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GEOSTANDARDS and GEOANALYTICAL RESEARCH

Refining Boron Isotopic Measurements of Silicate Samples by Multi-Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS)

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Solution MC-ICP-MS is an established technique for high precision boron isotope measurement results ($\delta^{11}B_{SRM\ 951}$) in carbonates, yet its application to silicate rocks has been limited. Impediments include volatilisation during silicate dissolution and contamination during chemical purification. To address this, we present a low-blank sample preparation procedure that couples hydrofluoric acid-digestion and low-temperature evaporation (mannitol-free), to an established MC-ICP-MS measurement procedure following chemical purification using B-specific Amberlite IRA 743 resin. We obtain accurate $\delta^{11}B_{SRM\ 951}$ values (intermediate precision ±0.2‰) for boric acid (BAM ERM-AE121 19.65 ± 0.14‰) and carbonate (NIST RM 8301 (Coral) 24.24 ± 0.11‰) reference materials. For silicate reference materials covering mafic to felsic compositions we obtain $\delta^{11}B_{SRM\ 951}$ with intermediate precision < ±0.6‰ (2*s*), namely JB-2 6.9 ± 0.4‰; IAEA-B-5 -6.0 ± 0.6‰; IAEA-B-6 -3.9 ± 0.5‰ (2*s*). Furthermore, splits of these same reference materials were processed by an alternative fusion and purification procedure. We find excellent agreement between $\delta^{11}B_{SRM\ 951}$ measurement results by MC-ICP-MS of the reference materials using both sample processing techniques. These measurement results show that our sample processing and MC-ICP-MS methods provide consistent $\delta^{11}B_{SRM\ 951}$ values for low B-mass fraction samples. We present new data from Mid Ocean Ridge Basalt (MORB) glass, documenting a range in $\delta^{11}B_{SRM\ 951}$ from -5.6 ± 0.3‰ to -8.8 ± 0.5‰ (2*s*), implying some upper mantle $\delta^{11}B_{SRM\ 951}$ heterogeneity.

Keywords: $\delta^{11}B_{SRM\ 951}$, MORB volcanic glass, OIB volcanic glass, silicate reference materials, MC-ICP-MS, HF digestion, boron isotopes.

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Isotopic fractionation of boron during surface (e.g., Spivack *et al.* 1987) and subduction processes (Ishikawa and Nakamura 1993, De Hoog and Savov 2018) followed by its deep recycling can strongly influence the present-day boron isotopic composition of the mantle (see review in Marschall 2018). The $^{11}B/^{10}B$ ratio (expressed as $\delta^{11}B_{SRM\ 951}$, relative to National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 951 Boric Acid Isotopic Standard, in parts per thousand:

$$\delta^{11}B_{SRM\ 951} = \left(R(^{11}B/^{10}B)_{Sample}/R(^{11}B/^{10}B)_{SRM\ 951}\text{-}1\right) \qquad (1)$$

varies by ~ 50‰ between chondrites and modern seawater (Foster *et al.* 2018), making it a powerful means to differentiate between reservoirs within the mantle with different contributions of recycled components, providing sufficient precision can be attained.

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Characterising the boron isotopic composition of the upper mantle, as sampled by MORB is important, but challenging, as these depleted samples often contain < 1 µg g^{-1} boron mass fraction (Ryan and Langmuir 1993). A recent, comprehensive set of MORB measurement results by a refined secondary ionisation mass spectrometry (SIMS) approach reported an isotopic range of ~ 4‰ (δ^{11}B$_{SRM\ 951}$ of -4.0 to -7.8‰ (Marschall *et al.* 2017)). However, large measurement uncertainties (typically ±2 to ±4‰; 2*s*), make it difficult to resolve possible source variability from measurement imprecision (Marschall *et al.* 2017). Advances in the use of boron isotope ratio measurements to investigate the composition of the Earth's upper mantle therefore requires improvement in measurement uncertainties (Foster *et al.* 2018). The determination of boron isotopes by solution MC-ICP-MS offers a means to obtain high signal to noise ratios given sufficient sample (10 to 50 ng of B, this study) (e.g., Wei *et al.* 2013, Zhu *et al.* 2021, Cai *et al.* 2021, Li *et al.* 2019). If this can be combined with control of instrumental mass bias via regular sample-standard-bracketing, and chemical purification of boron with minimal isotopic fractionation and contamination, then higher precision measurement results are viable (Li *et al.* 2019). Boron isotope ratio measurements by MC-ICP-MS sample-standard-bracketing techniques do not require close matching of boron concentration in samples and isotope standards (i.e., samples in the range of 5 to 50 ng g^{-1} boron mass fraction can be bracketed by a 50 ng g^{-1} boron isotope standard (Foster 2008, Rae *et al.* 2011, Devulder *et al.* 2013)). Matrix impurity has not shown to result in significant deviation of δ^{11}B$_{SRM\ 951}$ results in experimental runs (e.g., Devulder *et al.* 2013). Yet, we find that monitoring buffer reagent signal intensity correlates to some extent with larger measurement uncertainty in our early experimental runs.

The extraction and separation of boron from silicate matrices is challenging compared with carbonate samples, and numerous techniques have been trialled, including pyrohydrolysis, acid digestion, and flux fusion in preparation for analysis (Nakamura *et al.* 1992, Spivack *et al.* 1987, Tonarini *et al.* 1997). The standard-sample bracketing approach used in MC-ICP-MS critically requires matrix removal to achieve similar measurement conditions (matrix effects) between samples and isotope standards. However, certain boron species are volatile, particularly when drying samples in aqueous/acidic solution (e.g., Xiao *et al.* 1997), and procedural blank contributions are also a significant concern during sample processing. Achieving sufficient purification of boron from silicate samples for bias free measurement results without isotopic fractionation during dissolution and chromatographic separation remains problematic. In previous studies, significant emphasis has been placed on the matrix removal through multiple ion-exchange columns (e.g., Tonarini *et al.* 1997), however recent studies have sought to reduce the column procedure complexity (e.g., Li *et al.* 2019). Some studies have trialled the use of acids (e.g., HF) to dissolve silicate samples as an alternative to flux fusion techniques, with the aim of eliminating the need for expensive platinum crucibles and reducing the procedural blank. Reasonable agreement has been achieved (δ^{11}B$_{SRM\ 951}$ values within 0.7‰) between these flux fusion and hydrofluoric acid (HF) digestion experiments using thermal ionisation mass spectrometry (TIMS) (e.g., Rosner *et al.* 2003). These difficulties have at least in part delayed the application of the advantages of the MC-ICP-MS methodology, routinely applied to carbonates (Foster *et al.* 2008, Stewart *et al.* 2020, Gutjahr *et al.* 2020), to boron isotope measurement of silicate samples.

Here we present a hydrofluoric acid (HF) dissolution and dry down technique followed by a three-step chemical separation, involving no further sample dry down between columns. This protocol draws on previously documented insights on boron volatilisation and processing, which have been performed over the last three decades (Nakamura and Ishikawa *et al.* 1992, Xiao *et al.* 1997, Gaillardet *et al.* 2001). This chemical purification approach is coupled with a precise MC-ICP-MS technique (Foster 2008, Rae *et al.* 2011, Stewart *et al.* 2020), that has been calibrated against widely used carbonate reference materials (Foster *et al.* 2013, Gutjahr *et al.* 2020, Stewart *et al.* 2020). In light of the previously discussed poor to moderate reproducibility of boron isotopic measurements on silicate samples by different measurement techniques and independent sample preparation procedures (e.g., Gonfiantini *et al.* 2003), we compare MC-ICP-MS measurement results of sub-samples from the same batches of reference materials purified by our new HF digestion method and a flux fusion technique (Tonarini *et al.* 1997), traditionally used in conjunction with TIMS. Given notable differences in these sample preparation techniques, this test of consistency is a valuable assessment of the robustness of our approach.

Materials and sample preparation

Synthetic isotope certified RM solutions and natural silicate reference materials

As is conventional, we used NIST SRM 951 as our bracketing reference isotope standard for mass spectrometry.

We monitored intermediate precision, independent of column chemistry, using the BIG D boric acid solution (Foster *et al.* 2013) and BAM ERM-AE121 (Boric Acid in Water certificate value of 19.9 ± 0.6‰; (Vogl and Rosner 2012)). To test for possible fractionation during chemistry and sample preparation, we used the NIST RM 8301 (Coral). This solution, with a composition mimicking a dissolved coral, has well-characterised $\delta^{11}B_{SRM\ 951}$ from a recent inter-laboratory comparison exercise (certificate value of 24.17 ± 0.18‰, Stewart *et al.* (2020)).

For natural rock reference materials, we have focussed on three volcanic samples widely analysed in previous inter-laboratory comparisons (Table 1). These include two basaltic samples: the Japanese Geological Survey JB-2 (which is a subduction zone basalt from the Izu volcanic arc (Japan)) and IAEA-B-5 (which is a basalt from Mount Etna (Italy)), distributed by the International Atomic Energy Agency for interlaboratory calibration of boron isotope measurements (Tonarini *et al.* 2003). Although basalts are our prime interest, we additionally analysed the International Atomic Energy Agency standard, IAEA-B-6, a natural rhyolite glass (obsidian) from Lipari Island (Italy).

To illustrate the utility of our approach we also present a small set of $\delta^{11}B_{SRM\ 951}$ measurement results of MORB glasses, from three major ocean basins comprising three normal and one enriched MORB (Table 2) (Niu *et al.* 1999, Regelous *et al.* 1999, Robinson *et al.* 1996, Niu and Batiza 1994). These samples were previously analysed by SIMS (Marschall *et al.* 2017) and thus provide inter-comparison of SIMS and MC-ICP-MS techniques. The sample set includes two samples with a Cl/K ratio of < 0.08, which is considered to be the threshold for MORB glass uncontaminated by seawater (Marschall *et al.* 2017). Our Pacific E-MORB sample has higher Cl/K and so we compare this with a Pacific N-MORB sample, which also has elevated Cl/K (Table 2). As another more B-enriched basaltic sample, we also analysed one glassy ocean island basalt from Pitcairn Island (Table 2), which has been analysed previously by SIMS (Walowski *et al.* 2021).

Experimental

Measurement procedure for volcanic glass

Shards of volcanic glass, free of visible inclusions, were hand picked under a binocular microscope, avoiding contaminant mineral phases or whole rock particles and clasts. Typically, 30 to 60 mg were separated for analysis. The hand picked glass shards were then gently washed in de-ionised boron free water and treated ultrasonically for 5 min. The samples were then partly covered using para-film and left to dry in a low airflow box fitted with B-free HEPA filters.

Hydrofluoric acid digestion of silicate materials

Samples were prepared in a clean laboratory fitted with a B-free HEPA air filtration system (University of Bristol). Sufficient sample was weighed out to yield approximately 10 to 100 ng of boron and placed into a 7 ml PFA screw-top beaker before the following dissolution and drying steps were carried out in a class 100 fume hood. Concentrated HF (Romil UltraPure grade) was added to samples in a proportion 10:1 by mass for dissolution. The beaker was sealed and placed on a hot plate at 60 °C for 24 to 48 h (class 100 fume hood). During dissolution, condensate on the sides and top were carefully tapped back to the bottom of the beaker. This experimental set-up was tested on low-SiO_2 bulk rock materials and volcanic glasses only therefore its application to higher-SiO_2 bulk rock material was not tested in this study. Beaker lids were removed for dry down, and in their place, a second 7 ml uncapped beaker was placed upside down on top of the sample beaker with a small gap (~ 1 mm) left between upright and inverted beakers (Figure 1).

This arrangement, which is a modification after Gaillardet *et al.* (2001), allows for controlled evaporation, in an equilibrated environment and protects the sample from particles falling in during the protracted, low temperature dry down (Gaillardet *et al.* 2001). The time elapsed until dryness was a function of total acid used for digestion and varied between 6 and 12 h, at 60 °C on the hot plate. Earlier studies used mannitol ($C_6H_{14}O_6$) to minimise boron volatilisation during dry down (Nakamura *et al.* 1992), but others have questioned the value of its addition (Gaillardet *et al.* 2001). Although practitioners who use mannitol have appropriately minimised its impact on the boron blank, we have adopted an approach that does not include mannitol, thus removing this potential source of boron contamination altogether.

The dried samples were re-dissolved in 200 µl of 0.5 mol l^{-1} distilled nitric acid. This re-dissolution was often incomplete, likely due to insoluble fluorides, but these residues have been found not to fractionate boron from the sample (Rosner *et al.* 2003, Pi *et al.* 2014, Liu *et al.* 2018). The amount of insoluble fine particles typically correlates with digested sample mass. A minimum of 150 µl (depending on the

Table 1.
Measured $\delta^{11}B_{SRM951}$ values of silicate reference materials and previously published values

	JB-2	2*s*	*n*	Dissolution	Reference		IAEA-B-5	2*s*	*n*	Dissolution	Reference
MC-ICP-MS	6.90	0.40	12	HF	***This study***	**MC-ICP-MS**	-6.00	0.60	6	HF	***This study***
	6.90	0.10	1	Flux fusion	***This study***		-6.10	0.40	1	Flux fusion	***This study***
	6.96	0.22	2	HF	Pi *et al.* (2014)		-3.63	0.68	3	*	Gonfiantini *et al.* (2003)
	7.38	0.65	6	HF	Li *et al.* (2019)		-3.60	0.69	3	HF	Wei *et al.* (2013)
	7.20	0.53	7	HF	Wei *et al.* (2013)		-3.86	0.64	2	HF	Pi *et al.* (2014)
	7.38	0.00		HF	Le Roux *et al.* (2004)		-4.43	0.80	5	HF	Zhu *et al.* (2021)
	7.22	0.45	5	HF	Zhu *et al.* (2021)		-4.90	0.30	15	Flux fusion	Cai *et al.* (2021)
	7.30	0.60	9	Flux fusion	Cai *et al.* (2021)	**P-TIMS**	-4.69	0.60	6	HF	Li *et al.* (2019)
LA-MC-ICP-MS	7.30	0.14		*in situ*	Le Roux *et al.* (2004)		-3.95	0.32	5	Flux fusion	Tonarini *et al.* (2003)
N-TIMS	7.12	0.34	4	Flux fusion	Kasemann *et al.* (2001)		-1.64	0.78	3	*	Gonfiantini *et al.* (2003)
	6.90	0.80		Flux fusion	Kasemann *et al.* (2000)		-4.16	0.36	4	*	Gonfiantini *et al.* (2003)
P-TIMS	7.14	1.54	9	Flux fusion	Kasemann *et al.* (2001)		-4.39	0.53		Flux Fusion	Xiao *et al.* (2011)
	7.09	0.19		Flux fusion	Nakamura *et al.* (1992)	**SIMS**	-5.46	1.04	5	*in situ*	Gonfiantini *et al.* (2003)
	7.23	0.48		Flux fusion	Tonarini *et al.* (1997)		-9.20	4.40	1	*in situ*	Gonfiantini *et al.* (2003)
	7.33	0.37	14	Flux fusion	Tonarini *et al.* (2003)						
	7.66	0.20	8	Flux fusion	Dyar *et al.* (2001)**						
	7.66	0.20	11	Flux fusion	Leeman and Tonarini (2001)**						
	6.85	-	2	HF	Deyhle (2001)						
	7.50	1.20	15	Flux Fusion	Vils *et al.* (2009)***						
	5.79	0.41	38	Flux Fusion	Leeman *et al.* (2004)**						

* Gonfiantini *et al.* (2003) report results of anonymous participants, therefore detail information on laboratory procedures is unavailable.
** $\delta^{11}B_{SRM951}$ calcualted based on given $^{11}B/^{10}B$ ratios in the reference for JB-2 and NIST SRM 951.
*** intermediate precision reported.

volume of largely precipitate free solution) was transferred into a plastic micro centrifuge tube and centrifuged for 5 min (at 13,000 rpm) to separate remaining fine particles that did not re-dissolve. After centrifuging, the supernatant from the step above was carefully pipetted off and loaded onto the first chromatography column.

Ion exchange column chromatography procedure for boron extraction and purification

Ion exchange procedures, summarised in Figure 2, are modified from well-tested boron separation techniques from carbonate matrices established in the Bristol laboratory (Foster 2008, Rae *et al.* 2011), with the addition of cationic columns either side of the boron specific separation, to remove the greater matrix load from typical silicate samples (Tonarini *et al.* 1997). These extra steps were implemented in a protocol that does not require intermediate sample dry down between column separations and the associated risk of sample loss or fractionation. Thus, in our preparation procedure, samples are only evaporated to dryness after initial dissolution (see previous section).

Samples were first passed through a micro-cation exchange column (resin: Dowex AG50W-X8 100–200 mesh, 200 µl volume, see Figure 2), to remove the majority of the major element fraction. Centrifuged samples were loaded and then eluted with an additional 50 µl of 0.5 mol l^{-1} nitric acid. All eluents from this initial column were collected. Experiments with reference solutions (NIST SRM 951 and NIST RM 8301 (Coral)) did not reveal significant boron isotopic fractionation from this cation exchange resin (a known problem when using the boron specific anion exchange resin Amberlite IRA 743 if < 99% of boron is recovered (Lemarchand *et al.* 2002, Nakamura *et al.* 1992)).

Solutions were then buffered to a pH of 5 using an equal volume of 2 mol l^{-1} Na acetate and 0.5 mol l^{-1} acetic acid buffer. The buffer itself was first purified by passing through a ~ 500 µl volume Amberlite IRA 743 column, twice. The buffered sample was loaded stepwise (100 µl at a time) onto a 20 µl column (see Figure 2) containing Amberlite IRA 743 anion-exchange resin. Samples were purified by elution of matrix components with B-free high purity water (HPW Milli-Q company, resistivity: 18.2 MΩ cm),

	IAEA-B-6	2*s*	*n*	Dissolution	Reference
MC-ICP-MS	-3.90	0.50	10	HF	***This study***
	-2.90	0.10	1	Flux fusion	***This study***
	-4.46	1.68	3	*	Gonfiantini *et al.* (2003)
	-1.60	0.60	4	HF	Wei *et al.* (2013)
	-2.76	0.48	6	HF	Li *et al.* (2019)
	-1.61	0.44	4	Flux fusion	Tonarini *et al.* (2003)
	-2.89	0.55	8	HF	Devulder *et al.* (2013)
	-2.71	0.29	5	HF	Zhu *et al.* (2021)
	-1.9	0.2	19	Flux fusion	Cai *et al.* (2021)
P-TIMS	-0.45	0.60	13	*	Gonfiantini *et al.* (2003)
	-1.56	0.60	4	*	Gonfiantini *et al.* (2003)
	-3.35	0.24	3	*	Gonfiantini *et al.* (2003)
LA-MC-ICP-MS	-2.4	0.3	10	*in situ*	Fonseca *et al.* (2017)
	-3.29	1.12	35	*in situ*	Hou *et al.* (2010)

	BCR-2	2*s*	*n*	Dissolution	Reference
MC-ICP-MS	-4.4	0.2	1	HF	***This study***
	-5.93	0.53	4	HF	Liu *et al.* (2018)
	-5.70	0.35	5	HF	Zhu *et al.* (2021)
	-4.43	0.50	4	Flux fusion	Cai *et al.* (2021)
	-5.90	0.20	4	HF	Wei *et al.* (2013)

	BHVO-2	**2*s***	***n***	**Dissolution**	**Reference**
MC-ICP-MS	-3.2	0.2	1	HF	***This study***
	-1.61	0.62	4	HF	Liu *et al.* (2018)
	-2.38	0.47	6	HF	Zhu *et al.* (2021)
	-0.53	0.50	11	Flux fusion	Cai *et al.* (2021)
	-0.70	0.10	5	HF	Wei *et al.* (2013)

before the sample fraction containing boron was eluted with 0.5 mol l^{-1} nitric acid (5 × 110 µl). An additional elution step (the "tail") was performed after sample collection and analysed for boron concentration to ensure recovery from columns was complete (> 99%). These resin volumes are deliberately small (20 µl) so that matrix free samples can be obtained in low volumes of eluted acid (i.e., only 550 µl) that require no further dry-down prior to analysis. Resin within the columns should be routinely refloated prior to use to ensure no air bubbles or resin displacement.

Large volume silicate samples at this point may still have retained some matrix elements. Therefore, for further purification we pass samples through another cation exchange procedure, identical to the first column. This final column should also remove occasional contamination of sample with buffer that can occur from breakthrough in the Amberlite IRA 743 column.

Instrumentation – solution mode MC-ICP-MS

All isotope ratio measurements were performed at the University of Bristol using a Thermo-Finnigan Neptune MC-ICP-MS fitted with an ESI sapphire injector, a PFA Scott barrel spray chamber and a 50 µl min^{-1} PFA nebuliser for sample introduction. Nickel skimmer (X-geometry) and standard sample cones were used. The Neptune is equipped with two amplifier boards containing 10^{12} Ω resistors that are used for measurement of ^{10}B$^+$ and ^{11}B$^+$ (at mass to charge ratio (*m/z*) = 10 and 11 respectively).

The NIST SRM 951 bracketing isotope reference material was run at a boron concentration of 50 µg l^{-1}. Prior to analysis, a 10 µl aliquot of each 550 µl sample solution was diluted and pre-screened for boron concentration and matrix (sodium concentration) content so that remaining sample solutions could also be diluted to 50 µg l^{-1} boron concentration. Some samples did not have enough boron to yield a 50 µg l^{-1} solution in the 550 µl eluted from the final column – these samples were analysed undiluted at lower concentrations (note none were below 19 µg l^{-1} boron concentration). Previous work has shown that samples with boron concentration as low as 10 µg l^{-1} can be bracketed with 50 µg l^{-1} NIST SRM 951 solutions while still obtaining accurate results (Foster 2008, Rae *et al.* 2011).

Table 2.
Comparison of new MC-ICP-MS data with literature values obtained by SIMS, and relevant geochemical information. $\delta^{11}B_{SRM951}$ (‰) measurement precision of new data reported for intermediate precision determined in this study (0.6‰)

Sample	$\delta^{11}B_{SRM951}$ (‰) MC-ICP-MS	Sample mass (g)	$\delta^{11}B_{SRM951}$ (‰) SIMS	B (µg g^{-1}) SIMS	Cl/K	La/Sm$_n$	Ridge	Reference
	(This study)		(Marschall *et al.* 2017)					
PH103-2	-5.6 ± 0.6	47.8	-4.2 ± 3.0	1.95	0.74	1.07	East Pacific Rise	1
PH54-3	-6.5 ± 0.6	63.2	-9.8 ± 3.0	0.87	0.42	0.61	East Pacific Rise	2
D27-1	-6.2 ± 0.6	55.9	-7.5 ± 6.1	0.87	0.04	0.57	Mid Atlantic Ridge	3
5/15g	-8.8 ± 0.6	44.0	-6.8 ± 3.9	1.50	0.01	0.75	South-West Indian Ridge	4
	(This study)		(Walowski *et al.* 2021)					
SO-65-51-DS9	-5.0 ± 0.6	47.4	-5.3 ± 0.9 (mean, *n* = 6)	2.05			Pitcairn Islands	
SO-65-51-DS9	-5.1 ± 0.6	25.9						

References.
1. Niu *et al.* (1999).
2. Regelous *et al.* (1999).
3. Niu and Batiza (1994).
4. Robinson *et al.* (1996).

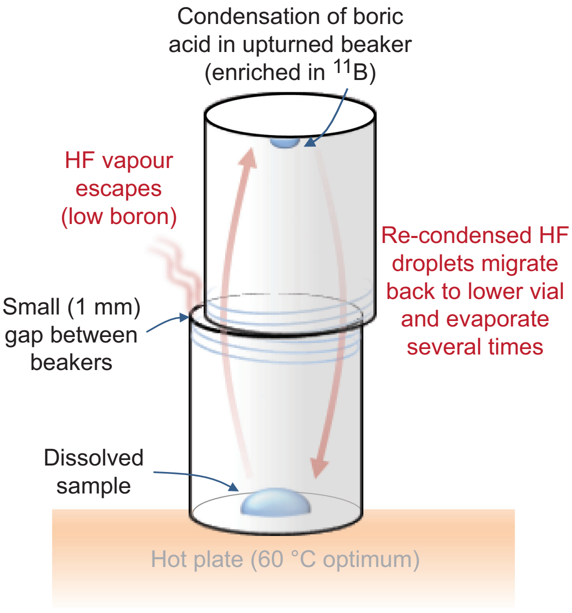


Figure 1. Schematic drawing of the beaker arrangement for the sample dry-down after HF digestion.

Concentrated HF (6 µl) is added to all sample solutions immediately prior to analysis to yield a solution of 0.3 mol l^{-1} HF and 0.5 mol l^{-1} HNO_3. Similarly, all wash, blanks and bracketing standards are run as 0.3 mol l^{-1} HF and 0.5 mol l^{-1} HNO_3 solution, ensuring all boron is present as soluble BF_4^- and not volatile $B(OH)_3$ (Zeebe and Rae 2020). Using this HF addition approach, instrumental blank is reduced to < 1 % of sample after 2 min wash. This method avoids poor instrumental washout that can occur due to boron volatilisation from other acid media (Misra *et al.* 2014) and is more effective than the previous use in the Bristol laboratory of ammonia gas addition during sample introduction (Al-Ammar *et al.* 2000, Foster 2008).

Acquisition time per measurement was 120 s (integration time of 4 s, thirty ratios, one block). Together with up-take time, this means that each purified sample can be analysed up to three times using a 50 µl min^{-1} nebuliser. Typically, samples are run twice, in different parts of the sequence, to reflect representative instrumental variability. The boron isotope ratio reported for a sample is the mean of the measurement results. As there is enough material for triplicate runs, if a particular part of a run is noisy, or uptake imperfect, a third measurement is possible. When made, a pooled mean and 2s of the three analyses are reported. Each individual analysis was blank corrected by subtracting from the sample intensities at *m/z* 10 and 11 interpolated between measurement results from bracketing 'blank pots', which are beakers containing equal volumes of blank acid, run in the same fashion as the samples to monitor the small cumulative addition of airborne boron over the analysis time of a given sequence (Rae *et al.* 2011).

Step description	Ion exchange column
	Cation (AG50Wx8; Column volume 200 µl)
Cleaning	3 × 6 mol l^{-1} HCl (1 ml)
Conditioning	2 × 0.5 mol l^{-1} HNO_3 (1 ml)
Sample loading	150 µl 0.5 mol l^{-1} HNO_3
Sample elution	50 µl 0.5 mol l^{-1} HNO_3
Column cleaning	3 × 6 mol l^{-1} HCl (1 ml)
Column cleaning	2 × H_2O (1 ml)
	Anion (Amberlite IRA 743; Column volume 20 µl) *After Foster (2008) and Rae et al. (2011)*
Pre-conditioning	1 × 0.5 mol l^{-1} HNO_3 (cr)
Pre-conditioning	1 × 0.5 mol l^{-1} HNO_3 (150 µl)
Conditioning	2 × H_2O (150 µl)
Sample loading	4 × (100 µl steps)
Sample purification	10 × H_2O (160 µl dropwise)
Sample elution	5 × 0.5 mol l^{-1} HNO_3 (110 µl)
Sample tail elution	1 × 0.5 mol l^{-1} HNO_3 (150 µl)
Column cleaning	2 × 0.5 mol l^{-1} HNO_3 (1 ml)
Column cleaning	2 × H_2O (1 ml)
	Cation (AG50Wx8 ; Column volume 200 µl) Second pass
Cleaning	3 × 6 mol l^{-1} HCl (1 ml)
Conditioning	2 × 0.5 mol l^{-1} HNO_3 (1 ml)
Sample loading	550 µl 0.5 mol l^{-1} HNO_3
Sample elution	50 µl 0.5 mol l^{-1} HNO_3
Column cleaning	3 × 6 mol l^{-1} HCl (1 ml)
Column cleaning	2 × H_2O (1 ml)

(cr) = column reservoir

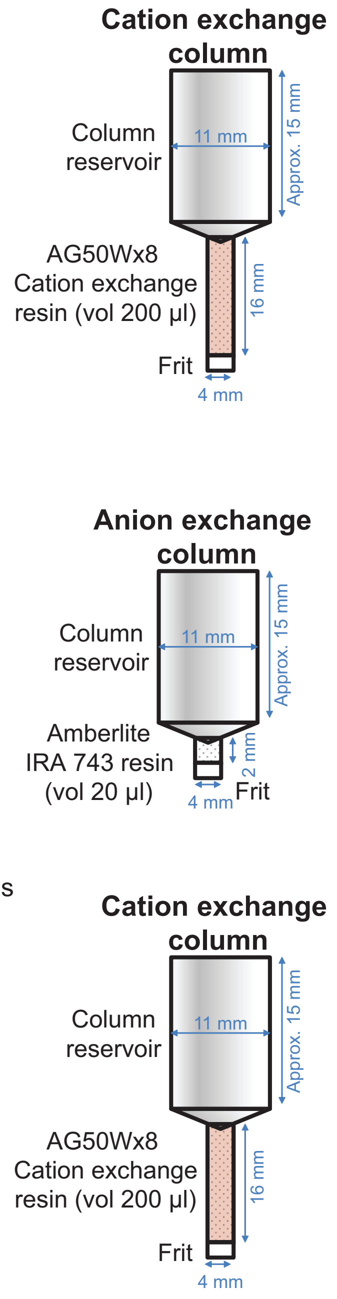


Figure 2. Procedure of the ion exchange chromatography in table format with schematic drawings of the column design and dimensions used in this study, for the respective steps.

Intercomparison method – K_2CO_3 flux fusion (IGG-Pisa) sample preparation procedure

The three selected silicate reference materials were also prepared at IGG-CNR in Pisa (Italy), using the B-separation method described by Agostini *et al.* (2021). Approximately 0.2 to 0.4 g of powdered rock samples were mixed with purified, powdered K_2CO_3 in Pt-Ir (95%-5%) crucibles, at a K_2CO_3/rock ratio > 4. K_2CO_3 is used since its high solubility facilitates rapid aqueous leaching of the resulting fusion cake. The sample+flux mixtures are fused at a temperature of ~ 1000 °C. After cooling, boron was brought into aqueous solution over-night by addition of B-free water. The solution, along with the insoluble phases, was transferred into polypropylene tubes, prior to centrifugation. Boron was then extracted and purified from the solution with an optimised three-step chemical separation procedure, as described in Agostini *et al.* (2021).

Initial sample purification was achieved using boron-specific Amberlite IRA 743 20-50 mesh resin, in ~ 2.35 ml volume PFA columns (resin radius = 5 mm, resin height = 30 mm, frit thickness = 2 mm). The Amberlite IRA 743 was used once per chemistry and discarded afterwards. The resin was cleaned using 1.5 mol l^{-1} HCl (2 × reservoir volume) and pre-conditioned using an aqueous NH_3 (pH ~ 10). The sample was loaded at pH > 10 and rinsed with an aqueous NH_3 (pH ~10), followed by boron elution using 1.5 mol l^{-1} HCl, collected in concave bottom PFA beakers (Savillex) and dried overnight. To avoid boron-loss and fractionation during this step, mannitol was added to the eluted sample, and the hot plate temperature maintained < 70 °C.

The day after, samples were re-dissolved in 0.015 mol l^{-1} HCl and then passed through AG50W-X8x (200 to 400 mesh) cation-exchange resin (2.35 ml volume, radius = 5 mm, height = 30 mm, Tonarini *et al.* 1997). Boron was immediately collected with 0.015 mol l^{-1} HCl. The sample solution was adjusted to pH > 10 adding 0.8 ml of 1.5 mol l^{-1} NH_3, following a third purification step. The sample was passed through 20 to 50 mesh Amberlite IRA 743 resin, following the procedure outlined above, modified by collecting boron from Amberlite IRA 743 in w = 2% HNO_3, ready to be measured via MC-ICP-MS.

All the chemical purification steps were performed in a class 1000 clean room, using B-free ultrapure reagents. High purity water (HPW) was obtained by sub-boiling distillation using a Savillex DST-1000; HCl was obtained starting from azeotropic solution of Supelco (Sigma-Aldrich) HCl and two subsequent steps of sub-boiled distillation using a Savillex DST-1000; HNO_3 was obtained starting from Suprapur (Merck) HNO_3 and two subsequent steps of sub-boiling distillation using a Savillex DST-1000; B-free NH_3 was obtained with sub-boiling distillation of ultrapure NH_3, adding mannitol to the starting solution to prevent boron volatilisation.

Again, prior to analysis by MC-ICP-MS (Bristol), a 10 µl aliquot of each 550 µl sample solution was diluted and pre-screened for boron and matrix (Na^+) content so that remaining sample solutions could also be diluted to 50 µg l^{-1} boron concentration.

Results

Synthetic isotope standard solutions

Boric acid reference materials BIG D and BAM ERM-AE121, measured in each analytical sequence (without purification by columns), yielded mean $\delta^{11}B_{SRM\ 951}$ of 14.80 ± 0.09‰ (*n* = 27, 2*s*) and $\delta^{11}B_{SRM\ 951}$ of 19.65 ± 0.14‰ (*n* = 9, 2*s*) (Table 3), within intermediate precision of previous measurement results of these unprocessed reference materials by MC-ICP-MS (14.76 ± 0.3‰ (95% confidence interval) (Foster *et al.* 2013) and 19.9 ± 0.6‰ (expanded uncertainty) (Vogl and Rosner 2012)). Moreover, our measured value for the BAM ERM-AE121 reference material is extremely close to its recently revised interlaboratory consensus value of 19.64 ± 0.17‰ (2*s*) (Stewart *et al.* 2020).

The synthetic coral solution NIST RM 8301 (Stewart *et al.* 2020) was used to monitor potential influences of the column chemistry procedure both with and without HF dry down (Table 3). The long-term mean $\delta^{11}B_{SRM\ 951}$ of artificial coral solution NIST RM 8301 (Stewart *et al.* 2020) purified following our new three-step column procedure is 24.24 ± 0.11‰ (*n* = 23), which is within uncertainty of interlaboratory consensus values (24.17 ± 0.18‰ (Stewart *et al.* 2020)). This provides a useful assessment of intermediate precision for 10 to 100 ng boron samples processed through our full boron purification procedure.

Blanks

Particularly for the small amounts of boron possible to analyse by MC-ICP-MS, laboratory and procedural blanks can be a significant concern at low sample/blank ratios (e.g., when the sample has less than 5 ng of boron). In the previous section we reported how instrumental memory is reduced by aspirating 0.3 mol l^{-1} HF solutions and cumulative 'fall-in' during measurement is corrected using 'blank pots' of equal volume (see section Instrumentation – solution mode MC-ICP-MS) which are used to subtract the boron 'fall-in' from the air during the period of sample measurements, which is typically 12 h. These contributions are subtracted directly from beam intensities during the analysis routine.

We have also monitored total procedural blanks for our full chemical separation procedure. Total procedural blanks for the method described here were established by running blank samples through the complete procedure (using all reagents as used for samples and including dry down).

Table 3.
Individual run results of reference materials measured in this study. Within-run measurement precision represents the mean of two to three repeat measurement results of the same aliquot

Sample	NIST RM 8301 (Coral)*			NIST RM 8301 (Coral)**			BIG D***			BAM ERM-AE121***	
	$\delta^{11}B_{SRM\ 951}$ (‰)	2*s*		$\delta^{11}B_{SRM\ 951}$ (‰)	2*s*		$\delta^{11}B_{SRM\ 951}$ (‰)	2*s*		$\delta^{11}B_{SRM\ 951}$ (‰)	2*s*
	24.18	0.11		24.21	0.11		14.83	0.09		19.82	0.38
	24.10	0.23		24.18	0.11		14.80	0.08		19.58	0.18
	24.18	0.28		24.31	0.09		14.81	0.32		19.61	0.17
	24.29	0.09		24.28	0.07		14.81	0.02		19.70	0.17
	24.19	0.05	***Mean***	***24.24***	***0.10***		14.67	0.15		19.68	0.12
	24.24	0.11					14.78	0.20		19.60	0.19
	24.24	0.04					14.74	0.02		19.63	0.18
	24.27	0.18					14.78	0.21		19.65	0.14
	24.26	0.03					14.76	0.06		19.62	0.13
	24.18	0.00					14.81	0.14	***Mean***	***19.65***	***0.14***
	24.24	0.28					14.89	0.12			
	24.34	0.14					14.77	0.29			
	24.25	0.07					14.73	0.15			
	24.24	0.01					14.76	0.11			
	24.26	0.18					14.76	0.09			
	24.20	0.13					14.77	0.10			
	24.33	0.09					14.82	0.38			
	24.31	0.07					14.80	0.02			
	24.26	0.06					14.77	0.14			
	24.18	0.22					14.93	0.10			
	24.19	0.07					14.89	0.02			
	24.25	0.15					14.78	0.12			
	24.21	0.20					14.76	0.18			
Mean	***24.24***	***0.11***					14.84	0.16			
							14.84	0.10			
							14.84	0.10			
						Mean	***14.80***	***0.09***			

* denotes solutions treated with full carbonate procedure (e.g., Rae *et al.* 2011).
** denotes solutions treated with full HF procedure, including dry down.
*** untreated boric acid reference materials.

These blanks are measured by the same sample-standard-bracketing procedure as samples. Measured boron signals for these total procedural blanks barely exceeded the background on the MC-ICP-MS. For this reason, it was only possible to obtain reliable mass estimates (in pg) for these blank solutions and their $\delta^{11}B_{SRM\ 951}$ ratios should be considered as a guide only. Four total procedural blanks measured alongside the measurement results reported here vary from 28 to 58 pg (Appendix S1), which are in keeping with a mean of 38 ± 36 pg for larger number of total procedural blanks (n = 41) for Amberlite column chemical separation alone over a longer, three-year period (Appendix S1). Even for our smallest sample sizes of 10 ng, the contribution of this total procedural blank is negligible, and we make no correction for it (the lowest sample boron mass fraction (10268 pg) was 270 times greater than the mean total procedural blank of 38 pg). Typical ranges for blank $\delta^{11}B_{SRM\ 951}$ are approximately -10 to 10‰ (Tonarini *et al.* 1997), in agreement with our mean estimate of -10‰ for the silicate processing (Appendix S1). In our worst case (sample 10 ng and blank 58 pg), the blank contributes ~ 0.58% towards the $\delta^{11}B_{SRM\ 951}$. A good overview of blank correction effects is given in Tonarini *et al.* (1997), and there a 2% blank contribution is needed to result in an 0.2‰ shift of the unknown. This is well within the limit of our here suggested intermediate precision of 0.6‰ for silicates. Additionally, we achieve a better sample/blank than in Tonarini *et al.* (1997), which further diminishes the effect of blank composition on our unknowns.

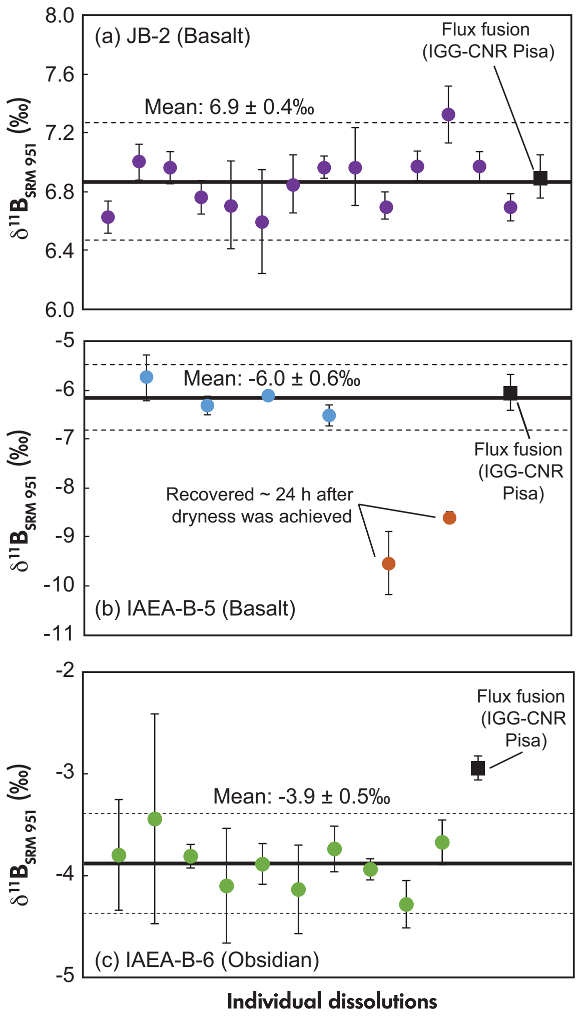
Total procedural blanks for IGG-Pisa column chemistry are in the range of 10 to 40 pg and are similarly insignificant for the sample sizes studied here (10 to 50 ng).

$\delta^{11}B_{SRM\ 951}$ of silicate rock reference materials

Our results for silicate reference materials and a comparison with literature values is given in Table 1, Figure 3 and briefly summarised below.

The natural silicate rock reference material best characterised for its $\delta^{11}B_{SRM\ 951}$ is the JB-2 basalt, with a relatively well-defined consensus $\delta^{11}B_{SRM\ 951}$ value between 6.7 and 7.7‰ based on results from several laboratories and their digestion methods (see Table 1). The mean $\delta^{11}B_{SRM\ 951}$ value for JB-2 obtained here using our HF digestion method is 6.9 ± 0.4‰ (n = 12, 2s). Our measured value is identical to that we obtain from the same powder lot processed by the flux fusion and chemical separation procedure of the Pisa CNR-IGG laboratory (6.9 ± 0.1‰; n = 1, 2SE).

We obtained mean $\delta^{11}B_{SRM\ 951}$ values of -6.0 ± 0.6‰ (n = 6) and -6.1‰ (n = 1) for the same material lot of International Atomic Energy Agency reference material IAEA-B-5 (Mt. Etna volcano basalt) using our HF digestion and the flux fusion protocol respectively. The concordant results of this study are significantly lower than the literature value ($\delta^{11}B_{SRM\ 951}$ ~ -4.0‰, Gonfiantini *et al.* 2003).



Agreement between samples processed by HF dissolution and flux fusion are poorer for the obsidian glass (IAEA-B-6). This yields a mean $\delta^{11}B_{SRM\ 951}$ of -3.9 ±0.5‰ using our HF digestion protocol, but $\delta^{11}B_{SRM\ 951}$ of -2.9 ± 0.1‰ for the aliquot processed by flux fusion. Yet both values lie within the wide bounds of literature data ($\delta^{11}B_{SRM\ 951}$ = -0.45 to -4.46‰).

$\delta^{11}B_{SRM\ 951}$ of oceanic basalts

Our four MORB samples show a range of $\delta^{11}B_{SRM\ 951}$ from -5.6 ± 0.3‰ to -8.8 ± 0.5‰ (Table 2). The difference between the mean $\delta^{11}B_{SRM\ 951}$ of MC-ICP-MS and SIMS measurement results is statistically insignificant, but in contrast to the SIMS data, MC-ICP-MS measurement results show resolvable differences (at measurement precision level) in $\delta^{11}B_{SRM\ 951}$ between samples (Figure 4).

The Pitcairn Island glass provides a clearer comparison between our bulk measurement results and SIMS, given its higher boron mass fraction the latter measurement result is more precise than for the depleted MORB samples. The agreement between the two approaches is good (Table 2),

Figure 3. $\delta^{11}B_{SRM\ 951}$ of silicate reference materials using the HF digestion and three-column (cation-anion-cation) ion exchange procedure presented in this study. The range bars are 2*s* of replicate measurement results. Thick black lines represent mean values measured here and the dashed black line the standard deviation. The silicate reference material JB-2 (a) yielded the greatest reproducibility. Note that two samples (orange points) in (b) were left intentionally on the hot plate after dryness to investigate the effect of isotope fractionation from a dry medium – these are not included in our mean value. The approximately 2 to 4‰ lighter isotopic composition measured is consistent with other excessive dry down experiments (Nakamura *et al.* 1992, Gaillardet *et al.* 2001). In (c), one IAEA-B-6 triplicate analysis ($\delta^{11}B_{SRM\ 951}$ -3.44 ± 1.03‰) is constituted of the values: -3.61 ± 0.26‰, -3.95 ± 0.23‰ and -2.94 ± 0.23‰ (all 2*s*). In the absence of indicators that would suggest anomalous run conditions (Rae *et al.* 2011), the value of -2.94 ± 0.23 is retained in the triple replicate calculation. Black squares denotes flux fusion with measurements in Bristol, whereas whites square with black outline denotes flux fusion and measurement at Pisa CNR (MC-ICP-MS).

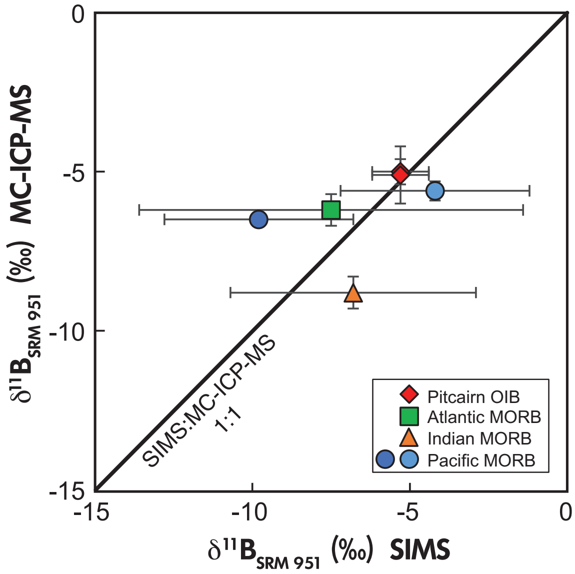


Figure 4. **$\delta^{11}B_{SRM\ 951}$ of volcanic glass obtained by *in situ* SIMS (*x*-axis, Marschall *et al.* 2017) and MC-ICP-MS using HF digestion (*y*-axis) in this study (2*s* range bars shown). Samples with higher boron mass fraction (≥ 2 μg g^{-1}) exhibit better correlation between SIMS and MC-ICP-MS data (Pitcairn OIB).**

with a mean of -5.3 ± 0.9‰ (n = 6) from repeat SIMS measurement results versus -5.1 ± 0.1‰ (n = 4) from a mean of measurement results of two different glass shards by MC-ICP-MS (Table 2).

Discussion

Incorporation of previous study observations on boron volatilisation

Volatilisation of boron during sample processing of silicate samples is a well-known concern (Nakamura *et al.* 1992). Some studies exploited this boron volatilisation, by achieving total evaporation and collecting and condensing the vapor fraction, which serves as a first matrix removal step by leaving behind non-volatile elements and compounds (Xiao *et al.* 1997, Gaillardet *et al.* 2001, Liu *et al.* 2013, Van Hoecke *et al.* 2014). The use of HF in silicate dissolution raises the spectre of possible boron loss as BF_3 and has commonly led to the addition of mannitol during dissolution to guard against this (Nakamura *et al.* 1992, Tonarini *et al.* 1997). Not only has the effectiveness of mannitol in binding to boron through complexation in typical dissolution scenarios been questioned (Xiao *et al.* 1997, Gaillardet *et al.* 2001), but recent calculations have further shown that the highly soluble BF_4^- is the dominant species in strong solutions of HF (Zeebe and Rae 2020). Studies by Xiao *et al.* (1997) and Gaillardet *et al.* (2001) concluded that boron isotopic fractionation is not necessarily prevented by the addition of mannitol, but instead that samples slowly dried at temperatures < 65 °C, from acids such as HCl and HF, retain their true boron isotopic composition, if recovered (i) immediately or (ii) just before dryness is achieved.

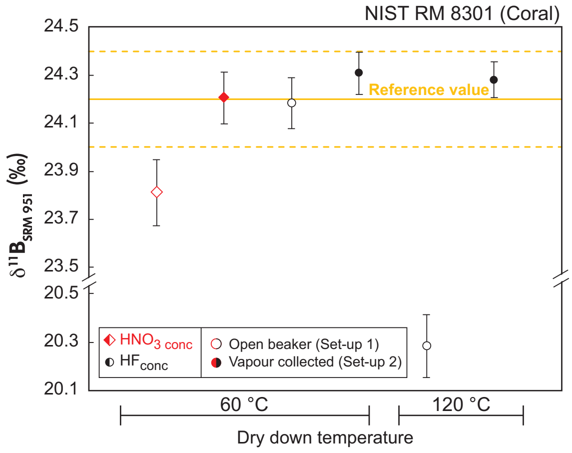


Figure 5. **$\delta^{11}B_{SRM\ 951}$ of synthetic coral isotope reference material (NIST RM 8301 (Coral)), that was dried to convert from strong HF or HNO_3 acid to 0.5 mol l^{-1} HNO_3, simulating the dissolution procedure. The dashed yellow lines represent the 2*s* variability of the interlaboratory consensus value, Stewart *et al.* (2020). Open circles denote samples where vapour was allowed to escape rapidly during the drying process (uncovered beakers), while filled circles represent samples where evaporation was carried out in a semi-enclosed environment (see Figure 1). Red symbols indicate HNO_3 acid matrix, black symbols indicate HF acid matrix.**

We have conducted a series of evaporation experiments of our own, in an attempt to reproduce the observations of Gaillardet *et al.* (2001), in the context of silicate rock samples. We changed multiple parameters to test their impact on $\delta^{11}B_{SRM\ 951}$ results: (i) acid matrix was either HF_{conc} or $HNO_{3\ conc}$, (ii) the dry down temperature set at 60 °C and 120 °C and (iii) the vapour was allowed to escape rapidly or in a semi-enclosed set-up that allows only slow vapour loss. Our experimental results support the finding of Gaillardet *et al.* (2001), in that open evaporation in a nitric acid medium causes obvious isotopic fractionation (Figure 5, Table 4).

Table 4.
Data presented in Figure 4

Sample	Temperature (°C)	Set-up detail	Acid matrix	$\delta^{11}B_{SRM\ 951}$ MC-ICP-MS (‰)
NIST RM 8301 (Coral)	60	1	HNO_3	23.8
NIST RM 8301 (Coral)	60	2	HNO_3	24.2
NIST RM 8301 (Coral)	60	1	HF	24.2
NIST RM 8301 (Coral)	60	2	HF	24.3
NIST RM 8301 (Coral)	120	1	HF	20.3
NIST RM 8301 (Coral)	120	2	HF	24.3

1 = open beaker.
2 = vapour collection.

In one experimental run, samples were dried excessively, which led to an approximately 3 to 4‰ isotopic shift towards lower $\delta^{11}B_{SRM\ 951}$ in the evaporated residue (Figure 3b). Subsequently, we adopted drying at 60 °C for our final procedure of silicate sample processing, removing samples from the hot plate just before or when dryness is achieved. When collecting before dryness was achieved, residual HF was neutralised by addition of Na-acetate, forming NaF, visible as precipitate occasionally. Testing of pH is necessary for samples collected prior to dryness, to ensure effective ion exchange resin performance.

Residual matrix contamination

Residual matrix components (major ions: Si, Ca, Na, Mg, etc.) in samples can cause differences in mass bias and shifts in the measured $^{11}B/^{10}B$ ratio of the following bracketing isotope standard (Xiao *et al.* 1997). While a good separation of boron from other elements is achieved by our chromatographic procedures, in a very few instances, some sample matrix and/or Na^+ still leaked through into the sample aliquot during the testing and adjustment phase of the method development. Before analysis we therefore measured the $m/z = 23$ (Na^+) beam intensity during the boron concentration screening measurement, to ensure all matrix cations had been separated from the boron (Rae *et al.* 2011). During the evolution of our procedure, we found using a second cationic column, guarded against this eventuality and further purified the boron from silicate matrix components. The intermediate precision of JB-2 basalt improved as we developed our modified measurement procedure by adding the final cation exchange column step. All data we report here were processed using this second cation exchange column.

Despite our three-step purification chemistry at Bristol and sample screening for Na, we infer from the poorer intermediate precision of the measurement result of silicate reference materials (~ ±0.6‰; 2*s*) compared with the simpler matrix boric acid and calcium carbonate reference materials (± < 0.2‰; 2*s*; Table 3) that matrix separation may still be imperfect for silicate samples (presumably matrix ions other than Na^+). We employed a cut-off for sample rejection and/or re-processing through the cationic column when the raw $m/z = 23$ (Na^+) beam intensity of the pre-screening test (fifteen-fold dilution of 10 µl sample aliquot; see section Instrumentation - solution mode MC-ICP-MS)) exceeded 0.5 V prior to sample analysis. Future testing of matrix sensitivity of silicate bulk rock samples following the procedures outlined in Chen *et al.* (2016) and Devulder *et al.* (2013) may provide an angle for further improvement of the method described here. Previous work by Devulder *et al.* (2013) showcased promising results using lithium as an isotope dopant, which encourages further research. Based on the intermediate precision of boron in silicate materials of 0.6‰ (discussed here) *vs.* the typical intermediate precision of 0.2‰ for carbonate materials, we infer that up to 0.4‰ of the total measurement precision derives from matrix effects. This, however, conflicts with observations by Devulder *et al.* (2013), Foster (2008) and Rae *et al.* (2011), who find no significant effect of matrix elements studied by them. An extensive study of elements interfering with B in MC-ICP-MS would thus be required to solve this discrepancy.

$\delta^{11}B_{SRM\ 951}$ comparability – diminishing inter-laboratory differences for basalt matrixes

A recurring problem in studies of silicate rocks is the large variability of reported $\delta^{11}B_{SRM\ 951}$ for silicate reference materials (Gonfiantini *et al.* 2003), particularly when comparing different sample preparation and measurement procedures (Gonfiantini *et al.* 2003). Several permil differences between analytical set-ups are commonly observed, but large discrepancies can still occur within datasets obtained by similar measurement procedures (Gonfiantini *et al.* 2003) (Table 1). In this light, we compare our new $\delta^{11}B_{SRM\ 951}$ results with literature data.

We stress the excellent agreement between the $\delta^{11}B_{SRM\ 951}$ we report for basaltic reference materials JB-2 and IAEA-B-5 using our two preparation techniques. Given our MC-ICP-MS applied measurement procedure approach has been benchmarked against a wide number of pure isotope reference materials, we expect that silicate sample processing (dissolution and matrix separation) should be the most critical aspect of sample accuracy. Therefore, the concordant results for basaltic reference materials obtained by (i) HF dissolution followed by our three-column sample preparation procedure at Bristol and (ii) alkali flux fusion followed by three steps of purification in Pisa, is strongly supportive of the reliability of these values.

In a previous section we noted the sensitivity of sample measurement precision of the measurement results to the inferred difference in residual matrix between purified silicate samples and boric acid solution reference materials. Matrix sensitivity has also been emphasised by Chen *et al.* (2016). Contrasting residual matrix compositions may therefore provide a possible explanation of differences between recent MC-ICP-MS measurement results of the same reference materials (Table 1). For example, Li *et al.* (2019) and Wei *et al.* (2013) who use a single column separation procedure, obtain $\delta^{11}B_{SRM\ 951}$ for B5 > 1.5‰ higher than our measurement results at measurement precision. Such discrepancies require further investigation and quantification of abundances of residual species after boron purification seems worthwhile. However, we also note that unlike the $\delta^{11}B_{SRM\ 951}$ we obtained for BAM ERM-AE121 (19.65 ± 0.14‰), the value reported by Li *et al.* (2019) is (1.5‰ lower) outside of uncertainty of both the certified value of 19.9 ± 0.6‰ (Vogl and Rosner 2012) and the recent inter-laboratory consensus value (19.64 ± 0.17‰; 2*s* of measurement results from five boron isotope laboratories (Stewart *et al.* 2020)) for this matrix-free reference material. Further inter-lab calibration work and measurement uncertainty budget evaluation is therefore required, for instance, testing of common analyte internal standardisation (e.g., addition of a lithium isotope spike to samples) that may help to improve sample-standard-bracketing techniques (e.g., Devulder *et al.* (2013)).

Agreement between $\delta^{11}B_{SRM\ 951}$ values for the obsidian glass reference material IAEA-B-6 between our HF acid dissolution and flux fusion approaches is imperfect. Yet Tonarini *et al.* (1997) report scepticism about their IAEA-B-6 results, suggesting the flux fusion to have formed silicate structures that retained boron in the fusion cake; this may explain the differences we obtained. Indeed, high silica samples such as IAEA-B-6 obsidian potentially fractionate boron during fusion (Tonarini *et al.* 2003). Our HF dissolution measurement results are again isotopically lighter than recent MC-ICP-MS measurement results of Li *et al.* (2019) and Wei *et al.* (2013), but are in agreement with two recent analyses of another IAEA-B-6 batch carried out at IGG-Pisa after flux fusion. Those measurement results are -3.60 ± 0.07‰ (2SE) and -3.48 ± 0.04‰ (2SE), within uncertainty of our value (-3.9 ± 0.5‰). In the latter, special care was taken to avoid incomplete fusion and residue in the fusion cake. To this end, the amount of sample powder was reduced to 100 mg, and the amount of K_2CO_3 flux was increased to 1 g, raising the flux/sample ratio > 10. This reduction of sample volume may (i) increase the role of potential B inhomogeneity, negatively impacting uncertainty of measurement results and (ii) increase blank contribution to the measurement uncertainty budget.

However, petrographic observations of IAEA-B-6 have shown that the parental material for this reference material is heterogeneous (Cooper *et al.* 2019). Li *et al.* (2019) further reported lighter $\delta^{11}B_{SRM\ 951}$ isotopic composition (by up to 1.5‰) for IAEA-B-6 after leaching, indicative of alteration phases in the powder. It is possible that different batches of IAEA-B-6 are heterogeneous and so it is not the best reference material with which to compare data reproducibility between laboratories.

Generally, the HF dissolution and flux fusion procedure discussed and tested here returned comparable results. We would therefore recommend the use of HF dissolution for labs without flux fusion capabilities and particularly advocate its use for small sample volumes (< 600 μl).

Applications of boron isotopes in source reservoir identification

A growing body of data show a mean MORB $\delta^{11}B_{SRM\ 951}$ of ~ -7.5‰ (Dixon *et al.* 2017, Marschall *et al.* 2017), but discerning significant $\delta^{11}B_{SRM\ 951}$ variability within these relatively imprecise (typically ±2‰) *in situ* measurement results is difficult. While several MORB have previously been identified with $\delta^{11}B_{SRM\ 951}$ distinctly higher than this mean, they are also associated with anomalously high Cl/K (Marschall *et al.* 2017, Li *et al.* 2019) or water contents (Dixon *et al.* 2017) indicative of the influence of crustal contamination. By contrast, South Atlantic MORB with $\delta^{11}B_{SRM\ 951}$ as low as -11.7 ± 2‰ appear to resolve a component with isotopically lighter boron (Dixon *et al.* 2017).

In general, our new MORB data have $\delta^{11}B_{SRM\ 951}$ values in keeping with the literature (Figures 4 and 6), including the recent MC-ICP-MS study of Li *et al.* (2019). Yet it is notable that for samples that show no evidence of seawater contamination, we demonstrate variability in $\delta^{11}B_{SRM\ 951}$ beyond our intermediate precision (±0.6‰). Namely, two samples with low Cl/K (< 0.08) have

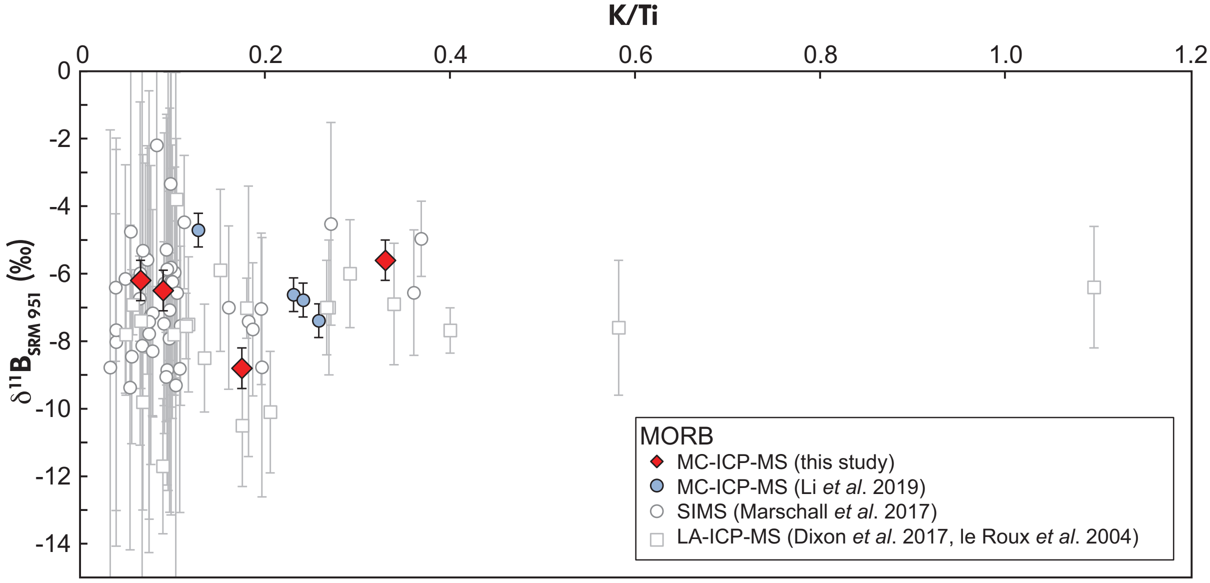


Figure 6. Solution MC-ICP-MS measurement results (red diamonds) for glasses previously measured by SIMS. MC-ICP-MS data plotted with uncertainty of ±0.6‰, reflecting the intermediate precision of basalt reference materials. Detailed information on individual measurement precision is given in Table 1. The $\delta^{11}B_{SRM\ 951}$ of volcanic glass obtained by SIMS (open circles) with uncertainty indicated at the 2*s* level. The $\delta^{11}B_{SRM\ 951}$ of volcanic glass obtained by LA-ICP-MS (open squares) with uncertainty indicated at the 2*s* level. Sources of data ($\delta^{11}B_{SRM\ 951}$ and K/Ti) displayed: Li *et al.* (2019), Marschall *et al.* (2017), Dixon *et al.* (2017), le Roux *et al.* (2004). We analysed the same material as Marschall *et al.* (2017) and utilise the K/Ti values from Marschall *et al.* (2017) together with our new, solution MC-ICP-MS $\delta^{11}B_{SRM\ 951}$ values.

$\delta^{11}B_{SRM\ 951}$ that ranges from -6.2 to -8.8‰, implying significant variability in the upper mantle source (Table 2).

We note that the sample volume of the SIMS measurement results is significantly lower than the bulk glass (25.9 to 63.2 g) measurement with which we compare it here. The low abundance of boron in mafic volcanic glass means it is not easy to decipher heterogeneity at the micrometre scale that would be homogenised when using several grams of glass shards. This requires either further reduction of sample volumes analysed by solution MC-ICP-MS or higher precision for *in situ* techniques. Future work could include further sequential leaching experiments of reference materials (e.g., Li *et al.* (2019)). This, however, first requires a better consensus on natural reference material $\delta^{11}B_{SRM\ 951}$ values.

As in other studies, there is no clear trend of $\delta^{11}B_{SRM\ 951}$ with upper mantle enrichment (Figure 4). Our E-MORB from the East Pacific Rise and enriched oceanic basalt from Pitcairn Island have $\delta^{11}B_{SRM\ 951}$ indistinguishable from two of our three N-MORB samples (Figure 2, Table 2). This shows that substantial mantle enrichment can occur without markedly influencing $\delta^{11}B_{SRM\ 951}$. The preliminary observation is that there is greater variability in boron isotope ratios in the more depleted samples.

Conclusions

The dissolution of silicate materials using hydrofluoric acid prior to column chemistry and measurement by MC-ICP-MS presented here permit the investigation of samples limited by mass and low-B mass fraction samples, such as MORB glass. Key findings include:

(1) Boron can be liberated from silicate rock materials without isotopic fractionation by use of HF acid digestion in the absence of volatilisation suppression agents (e.g., mannitol). This requires careful, low temperature (< 60 °C) dry down following dissolution. Evaporating samples from a beaker largely covered by an upturned beaker helps control evaporation, prevents particle fall in and appears to guard against sample fractionation during higher temperature evaporation, for a short duration of time.

(2) Our three-column (cation-anion-cation) method of removing matrix elements and measurement of low-B samples by solution MC-ICP-MS yields marked improvement in measurement precision over results from previous thermal ionisation (TIMS) and *in situ* (SIMS, LA-MC-ICP-MS) techniques, with measurement precision now better than ±0.6‰ (2*s*). We obtain consistent $\delta^{11}B_{\text{SRM 951}}$ for basaltic reference materials with boron separated by our acid digestion approach and an independent, flux fusion technique.

(3) A comparison of SIMS and newly acquired MC-ICP-MS data of volcanic glasses from MORB settings shows a general overlap of SIMS and MC-ICP-MS results, but considerably better measurement precision is offered by MC-ICP-MS for samples with B mass fractions < 2 µg g^{-1}. This allows us to resolve boron isotopic heterogeneity in the upper mantle.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting information

The following supporting information may be found in the online version of this article:

Appendix S1. Total procedural blanks for the new three-column procedure and the single-column carbonate procedure.

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