in rocks. The isotopic data were compared with those from SIMS with a Cameca IMS 1280 ion microprobe. The LA-ICPMS method was suitable for B isotopic analysis in subduction-related rocks (silicates) with boron concentrations that exceeded 5  $\mu\text{g/g}$ , with an external reproducibility of  $\pm 2.88$  to 3.31‰ (2 SD) and in a short time of 2 min/analysis. *In situ* studies for boron isotopic analysis were also reported in carbonates (Fietzke et al., 2010) and tourmalines (Mikova, Kosler, & Wiedenbeck, 2014).

Femtosecond LA (200 nm) was used (Jochum et al., 2014) to determine 47 trace elements, including boron, in 22 reference materials, and the results were compared with those obtained with two commonly used ns lasers (193 nm excimer and 213 nm Nd:YAG). A detailed study was reported for the matrix effects,

which included elemental fractionation and mass loading matrix effects. It was shown that, with fs LA-ICPMS and use of line scan instead of spot scan, significant elemental-fractionation effects do not occur, and that a non-matrix matched calibration standard can be used to determine trace elements in geological and environmental samples.

LA-ICPMS with a fs Ti-sapphire laser, fourth-harmonic generated 194 nm beam, and an ion-counting system that consisted of compact discrete dynode multipliers (CDD) instead of Faraday cups in MC-ICPMS for  $\delta^{11}\text{B}$  measurements, and simultaneous use of an ICP-OES system for B/Ca ratios, was employed recently (Kaczmarek et al., 2015). Measurements performed on cultured, benthic foraminifer *Amphistegina lessoni*, yielded an average boron concentration of  $53 \pm 7 \mu\text{g/g}$  (1 SD) and  $\delta^{11}\text{B}$  as  $18.0 \pm 0.83\%$  (1 SD), in agreement with those available in the literature. Mean internal precision values of 0.52 and 0.29‰ were obtained for  $\delta^{11}\text{B}$  in foraminifera and coral samples, respectively, with B/Ca ratios of  $0.588 \pm 0.08$  (1 SD) and  $0.564 \pm 0.026$  (1 SD) mmol/mol. The estimated amount of ablated calcite was 0.73  $\mu\text{g}$  equivalent to 0.024 ng of boron, nearly eight times less than that used previously (Fietzke et al., 2010).

B isotope compositions were determined in different geological materials with LA-MC-ICPMS that used a 193 nm ArF excimer laser (Lin et al., 2014). Three different sample and skimmer cone combinations (i.e., standard sample cone + H skimmer cone, standard sample cone + X skimmer cone, and a jet sample cone + X skimmer cone) were used with and without addition of  $\text{N}_2$  into one of the three ICP gas flows. The combination of jet sample cone + X skimmer cone improved precision by a factor of 2–10 for low B-containing (11 and 31 ppm) materials.

Coral bleaching events were investigated recently by determining decrease of  $\delta^{11}\text{B}$  with fs LA-MC-ICPMS in corals (Dishon et al., 2015). These studies are useful to study global decline in coral reefs and correlate paleo-coral bleaching with environmental changes.

## V. INTERLABORATORY COMPARISON/EVALUATION EXPERIMENTS

Interlaboratory intercomparisons are highly useful to evaluate different researchers who perform similar analyses with the same or different mass spectrometric technique. These comparisons also identify unknown problems /limitations of the procedures followed by researchers at various laboratories. Participation in such exercises provides an opportunity to the researcher to evaluate himself/herself and also enhances the confidence in terms of the capability to compare/compete/match all other participating researchers. A number of international intercomparisons have been conducted, from time to time, to evaluate the status of boron isotopic analysis by various mass spectrometric techniques in different materials. Three inter-laboratory inter-comparisons have been reported by the earth scientists and marine geochemistry community to evaluate developments in  $\delta^{11}\text{B}$  determination at various international laboratories.

The first inter-laboratory inter-comparison to determine the isotopic composition and/or concentration of boron was planned by the Instituto di Geoscienze e Georisorse (IGG) at Pisa, Italy with the support of the International Atomic Energy Agency

(IAEA; Tonarini et al., 2003). A total of eight samples that consisted of three natural waters and five rocks and minerals, were distributed. The natural water samples were Mediterranean seawater (B1) and ground water (B2 and B3), and the rocks and minerals were tourmaline (B4), basalt (B5), obsidian (B6), limestone (B7), and clay (B8). Out of the 27 researchers who agreed to participate, only 15 submitted the results. Data analysis showed an interlaboratory reproducibility that was poor compared to the precision values reported by the each individual researcher. During this exercise, seven researchers used P-TIMS and N-TIMS, ICPMS (4), MC-ICPMS (1), and SIMS (3). An evaluation of the data received from various researchers in different laboratories showed most consistent results for water (B3,  $1.795 \text{ mg L}^{-1}$  of B,  $\delta^{11}\text{B} -21.33\text{‰}$ ) and clay (B8,  $101.6 \text{ mg kg}^{-1}$  of B,  $\delta^{11}\text{B} -5.4\text{‰}$ ) in view of the simple matrices. The largest variation was seen for ground water (B2,  $0.2085 \text{ mg L}^{-1}$  of B,  $\delta^{11}\text{B} +13.6\text{‰}$ ) and limestone (B7,  $1.91 \text{ mg kg}^{-1}$  of B,  $\delta^{11}\text{B} +7.2\text{‰}$ ) due to the low boron concentrations compared to other six samples. The spread of data on B1 (sea water), B5 (basalt), and B6 (obsidian) was attributed to complex matrices to highlight the need to develop methods for extraction and purification of boron. No definite conclusion was drawn about the poor precision, whether due to contamination, fractionation during sample processing, or mass spectrometric technique used (Gonfiantini et al., 2003; Tonarini, Pennisi, & Gonfiantini, 2009).

During the second inter-laboratory inter-comparisons, two standards were prepared by gravimetrically mixing solutions of 96% enriched isotopes of  $^{10}\text{B}$  and  $^{11}\text{B}$  in the form of boric acid (Aggarwal et al., 2009a). These standards—(viz, JABAA and JABAB) were prepared with  $\delta^{11}\text{B}$  values of  $9.86\text{‰}$  and  $-23.65\text{‰}$ , with B concentration of  $10 \mu\text{g mL}^{-1}$ . These two standards, along with NIST-SRM-951 solution with approximately 10 ppm boron, were sent to researchers in 28 laboratories that showed interest in participating; however only 15 researchers submitted their results. Researchers used different mass spectrometric techniques (e.g., P-TIMS [3 labs] and N-TIMS [6 labs] [both with and without total evaporation], Q-ICPMS [3 labs], HR-ICPMS [1 lab], and MC-ICPMS [5 labs]); some researchers used more than one technique. The data reported with various analytical techniques could be compared in this exercise. It was concluded (Aggarwal et al., 2009a) that  $\delta^{11}\text{B}$  results with N-TIMS can be lowered by the isobaric interference from  $\text{CNO}^-$  at  $m/z$  42, and that ICPMS data can be positively biased due to incomplete resolution of isobaric interference from  $\text{Ar}^{4+}$ . It was recommended that all researchers who analyze boron should carefully control, assess, and report boron blank data. The weighted mean values of  $9.99 \pm 0.08$  and  $-23.66 \pm 0.10\text{‰}$  estimated for JABAA and JABAB, respectively, were in good agreement with results from gravimetry, after consideration of the uncertainty values.

Recently, during 2013, the results of the third inter-laboratory inter-comparison experiment organized for the isotopic analysis of boron in boric acid, sea water, and marine  $\text{CaCO}_3$  were published (Foster et al., 2013). Samples were not distributed openly but researchers from four laboratories were involved with their specific interest of analyses. These researchers were from Bristol Isotope Group (BIG), UK; Lamont-Doherty Earth Observatory (LDEO) of Columbia University, USA; Institut de Physique du Globe de Paris (IPGP), France; and Duke University, USA. Fifteen samples of  $\text{CaCO}_3$  that

ranged from inorganic calcite to aragonitic corals, and three samples of boric acid, were given to each researcher. Researchers in two laboratories (BIG and IPGP) used MC-ICPMS, and the other two (LDEO and Duke) employed N-TIMS. B/Ca ratios of the 15 samples determined with Thermo Scientific Element 2 ICPMS ranged from 65 to  $522 \mu\text{mol/mol}$ . Researchers in each laboratory followed their own protocol of sample digestion/analysis, and used in-house available sea water reference material. The group at Bristol used ammonia add-gas to improve boron wash-out, whereas at IPGP, direct injection nebulisation was employed (Louvat, Bouchez, & Paris, 2010; Louvat et al., 2014) and washing was done only with  $0.5 \text{ M HNO}_3$  for 100 sec. At LDEO and Duke, strict analytical protocols were followed to keep the time-dependent mass fractionation under control in N-TIMS, by loading 1–10 ng of boron on the filament.

The results from this inter-laboratory comparison showed that there was no significant difference in the data obtained by researchers in the four laboratories for simple matrices like boric acid and sea water. The significant variation noted for  $\text{CaCO}_3$  samples was attributed either to size of the sample (with small amounts of boron) or due to differences in B/Ca ratios of these samples (Foster et al., 2013). A need was expressed to organize in future interlaboratory comparison experiments and to keep in mind the experiences gained from these experiments.

Another interlaboratory study was reported for reference corals aragonite (Hathorne et al., 2013), in which researchers from a limited number of laboratories out of a total of 21, submitted their results on B/Ca ratios. The experiment was aimed to evaluate different analytical methodologies, including mass spectrometry, for coral Sr/Ca and other-element/Ca ratios for palaeothermometry (i.e., past sea-surface temperature). Mean values of B/Ca ratios of  $459.6 \pm 22.7$  (1 SD) and  $191.0 \pm 9.3$  (1 SD)  $\mu\text{mol/mol}$  were obtained from the data reported by researchers from six and 3 laboratories for *Porites* coral reference material JCP-1 and giant clam reference material JCT-1, respectively. It was recommended that in future, all the studies determining coral element/Ca ratios should also report the values determined in a reference material such as JCP-1 (Hathorne et al., 2013).

## VI. CERTIFIED ISOTOPIC REFERENCE MATERIALS (CRMS) FOR BORON

Certified reference materials (CRMs) are required to validate any methodology with respect to repeatability, reproducibility, and evaluate the accuracy. These CRMs are also necessary from the traceability point of view to bring the measurements performed by researchers in different laboratories around the world at a common platform. The Isotopic reference materials are generally prepared by gravimetric mixing of the characterized high-purity elements, or stoichiometric compounds of the enriched isotopes. The certified isotope ratios are determined by theory with the amounts mixed, enrichment level of the isotopes, other impurities present, etc., and the overall uncertainty is given by compounding the uncertainties on different parameters.

In the case of boron, there are problems because boric acid ( $\text{H}_3\text{BO}_3$ ) is not a primary standard. Boric acid is always associated with small amounts of water and on heating it to about  $100^\circ\text{C}$ , it dehydrates to form  $\text{HBO}_2$  (Vogl & Rosner, 2011). Until 2001, there were only two isotopic reference materials of boron available from NIST— viz, natural B (SRM-

951) and highly enriched B (SRM-952). These CRMs were mainly used in the nuclear industry. With the increased interest in  $\delta^{11}\text{B}$  studies with MC-ICPMS as well as MC-TIMS techniques over the last two decades, there is a growing demand for isotopic reference materials (IRMs) that span the natural variations in the  $^{11}\text{B}/^{10}\text{B}$  isotope ratios. The need for isotopic reference materials and the details of preparation and characterization of new reference materials for boron have been discussed recently (Vogl & Pritzkow, 2010; Vogl & Rosner, 2011).

A list of the boron isotopic reference materials (IRMs) available commercially is given in Table 2. There are two types of IRMs required for mass spectrometric analysis of boron—viz, (i)  $\delta^{11}\text{B}$  for geochemical, environmental, and provenance studies, and (ii)  $^{10}\text{B}$ -enriched materials for the nuclear industry. These isotopic reference materials are now commercially

**TABLE 2.** Certified isotopic reference materials (IRMs) for isotope ratio of boron

| Isotopic reference material | Matrix                                 | $^{11}\text{B}/^{10}\text{B}$ or $\delta^{11}\text{B}$  |
|-----------------------------|--|---|
| NIST-SRM-951a               | Boric acid (solid)                     | $^{10}\text{B}/^{11}\text{B} = 0.2473 \pm 0.0002$ (1 sd) (natural B), Primary                     |
| NIST-SRM-952                | Boric acid (solid)                     | $^{10}\text{B}/^{11}\text{B} = 18.80 \pm 0.02$ (1 sd), $^{10}\text{B}$ (95%)                      |
| IRMM-011                    | Crystalline boric acid                 | +0.16‰, -0.375‰ (sd not given)  |
| NIST SRM 610                | Silicate glass                         | -0.52 ± 0.53‰ (1 sd) (from GeoReM)  |
| NIST-SRM-612                | Silicate glass                         | -1.07 ± 1.7‰ (2sd), -0.51‰ (from GeoReM)  |
| OSIL-IAPSO                  | Sea water                              | +39.64 ± 0.42‰ (1 sd)   |
| NRCC NASS-5                 | Sea water                              | +39.88 ± 0.27‰ (1 sd), Louvat et al., 2011  |
| IAEA-B1                     | Sea water                              | +38.76 ± 0.79‰ (1sd)  |
| IAEA-B2                     | Ground water                           | +13.8 ± 0.79‰ (1sd)   |
| IAEA-B3                     | Ground water                           | -21.4 ± 0.89‰ (1sd)   |
| IAEA-B4                     | Tourmaline                             | -8.7 ± 0.18‰ (1sd)  |
| IAEA-B5                     | Basalt                                 | -3.8 ± 2.0‰ (1sd)   |
| IAEA-B6                     | Obsidian                               | -1.8 ± 1.5‰ (1sd)   |
| IAEA-B7                     | Limestone                              | +9.7 ± 5.9‰ (1sd)   |
| IAEA-B8                     | Clay                                   | -5.1 ± 0.87‰ (1sd)  |
| GSJ-Jcp-1                   | Carbonate standard (coral powder)      | 24.3 ± 0.34‰ (2sd)  |
| GSJ-Jct-1                   | Carbonate, Tridacna giant clam (coral) | 16.2 ± 1.62‰ (2sd, oxidized)<br>16.4 ± 1.64‰ (2sd, un-oxidized)                                   |
| GSJ-JB-2                    | Basalt rock powder                     | +7.24 ± 0.33‰ (2sd)   |
| ERM-AE101                   | Boric acid solution                    | $^{10}\text{B}/^{11}\text{B} = 0.28197$ , (-123.01 ± 0.41‰), (21.99% $^{10}\text{B}$ , secondary) |
| ERM-AE102a                  | Boric acid solution                    | $^{10}\text{B}/^{11}\text{B} = 0.4285 \pm 0.0006$ (2 sd), (29.99% $^{10}\text{B}$ , secondary)    |
| ERM-AE103                   | Boric acid solution                    | $^{10}\text{B}/^{11}\text{B} = 0.9895$ (49.74% $^{10}\text{B}$ , secondary)                       |
| ERM-AE104a                  | Boric acid solution                    | $^{10}\text{B}/^{11}\text{B} = 0.4596 \pm 0.0006$ (2 sd), (31.49% $^{10}\text{B}$ , secondary)    |
| ERM-AE120                   | Aqueous solution (boric acid)          | $\delta^{11}\text{B}$ : -20.2 ± 0.6‰ (2 sd)   |
| ERM-AE121                   | Aqueous solution (boric acid)          | $\delta^{11}\text{B}$ : +19.9 ± 0.6‰ (2 sd)   |
| ERM-AE122                   | Aqueous solution (boric acid)          | $\delta^{11}\text{B}$ : +39.7 ± 0.6‰ (2 sd)   |
| ERM-ED102                   | Boron carbide powder                   | -5.0‰ (sd not given)  |
| BCR-679                     | Cabbage                                | -23.8 ± 1.15‰ (1 sd)  |
| NIST-RM-8433                | Corn bran                              | +8.3 ± 1.69‰ (1 sd)   |
| NIST-RM-1547                | Peach leaves                           | +41.1 ± 1.12‰ (1 sd)  |

NIST, National Institute for Standards and Technology, Gaithersburg, USA, <http://www.nist.gov>; IRMM, Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, Geel, Belgium, <http://irmm.jc.ec.europa.eu>; ERM, European Reference Materials, <http://www.erm-crm.org>; BAM, Federal Institute for Materials Research and Testing, Berlin, Germany, <http://www.bam.de>.

available from NIST, USA; IRMM, Belgium; and BAM, Germany. Most are secondary reference materials primarily used for quality control and to validate the mass spectrometric analysis procedures. The  $^{10}\text{B}$ -enriched materials are primarily used to determine the mass discrimination factor in TIMS. One such attempt to prepare and characterize the  $^{10}\text{B}$  enriched secondary isotopic reference materials to be used for quality control in  $^{10}\text{B}$ -enrichment plant and for nuclear industry was published recently (Rao, Parab, & Aggarwal, 2012).

Because NIST-SRM-951 isotopic reference material is used most commonly by most researchers in a variety of applications, a few aspects about this certified isotopic reference material are given here. NIST-SRM-951 was prepared from Searles Lake Borax, and the certified value was obtained at NBS (Catanzaro et al., 1970) with  $\text{Na}_2\text{BO}_2^+$  in P-TIMS. A large number of researchers have determined  $^{11}\text{B}/^{10}\text{B}$  ratio in NIST-SRM-951 with different mass spectrometric methodologies and instruments. SRM-951 is a routinely used standard to determine  $\delta^{11}\text{B}$  values with MC-ICPMS employing SSB approach.

## VII. DETERMINATION OF B/Ca RATIOS

B/Ca ratios are of interest (Coadic et al., 2013) to reconstruct seawater chemistry and environmental conditions of the ocean in the past 20 million years. These ratios in benthic foraminifera have the potential to reconstruct the carbonate ion history of their habitat. Studies on B/Ca ratio proxy for marine carbonate chemistry are relatively new and culture experiments under controlled environmental conditions are also done in a few laboratories (Allen et al., 2011, 2012; Allen & Hönisch, 2012). However, a lot more needs to be done to make the proxy robust and allow B/Ca ratios of planktic foraminifera to unravel the ocean surface chemistry (Allen & Hönisch, 2012). The dependence of boron incorporation, and therefore B/Ca ratios on temperature, salinity, carbonate chemistry, sea-water boron concentration, and other parameters in different foraminifera species need to be constrained to arrive at conclusive interpretations. A variety of mass spectrometric techniques are used to determine B/Ca ratios in various types of samples, as discussed below.

A quadrupole ICPMS (Perkin–Elmer Elan DRC II) was used (Yu et al., 2005) to determine B/Ca ratios along with other element/Ca ratios in foraminiferal calcite samples. A quartz cyclonic spray chamber was used to minimize the boron blanks from about 30% with a glass spray chamber to about 5%. In addition, a small-diameter peristaltic pump tubing (ID 0.03 mm) and a glass micro-concentric nebulizer with a narrow orifice were used to reduce solution consumption to 60  $\mu\text{L}/\text{min}$ . The cleaned foraminiferal tests (Barker, Greaves, & Elderfield, 2003) after dissolution in 0.075 M  $\text{HNO}_3$  were used for ICPMS measurements with pulse-counting mode to avoid the need for cross-calibration of detectors. The effect of Ca deposition on the sampling cones, which decreases sensitivity, was circumvented with cone-conditioning procedure that consisted of injection of a 100 ppm pure Ca solution for 30–60 min prior to the analysis of foraminiferal sample solutions. External standardization with matrix-matched multiple calibration standards was used to determine B/Ca (about 1–10 ppb of B) and other-elements/Ca ratios. Longer wash-out and uptake times were used to minimize the B memory effect. Long-term relative standard deviation (RSD) of 2–7% was reported for planktonic foraminiferal

samples, which usually have small B/Ca ratios, in the range of 41–78  $\mu\text{mol/mol}$ , with a foraminiferal sample amount of about 60  $\mu\text{g}$ .

Recently, a triple quadrupole-based ICPMS system QQQ-ICPMS (Agilent 8800, Tokyo, Japan) was employed to determine the low B/Ca ratios (a few  $\mu\text{mol}$  of B/mol of Ca) in carbonate samples (Fernandez et al., 2015). In this system, there is an octopole collision/reaction cell between the two hyperbolic quadrupole mass filters Q1 and Q2. This triple quadrupole system offers the advantage to remove isobaric and polyatomic interferences with two approaches (i.e., *on mass MS/MS mode* with precursor-ion scan, and *mass shift mode* with product-ion scanning (Agilent, 2013)). The system provided a high abundance sensitivity (more than  $10^8$ ), which minimized the tail contribution of  $^{12}\text{C}^+$  at the  $^{11}\text{B}^+$  peak. Oxygen gas was used in the octopole collision cell to chemically resolve  $^{46}\text{Ti}$  and  $^{46}\text{Ca}$  (reaction enthalpies of  $\text{Ca}^+$ ,  $\text{Ti}^+$ , and  $\text{B}^+$  with  $\text{O}_2$  are +1.53, -1.63 and +1.39 eV, respectively) and perform *on mass* measurements for  $^{11}\text{B}^+$ . B/Ca ratios close to 1  $\mu\text{mol/mol}$  were measured in calibration standards as well as for cultured samples (Fernandez et al., 2015). These results on B/Ca ratios were quite low compared to those reported with isotope dilution-TIMS and SIMS, and, therefore, further investigations are required to look into this discrepancy.

B/Ca ratios (range from 42.4 to 98.8  $\mu\text{mol/mol}$ ) were determined in natural carbonates (planktonic foraminiferal shells) with single-collector sector-field HR-ICPMS (Thermo-Element XR; Misra et al., 2014). A detection limit of 2  $\mu\text{mol/mol}$ , with the possibility to analyze a single foraminiferal shell, was reported, compared to a previous detection limit of higher than 10  $\mu\text{mol/mol}$  (Yu et al., 2005, 2007, 2010; Rae et al., 2011).

LA and solution based Q-ICPMS were used to determine B/Ca ratios (Allen et al., 2011) in *Orbulina universa* from culture experiments in living planktic foraminifera. The bulk analysis of B/Ca was done with Perkin-Elmer SCIEX DRC-II Q-ICPMS, and Rh and In were used as internal standards for quantitation. The B/Ca profiles in inner and outer parts of the cultured shells were determined with pulsed ArF excimer laser (193 nm) in an Agilent 7500s ICPMS system. Variations were observed in B/Ca determined from individual shell profiles as well as in the shells cultured under identical experimental conditions. The need to perform more culture experiments to constrain the dependence of B/Ca on various parameters and in various foraminifera species was highlighted (Allen et al., 2011).

A SIMS study to determine B/Ca in coccoliths from three different strains of *Emiliania huxleyi* and one strain of *Coccolithus braarudii braarudii* cultured under different seawater pH conditions, illustrated the response of coccolithophorids algae to changing pH of the ocean (Stoll et al., 2012). ICPMS cannot be used for these studies because B/Ca of the cultured coccoliths is much lower than those of foraminifera and corals (Yu et al., 2005). In this study, a primary ion beam of  $^{133}\text{Cs}^+$  with 12.7 keV energy, 5–6 nA current focused to a spot of about 20  $\mu\text{m}$  diameter, was used on a Cameca IMS 1280. The yield of  $\text{B}^-$  secondary ions from carbonate samples with  $\text{Cs}^+$  bombardment was about five times more than that of  $\text{B}^+$  ions produced by bombarding with  $\text{O}^-$  primary ions. Culture samples were cleaned to remove organic phases with an oxidizing solution and after oven drying at 110°C for 12 hr, were mounted in an aluminum holder with indium substrate, and a thin gold film

(30 nm) was coated prior to ion-probe analysis. B/Ca ratios in the range of  $8.2 \pm 0.5 \mu\text{mol/mol}$  (2 standard error) to  $56 \pm 9.1 \mu\text{mol/mol}$  were determined in various coccoliths.

## VIII. CONCLUSIONS AND RECOMMENDATIONS

Table 3 lists the various kinds of mass spectrometers available from different vendors for isotope ratio measurements. Because MC-TIMS and MC-ICPMS are most commonly used for isotope ratio and amount determination of boron, a comparison of their salient features is included in Table 4. Figure 2 compares the relative precision achievable and the amounts required for isotope analysis of boron with TIMS, ICPMS, and SIMS. MC-ICPMS, undoubtedly, provides an easy way to determine  $\delta^{11}\text{B}$  values in a variety of matrices with SSB. Researchers experience in different laboratories over the past decade has demonstrated that it is possible to achieve relative precisions better than 1‰, if the samples to be measured do not have large variations in the isotope ratios (e.g.,  $\delta^{11}\text{B}$  between -50‰ and +50‰) and about 10–50 ng/mL of boron in the solution is available. MC-ICPMS is the most preferred technique for paleo-proxy studies with B solutions of about 20 ppb concentration and satisfies the requirement of high precision (0.2–0.4‰) for practical use of the isotope ratio data. Further, for samples with less than nanogram amounts of boron (e.g., foraminiferas, coccoliths), the technological advances with the use of  $10^{12}$  and  $10^{13} \Omega$  resistors with MC-ICPMS will further reduce the sample size requirements and allow analysis of much smaller  $^{11}\text{B}$  signals (Makishima & Nakamura, 2012; Koornneef et al., 2014). MC-TIMS (positive and negative) has the biggest

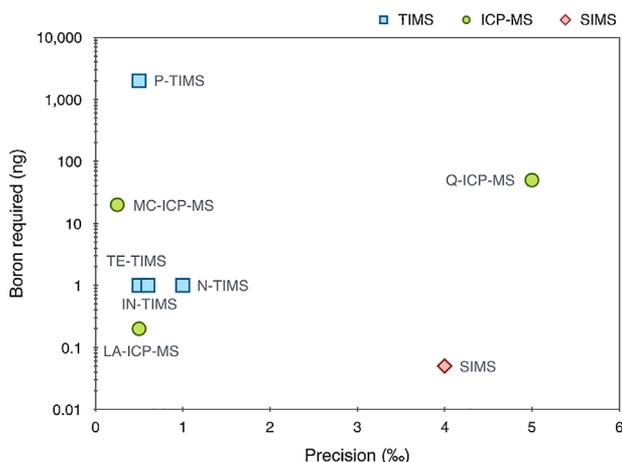
**TABLE 3.** Different types of mass spectrometers available for isotopic analysis of boron

| Type of MS | Model                                     | Vendor                                   | Remarks   |
|------------|---|--|---|
| TIMS       | TRITON PLUS                               | Thermo Fisher, Germany                   | MC, RPQ filter  |
|            | Phoenix                                   | Isotopx, UK                              | MC, WARP filter   |
|            | Nu-TIMS                                   | Nu Plasma, UK                            | MC, with zoom lens                                      |
| ICP-MS     | NuPlasma II                               | Nu Instruments, Wrexham, Great Britain   | HR-MC-ICPMS   |
|            | Neptune MC-ICPMS                          | Thermo Fisher, Bremen, Germany           | 9 Faraday cups and $10^{11} \Omega$ amplifiers          |
|            | Element XR                                | Thermo Fisher                            | Single Faraday cup                                      |
|            | Attom ES                                  | Nu Instruments                           | Single Faraday cup                                      |
|            | NuPlasma 1700                             | Nu Instruments                           | Large geometry and high dispersion MC                   |
|            | ICAP-Q ICPMS                              | Thermo Fisher                            | Quadrupole analyser                                     |
|            | Plasma Quant MS and Plasma Quant MS Elite | Analytika Jena                           | Quadrupole analyser, integrated collision reaction cell |
| SIMS       | 7700x Q-ICPMS                             | Agilent Technologies, Waldbronn, Germany | Quadrupole based  |
|            | Agilent QQQ-ICPMS-8800                    | Agilent Technologies, Japan              | MS/MS possible  |
|            | Nexion Q based with DRC                   | Perkin Elmer, USA                        | Quadrupole based with dynamic reaction cell             |
|            | ToF based ICPMS                           | GBC Scientific, Australia                | Good for transient signals                              |
|            | Cameca IMS 1270 and 1280                  | Cameca, France                           | Multicollector large geometry SIMS                      |
|            | IMS 7f, magnetic sector and ESA analyser  | Cameca, France                           | Ion microprobe and ion microscopy possible              |

**TABLE 4.** A comparison of isotopic analysis of B by MC-ICPMS and MC-TIMS

| Parameter                                | MC-ICPMS   | P-TIMS   | N-TIMS                                       | Remarks  |
|--|--|--|--|--|
| Ions monitored                           | B <sup>+</sup> (m/z 10 and 11)   | M <sub>2</sub> BO <sub>2</sub> <sup>+</sup> (308 and 309; Cs <sub>2</sub> BO <sub>2</sub> <sup>+</sup> ) | BO <sub>2</sub> <sup>-</sup> (m/z 42 and 43) | Single filament (Ta for P-TIMS, Re for N-TIMS)                                   |
| Ionisation efficiency                    | 50%  | 1%   | >5%  | ICPMS gives the highest efficiency due to high plasma temperature                |
| Mass fractionation /amu                  | About 15%  | 0.1-0.2%   | 2-3%, variable                               | Least fractionation in P-TIMS using Cs <sub>2</sub> BO <sub>2</sub> <sup>+</sup> |
| B amount needed                          | Solution with 20-50 ppb of B in 0.5 M HNO <sub>3</sub>   | 2 µg   | 1 ng   | N-TIMS gives the highest sensitivity, solution to be dried on filament           |
| Sample Chemistry/Purity                  | Not very strict (Sample matrix with lot of Na unaccepted)  | Complex purification required  | Moderate purification OK                     | P-TIMS requires strict analytical chemistry                                      |
| Isobaric interferences                   | Ar <sup>+</sup> and Ne <sup>+</sup> at <sup>10</sup> B, <sup>10</sup> BH <sup>+</sup> at <sup>11</sup> B | Nil at m/z 308 and 309   | CNO <sup>-</sup> at m/z 42 and 43            | Organic interferences suppress ionisation in TIMS and lower the accuracy         |
| Memory effect                            | Yes (needs washing)  | No   | No   | TIMS does not give any memory effect   |
| Time of analysis                         | 30 min   | 60-120 min   | 60 - 120 min                                 | Time in TIMS depends upon method used for isotope fractionation accounting       |
| Isotopic reference material (IRM) needed | Y (for signal drift correction)  | N  | N  | IRM is a must in ICPMS to use sample-standard bracketing approach                |
| Precision achievable (2sd)               | 0.25‰  | 0.5‰   | 0.5-1‰                                       | MC-ICPMS gives the highest precision   |

advantage of complete absence of any memory effect, and thus will continue to be used, in particular in the nuclear industry, where samples with wide ranges of <sup>11</sup>B/<sup>10</sup>B isotopic ratios need to be analysed for enrichment and reactor applications, and precision and accuracy of about 1‰ is acceptable. As of now, N-TIMS with BO<sub>2</sub><sup>-</sup> ions is the only method to provide the highest sensitivity, despite the problem of isotope fractionation, which can be partly accounted for with total evaporation or internal normalization based on <sup>18</sup>O/<sup>16</sup>O isotope ratios. P-TIMS

**FIGURE 2.** A comparison of the precision obtained (‰, 2σ) and amount required (ng) for isotopic analysis of boron by various mass spectrometric techniques (Adapted from: Kaczmarek et al., 2015). TE, Total evaporation; IN, Internal normalization.

with the Cs<sub>2</sub>BO<sub>2</sub><sup>+</sup> ion will be the most-preferred approach to characterize isotopic reference materials. For applications in nuclear technology that do not demand ultra-high precision, and for samples with sufficient amounts of boron, P-TIMS with Na<sub>2</sub>BO<sub>2</sub><sup>+</sup> ions can also be used. SIMS and LA-ICPMS will continue to play a major role for *in situ* micro-analysis with high spatial resolution. It will be interesting to explore the use of LA-ICPMS for isotopic analysis and concentration of boron with dried sample solutions deposited on filter paper disks (Nischkauer et al., 2014) and use a radial line scan to circumvent the problem of non-representative sampling. A combination of multiple ion counting with compact discrete dynode multipliers in MC-ICPMS with laser ablation and ICP-OES to simultaneously determine δ<sup>11</sup>B and B/Ca amount ratio reported recently sounds very promising (Kaczmarek et al., 2015) to analyze single foraminiferal tests. The precision and accuracy of this approach is not yet good enough to be of practical use to produce useful palaeo records.

The novel methodology (Aggarwal et al., 2009b) to use <sup>18</sup>O/<sup>16</sup>O isotope ratios determined *in situ* with ReO<sub>4</sub><sup>-</sup> ions in TIMS, for internal normalization, in (m/z 43)/(m/z 42) boron isotope ratios from BO<sub>2</sub><sup>-</sup>, needs to be evaluated and compared by researchers in various laboratories with total evaporation in N-TIMS. This internal normalization approach, along with loading solution prepared by mixing high-purity salts of Mg, Ca, Na, and K (Dwyer & Vengosh, 2008), must be tried and evaluated for automatic data acquisition. The heavier δ<sup>11</sup>B values (about 2‰) obtained with N-TIMS ubiquitously in foraminifera compared to those with MC-ICPMS must be investigated further (Ni, Foster, & Elliott, 2010). The large positive off-set in δ<sup>11</sup>B values for core-top *G. sacculifer*, with N-TIMS versus MC-ICPMS, is not well understood and may be matrix dependent (Foster, Lear, & Rae, 2012; Foster et al., 2013; Martinez-Boti et al., 2015). Use of polyatomic ions (Aggarwal & Jain, 1995) Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> and Rb<sub>2</sub>BO<sub>2</sub><sup>+</sup> with an internal normalization methodology based on <sup>6</sup>Li/<sup>7</sup>Li (Sahoo & Masuda, 1995) and <sup>85</sup>Rb/<sup>87</sup>Rb isotope ratios (Rao et al., 2010a), respectively, to account for isotope fractionation requires investigations at different laboratories with different TIMS instruments.

Studies are needed to explore the use of B isotopes for provenance in crop plants and to gain insight into plant physiology (Rosner et al., 2011). Differences in the isotopic data for B hold a great potential to authenticate the origin of agricultural products like *Coffea Arabica* beans (Wieser et al., 2001). Because boron is an essential element for crops, these studies will also be useful to improve the quality of agricultural produce. The overall uncertainty of applying δ<sup>11</sup>B determined mass spectrometrically, in calcium carbonate skeletons, to reconstruct paleo-ocean pH depends strongly on the exact value of isotope fractionation factor between the two main dissolved boron species <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>4</sub><sup>-</sup>. Recent experimental results (Klochko et al., 2006; Nir et al., 2015) show good agreement with theoretical studies (Liu & Tossell, 2005; Rustad et al., 2010). A recent review on controlling factors of the δ<sup>11</sup>B-pH proxy suggests the need to confirm the assumption whether only anionic form of boron (i.e., B(OH)<sub>4</sub><sup>-</sup>) is incorporated into marine carbonates (Xiao et al., 2014; Noireaux et al., 2015). It is recommended to use larger foraminiferal shells (>515 µm) to reduce the isotopic offsets between foraminifera species, shell size and dissolution effects (Hönisch & Hemming, 2004). The B isotopic composition of

brachiopods is of interest in view of their tolerance to a wide range of depth, temperature, and pH conditions. Additionally, foraminifera-bearing deep sea sediments are limited only to the past about 180 million years (Penman et al., 2013). Studies reported (Joachimski et al., 2005; Penman et al., 2013) recently have shown that the brachiopods are internally inhomogeneous and there are huge interspecies and inter-individual offsets. The  $\delta^{11}\text{B}$  studies on laboratory cultures of brachiopods are important to understand and resolve these issues. Recent studies reported on  $\delta^{11}\text{B}$  for aragonite bivalve shell of cultured *Arctica islandica* point towards a species-specific boron isotope fractionation factor (Liu et al., 2015).

The observations reported from the latest inter-laboratory inter-comparison experiment (Foster et al., 2013) call for a better control and understanding of the contribution of boron blank in  $\delta^{11}\text{B}$  values, particularly for samples with small amounts of boron. This experiment also highlighted the need to make available well-characterized marine carbonate reference materials with certified boron isotope ratios. There is a strong need to develop primary isotopic reference materials for boron for  $\delta^{11}\text{B}$  and  $^{10}\text{B}$  enriched samples. Finally, the  $\delta^{11}\text{B}$  values reported on foraminifera samples with TE-NTIMS are ubiquitously heavier by +2‰ with respect to those determined with MC-ICPMS (Ni, Foster, & Elliott, 2010; Foster et al., 2006); that difference must be addressed. As of now, it is believed that the organic residues present in the purified boron solution suppress the ionization of the lighter isotope in N-TIMS during the early stages of TIMS analysis. The presence of organic residues that affect the isotope ratio can be checked in MC-ICPMS with a standard addition approach, but not in TE-NTIMS.

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## ABBREVIATIONS

|       |  |
|-------|--|
| BNCT  | boron neutron capture therapy              |
| CCR   | coal combustion residue                    |
| CRM   | certified reference material               |
| DIHEN | direct injection high efficiency nebulizer |
| DRC   | dynamic reaction cell                      |
| EHD   | 2-ethyl-hexane 1,3 diol                    |

|           |  |
|-----------|--|
| FT-IR     | fourier transform-infra red  |
| GSMS      | gas source mass spectrometer   |
| HEPA      | high efficiency particulate air                                      |
| HR-ICPMS  | high resolution inductively coupled plasma mass spectrometer         |
| ICPMS     | inductively coupled plasma mass spectrometer                         |
| ICP-OES   | inductively coupled plasma optical emission spectroscopy             |
| IN-NTIMS  | internal normalization negative thermal ionization mass spectrometry |
| IRM       | isotopic reference material  |
| KEMS      | Knudsen effusion mass spectrometry                                   |
| LA        | laser ablation   |
| MC-ICPMS  | multi-collector inductively coupled plasma mass spectrometer         |
| MC-TIMS   | multi-collector thermal ionization mass spectrometer                 |
| m/z       | mass to charge ratio   |
| NIST      | National institute of standards and technology                       |
| N-TIMS    | negative thermal ionization mass spectrometry                        |
| PFA       | per fluoro alkoxy  |
| PHWR      | pressurized heavy-water reactor                                      |
| PN        | pneumatic nebulizer  |
| PTFE      | poly tetra fluoro ethylene   |
| P-TIMS    | positive thermal ionization mass spectrometry                        |
| PWR       | pressurized water reactor  |
| Q-ICPMS   | quadrupole inductively coupled plasma mass spectrometer              |
| SD        | standard deviation   |
| SIMS      | secondary ion mass spectrometry                                      |
| SNMS      | sputtered neutral mass spectrometry                                  |
| SRM       | standard reference material  |
| SSB       | standard sample bracketing   |
| TEM       | transmission electron spectroscopy                                   |
| TE-NTIMS  | total evaporation-negative thermal ionization mass spectrometry      |
| TG        | thermogravimetry   |
| TG-DSC-MS | thermogravimetry-differential scanning calorimetry-mass spectrometry |
| TIMS      | thermal ionization mass spectrometry                                 |
| ToF       | time-of-flight   |

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