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Abstract

Over the last twenty years applications of the boron isotope system have expanded from the analysis of boron-rich phases (e.g., tourmaline, borates) to include other materials with low B concentrations (e.g., carbonates, basaltic glass). The accurate and precise determination of the boron isotopic composition of geological materials is however a difficult task, particularly for those where boron is present in low-concentration. For solution methods, this difficulty arises principally from the near ubiquitous level of boron contamination in most standard clean laboratories, the light mass of the element, the occurrence of only two stable isotopes, and the large mass difference between them. For in situ approaches, such as secondary-ion mass spectrometry, additional difficulties arise from the restricted availability of well-characterized reference materials, from surface contamination, from limited precision in low-concentration samples, and limitations in reproducibility in high-concentration samples that may partly arise from small-scale heterogeneities in the analyzed materials. Nevertheless, a variety of novel techniques, strategies and methodologies have been developed over the past two decades to meet these challenges. We describe here some of these developments and focus on those that we feel are going to play a major role in the growing use of the boron isotope system in the earth and planetary sciences in decades to come.

Keywords

Analytical methods · Sample digestion · Sample purification

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2.1 Introduction

Boron has two naturally occurring stable isotopes: ^{11}B and ^{10}B that occur approximately in a 4:1 ratio in terrestrial materials. The large relative mass difference between the two isotopes ($\sim 10\%$), and the behavior of boron in aqueous solutions, results in variations in the isotopic composition of boron in Earth and extra-terrestrial materials providing numerous and unique insights into low- and high-temperature geochemical processes. As with other stable isotope systems, boron isotope variations are expressed in delta notation with reference to a standard: in this case, a boric acid (NIST SRM 951; Catanzaro et al. 1970; Brand et al. 2014). Despite its utility, the applicability of the boron isotope system is often restricted by the analytical challenges involved in its precise and accurate measurement. Some of the difficulties are common to other dual isotope systems (e.g., Li and Cu isotopes), whilst others, such as the volatility of boron in acidic solutions and the near ubiquitous level of blank contamination in most clean laboratories, are unique to the boron isotope system. Despite these complications boron isotope measurement of geological materials has a long history (e.g., McMullen et al. 1961; Marshall and Foster 2017). In recognition of the important information that can be gained from boron isotope studies, analytical techniques have evolved considerably, and there are now many dissolution, purification and mass spectrometric methods available, each with its own advantages and disadvantages. Several publications reviewed the methods in use by the late 1990s (e.g., Aggarwal and Palmer 1995; Swihart 1996), so here we will focus only on those methods that are most commonly used today (also see the recent review of analytical techniques by Aggarwal and You 2016). In the following sections, the required purification methods and the analytical methodology are discussed briefly in turn, and the more commonly used analytical techniques are summarized in Table 2.1. The $\delta^{11}\text{B}$ values of commonly used standards and reference materials for boron isotope research are shown in Table 2.2. Note that many of the standards listed in Table 2.2 are not commercially

available; we therefore recommend that the interested reader contact the lead author of the appropriate study to enquire about availability.

2.2 Digestion and Purification Methods for Boron Isotope Analysis of Geologic Materials

For the most accurate bulk sample isotopic analysis the sample is first dissolved and then boron is generally purified from the sample matrix to remove isobaric interferences and enhance ionization. This requirement applies to all analyses by Inductively Coupled Plasma Mass Spectrometry (ICPMS) and for most, but not all, Thermal Ionization Mass Spectrometry (TIMS) techniques.

2.2.1 Sample Digestion

A number of procedures are available for digestion of a geological sample. These include: pyro-hydrolysis, alkali fusion and acid digestion. Pyro-hydrolysis is time consuming and is perhaps most suitable for boron-rich materials such as tourmalines (Spivack and Edmond 1986). Acid digestion is currently popular due to the small volumes of reagents needed and hence lower levels of contamination. For carbonates cold HNO_3 (or HCl ; e.g., Foster et al. 2013) is sufficient to completely dissolve a sample, whereas silicates are most commonly dissolved for geochemical analysis by heating the sample together with high concentrations of HF (to volatilise Si in the sample) and HNO_3 (to retain the dissolved cations in solution), with additional acids (e.g., HClO_4) being employed for particularly refractory/organic-rich samples. This creates problems for boron analyses of silicates because BF_3 is highly volatile and can easily be lost from solution. Hence, studies employing the acid dissolution technique typically add mannitol to the dissolution cocktail to form a boron-mannitol complex that is stable in acid solution (Nakamura et al. 1992). Alternatively, by using the alkali fusion method the

Table 2.1 Summary of boron isotope measurement techniques

Analytical technique	Acronym	Chemical purification commonly performed	Sample types	Sample size (ng)	Precision (‰)	Example references
Positive ion thermal ionisation mass spectrometry	PTIMS	Cation and anion (typically Amberlite IRA743) exchange resin	Carbonates, silicates, waters	20–1000	0.1–0.3	He et al. (2013), Trotter et al. (2011)
Negative ion thermal ionisation mass spectrometry	NTIMS	None or cation and anion (typically Amberlite IRA743) exchange resin	Carbonates, waters	1–10	0.3–1.0	Hemming and Hönisch (2007), Kasemann et al. (2009), Foster et al. (2013), Clarkson et al. (2015)
Total evaporation negative ion thermal ionisation mass spectrometry	TE-NTIMS	None	Carbonates, waters	0.3–1	1–2	Foster et al. (2006), Ni et al. (2010), Liu et al. (2013)
High-resolution inductively coupled plasma mass spectrometry	HR-ICPMS	Microsublimation or cation and/or anion (typically Amberlite IRA743) exchange resin	Carbonates, waters	3–5	0.5–0.7	Misra et al. (2014)
Multi-collector inductively coupled plasma mass spectrometry	MC-ICPMS	Microsublimation or cation and/or anion (typically Amberlite IRA743) exchange resin	Carbonates, silicates, waters	5–50	0.2–0.3	Foster et al. (2013), Louvat et al. (2011), Foster (2008)
Laser ablation multi-collector inductively coupled plasma mass spectrometry	LA-MC-ICPMS	None required-in situ technique	Carbonate, silicates	0.1–0.3	0.5–1.75	Fitzke et al. (2010), Thil et al. (2016)
Secondary ion mass spectrometry	SIMS	None required-in situ technique	Carbonate, silicates	0.001–0.00001	0.5–3	Chaussidon et al. (1997), Marschall and Monteleone (2015), Kasemann et al. (2009), Liu et al. (2010)

aluminosilicate matrix can be broken down by high temperature fusion of the sample with a fluxing agent, typically K_2CO_3 , followed by dissolution of the fusion cake in pure water (Tonarini et al. 1997).

For all digestion methods any further chemical treatments prior to purification (e.g., the conversion of the dissolved silicate sample to chloride) must be done with care to avoid any isotopic fractionation arising from the volatility

Table 2.2 Summary of boron isotope reference materials and commonly used standards

Description	Material	$\delta^{11}\text{B}_{951}$	Uncertainty	Suitable for:				References	
				PTIMS	NTIMS	ICPMS	SIMS		
NIST SRM 951 (951a)	Boric acid	0		x	x	x			Brand et al. (2014) and references therein
IRMM-011	Boric acid	0.16/ −0.375		x	x	x			Brand et al. (2014) and references therein
ERM-AE101	Boric acid (aqueous)	−122.96		x	x	x			Brand et al. (2014) and references therein
		−123.01	0.41						Brand et al. (2014) and references therein
ERM-AE120	Boric acid (aqueous)	−20.2	0.6	x	x	x			Vogl and Rosner (2011)
ERM-AE121	Boric acid (aqueous)	19.9	0.6	x	x	x			Vogl and Rosner (2011)
ERM-AE122	Boric acid (aqueous)	39.7	0.6	x	x	x			Vogl and Rosner (2011)
NRC NASS-5	Seawater	39.89		x	x	x			Brand et al. (2014) and references therein
OSIL IAPSO	Seawater	39.64	0.42	x	x	x			Brand et al. (2014) and references therein
Natural seawater	Seawater	39.61	0.2	x	x	x			From Foster et al. (2010)
IAEA-B-1	Seawater	38.6	1.66	x	x	x			Brand et al. (2014) and references therein
		38.76	0.79						Brand et al. (2014) and references therein
IAEA-B-2	Groundwater	13.8	0.79	x	x	x			Brand et al. (2014) and references therein
		14.38	1.2						Brand et al. (2014) and references therein
IAEA-B-3	Groundwater	−21.4	0.89	x	x	x			Brand et al. (2014) and references therein
		−20.82	0.86						Brand et al. (2014) and references therein

(continued)

Table 2.2 (continued)

Description	Material	$\delta^{11}\text{B}_{951}$	Uncertainty	Suitable for:					References
				PTIMS	NTIMS	ICPMS	SIMS	LA-ICPMS	
IAEA-B-4	Tourmaline (schorl)	-8.7	0.18	x	x	x	x	x	Brand et al. (2014) and references therein
IAEA-B-5	Basalt	-3.8	2	x	x	x			Brand et al. (2014) and references therein
IAEA-B-6	Obsidian	-1.8	1.5	x	x	x	x	x	Brand et al. (2014) and references therein
IAEA-B-7	Limestone	9.7	5.9	x	x	x			Brand et al. (2014) and references therein
IAEA-B-8	Clay	-5.1	0.87	x	x	x			Brand et al. (2014) and references therein
H112566	Tourmaline (schorl)	-12.5	1.5	x	x	x	x	x	Leeman and Tonarini (2001)
H108796	Tourmaline (dravite)	-6.6	0.6	x	x	x	x	x	Leeman and Tonarini (2001)
H98144	Tourmaline (elbaite)	-10.4	0.3	x	x	x	x	x	Leeman and Tonarini (2001)
GOR-128-G	Komatiitic glass	13.55	0.21	x	x	x	x	x	Rosner and Meixner (2004)
GOR-132-G	Komatiitic glass	7.11	0.97	x	x	x	x	x	Rosner and Meixner (2004)
StHs6/80-G	Andesitic glass	-4.48	0.29	x	x	x	x	x	Rosner and Meixner (2004)
TB	Shale rock powder	-12.6	1.3	x	x	x			Rosner and Meixner (2004)
Am-21805	Amphibole	-0.4	0.9	x	x	x	x	x	Pabst et al. (2012)
Phe-80-3	Phengite (white mica)	-13.5	0.7	x	x	x	x	x	Pabst et al. (2012)
NIST SRM 610	Silicate glass	-0.52	0.53	x	x	x	x	x	Brand et al. (2014) and references therein
NIST SRM 612	Silicate glass	-0.51	0.52	x	x	x	x	x	Brand et al. (2014) and references therein
GSI JB-2	Basalt rock powder	7.24	0.33	x	x	x	x	x	Brand et al. (2014) and references therein
GSI JB-3	Basalt rock powder	5.9	0.8	x	x	x			Rosner and Meixner (2004)
GSI JGb-1	Gabbro rock powder	4.0	2.8	x	x	x			Rosner and Meixner (2004)

(continued)

Table 2.2 (continued)

Description	Material	$\delta^{11}\text{B}_{951}$	Uncertainty	Suitable for:				References
				PTIMS	NTIMS	ICPMS	SIMS	
GSI JA-1	Andesite rock powder	5.3	0.3	x	x	x		Rosner and Meixner (2004)
GSI JR-2	Rhyolite rock powder	2.9	0.2	x	x	x		Rosner and Meixner (2004)
GSI JR-2e	Rhyolite	2.57	1.06	x	x	x	x	Brand et al. (2014) and references therein
GSI JCP-1	Coral powder	24.24		x	x	x		Brand et al. (2014) and references therein
NIST RM 1547	Peach leaves	41.09	1.12	x	x	x		Brand et al. (2014) and references therein
NIST RM 8433	Corn bran	8.3	1.69	x	x	x		Brand et al. (2014) and references therein
BCR-679	White cabbage	-23.8	1.15	x	x	x		Brand et al. (2014) and references therein
BIG-D	Boric acid (aqueous)	14.56	0.61	x	x	x		Foster et al. (2013)
BIG-E	Boric acid (aqueous)	24.96	0.31	x	x	x		Foster et al. (2013)
UMD	Boric acid (aqueous)	-12.87	0.29	x	x	x		Foster et al. (2013)
IC _A	Deep ocean carbonate	15.96	1.50	x	x	x		Foster et al. (2013)
IC _B /UWC-1	Inorganic calcite rhomb	8.99	1.64	x	x	x	x	Foster et al. (2013)
		8.08	1.16					Kasemann et al. (2009)
IC _C /PS69/318-1	Cold water octocoral	15.90	0.65	x	x	x	x	Foster et al. (2013)
		16.07	0.67					Kasemann et al. (2009)
IC _D /M93-TB-FC-1	Aragonitic <i>Porites</i> (sp) coral	25.23	0.67	x	x	x	x	Foster et al. (2013)
		24.8						Kasemann et al. (2009)
IC ₁	<i>Porites cylindrica</i> coral	24.86	0.89	x	x	x		Foster et al. (2013)
IC ₂	<i>Acropora nobilis</i> coral	24.03	1.81	x	x	x		Foster et al. (2013)
IC ₃	<i>Porites cylindrica</i> coral	23.75	1.35	x	x	x		Foster et al. (2013)

(continued)

Table 2.2 (continued)

Description	Material	$\delta^{11}\text{B}_{951}$	Uncertainty	Suitable for:				References	
				PTIMS	NTIMS	ICPMS	SIMS		
IC ₄	<i>Acropora nobilis</i> coral	22.72	0.92	x	x	x		Foster et al. (2013)	
IC ₅	<i>Acropora nobilis</i> coral	22.04	1.37	x	x	x		Foster et al. (2013)	
IC ₆	Planktic foraminifers (<i>Globigerinoides sacculifer</i>)	20.16	2.27	x	x	x		Foster et al. (2013)	
IC ₇	Planktic foraminifers (<i>Globigerinoides sacculifer</i>)	20.87	1.73	x	x	x		Foster et al. (2013)	
IC ₈	Planktic foraminifers (<i>Globigerinoides sacculifer</i>)	19.99	2.24	x	x	x		Foster et al. (2013)	
IC ₉	Planktic foraminifers (<i>Globigerinoides sacculifer</i>)	20.78	2.15	x	x	x		Foster et al. (2013)	
IC ₁₀	Brachiopod (<i>Terebratalia transversa</i>)	16.95	2.86	x	x	x		Foster et al. (2013)	
IC ₁₁	Brachiopod (<i>Terebratalia transversa</i>)	15.38	1.60	x	x	x		Foster et al. (2013)	
KW-T6	<i>Tridacna gigas</i> bivalve	15.53	0.64	x	x	x	x	Kasemann et al. (2001)	

Uncertainty is typically at a 95% confidence level but the reader should refer to the cited reference. For Vogl and Rosner (2011) quoted values are the mean of gravimetric determination and two measurements, uncertainty is 2sd of these. For the data from Foster et al. (2010) uncertainty is mean and 2sd of 28 seawater samples. For standards from Foster et al. (2013) the quoted value is the mean of all laboratories and the uncertainty is the 2sd about this mean. For the data from Kasemann et al. (2009) the quoted values are the mean and uncertainty from their Table 2.2

of boron. The alkali fusion method was developed with this limitation in mind, especially with regard to silicates where the formation of a K_2CO_3 fusion cake avoids the need for HF for dissolution (e.g., Tonarini et al. 1997). Regardless of the sample type, all reagents must have very low boron concentrations ($\ll 1$ ng/g) to keep the procedural blank contamination sufficiently low. To this end, most clean laboratories carrying out boron isotope analysis are fitted with boron-free HEPA filters to reduce the blank contamination during sample handling (e.g., Rosner et al. 2005).

Once a sample is dissolved, there are two principal methods currently in use to purify boron prior to analysis. These are discussed in turn below.

2.2.2 Ion Exchange

For carbonate samples, boron purification from the relatively simple $CaCO_3$ matrix typically involves the use of the boron specific ion-exchange resin Amberlite 743 (Kiss 1988) either in a one-step (Foster 2008) or two step procedure (Lemarchand et al. 2002; McCulloch et al. 2014). The Amberlite 743 resin contains a hydrophobic styrene backbone and tertiary amine group that only absorbs boron in the borate form ($B(OH)_4^-$; Yoshimura et al. 1998). In the one-step method of Foster (2008), the dissolved $CaCO_3$ sample is added to a 2 M Na acetate–0.5 M acetic acid buffer to ensure that the loading pH is ~ 5 . This pH is sufficient to ensure quantitative retention of boron on the column and low enough to prevent Ca precipitation prior to loading. In the two-step process (Foster et al. 2013; Lemarchand et al. 2002; McCulloch et al. 2014), dissolved cations (e.g., Ca, Mg) are first removed using a cationic exchange resin (e.g., Dowex AG50X8; Lemarchand et al. 2002; McCulloch et al. 2014). The pH of the solution from this first step is then increased to ~ 9 using NH_4OH without fear of forming precipitates and is then further purified using Amberlite 743 (Lemarchand et al. 2002; McCulloch et al. 2014). Following rinses with MQ water, and in some

methods with $NaNO_3$ as well to remove the matrix (Foster et al. 2013; Lemarchand et al. 2002), quantitative elution of boron from Amberlite 743 is typically achieved using 0.1–0.5 M HNO_3 . Experiments by Lemarchand et al. (2002) illustrate that relatively large isotopic fractionations can result if recovery is not close to 100%, although this is relatively easy to achieve and monitor (e.g., Foster et al. 2013; Lemarchand et al. 2002). The volume of HNO_3 required to elute all the boron depends on its molarity, resin mesh size, column volume and column geometry. Due to the volatility of boron in acidic solutions further concentration of the eluant via a dry-down step is generally avoided. Hence, column design has to be optimized to recover boron in sufficiently low quantities of HNO_3 such that final boron concentration is not diluted beyond that required for precise measurement by mass spectrometry. Hence, for measurement of $CaCO_3$ samples that generally have low boron contents (10–50 $\mu g/g$ B; Hemming and Hansen, 1992), the columns are typically small volume (< 50 μl) and reagent volumes are also small (< 1 ml HNO_3). Thus blank contamination from purification is low: typically < 1 ng and in some instances < 50 pg (Foster et al. 2013; Henahan et al. 2013).

Purification of boron contained within aluminosilicate geological samples is more complex. This is partly because rock samples contain a more diverse suite of cations that must be removed from the sample, but the complexities of purification largely arise because of the more aggressive procedures that are required to release boron from the rock matrix (see above). Regardless of whether the rock is dissolved or fused, the boron must then be purified from a concentrated solution containing high concentrations of a wide range of dissolved species. Hence, the purification method has typically involved at least three separate ion-exchange columns (Nakamura et al. 1992; Tonarini et al. 1997). This is time-consuming and problematic in terms of controlling potential contamination of the sample from the large volumes of reagents required and prolonged sample processing. More recently, Romer and Meixner (2014) have

developed an improved two-step method and Wei et al. (2013) developed a single column procedure using Bio-Rad AG MP-1 (an anion exchange resin) for separation of rock samples that had undergone acid dissolution. This latter technique greatly simplifies the purification stage but, in its current incarnation, requires large volumes of 24 M HF (~24 ml per sample) in nine separate aliquots during the column chemistry. Recent tests by one of us (Palmer and Cooper, in prep) however suggest the approach is well-suited to miniaturisation allowing for a reduction in blank and HF volume.

2.2.3 Purification by Non Exchange Resin Methodologies

A number of methods exist to purify boron that do not rely on anion/cation exchange resins. The earliest of these, methyl borate distillation, exploits the volatility of trimethyl borate to separate boron from more refractory species such as Si (Aggarwal and Palmer 1995; Spivack and Edmond 1986). More recently, a method initially used as a final purification step to remove organic contamination (Gaillardet et al. 2001; Lemarchand et al. 2002) known as “microsublimation” is being used to separate boron from CaCO_3 and other matrices (Misra et al. 2014; Pi et al. 2014; Wang et al. 2010). The microsublimation approach exploits the volatility of boron and its ability to sublime from a solid at low temperatures (~75–100 °C). In this separation method CaCO_3 samples are dissolved in a small volume (<50 μl) of HNO_3 or HCl with $\text{pH} < 2$ and loaded onto the center of the cap of a 5 ml Savillex Teflon fin legged screw top beaker (Misra et al. 2014; Wang et al. 2010). The inverted beaker with sample loaded on the lid is then placed on a hotplate at a relatively well-controlled temperature ideally with wells or digestion blocks to ensure an even heating of the vial (Liu et al. 2013; Wang et al. 2010). The distillation process is then carried out for >12 h and the purified boron is simply recovered from the drop that forms in the conical end of the inverted beaker. The potential for fractionation if recovery is not

quantitative, as with the column procedures above, is large (Gaillardet et al. 2001; Misra et al. 2014; Wang et al. 2010) and incomplete recovery can occur through loss of sample through the screw-top seal of the distillation vial or because complexes can form in the residue that bind to boron (Gaillardet et al. 2001). The extent of recovery when applied to CaCO_3 purification is checked by analyzing the B/Ca ratio of what was loaded on the lid and the B concentration of the final distillate and residue (Misra et al. 2014), although the accuracy of these approaches limits these assessments of B concentration to ± 1 –12% and significant fractionation occurs if B recovery is <90% (Misra et al. 2014). Due to the limited handling and small volume of reagents used the total procedural blanks, provided B-clean reagents are used, tend to be smaller for this method than for column-based approaches (e.g., <10 pg).

2.3 Analytical Methods for Boron Isotope Analysis of Geological Materials

Boron isotopes are commonly measured using a variety of analytical techniques. Figure 2.1 provides an up-to-date summary of the state of the art with regard to the precision and sample size required for each of the techniques and Table 2.2 lists some of the commonly used reference materials. In the following we attempt to briefly summarize the relevant methodologies, paying particular attention to their strengths and weaknesses.

2.3.1 The Isotopic Analysis of Boron in Solution Mode

2.3.1.1 Positive Ion Thermal Ionization Mass Spectrometry

The first boron isotope measurement technique suitable for high precision analysis of geological materials was Positive ion Thermal Ionization Mass Spectrometry (PTIMS; e.g., Ramakumar et al. 1985). Initial attempts using a

sodium-borate complex only achieved a precision of around $\pm 2\%$ (at 95% confidence; e.g., Swihart et al. 1986) due to the relatively light mass of the Na_2BO_2^+ ion (mass 88 and 89 for ^{10}B and ^{11}B , respectively). Better precision was achieved with using Cs-borate complexes (Cs_2BO_2^+ ; masses 308 and 309) due its heavier mass minimizing instrumental fractionation ($\pm 0.4\%$ at 95% confidence; Ramakumar et al. 1985). However the relatively low ion yield from these heavy alkali-borate complexes, the requirement for dynamic runs due to the close spacing of masses 308 and 309, and the potential high level of B-contamination during purification of the boron prior to mass spectrometric analysis, typically resulted in sample size being relatively large for these early PTIMS methods (5000 ng; Spivack and Edmond 1986). Since the initial development of the Cs-borate TIMS method there has been a series of improvements to sample size and precision. For example, improved signal intensity and reproducibility was

achieved by coating the filament with graphite (Xiao et al. 1988) and changes to the sample dissolution method and boron purification process (Nakamura et al. 1992; Tonarini et al. 1997). In addition, the introduction of a specially designed double collector package allowed for static multi-collection of both boron isotopes (Nakano and Nakamura 1998) that further improved precision and reduced the required sample size, such that it is now possible to achieve accuracy and precision of around $\pm 0.3\%$ (at 95% confidence) on sample sizes as small as 20 ng of boron (Deyhle 2001; He et al. 2013). These latest methods therefore offer the potential for achieving precise data on small samples using PTIMS.

2.3.1.2 Negative Ion Thermal Ionization Mass Spectrometry

Negative ion thermal ionization mass spectrometry (NTIMS) approaches to the measurement of

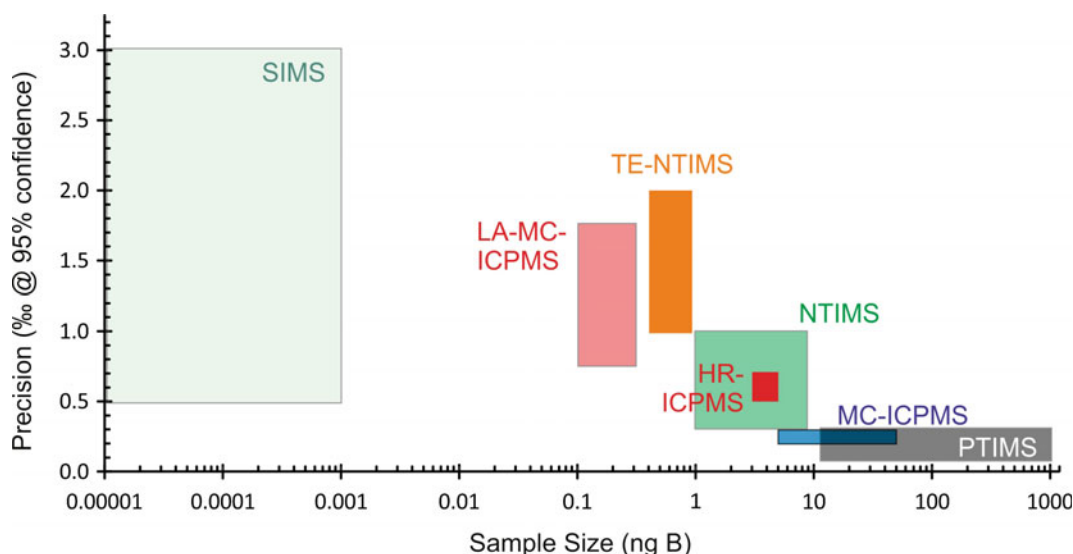


Fig. 2.1 Summary of the sample size and reported precision (at 95% confidence) for the commonly used techniques for boron isotope analysis from a selection of contributions. *Sources* Secondary ion mass spectrometry (SIMS; Marschall and Monteleone 2015); laser ablation multi-collector inductively-coupled plasma mass spectrometry (LA-MC-ICPMS; Fietzke et al. 2010); total evaporation negative ion thermal ionization mass spectrometry

(TE-NTIMS; Foster et al. 2006; Ni et al. 2010); high-resolution ICPMS (Misra et al. 2014); negative ion thermal ionization mass spectrometry (NTIMS; Hönisch and Hemming 2007; Kasemann et al. 2009); multi-collector ICPMS (MC-ICPMS; Foster et al. 2013); positive ion thermal ionization mass spectrometry (PTIMS; He et al. 2013; Trotter et al. 2011). Note that across the techniques as sample size increases precision tends to improve

boron were first developed by Zeininger and Heumann (1983). This approach, where $^{10}\text{B}^{16}\text{O}_2^-$ and $^{11}\text{B}^{16}\text{O}_2^-$ are measured statically at masses 42 and 43, has a very high ion yield when an activator (e.g., lanthanum nitrate or boron-free seawater) is used, meaning samples as small as 1 ng can be measured to relatively high precision ($\pm 0.4\text{--}0.7\text{‰}$ at 95% confidence; Hemming and Hanson 1992; Kasemann et al. 2001; Clarkson et al. 2015; Farmer et al. 2016). Hemming and Hanson (1994) noted that a complex ionic electrolyte like acidified seawater or dissolved calcium carbonate also resulted in very high ion yields with NTIMS. Hemming and Hanson (1992) therefore proposed that for carbonates and natural waters no boron purification was necessary provided the same boron-free seawater was added to samples (dissolved carbonate or natural water) and standards (boric acid NIST SRM 951) to ensure some similarity in matrix. The principal difficulties of this approach are: (i) the accurate correction of machine induced mass fractionation of the two relatively light isotopologues of BO_2^- at masses 42 and 43; (ii) interference of minor borate isotopologues (e.g., $^{10}\text{B}^{16}\text{O}^{17}\text{O}^-$ on mass 43, and CNO^- from organic contamination on mass 42). Whilst the interference of CNO^- can be adequately monitored using CN^- and the other borate isotopologues are typically minor, it is the accurate correction of machine-induced bias that has proven most difficult to overcome. Several approaches exist that all require a high level of operator skill and care, from using a linear regression to correct for the time-dependent fractionation relating to ionization (e.g., Kasemann et al. 2001), to total evaporation (TE-NTIMS) whereby the entire sample is ionized and the $^{11}\text{B}/^{10}\text{B}$ ratio is determined from the total ^{11}B measured/total ^{10}B measured (Foster et al. 2006; Liu et al. 2013). The degree of instrumental mass fractionation and the precision of NTIMS analyses are improved if care is taken to control the filament temperature during warm-up of the filament (up to $\sim 970^\circ\text{C}$) and during the data acquisition (approximately $950\text{--}1000^\circ\text{C}$) (Hemming and Hanson 1994; Hemming and Hönisch 2007). For some, but not all (e.g., Foster et al. 2013; Kasemann et al. 2009),

NTIMS methodologies, the accuracy of CaCO_3 analysis remains an issue and biases of 0.5 to 2.7‰ are evident and appear to be related to sample matrix in some way (e.g., Foster et al. 2013; Farmer et al. 2016).

2.3.1.3 Inductively Coupled Plasma Mass Spectrometry

The measurement of boron isotopes by ICPMS also has a relatively long history, with the first study by Gregoire (1987). These early attempts however were associated with high uncertainty ($\pm 3\text{‰}$ at 95% confidence; Gregoire 1987) making the methodology unsuitable for most geochemical applications. The last 20 years or so have seen a dramatic growth in the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS; e.g., Walder and Freedman 1992; Halliday et al. 1998). This new technology was rapidly adopted for boron isotope measurement with early applications meeting some success (e.g., Aggarwal et al. 2003; Lecuyer et al. 2002). However the challenges of boron isotope analysis by MC-ICPMS (and ICPMS) are also manifold: (i) due to the volatility of boron in acidic solutions wash out between samples can be very long (Al-Amar et al. 2000); (ii) $^{40}\text{Ar}^{4+}$ and/or $^{20}\text{Ne}^{2+}$ from the ionization gas interfere on ^{10}B (Wang et al. 2010); (iii) mass fractionation is large although typically relatively stable (up to 16‰; Foster 2008); (iv) due to its light mass, boron has very low transmission across the plasma interface leading to poor sensitivity; (v) matrix effects mean solutions must be purified first in order to obtain accurate and precise data (e.g., Guerrot et al. 2011; Pi et al. 2014). Improved analytical and abundance sensitivity, and mass fractionation stability with the most recent generations of MC-ICPMS has overcome many of these problems (Foster 2008). Purification is typically achieved using one of the options discussed in Sect. 2.2 and several strategies are also available to overcome the wash-out problem, including: (a) the addition of small quantities of NH_3 gas to ensure spray chamber pH is high enough that boron is present in the non-volatile borate form (Foster 2008); (b) protracted wash-outs and the

use of dilute solutions (Wang et al. 2010; McCulloch et al. 2014); (c) the use of a mixed 0.3 M HF/0.4 M HNO₃ reagent for the introduction of samples, standards, blanks and wash (Misra et al. 2014); (d) the use of direct injection where the volume of wetted parts is small and hence the boron wash-out is relatively quick (Louvat et al. 2011). Regardless of which strategy is used to overcome the wash out issue, the most precise $\delta^{11}\text{B}$ data are obtained when sample-standard bracketing is as fast as possible (i.e. <5 min between sample and standard), wash out is stable and machine-blank is <2% of analyte signal, and the MC-ICPMS is optimized for mass fractionation stability rather than maximum signal (e.g., Foster 2008; Guerrot et al. 2011; Louvat et al. 2011; Wang et al. 2010). Until recently, analytical sensitivity placed a lower limit on sample size (~ 10 ng of B), however improved electronics ($10^{12} \Omega$ resistors for Faraday cup amplifiers; e.g., John and Adkins 2010) now allow a further reduction in sample sizes (<5 ng of B) making laboratory blank contamination, rather than total available boron, the limiting factor.

2.3.2 The Isotopic Analysis of Boron in Situ

Many geological materials show small-scale chemical and isotopic heterogeneities that contain a wealth of relevant information but are inaccessible by bulk methods, as these only reveal average compositions of the dissolved sample mass. This is where in situ methods of boron isotope analyses become indispensable, and the two most common techniques are discussed here.

2.3.2.1 Secondary Ion Mass Spectrometry (SIMS)

Secondary-ion mass spectrometry (SIMS) employs a beam of focused ions to sputter and ionize small amounts of material from the surface of a solid sample. The secondary ions created in this process are accelerated by a homogenous high-voltage electric field into a mass

spectrometer. The mass spectrometer may employ a time-of-flight mass separation system (e.g., Lyon et al. 2007) or a quadrupole filter, but more typically for boron isotope analysis consists of an electrostatic filter and a sector magnet (e.g., Straub and Layne 2002). More recently, the NanoSIMS, which enables higher lateral resolution than standard ion probes, has been employed to analyze B isotopes in meteorites (Liu et al. 2010).

SIMS is a method that requires introduction of the sample in solid form into the mass spectrometer. Typically, these include silicate minerals, glass, and biogenic carbonates that may contain trace concentrations of boron or are boro-silicates or borates that contain boron as a major component. Ideally, the samples should be very well polished to provide a flat, smooth surface. This is important, because the sample surface is part of the extraction lens for the secondary ion beam, and surface topography leads to distortion of the electric field that may result in irreproducible boron isotope fractionation. SIMS has also been applied to analyze boron isotopes of water samples and clay suspensions. These liquid materials were dried on Si wafers or glass slides, and the dry residues were analyzed by ion probe (Rose-Koga et al. 2006; Williams et al. 2001).

The prominent advantage of SIMS compared to any alternative analytical method lies in the very high spatial resolution of the method. This follows from the gentle sputtering process with slow depth progress (compared with laser-ablation methods) and from the ability to focus the primary ion beam to spot sizes of 5–100 μm , depending on required signal intensity and B concentration in the sample. In NanoSIMS, spot diameters below 1 μm are possible. The sputter rate depends on the material and the primary beam density and is typically on the order of 0.1–5 nm/s for beam currents of 1–40 nA in carbonates, silicates and silicate glasses (e.g., Marschall and Monteleone 2015; Rollion-Bard et al. 2007). This translates to a pit depth of 0.1–5 μm for typical B isotope analyses that take 10–30 min total analysis time for a single spot. These small volumes of sputtered

material make SIMS the ideal method for resolving spatial heterogeneity, for instance in foraminifera and coral skeletons (e.g., Rollion-Bard et al. 2003; Blamart et al. 2007) and for material with limited volume, such as melt inclusions (e.g., Schmitt et al. 2002). The small analyzed volume also translates to a very small mass boron required for a SIMS isotope analysis, which is several orders of magnitude lower than for any other method, and may range from approximately 10 femto grams to several pico grams (Fig. 2.1).

For high-concentration samples ($\geq 20 \mu\text{g/g}$ B, depending on the instrument), the analytical precision of SIMS depends on the stability of the mass spectrometer, most importantly the stability of the magnet, the detection system (electron multiplier = ion counter; or Faraday cups), and the primary beam. Most published B isotope analyses from magnetic-sector field SIMS have been completed using a single collector and magnet cycling between the collection of $^{10}\text{B}^+$ and $^{11}\text{B}^+$. Two electron multipliers in multi-collection mode have also been used, but precision was not significantly better compared to mono-collection (Kobayashi et al. 2004). More recently, the B isotope ratio of tourmaline (ca. 30,000 $\mu\text{g/g}$ B) has been analyzed in multi-collection mode using two Faraday cups, which reduced the total analysis time to 2 min per spot at a precision of $\pm 0.8\%$ (2SE; Büttner et al. 2016). A $^{16}\text{O}^-$ primary beam was used in all cases, including small- and large-radius spectrometers and NanoSIMS. Fluctuations of the primary beam intensity that are on the same time scale as the integration cycles of the measurement will directly affect internal precision in single-collection mode and cannot be corrected. Magnet stability has been improved over the years through better electronic hardware, laminated magnets, software improvements, and the introduction of a nuclear magnetic resonance magnet control. The combined instrument stability translates to an internal precision of typically between 0.4 and 1.0‰ (2SE) for a $^{11}\text{B}/^{10}\text{B}$ analysis of a high-concentration sample (Büttner and Kasemann 2007; Drivenes et al. 2015; Marschall and Monteleone 2015). Internal

precision refers to the standard deviation among the analyzed ^{11}B – ^{10}B cycles in a single measurement divided by the square root of the number of cycles in that measurement.

For low-concentration analysis, the internal precision depends on the number of counted ions and can be predicted from counting statistics (Fitzsimons et al. 2000). The total counts of the measurement depend on the boron concentration in the sample, the primary beam current (or beam density and the analyzed area), the composition of the analyzed sample, and the sensitivity of the instrument.

A way to express instrument sensitivity is through the useful ion yield, which depicts the fraction of ions counted at the conditions of the measurement relative to the amount present in the sputtered sample volume. For boron, this value ranges from approximately 0.15–0.3% for small-radius instruments to 1.8% for the large-radius instruments (Hervig et al. 2006; Marschall and Monteleone 2015). That means that >98% of the boron present in the sample is currently wasted, mostly because of poor ionization during the sputter process. Large-radius magnet SIMS instruments now achieve precisions of $\pm 3\%$ (2 σ) in samples with 1 $\mu\text{g/g}$ boron in a single-spot 30-min analysis (Marschall and Monteleone 2015).

Strong or systematic deviations of the precision of low-concentration analysis from the precision predicted from counting statistics may be due to small-scale sample heterogeneity, or they may be a sign of an analytical problem, for example caused by insufficient instrument stability or by surface contamination of the sample. Surface contamination is a challenge in SIMS particularly for boron analysis (e.g., Chaussidon et al. 1997; Marschall and Ludwig 2004; Shaw et al. 1988). Several measures have been applied to reduce and quantify surface contamination: (i) avoid boron-bearing lubricants and polishing materials during sample preparation; (ii) produce a sample surface that is as smooth as possible without roughness, cracks, pits, or other topography; (iii) clean sample mounts (or thin sections) in ultra-sonic bath with B-free de-ionized water immediately before gold-coating and

introduction into the air-lock system of the mass spectrometer; (iv) use sufficient pre-sputter time to remove remaining surface contamination prior to signal integration; (v) raster the beam over a larger area during pre-sputter and reduce the rastered area (or fixed spot) during collection of the analysis signal; (vi) use a field aperture to block the margin of the secondary beam, so that only the central, low-contamination part of the sample is analyzed (Chaussidon et al. 1997; Liu et al. 2009; Marschall and Ludwig 2004; Marschall and Monteleone 2015). The best way to quantify any remaining contamination is by the analysis of a material that contains as little B as possible. Silica glass Herasil-102 was suggested for this purpose, which contains ≤ 1 ng/g boron (Marschall and Ludwig 2004).

Mass interferences are not a problem for B isotope analysis by SIMS, and a mass resolving power ($m/\Delta m$ at 10% peak height) of approximately 1200 is sufficient to suppress the principle interferences ($^9\text{BeH}^+$ and $^{30}\text{Si}^{3+}$ on $^{10}\text{B}^+$; $^{10}\text{BH}^+$ on $^{11}\text{B}^+$). Machine drift is typically slow ($\leq 0.3\%/h$) and can be corrected for by completing regular analysis of well-characterized (ideally internationally distributed) reference materials or standards. Reproducibility of the measurements is quantified by repeated analyses of a homogenous material, which may include the reference materials. Reported reproducibility (2 SD) for SIMS boron isotope analysis ranges from 0.4 to 4.7‰, but is typically on the order of 1.5‰, as summarized by Marschall and Monteleone (2005) (see also Büttner and Kasemann 2007; Büttner et al. 2016; Kasemann et al. 2009; Nakano and Nakamura 2001; Trumbull et al. 2008).

Accuracy is the most difficult aspect to quantify in any measurement, and B isotopes by SIMS are no exception. Instrumental mass fractionation of $^{11}\text{B}/^{10}\text{B}$ in SIMS is typically between 2 and 6%, and it may vary among different instruments, from session to session on a particular instrument, and even within an analytical session (e.g., Chaussidon et al. 1997). The primary B isotope standard (NIST SRM951) is boric acid, a white crystalline powder that is water soluble and widely used for TIMS and

ICP-MS analyses, but for most applications it is not suitable for SIMS.

The mass fractionation of SIMS may depend on the chemical composition of the analyzed material. This so-called “chemical matrix effect” requires that reference materials used for correction of instrumental mass fractionation need to be similar to the analyzed samples, or at least it needs to be demonstrated through the analysis of a range of materials that the matrix effect is negligible or can be quantified for data correction. A range of silicate glasses has been distributed internationally and has been characterized for their B isotopic compositions. They are homogeneous at the level of current analytical precision, and range from komatiitic to basaltic to andesitic to rhyolitic in composition (e.g., Jochum et al. 2006; see Table 2.2).

The matrix effect for SIMS boron isotope analyses among this wide range of naturally occurring glass compositions was analytically not resolvable (less than 0.5‰) in a study by Marschall and Monteleone (2015). This had also been demonstrated previously for a similar set of basaltic to rhyolitic glasses in two other SIMS labs at a level of ≤ 1.3 and $\leq 2.1\%$, respectively by Rosner et al. (2008), showing that matrix effects are not limiting the accuracy of B isotope analyses of natural silicate glasses by SIMS. In contrast, the widely distributed NIST glasses of the 61X series (e.g., SRM610, SRM612) are not suitable for SIMS boron isotope analyses as a reference for instrumental mass fractionation correction; they consistently produce fractionation factors that are 2–4‰ different from all glasses with natural compositions (Rosner et al. 2008; Gurenko and Kamenetsky 2011). These glasses are, therefore, generally avoided for SIMS boron isotope work in modern studies.

Chaussidon et al. (1997) investigated boric acid solution and seawater evaporated on a Si wafer, silicate glasses, and tourmaline, and found less than 1.6‰ matrix effect among all these materials. In an earlier study, the same group had reported a strong effect of tourmaline chemistry on instrumental mass fractionation, amounting to approximately 15‰ between the Fe–Mg-rich types (schorl-dravite) on the one hand and the

Li-rich elbaite on the other. However, the reported relationship is mostly anchored on one elbaite sample, and this set of tourmalines was only used in that particular lab. A set of three tourmaline reference materials (dravite, schorl and elbaite) has subsequently been established and is now widely distributed through the Harvard museum (Leeman and Tonarini 2001). Small (<2‰) or negligible matrix effects among various tourmaline compositions have been reported by a number of labs (e.g., Büttner and Kasemann 2007; Drivenes et al. 2015; Ludwig et al. 2011; Nakano and Nakamura 2001). However, recently McGregor et al. (2013) reported difference in instrumental mass fractionation of approximately 5‰ among the Harvard reference tourmalines, in addition to a matrix effect of 4–5‰ for the B-rich silicate prismatic depending on its Fe content. It is, therefore, recommended that a range of reference materials should be analyzed in each laboratory and during each analytical session (Table 2.2).

Few other minerals have been investigated for their matrix effect in SIMS (e.g., Pabst et al. 2012), but the growing number of laboratories that specialize on B isotope studies may lead to the establishment of a wider range of reference materials. For the analysis of carbonates, a characterized standard of inorganic calcite and a Porites coral sample are in use for mass fractionation correction; the latter has been analyzed by NTIMS and MC-ICP-MS (Kasemann et al. 2009; Table 2.2).

2.3.2.2 Laser Ablation Inductively Coupled Mass Spectrometry

The rapid growth in the adoption of MC-ICPMS for isotopic analysis stems partly from the utility of the plasma interface, as it is able to efficiently ionize both wet and dry aerosols (Halliday et al. 1998). This allows the direct coupling of the MC-ICPMS with a laser ablation (LA) system for high spatial resolution sample introduction. Shortly after the first applications of solution mode MC-ICPMS for boron isotope analysis (e.g., Lecuyer et al. 2002), LA-MC-ICPMS was applied to the in situ determination of $\delta^{11}\text{B}$ (le

Roux et al. 2004). As with solution-mode MC-ICPMS, there has been a resurgence in recent years, following the enhanced analytical sensitivity and mass fractionation stability of the latest generation of MC-ICPMS. Several studies now report precise (<1‰ at 95% confidence) $\delta^{11}\text{B}$ in high boron matrices like tourmaline (e.g., Hou et al. 2010; Martin et al. 2015; Ribeiro da Costa et al. 2014) and low boron matrices such as biogenic CaCO_3 with a spatial resolution of <100 μm (Fietzke et al. 2010; Yang et al. 2015). Although, as with the other approaches discussed here, demonstrating accuracy is challenging and requires the use of an appropriate standards and reference materials (e.g., Devulder et al. 2015; Table 2.2).

The LA-MC-ICPMS introduction system is very flexible allowing for a diverse range of sample sizes and types to be analysed, and is relatively rapid (1 sample every 2–5 min). However, despite this utility the sample/spot size of LA-MC-ICPMS is still larger than is achievable with SIMS. Focusing of the laser beam on the surface of the sample is not thought to be critical (Thil et al. 2016) so a high degree of polish on the sectioned sample is not necessary. As with all boron isotopic analytical techniques, blank contamination can however be an issue and many studies do a pre-analysis ablation to clean the surface of the sample immediately prior to analysis (e.g., Fietzke et al. 2010).

For most applications NIST 610 (356 $\mu\text{g/g}$ B) or NIST 612 (34.7 $\mu\text{g/g}$ B) are used to correct for machine induced isotopic fractionation (Table 2.2) through a sample-standard bracketing routine (e.g., Fietzke et al. 2010). The importance of matrix matching sample and standard is currently unclear, with some studies reporting that there is no need (e.g., Fietzke et al. 2010; Hou et al. 2010) but others suggesting corrections of >2‰ are required if NIST glasses are used for sample-standard bracketing of CaCO_3 matrixes (e.g., Thil et al. 2016). This debate is well illustrated for tourmaline, for which Mikova et al. (2014) proposed that variations in major element chemistry were sufficient to impart significant matrix effects, whereas Ribeiro da Costa et al. (2014) reported no

significant matrix dependence for 18 tourmaline samples covering a $\delta^{11}\text{B}$ range of -24.5 to $+3.2\text{‰}$ as determined by PTIMS (Palmer and Slack 1989). Indeed, in Ribeiro da Costa et al. (2014) the average deviation between solution and laser ablation was only 0.7% (maximum deviation of 2.3%; 15 of the 18 analyses differed by $<1\text{‰}$), despite the differences in sample size: the TIMS technique involved analysis of the total B extracted from multiple grains of tourmaline sometimes showing evidence of optical and isotopic zoning, whereas the LA-MC-ICPMS technique only analyses a small portion of individual tourmaline grains (using a 25 μm spot rastered over 100–200 μm).

Despite some difficulties, the advantage of the high spatial resolution and relatively quick throughput makes LA-MC-ICPMS analysis of $\delta^{11}\text{B}$ an attractive technique, albeit one where accuracy and precision approaching the bulk methods is a significant challenge.

2.4 Summary and Outlook

The last 20 years or so have seen the interest and application of stable isotope systems to key problems in the Earth sciences grow at a phenomenal rate. The stable isotopes of boron have a long history in this regard but analytical difficulties have always made the analysis of the $^{11}\text{B}/^{10}\text{B}$ ratio difficult and hard won. There are, however, a wealth of sample preparation, digestion, purification and analytical techniques available that allow for the analysis of boron at a wide range of scales and from a plethora of sample types (Table 2.1; Fig. 2.1). Given the ever wider proliferation of MC-ICPMS technology and the suitability of this technique for both bulk and in situ analysis, along with the installation of large-radius ion probes with high transmission in a number of laboratories worldwide, we are in no doubt that the years to come will continue to see a growth in the application and utility of boron isotopes. This, along with the continued growth in interest in boron isotopes in general, will lead to the establishment of new

standards and quality control materials for in situ and solid B isotope analyses.

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