In situ, multiple-multiplier, laser ablation ICP-MS measurement of boron isotopic composition (δ^{11}B) at the nanogram level

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Abstract

We present a new in situ, multiple electron-multiplier LA-ICP-MS technique for the analysis of boron isotopes (δ^{11}B) at $< 1‰$ 2σ precision and at the nanogram level. Sample materials analyzed were all natural and synthetic glasses, spanning a range of boron concentrations from 0.39 to 30.2 ppm and ^{11}B/^{10}B values from 4.0254 to 4.0799 (δ^{11}B $-6.08‰$ to $+7.35‰$). The in situ analyses were duplicated at higher concentrations by solution analyses of chemically separated boron using conventional nebulization on the same ICP-MS system.

Sample-standard switching between glass chips on an approximate 5-min cycle is used to monitor and correct for instrumental fractionation and drift. Instrumental fractionation of more than $100‰$ in measured ^{11}B/^{10}B ratios is successfully corrected and the final ^{11}B/^{10}B values are up to 100-fold more accurate than the measured ratios. Reproducibility of $<1‰$ at 2σ are routinely produced at natural sample boron concentrations as low as 0.39 ppm.

The amount of boron measured to produce these data is dependent on the boron concentration of the sample, and ranges from 0.014 μg at 30.2 ppm boron to 0.0008 μg at 0.39 ppm boron. These nanogram amounts of boron measured are approximately two orders of magnitude lower than conventional P-TIMS and solution multiple faraday ICP-MS methods which typically require 0.3–3.3 μg of boron. The advantages of this technique are the elimination of procedures for the chemical separation for boron, low instrument memory and background (<300 cps compared to $>100\,000$ cps for solutions), high sensitivity, small sample size, and spatial control on material analyzed. These characteristics will permit boron isotopic analysis on virtually any glass collection.

The boron isotope compositions of four fresh MORB glass samples from the northern EPR ($15–18°$N) were determined using the laser ablation technique presented here. The results indicate a narrow range of boron compositions for these samples (δ^{11}B $-6.92‰$ to $-7.68‰$), which overlap at the 2σ level. The light δ^{11}B composition of these samples precludes substantial seawater (δ^{11}B $+39.5‰$) contamination of their pre-eruptive MORB magmas.
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Keywords: Laser; Ablation; Glass; ^{11}B/^{10}B; Seawater; MORB

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1. Introduction

The light element boron and its isotopic composition have proved to be useful in diverse fields of geosciences: e.g., the composition of the mantle and

meteorites (Chaussidon and Jambon, 1994; Chaussidon and Libourel, 1993; Chaussidon and Marty, 1995; Gurenko and Chaussidon, 1997; Leeman and Sisson, 1996; Zhai et al., 1996), defining subduction zones processes (Benton et al., 2001; Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997, 1999; Ishikawa et al., 2001; Kopf and Deyhle, 2002; Rose et al., 2001; Schmitt et al., 2002; Straub and Layne, 2002), the compositional alteration of the oceanic crust and MORB magmas (Ishikawa and Nakamura, 1992; Marty et al., 2001; Shirey et al., 1998; Smith et al., 1995; Spivack et al., 1990; Spivack and Edmond, 1987; Williams et al., 2001), environmental monitoring (e.g., Gäbler and Bahr, 1999; Lemarchand et al., 2002a) and chemical palaeo-oceanography (Hemming et al., 1998; Hemming and Hanson, 1992; Lécuyer et al., 2002; Lemarchand et al., 2002b; Sanyal et al., 1995, 1997). Thermal ionization mass spectrometry analysis for boron isotopic composition has major complications particularly the associated laborious and notoriously difficult chemistry (Hemming and Hanson, 1994; Lécuyer et al., 2002; Nakamura et al., 1992; Spivack and Edmond, 1986; Swihart, 1996; Tonarini et al., 1997). Attempts with secondary-ion mass spectrometry, using single-collector, small-radius instruments (e.g., Cameca IMS 3f) (Chaussidon and Jambon, 1994; Chaussidon and Marty, 1995; Chaussidon et al., 1997; Straub and Layne, 2002), have been successful but at necessarily low useful ion yields that limited the precision of the boron isotopic measurement (2σ values of $\pm 3–6‰$) and hampered its application in settings where restricted ranges in boron isotopic composition occur.

We report here a new technique for in situ boron isotopic analysis that avoids sample chemistry, achieves high enough ion yield to obtain better than $1‰$ precision on even low boron abundance glasses, and permits correction of the high mass fractionation produced by the ICP-MS ($100–150‰$ for measured $^{11}B/^{10}B$ ratios) to better than $1‰$ absolute accuracy by sample-standard switching.

2. Standards

The certified reference materials NIST 610, NIST 612 and NIST 614 used in this study are synthesized $Si–Na–Ca–Al$-oxide glasses produced by the U.S.

National Institute of Standards and Technology (NIST, Kane, 1998). The trace-element compositions of these reference glasses span a broad range (NIST 610: ~ 500 ppm; NIST 612: ~ 50 ppm; NIST 614: ~ 1 ppm), making them the standard materials of choice for microanalysis in geosciences. These nominal trace-element concentrations have been well characterized for NIST 610 and NIST 612 (Pearce et al., 1997; Rocholl et al., 1997, 2000), and to a lesser extent for NIST 614 (Horn et al., 1997; Kurosawa et al., 2002). Some radiogenic isotope data are available for these glasses (Woodhead and Hergt, 2001), and recently oxygen and boron stable isotope data have appeared for NIST 610 and NIST 612 (Kasemann et al., 2001; Schmitt et al., 2002).

JB-2 (30.2 ppm B, Kasemann et al., 2001) is a natural basalt reference material from Oshima, Japan, supplied by the Geological Survey of Japan, in powdered form. The major- and trace-element compositions of JB-2 are well characterized (Govindaraju, 1994; Imai et al., 1995), and boron isotope compositions have also been determined by a number of studies on these powders (Kasemann et al., 2000, 2001; Nakamura et al., 1992; Tonarini et al., 1997).

The two natural MORB quenched glasses used in this study are both part of well-studied sample suites. Sample ALV519-4-1 (0.39 ppm B; DTM unpublished data) is from $36.82°N$, $33.26°W$ on the Mid-Atlantic Ridge (FAMOUS area), has a well-characterized composition (Langmuir et al., 1977) and has been included in a number of diverse studies (e.g., Hauri et al., 2002; Shimizu, 1998). Sample VE-32 (1.01 ppm B; DTM unpublished data) was dredged during the Venture Leg 2 cruise from $15.52°N$, $-105.40°W$ on the northern East Pacific Rise and also has well-characterized major- and trace-element compositions (Reynolds et al., 1992).

3. Analytical method

3.1. Solid sample preparation

All solid materials in this study were analyzed by laser ablation in the form of glass. The JB-2 powdered sample was fused in a platinum capsule, at 1500 °C and >7 kbar for ~ 10 min in a piston-cylinder apparatus. Resulting JB-2 glass shards, along with

ALV519-4-1 and VE-32 glass shards were mounted in epoxy, in holes drilled in 25 mm round aluminum discs. The discs were polished using only 180 grit silicon carbide grinding paper until the exposed surface area of most glass shards exceeded $\sim 2 \times \sim 1$ mm. All evidence of phenocrysts, alteration, cracks and fractures in the natural glass shards were avoided during handpicking.

As a final cleaning step, the polished sample discs and NIST 612 and NIST 614 wafers were immersed in boron-free water, in a boron-free Teflon beaker, and placed in an ultrasonic bath for ~ 5 min. This process was repeated three times, with fresh boron-free water after each cycle. Subsequently sample discs and NIST wafers were only handled while wearing latex gloves and the surfaces to be analyzed never touched. Without these steps, surface boron contamination increased the measured signal by variable amounts, up to double the true intensity.

The boron-free water was produced in-house using a Teflon, two-bottle still. All-teflon laboratory equipment was used to avoid boron contamination from borosilicate glassware. The Teflon bottles, joins, storage bottles and beakers were cleaned for ~ 24 h at sub-boiling temperatures in a 90% ~ 5 M HNO_3– 10% 28 M HF solution. The resulting "clean" still reservoir was loaded with 1 l Milli-Q water and 5 g mannitol powder. Heating tape was wrapped around the reservoir bottle, and the bottle was then covered in aluminum foil. The heating tape was set to yield a reservoir bottle temperature of ~ 40 °C. The reservoir bottle was emptied and recharged with Milli-Q– mannitol solution once approximate 0.5 l of the solution had been distilled.

3.2. Solution sample preparation

NIST 610, NIST 612, VE-32 chips and JB-2 powders were the starting materials for the solution multi-faraday ICP-MS analyses presented in this study. NIST 610 and NIST 612 material was cleaned according to the following procedure: immersion in methanol solution and ultrasonification for ~ 30 min; rinsing three times with methanol; and drying in an oven at ~ 80 °C. The VE-32 chips were handpicked and cleaned according to the following procedure: immersion in MeOH and ultrasonification for ~ 30 min; immersion in Milli-Q+0.5 ml mannitol solution

and ultrasonification for ~ 30 min; repetition of this step three times; rinsing in boron-free water (see preceding explanation); and drying in an oven at ~ 80 °C. The JB-2 powder was taken directly as supplied and digested.

Subsequent sample digestion and boron column chemistry followed published methodology (Nakamura et al., 1992), previously successfully employed in studies at DTM (e.g., Benton et al., 2001). After the column chemistry, the samples (boron–mannitol beads) were rehydrated with boron-free water, with one drop of ammonia added for every 10 ml of boron-free water used. The NIST 951 standard solution was diluted with boron-free water to yield a boron concentration of approximately 1 ppm, one drop of ammonia was added for every 10 ml of the solution.

3.3. In situ boron isotope measurements

A Cetac LSX200 Nd-YAg frequency-quadrupled laser, operating at 266 nm, was coupled to a VG Elemental Axiom double-focusing ICP-MS (Rehkämper et al., 2001). The Axiom is equipped with multiple electron multipliers, to make simultaneous signal collection of the ^{11}B and ^{10}B ion beams possible.

The following procedures were used to ensure a clean instrument system for these measurements. All tubing leading from the laser-ablation sample chamber to the plasma torch was regularly checked for build-up of material. The first section of tubing leading from the laser-ablation sample chamber was cleaned with compressed air before each half-day session and replaced after two to three sessions. All tubing was replaced on a regular basis, when discernable build-up of ablated glass dust was observed, and all valves, T-joins, etc., were carefully cleaned with compressed air. The laser-ablation sample chamber was thoroughly cleaned with compressed air and ethanol before each session to remove any previously ablated material. The ICP-MS torch was cleaned with compressed air prior to instrument start-up, and all build-up of ablated glass on the sampler and skimmer cones was thoroughly removed. The skimmer cone was immersed in 5% HNO_3, and placed in an ultrasonic bath for ~ 5 min, both cones were then cleaned with wet Polaris pumice powder and finally immersed again in 3% citrinox solution and placed in the ultrasonic bath for ~ 30 min. Once clean, the cones were rinsed with

distilled water and dried with compressed nitrogen gas.

The skimmer cone used was a standard 0.7 mm aperture nickel or platinum cone and the sampler cone was a 1.1 mm aperture, high sensitivity nickel/copper cone. This combination gave significantly improved sensitivity for boron.

The laser-ablation settings, listed in Table 1, were kept constant and only the ICP-MS settings were tuned and optimized for each session following instrument start-up. The laser was used in scan-mode; the selected area was kept constant at 1625×500 μm, resulting in two parallel trenches joined at one end (see Fig. 1). The total volume of material ablated

Table 1
Laser and ICP-MS operating settings[a]

	Laser settings
Energy level	20
Pulse repetition rate	20 Hz
Spot-size (diameter)	200 μm
Laser energy	~ 5 mJ
Distance between lines	250 μm
Scan speed	10 μm/s
Sample defocus	1000 μm
	ICP-MS settings
Torch	
x-position	− 120 ± 5
y-position	− 10 ± 5
z-position	− 150
Cooling gas	14.0 *l*/s
Auxiliary gas	1.0 ± 0.1 *l*/s
Nebulizer gas	1.35 ± 0.03 *l*/s
Beam	
Transfer lens 1	4350 V
Transfer lens 2	4300 V
X1 deflection	− 130 ± 5 V
Y1 deflection	0 ± 10 V
X lens	− 2100 V
Ion energy	4950 V
Multipliers	
Low and high mass discriminators	0
Low mass deflector 1	958 V
Low mass deflector 2	− 1349 V
Low mass tape-slit position	5440 ± 50
High mass deflector 1	393 V
High mass deflector 2	− 41 V
High mass tape-slit position	4950 ± 50

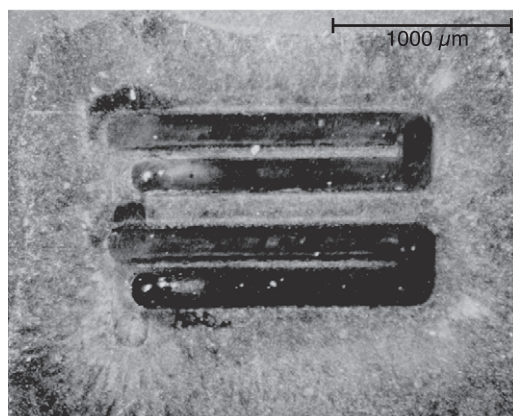[a] Ranges indicate typical limits within which optimal performance was found.

Fig. 1. Example of sample VE-32 glass following laser ablation. Trench depth represents four periods of ablation, and the long-dimension of each trench is 1650 μm.

was approximately 2.5×10^7 μm^3 (two trenches, ~ 200 μm wide, ~ 1650 μm long and ~ 20 μm deep). Given the scan speed of 10 μm/s, the total ablation time was approximately 6 min for the trench shown in Fig. 1.

The ICP-MS was tuned while ablating NIST 612 or NIST 614 and optimized for ^{11}B sensitivity; ^{11}B and ^{10}B peak positions in the mass calibration were updated for each session. Once the optimal torch, gas and beam settings were determined, subsequent adjustments between successive sessions were found to be small (see Table 1). The final adjustment was to align the ^{11}B and ^{10}B peaks on the high-mass and low-mass electron-multipliers (see Fig. 2). The flat-topped peaks in Fig. 2 are representative of the peak shapes routinely obtained, and ^{11}B and ^{10}B signals were measured simultaneously in static mode. The layout of the multiple multiplier assemblage installed on the ICP-MS at DTM is illustrated schematically in Fig. 3. A significant advantage of this design is the use of deflectors to direct the ion beams straight into the throat of the electron multipliers. The result is high relative gain stability and high sensitivity. Very rare adjustments to the voltage settings on the deflectors, to assure good peak shape, and the tape-slit positions, to fine tune peak coincidence, were the only settings in need of minor adjustment between sessions.

The most consistent and reproducible results were obtained while keeping the ^{11}B signal well below
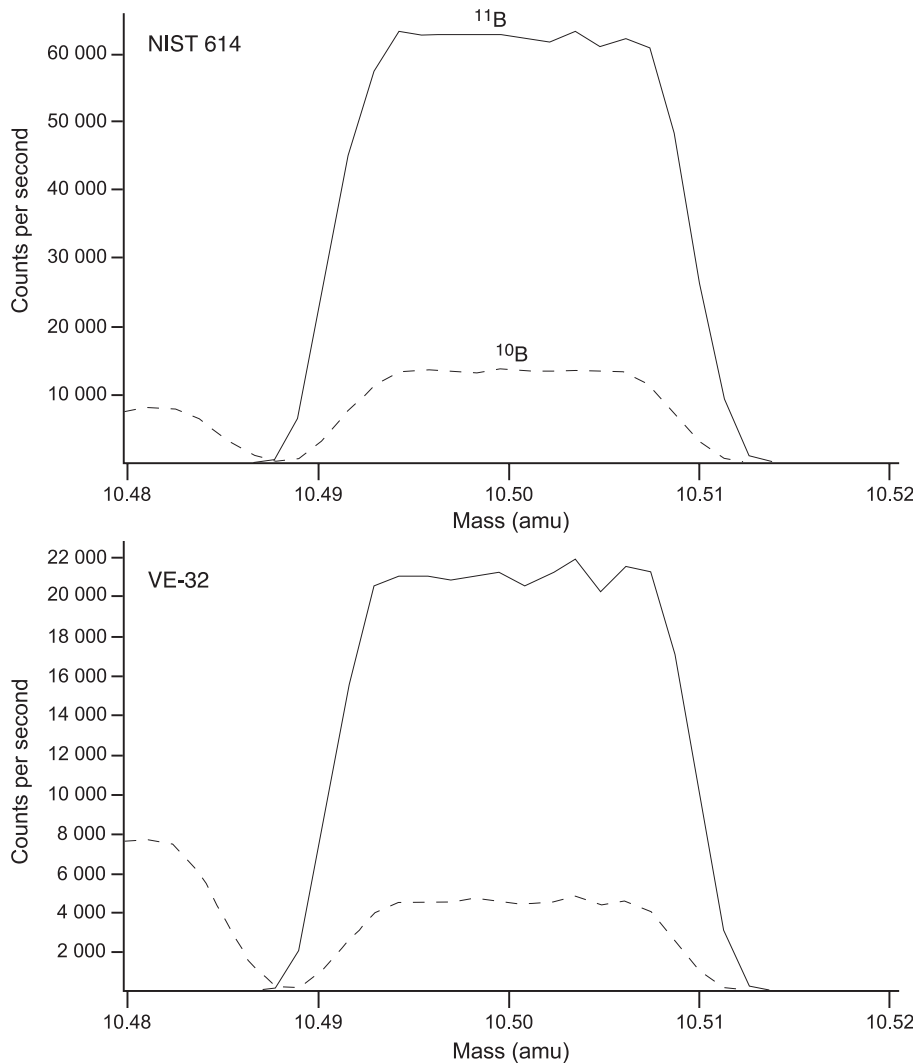
Fig. 2. Representative [11]B and [10]B peak size and shape obtained on the high-mass and low-mass electron multipliers, respectively; aligned for simultaneous acquisition.

100,000 cps, preferably below 50,000 cps. For NIST 614 and the low-boron MORB glass analyses [11]B sensitivity was comfortably in this range (< 50,000 cps). When analyzing the higher boron JB-2 and NIST 612 glasses the signal was much higher and the ICP-MS source-slit was narrowed from 400 resolution to 1000 resolution to bring the [11]B sensitivity into this optimal range for the electron multipliers. Numerous other options were explored to achieve this signal reduction such as changing laser spot-size, laser pulse rate, laser energy, and torch gas flow rate, all of

which produced changes in the instrumental fractionations on boron isotopic composition. Since the boron system has only two isotopes and no possible internal corrections for such fractionation, this effect produces large inaccuracies in final [11]B/[10]B ratios when sample/standard switching. Thus we settled on limiting the signal with the source resolution-defining slit as the most accurate way to adjust the signal between sample and standard.

Although the samples and standards were all thoroughly cleaned (as described above), it was
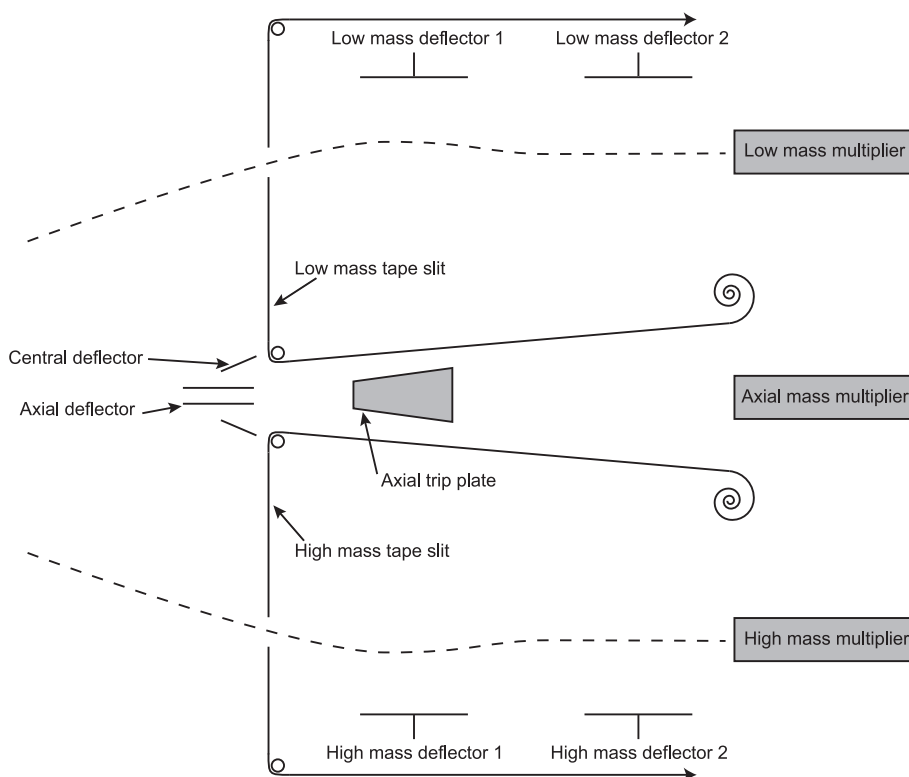
Fig. 3. Schematic layout of the multiple multipliers installed on the Axiom ICP-MS at DTM.

necessary to ablate the sample and standard surfaces with the laser immediately before data acquisition. The epoxy mounted glass shards were only roughly polished (as described earlier) and it is possible some boron contamination persists in scratches on the sample surface, contamination not commonly observed during secondary-ion mass spectrometry because of the small, scratch-free surfaces selected for such analyses. For a typical session, two areas of the standard and unknown were cleaned by ablation using the same laser settings as for data acquisition. One area of the standard and one area of the unknown were then analyzed alternatively and repeatedly, until three analyses of this single area of the unknown were interspersed and bracketed by four analyses of the single area of the standard. No laser firing was performed for a period of 1 min between analyses, to avoid any possible memory effect, and this time was sufficient to move the laser stage from the standard to the sample position or vice versa. The procedure was repeated for the second pair of "cleaned" areas, to produce six analyses of the unknown per session (see Fig. 4A). [11]B sensitivity decreased with time as the system got dirtier (e.g., tubing, cones) and six standard-bracketed analyses of an unknown were the maximum routinely obtained per session.

Initially, analyses of different areas of the standard were used to bracket and correct the analysis of the unknown. Later, analyses of the same area of the standard were used to bracket and correct an analysis of the unknown. The latter method yielded improved results. Subsequent technique developments (e.g., improved and more stable instrument and laser optimization) decreased the importance of the analysis location, although two analyses of the same area of the standard remained the most consistent measure of instrumental drift. Furthermore, this procedure yields more analyses from the limited standard and sample surface area available.
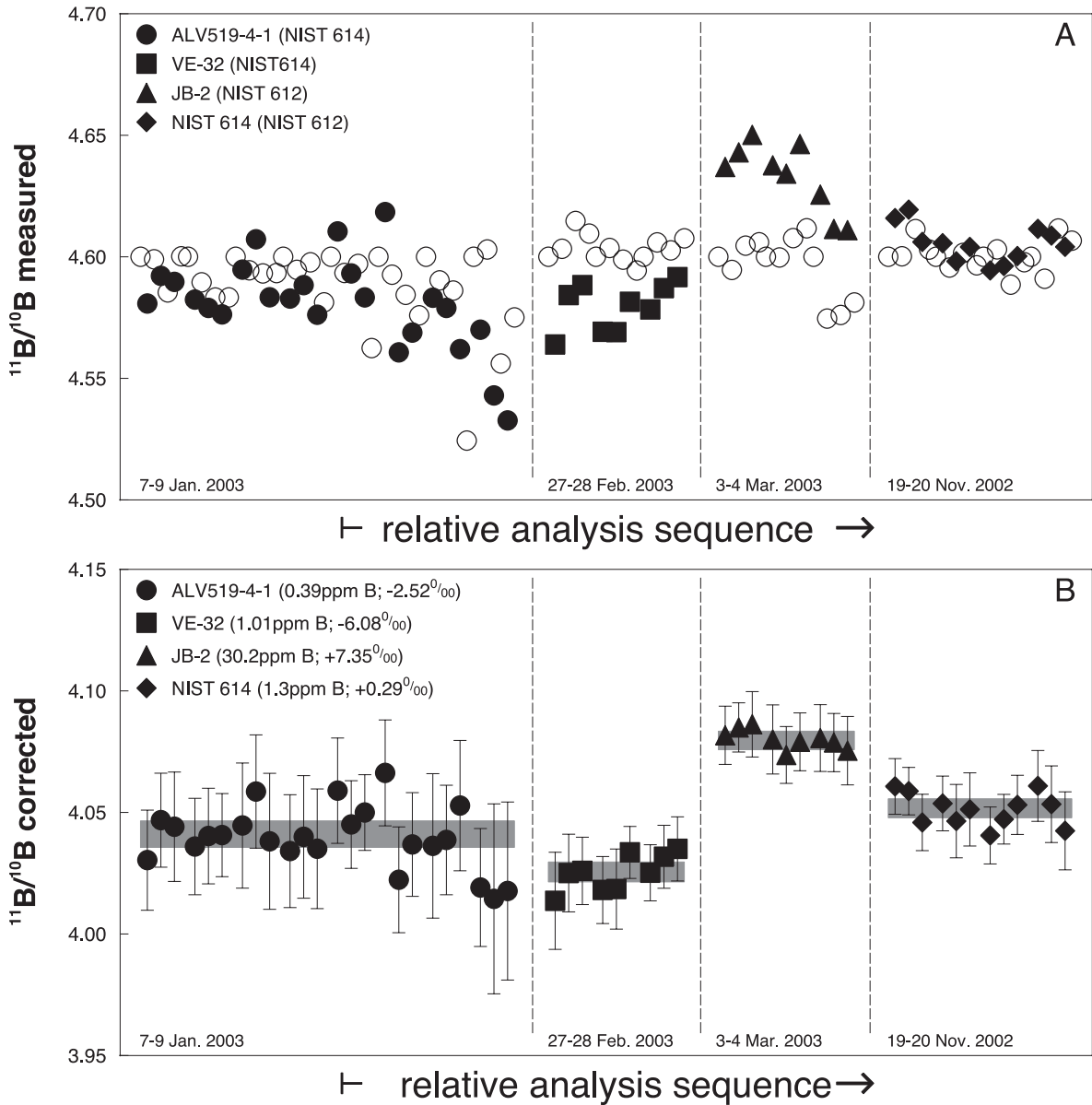
Fig. 4. (A) $^{11}B/^{10}B$ measured for analyses which constitute one of the final values in Table 2, for each unknown (unknown: filled marker; standard: open marker) analyzed in this study (see legend). Note the range in $^{11}B/^{10}B$ measured values of the standard and unknowns, and how using two analyses of the same area of the standard to bracket, and correct, an analysis of an unknown yields consistent final $^{11}B/^{10}B$ ratios for the unknowns in panel B. (B) $^{11}B/^{10}B$ corrected for instrumental fractionation, drift and calculated relative to NIST 951, with 2σ error bars for each individual analysis. Gray fields: range of LA-MM-ICP-MS values listed in Table 2 for respective sample or standard, including 2σ errors. The larger scatter, more analyses required and larger 2σ errors for ALV519-4-1 analyses relative to JB-2 analyses is due to the much lower boron concentration in ALV519-4-1 relative to JB-2 (see legend). In both diagrams, dashed vertical lines indicate temporal breaks in the relative analysis sequence. The dates listed on the diagrams indicate when these specific data were collected.

During data acquisition, a 120 s pre-ablation was followed by automatic centering of the ^{11}B peak in the high-mass electron multiplier (typically ~ 5 s). The background was subsequently simultaneously measured in the high- and low-mass electron multipliers 0.5 amu below each boron peak for 5 s. The 0.5 amu separation is sufficient to avoid interference from the doubly-charged neon peak (at ~ 9.9 amu) adjacent to the ^{10}B peak on the low-mass side. The ^{11}B and ^{10}B ion intensities were then simultaneously measured, without any further adjustments. The duration of a boron measurement was 5 s, and 36 measurements were made per analysis split into three sets of 12 measurements. Data acquisition totaled about 3 min, while the total time for an analysis, including pre-ablation, was approximately 5 min.

The 36 measured $^{11}B/^{10}B$ ratios of an analysis of an unknown were corrected for instrumental drift to the mean of the two bracketing analyses of the standard (see Eq. (1)). The drift-corrected ratios were further referenced to the accepted $^{11}B/^{10}B$ value of the standard (see x in Eq. (1)), itself referenced to NIST 951. For each unknown, the 36 drift-corrected and referenced $^{11}B/^{10}B$ ratios of all separate analyses were pooled and iteratively filtered to exclude ratios greater than three standard deviations of the mean (typically < 1% of ratios were eliminated). These filtered ratios were used to calculate the final $^{11}B/^{10}B$ value of the unknown, as well as the 2σ error for this final value.

$$^{11}B/^{10}B_{\text{unkn}}(\text{final}) = \frac{^{11}B/^{10}B_{\text{unkn}}(\text{measured})}{x}$$

$$x = \frac{^{11}B/^{10}B_{\text{std1}}(\text{measured}) + ^{11}B/^{10}B_{\text{std2}}(\text{measured})}{2}$$
$$\times \frac{1}{^{11}B/^{10}B_{\text{std}}(\text{reference})} \qquad (1)$$

The same reference value for the $^{11}B/^{10}B$ ratios of NIST 612 and NIST 614 was used on the assumption that, in the absence of direct boron isotopic measurements of NIST 614, both glasses included boron of the same isotopic composition. Recently, Woodhead et al. (2001) documented isotopic differences between Sr, Nd and Pb isotopic compositions of NIST 612 and 614 which was attributed to blank contamination

during preparation of the lower abundance NIST 614 glass. Our study rules out this effect for boron since no significant difference in boron isotopic composition was observed between these two standard glasses in this study (see Table 2). The boron isotopic composition used was the high-precision solution ICP-MS value, 4.04680($\pm$ 05), determined for NIST 612 in this study which agrees with previously published analyses of this standard, but with a smaller 2σ error (see Table 2).

3.4. Solution boron isotope measurements

The same VG Axiom double-focusing ICP-MS at DTM was used to make the boron isotope measurements of solutions, employing multiple faraday collectors. Solutions were introduced into the ICP-MS plasma torch via a quartz-glass spray-chamber and free aspiration. A 1 ppm boron solution of diluted NIST 951 was used to tune the ICP-MS, optimizing ^{11}B sensitivity on the axial faraday collector. The ^{11}B and ^{10}B peaks were aligned and centered in the high-4 and low-4 faraday collectors.

Data acquisition was divided into cycles, with each cycle comprised of a 90-s uptake, 40 consecutive boron measurements of 5 s each, and finally a 60-s wash. For the best results, each analysis cycle of an unknown or standard was followed by two cycles of the wash solution. This ensured no cross-contamination between standards and unknowns and an accurate measurement of the background.

Standard-sample switching was also followed for the solution analyses, and the data reduction was similar to that described for the laser-ablation analyses.

Obtaining useful boron isotope data by this solution technique was challenging for a number of reasons. The washout of boron between different solutions was difficult to quantify and necessitated constant monitoring. Even the low boron solution used as a wash solution still yielded significant boron intensities. Therefore, very high boron signals ($\gg 1-3 \times 10^6$ cps) were required for the standard and sample solutions to overcome this very significant background. The accuracy of the final analysis can be compromised by variable mixing of different boron reservoirs in the wet uptake and spray chamber system, especially at low boron signals. These effects provided measurement difficulties beyond the notori-

Table 2
Boron isotope results for laser-ablation multiple electron multiplier and solution multiple-faraday ICP-MS determinations from this study, with published data for the same standards and samples

Sample	μg B	B (ppm)	Type	Normalized to	$^{11}B/^{10}B_{unkn}$ (measured)	α (951)[a]	$^{11}B/^{10}B_{unkn}$ (corrected)[b]	Ref. range[b]	$δ^{11}B_{unkn}$ (‰)[b,c]	Ref. range (‰)[b]
NIST 610	3.3	363[1]	solution	951	4.5000	1.120165	4.0494 (± 09)	4.0453 (± 56)– 4.0468 (± 56)[1,2]	− 0.16 (± 0.21)	− 0.79 (± 1.40) to − 1.16 (± 1.40)[1,2]
NIST 610	3.3		solution	951	4.5386	1.120214	4.0486 (± 02)		− 0.36 (± 0.06)	
NIST 612	2.9	34.9[1]	solution	951	4.5397	1.121251	4.0489 (± 15)	4.0457 (± 69)[1]	− 0.29 (± 0.37)	− 1.06 (± 1.70)[1]
NIST 612	2.9		solution	951	4.4704	1.104733	4.0468 (± 05)		− 0.80 (± 0.13)	
NIST 614	0.0015	1.3[6]	LA/glass	612	4.4761	1.103770	4.0524 (± 32)		0.58 (± 0.79)	
NIST 614	0.0015		LA/glass	612	4.4987	1.109745	4.0512 (± 34)		0.29 (± 0.84)	
JB-2	3	30.2[1]	solution	951	4.5766	1.121794	4.0799 (± 09)	4.0790 (± 62)– 4.0793 (± 07)[1,3,4]	7.38 (± 0.22)	7.15 (± 1.54) to − 7.23 (± 0.20)[1,3,4]
JB-2	3		solution	951	4.5497	1.115300	4.0799 (± 17)		7.38 (± 0.42)	
JB-2	0.014		LA/glass	612	4.6736	1.145029	4.0794 (± 36)		7.25 (± 0.88)	
JB-2	0.014		LA/glass	612	4.7533	1.164288	4.0798 (± 36)		7.35 (± 0.88)	
ALV519-4-1	0.0008	0.39[7]	LA/glass	614	4.6140	1.141498	4.0427 (± 38)	4.0402 (± 09)[5]	− 1.80 (± 0.95)	− 2.40 (± 0.20)[5]
ALV519-4-1	0.0008		LA/glass	614	4.6026	1.141424	4.0398 (± 42)		− 2.52 (± 1.04)	
VE-32	0.6	1.01[7]	solution	951	4.4269	1.098214	4.0316 (± 09)		− 4.55 (± 0.20)	
VE-32	0.6		solution	951	4.4244	1.098041	4.0298 (± 09)		− 5.00 (± 0.20)	
VE-32	0.0014		LA/glass	614	4.5983	1.141004	4.0255 (± 41)		− 6.05 (± 1.03)	
VE-32	0.0014		LA/glass	614	4.6460	1.153103	4.0254 (± 35)		− 6.08 (± 0.89)	

[1]Kasemann et al. (2001); [2]Schmitt et al. (2002); [3]Tonarini et al. (1997); [4]Nakamura et al. (1992); [5]Ishikawa and Hauri (unpublished data) after, Ishikawa and Tera (1997); [6]NIST certified value; [7]DTM ion probe data.

[a] α (951): instrumental mass fractionation of measured $^{11}B/^{10}B$ ratio of standard relative to NIST 951.

[b] Value in brackets indicate $2σ$ errors in final two decimal places of ratio.

[c] $δ^{11}B = \frac{(^{11}B/^{10}B_{unkn} - {}^{11}B/^{10}B_{std})}{^{11}B/^{10}B_{std}} \times 1000$ where $^{11}B/^{10}B_{std} = 4.05003$ (NIST 951 Ishikawa and Tera, 1997; Ishikawa et al., 2001).

ous chemical procedures used to prepare the standard and sample solutions.

4. Results

The results for the laser-ablation multiple electron multiplier (LA-MM-ICP-MS) and solution multiple-faraday ICP-MS boron isotope determinations are presented in Table 2. It is important to notice the considerably smaller amount of boron analyzed by laser ablation in comparison with other TIMS techniques. P-TIMS studies routinely require enough material to provide $0.3–3$ μg of boron per analysis. The solution multiple-faraday ICP-MS analyses performed as part of this study required $0.6–3.3$ μg of boron per analysis, in particular to raise the sample/analytical blank ratio (see Section 3.4, above). For the LA-MM-ICP-MS determined boron isotope values listed in Table 2, the total amount of boron cumulatively analyzed for each boron isotopic determination was $0.0008–0.014$ μg of boron, depending on the boron concentration. The LA-MM-ICP-MS analysis therefore in some cases sampled 1000 times smaller amounts of boron compared to what is needed for P-TIMS even though the boron ion beam was reduced to optimize multiplier accuracy and reproducibility (see Section 3.3). The percentage boron ion yield (number of ions detected/number of ions ablated) for the LA-MM-ICP-MS technique ranged from $\sim 0.0001\%$ for the 0.39 ppm boron ALV519-4-1 ($\sim 3.6 \times 10^7$ boron ions detected; $\sim 4.5 \times 10^{13}$ boron ions ablated) analyses to $\sim 0.00001\%$ for the 30.2 ppm boron JB-2 ($\sim 5.1 \times 10^7$ boron ions detected; $\sim 7.8 \times 10^{14}$ boron ions ablated) analyses. The ion beam intensity during the analyses of JB-2 was reduced using the source resolution-defining slit (see Section 3.3), which accounts for the lower ion yield although JB-2 has the highest boron concentration of the natural samples analyzed in this study.

5. Discussion

5.1. Accuracy and precision

The data from this study, listed in Table 2, indicate the ability of the LA-MM-ICP-MS technique to re-

produce the $^{11}B/^{10}B$ isotopic composition of four different standard materials to an accuracy better than $1\%_o$ (2σ of the mean, with $n>300$) across a composition range spanning isotopically light boron ($^{11}B/^{10}B$ of 4.025; $\delta^{11}B$ of $-6\%_o$) to isotopically heavy boron ($^{11}B/^{10}B$ of 4.080; $\delta^{11}B$ of $+7.4\%_o$). This includes the synthetic NIST 614 glass, JB-2 experimentally fused glass (described earlier) and the two natural quenched MORB glasses. These results have been cross-checked against measured boron isotopic composition on chemically separated boron by P-TIMS (Nakamura et al., 1992; Tonarini et al., 1997) and ICP-MS (this study, Kasemann et al., 2001; Schmitt et al., 2002).

The standard-sample-standard analysis method described earlier provided an accurate monitor of the instrumental fractionation (see measured $^{11}B/^{10}B$ values in Table 2) and drift (see Fig. 4A). During LA-MM-ICP-MS analysis, this enabled the correction of the sample analysis and compensated for instrumental fractionation at the $\sim 100–150\%_o$ level (see α (951) values in Table 2), producing a final accuracy that is more than a 100-fold improvement over the measured value (compare $^{11}B/^{10}B_{unkn}$ (measured) with $^{11}B/^{10}B_{unkn}$ (corrected) in Table 2, and see Fig. 4B).

A particular strength of the standard-sample-standard analysis method is the inherent ability to correct for any systematic electron-multiplier gain bias in the measurements of the ^{11}B and ^{10}B signal intensities (i.e., the analyses of the standard and the sample would be similarly affected). All the material analyzed by LA-MM-ICP-MS in this study was glass, which limits the possibility of any significant matrix affect. Although the major-element compositions of the NIST glasses and glasses analyzed as unknowns differ, this made no significant impact on the ability of the LA-MM-ICP-MS method described here to reproduce previously determined boron isotope values for these glasses within $1\%_o$ 2σ levels (see Discussion below).

The ability of the LA-MM-ICP-MS and solution MF-ICP-MS techniques to reproduce published boron isotope values to within $1\%_o$ 2σ error is shown in more detail in Fig. 5. $\delta^{11}B$ values for the MORB quenched glass ALV519-4-1 (0.39 ppm B) determined by LA-MM-ICP-MS using NIST 614 as normalizing standard ($-1.80 \pm 0.95\%_o$ and $-2.52 \pm 1.04\%_o$) agree within 2σ error with the same measurement performed by P-TIMS at DTM ($-2.40 \pm 0.20\%_o$)
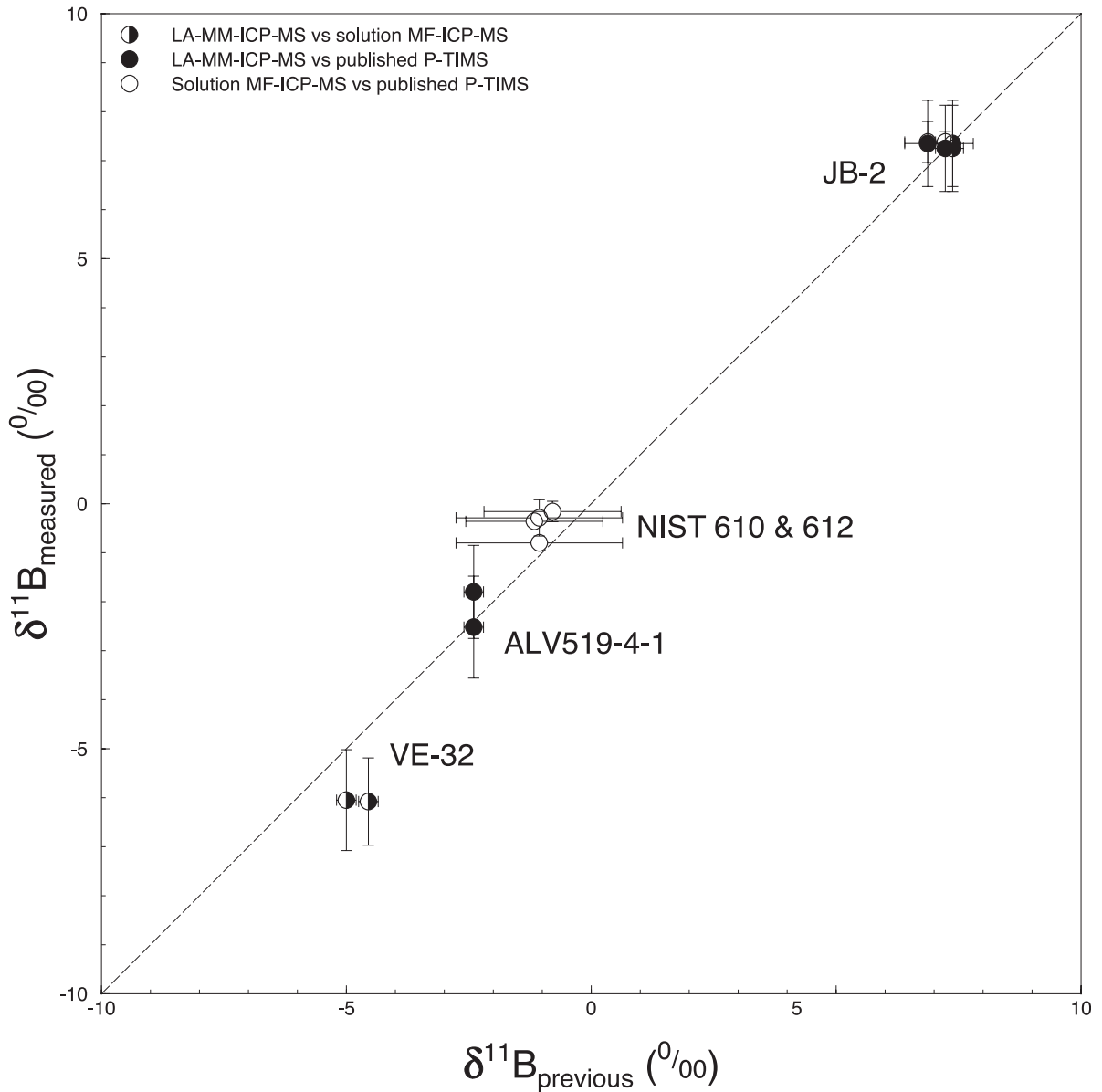
Fig. 5. $\delta^{11}B_{measured}$ versus $\delta^{11}B_{previous}$ for analyses of the same sample or standard (as labeled) by different analytical techniques (as indicated in the legend).

almost a decade earlier (Ishikawa and Hauri, unpublished data after Ishikawa and Tera, 1997). The $\delta^{11}B$ values of the other MORB glass VE-32 (1.01 ppm B) were all determined as part of this study, and the data from LA-MM-ICP-MS analysis using NIST 614 as normalizing standard ($-6.05 \pm 1.03\permil$ and $-6.08 \pm 0.89\permil$) are also in close agreement with

the results from solution MF-ICP-MS ($-4.55 \pm 0.20\permil$ and $-5.00 \pm 0.20\permil$). There is no evidence for boron isotope heterogeneity in VE-32 (including long-term repeat LA-MM-ICP-MS analyses), although it cannot be discounted. The solution MF-ICP-MS analyses of VE-32 were preformed on the same day and following analyses of high concentra-

tions boron material with significantly heavier boron isotope compositions (JB-2 and seawater). Although extreme care was taken to avoid memory effects between solution analyses, this was the largest source of difficulty during solution MF-ICP-MS analyses. Minimal wet uptake and spray-chamber contamination by these JB-2 or seawater solutions could account for the observed slight offset between VE-32 solution analyses and LA-MM-ICP analyses.

The published P-TIMS $\delta^{11}B$ values of the higher boron concentration (30.2 ppm B) natural basalt reference material JB-2, supplied by the Geological Survey of Japan, range from $+7.15 \pm 1.54‰$ to $+7.23 \pm 0.10‰$. The $\delta^{11}B$ values of JB-2 determined by LA-MM-ICP-MS, using NIST 612 as normalizing standard, ($+7.25 \pm 0.88‰$ and $+7.35 \pm 0.88‰$) are in close agreement with the published $\delta^{11}B$ range. The $\delta^{11}B$ values of JB-2 determined by solution MF-ICP-MS, using NIST 951 as normalizing standard, ($+7.38 \pm 0.22‰$ and $+7.38 \pm 0.42‰$) also overlap the published data, and data from LA-MM-ICP-MS.

As discussed above, NIST 614 (1.3 ppm B) was used as normalizing standard for the LA-MM-ICP-MS analysis of the low boron concentration MORB glasses. Some degree of concentration matching between sample and standard was found necessary to ensure similar ^{11}B and ^{10}B peak sensitivities, enabling constant ICP-MS optimization and similar instrumental drift. However, no previous boron isotope determination of NIST 614 has been published. In order to use NIST 614 as normalizing standard for low boron concentration samples, its boron isotope composition was measured by LA-MM-ICP-MS using NIST 612 as normalizing standard. This required the reduction of the NIST 612 ^{11}B and ^{10}B peak sensitivities by narrowing the ICP-MS source-slit, as discussed previously. The resulting $\delta^{11}B$ values for NIST 614 ($+0.29 \pm 0.84‰$ and $+0.58 \pm 0.79‰$) overlap the published P-TIMS $\delta^{11}B$ value for NIST 612 ($-1.06 \pm 1.70‰$) and NIST 610 ($-0.79 \pm 1.40‰$ and $-1.16 \pm 1.40‰$); as well as solution MF-ICP-MS $\delta^{11}B$ values for NIST 612 ($-0.29 \pm 0.37‰$ and $-0.80 \pm 0.13‰$) and NIST 610 ($-0.16 \pm 0.21‰$ and $-0.36 \pm 0.06‰$) from this study. The similar $\delta^{11}B$ values of NIST 610, 612, and 614 agrees with previous work on only NIST 610 and 612 (Kasemann et al., 2001). Therefore, the boron

isotopic composition of NIST 614 is not significantly different from that of NIST 610 and NIST 612, at the $1‰$ precision of this study, and we find no evidence of boron isotopic contamination of NIST 614 as was documented for Sr, Nd and Pb isotopes (Woodhead and Hergt, 2001).

The results presented in Table 2 also indicate the close agreement between the measured $^{11}B/^{10}B$ ratios for solution MF-ICP-MS and LA-MM-ICP-MS ($^{11}B/^{10}B_{unkn}$ (measured)). The instrumental mass fractionation of the normalizing standard (α value in Table 2) for the solution technique range between $100‰$ and $120‰$, and for the laser technique between $100‰$ and $160‰$. The slightly higher α values for the laser technique is likely due to additional fractionation of the $^{11}B/^{10}B$ ratio during laser ablation of the solid sample, different gains of the electron multipliers versus faraday collectors, and differential transport of the ablated material from the ablation chamber to the ICP-MS torch.

The theoretical 2σ errors of each LA-MM-ICP-MS analysis was calculated from counting statistics on the ^{11}B and ^{10}B peaks. The calculated theoretical errors of these analyses are in good agreement with the actually achieved 2σ errors which shows that gain stability fluctuations, mass centering, shot-to-shot laser power fluctuations, and variability in laser- and plasma-induced fractionation do not significantly add to measurement uncertainty.

5.2. Advantages

The main advantages of LA-MM-ICP-MS is the lack of any chemical separation of boron in the sample prior to analysis and the small sample size required, thus avoiding the numerous opportunities for contamination of the sample, and the tedious procedures needed to extract boron without fractionating its isotopic composition. In addition, the time required to process a sample from rock to final boron isotope value is cut dramatically (e.g., solution MF-ICP-MS approximately 2–3 weeks, LA-MM-ICP-MS approximately 2–3 days). Each value of VE-32 and JB-2 in Table 2 (constituent standard and sample analyses plotted in Fig. 4) required ∼126 min of data acquisition in less than a day, while each value of ALV519-4-1 required ∼336 min of data acquisition spread over 2 days.

Crystalline or powdered samples can be analyzed if they are fused first which opens up the technique beyond young, glassy samples. We have had success with solid-media apparatus at high confining pressures, as has Kasemann et al. (2001) at 0.1 GPa using a molybdenum strip furnace. The agreement of analyses of our fused powder of JB-2 with analyses of JB-2 powder put straight into chemistry shows that the boron isotopic composition, at least at the ~ 30 ppm level, is not affected by the fusion procedure. This opens up a wider spectrum of potential non-quenched igneous rocks for analysis according to the same procedure. Testing this possibility with a larger selection of powdered samples with known boron isotopic compositions, and from various geological settings, is required.

The LA-MM-ICP-MS technique presented here has been shown to accommodate samples with a wide range in boron concentrations (0.39 to 30.2 ppm B) and boron isotopic compositions (δ^{11}B approximately $-6.1‰$ to $+7.4‰$). The procedures are flexible enough to cover these ranges and robust enough to produce accurate data at all the extremities of these ranges. The capability is therefore established to analyze low boron content MORB samples, to high boron arc lavas and anything in between.

The in situ nature of the LA-MM-ICP-MS technique makes it possible to continuously monitor an analysis for the possible influence of microphenocryst, microlites, cracks and fractures in the sample. Knowingly avoiding these and the ability to reanalyze the same sample after repolishing makes it easier and quicker to be certain of observed anomalous boron isotopic compositions.

6. Application to fresh east pacific rise MORB glasses

The laser-ablation MM-ICP-MS technique was used to obtain the boron isotopic composition of four fresh MORB glass from the East Pacific Rise, at 15–18°N (see Table 3). The boron concentrations of these four samples range from 0.59 to 3.57 ppm, with the low-boron samples less-evolved (Mg#'s 59 to 65) and the high-boron samples more-evolved (Mg#'s 50–57). The samples are variably degassed, as indicated by the large variation in CO_2/Nb ratios (Saal et al., 2002). The

Table 3
Composition of four samples from the northern EPR

	D8-1	D22-1	D30-1	D61-4
Latitude (°N)	17.22	15.71	15.47	15.24
Longitude (°W)	−105.39	−105.43	−105.38	−104.85
Depth (mbsl)	2801	2314	2348	3372
SiO_2[a]	50.99	51.65	53.24	50.88
TiO_2	1.69	1.46	2.70	1.21
Al_2O_3	14.35	15.48	13.11	14.97
FeO*	11.29	10.52	7.88	9.14
MnO	0.20	0.16	0.27	0.18
MgO	7.38	7.59	3.89	8.20
CaO	10.77	10.04	14.01	12.23
Na_2O	2.73	2.91	3.79	2.56
K_2O	0.14	0.19	0.78	0.05
P_2O_5	0.19	0.14	0.75	0.08
Total	99.73	100.14	100.42	99.5
Mg#	57	59	50	65
δ^{11}B (2σ)[c]	−7.55‰ (±0.97)	−7.02‰ (±0.89)	−7.68‰ (±0.67)	−6.92‰ (±0.89)
Disc 2[d]	−8.79‰ (±0.95)	−5.98‰ (±0.98)	−7.73‰ (±0.73)	−5.68‰ (±0.86)
B (ppm)[b]	1.13	0.59	3.57	0.69
H_2O/Ce	0.018	0.012	0.017	0.016
CO_2/Nb	48	57	8.89	244
F/P	0.30	0.28	0.33	0.30
Cl/Nb	54	17	106	35
B/Ce	0.08	0.05	0.07	0.11

[a] Major element oxide in weight percent (Donnelly, unpublished PhD thesis).
[b] Boron concentrations, volatile, halogen and trace element data from DTM ion probe (le Roux et al., in preparation).
[c] Boron isotope compositions relative to NIST 951.
[d] Duplicate analyses of the same samples, but from glass shards in a disc prepared over 3 years ago.

elevated Cl/Nb ratios in sample D30-1 and to a lesser extent D8-1 indicate significant addition of chlorine to the magma. This excess chlorine is thought to come from assimilation of seawater-derived components in the oceanic crust (Michael and Cornell, 1998).

The boron isotope composition of these four samples all overlap at the 2σ level, from a low δ^{11}B of $-7.68‰$ to a high δ^{11}B of $-6.92‰$. Therefore, although the B/Ce ratios of these samples indicate slight addition of boron to some of these magmas (e.g., D61-4), no significant change of boron isotope composition accompanied the variable compositional contamination of these magmas. This eliminates unadulterated seawater as source of the magma contamination (seawater δ^{11}B $+39.5‰$ Spivack and

Edmond, 1987), and place significant compositional constraints on possible contaminants (le Roux et al., in preparation).

A set of duplicate LA-MM-ICP-MS analyses for these samples was made on glass shards prepared for secondary-ion mass spectrometry over 3 years ago (Table 3). These duplicates agree with the boron isotope values determined on samples prepared specifically for this study, at the stated 2σ levels. Thus, the boron isotope compositions of these MORB samples are homogeneous at the $\sim 1‰$ 2σ level and the boron isotope compositions of glass samples are not significantly affected by long-term storage.

7. Conclusions

This study presents an in situ, multiple electron-multiplier LA-ICP-MS technique for the analysis of boron isotopes (δ^{11}B) at the nanogram level, at $<1‰$ 2σ precision. The samples analyzed are all in the form of glass, and span a range of boron concentrations (0.39 to 30.2 ppm B) and boron isotopic compositions (δ^{11}B $-6.08‰$ to $+7.35‰$).

The procedure uses sample-standard switching on an approximate 5-min cycle to monitor and correct for instrumental fractionation and drift. Instrumental fractionation of more than $100‰$ are successfully corrected and the final ^{11}B/^{10}B values are up to 100-fold more accurate than the measured ratios. Precision of $<1‰$ 2σ errors are routinely produced at sample boron concentrations as low as 0.39 ppm.

The amount of boron measured to produce these data is dependent on the boron concentration of the sample, and range from 0.014 µg at 30.2 ppm boron to 0.0008 µg for 0.39 ppm boron. These nanogram amounts of boron measured are orders of magnitude lower than conventional P-TIMS and solution multiple faraday ICP-MS methods, which require 0.3 to 3.3 µg of boron.

The boron isotope compositions of four fresh MORB glass samples from the northern EPR (15–18°N) were determined using the LA-MM-ICP-MS technique presented here. The results indicate a narrow range of boron compositions between these samples (δ^{11}B $-6.92‰$ to $-7.68‰$), overlapping at the 2σ level. The light δ^{11}B composition of these samples precludes significant seawater (δ^{11}B $+39.5‰$) contamination of their pre-eruptive MORB magmas.

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