



Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine CaCO₃ by MC-ICPMS and NTIMS



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ABSTRACT

In this study we make the first attempt to inter-calibrate boron isotope ($\delta^{11}\text{B}$) measurements on marine biogenic carbonates measured by four different laboratories, each using a different analytical technique. The importance of such calibrations lies in the major implications of relatively small changes in $\delta^{11}\text{B}$ (<2‰), which are typical of palaeoclimate applications of the $\delta^{11}\text{B}$ –pH proxy. Despite the variety of mass spectrometric techniques used by the different laboratories in this study (two variants of negative ion thermal ionisation mass spectrometry and two variants of multicollector inductively coupled plasma mass spectrometry), for samples without a complex sample matrix, such as boric acid, there are no significant interlaboratory biases: the pooled 2sd of these samples is 0.39‰, which is within the measurement uncertainties reported by each laboratory (which range between 0.18 and 0.80‰). For seawater, a common in-house reference material, we find a similarly good agreement ($\delta^{11}\text{B} = 39.65 \pm 0.41\text{‰}$, 2sd) despite four different sample preparation procedures. Reported $\delta^{11}\text{B}$ for calcium carbonate samples have a pooled 2sd of 1.46‰, which is larger than the measurement uncertainty reported by each laboratory. We have attempted to identify the source of this interlaboratory variability, and find that overall sample size (in terms of available B) and B/Ca ratio (i.e. amount of boron relative to matrix) may play a role, but the exact mechanisms remain uncertain. Observed variations in reported $\delta^{11}\text{B}$ for the CaCO₃ samples are, however, relatively systematic for each laboratory for a given sample matrix (i.e. similar B/Ca and amount of boron for analysis). This implies that *relative* differences in $\delta^{11}\text{B}$ in a sample set of a given matrix can be reconstructed by the four laboratories involved in this study more accurately than the absolute boron isotope ratios.

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1. Introduction

Boron has two naturally occurring isotopes (^{11}B and ^{10}B) with proportions of ~80% and ~20%, respectively. In common with many stable isotope systems, variations in the $^{11}\text{B}/^{10}\text{B}$ ratio are expressed as parts per thousand deviations from a certified reference material, in this case NIST SRM 951 boric acid, as follows:

$$\delta^{11}\text{B}(\text{‰}) = \left[\left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{Sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{NIST951}}} \right) - 1 \right] \times 1000 \quad (1)$$

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where $^{11}\text{B}/^{10}\text{B}_{\text{NIST951}}$ is the $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951 (4.04363; Catanzaro et al., 1970). A number of natural processes fractionate boron isotopes and, by virtue of their large relative mass difference, there is a wide range of boron isotope compositions found in nature from –30‰ to +50‰ (Palmer and Swihart, 1996). Importantly for palaeoclimate applications, boron isotopes are fractionated by ~27‰ between aqueous borate and boric acid (Klochko et al., 2006), the two main boron species in seawater. Precise measurement of the boron isotope ratio by mass spectrometry is however difficult for a number of reasons. Firstly, the relatively large mass difference between the isotopes can result in large isotope fractionation during measurement. Secondly, boron has only two naturally occurring isotopes, and the lack of stable (or at least long lived) synthetic isotopes means it is impossible to use the double spike approach that has proved successful for other systems (e.g., Zn, Bermin et al., 2006) to correct machine induced isotope fractionation.

In the past 20 years or so there have been a number of important methodological and technological advances that help tackle these

Table 1
Materials used for interlaboratory comparison of boron isotope composition.

Code	Description and origin	Approx. [B] (ppm)	Amount distributed ^a
BIG-D	Mixture between NIST SRM 951 and enriched boric acid in 0.5 M HNO ₃	7	5 ml
BIG-E	Mixture between NIST SRM 951 and enriched boric acid in 0.5 M HNO ₃	7	5 ml
UMD	Boric acid diluted in 0.5 M HNO ₃	15	5 ml
IC _A	Miocene-aged deep ocean carbonate (ODP 871 6H cc)	7	100 mg
IC _B	Inorganic calcite rhomb from Valentine Wollastonite Mine in the Adirondacks	13	105 mg
IC _C	Cold water calcitic scleraxonian octocoral from the Pacific Sector of the Southern Ocean (1480–1788 m)	21	75 mg
IC _D	Massive aragonitic <i>Porites</i> (sp) coral from Papua New Guinea	40	75 mg
IC ₁	laboratory grown <i>Porites cylindrica</i>	52	4 mg
IC ₂	laboratory grown coral <i>Acropora nobilis</i>	55	2 mg
IC ₃	laboratory grown <i>Porites cylindrica</i>	51	3 mg
IC ₄	laboratory grown coral <i>Acropora nobilis</i>	51	4 mg
IC ₅	laboratory grown coral <i>Acropora nobilis</i>	51	3 mg
IC ₆	planktic foraminifers (<i>Globigerinoides sacculifer</i>), ~128 ka, ODP 668B	11	7 mg
IC ₇	planktic foraminifers (<i>Globigerinoides sacculifer</i>), ~141 ka, ODP 668B	10	3 mg
IC ₈	planktic foraminifers (<i>Globigerinoides sacculifer</i>), ~613 ka, ODP 668B	9	4 mg
IC ₉	planktic foraminifers (<i>Globigerinoides sacculifer</i>), ~657 ka, ODP 668B	11	4 mg
IC ₁₀	brachiopod (<i>Terebratalia transversa</i>) from Catalina Island, California	22	1 mg
IC ₁₁	brachiopod (<i>Terebratalia transversa</i>) from The Narrows, Tacoma, Washington	24	1 mg

^a Amount distributed varied between laboratories and this is only an approximate estimate.

analytical issues and boron isotopic analysis of natural materials is a rapidly growing field of research. Part of this growth in interest is because the boron isotopic composition of marine carbonates has been shown to be determined by the pH of the water from which the CaCO₃ precipitated (e.g., Vengosh et al., 1991; Hemming and Hanson, 1992; Gaillardet and Allegre, 1995; Sanyal et al., 1996, 2000, 2001; Hönisch et al., 2004; Rae et al., 2011), leading to the possibility of reconstructing past levels of atmospheric pCO₂ and ocean acidification (e.g., Sanyal et al., 1995; Pearson and Palmer, 2000; Hönisch and Hemming, 2005; Foster, 2008; Hönisch et al., 2009; Pearson et al., 2009; Seki et al., 2010; Foster et al., 2012). The large appeal of such studies lies in the relatively well-understood theoretical basis of the δ¹¹B-pH proxy (e.g., Zeebe and Wolf-Gladow, 2001) to which, perhaps unusually for palaeoclimate tracers, observations often closely match with minor or no “vital effects” (e.g., Sanyal et al., 1996, 2000, 2001; Rae et al., 2011). The full details of the boron isotope palaeo-pH proxy are described elsewhere (e.g., Hemming and Hönisch, 2007), but it is important to note that provided sufficient analytical accuracy and precision, accurate determination of palaeo-pH and hence pCO₂, can be reconstructed using this system (e.g. Sanyal et al., 1995; Hönisch and Hemming, 2005; Foster, 2008). Given the recent and growing importance of past climate research, such boron isotope studies tend to have a broad scientific and public interest and wide ranging implications. For instance, the Cenozoic record of pCO₂ and ocean pH of Pearson and Palmer (2000) based on δ¹¹B measurements of ancient foraminifers appears in the IPCC AR4 report as part of the case for CO₂ causing natural climate change (Jansen et al., 2007). Consequently, the requirement of a high level of analytical accuracy for boron isotope measurements is particularly pertinent. Such requisite accuracy was not apparent for previous interlaboratory comparisons for boron isotope measurements (Gonfiantini et al., 2003; Aggarwal et al., 2009), which showed an interlaboratory range in δ¹¹B of typically around 2–3‰ and up to 11‰ on the same sample. Such variability is incompatible with important palaeo-pH applications (where

distinguishing differences of <1‰ is often required) and typically exceeds the reproducibility thought to be achievable within each individual laboratory (<0.5‰; e.g., Pearson and Palmer, 2000; Foster, 2008; Hönisch et al., 2009; Louvat et al., 2011). Although the first interlaboratory comparison study by Gonfiantini et al. (2003) included a marine carbonate (IAEA-B7, a Miocene marine limestone from Maiella Italy), its boron concentration was lower than typical biogenic marine carbonates used for palaeo-pH studies (2 ppm vs. >10 ppm; throughout the text we use ppm to denote ng/g). There is therefore a pressing need to better assess the interlaboratory biases, and hence analytical accuracy, of boron isotopic measurements of the types of marine carbonates that are typically used for palaeo-pH applications (e.g., foraminifera and corals).

Here, in contrast to the previous boron isotope laboratory inter-comparison studies, we have chosen not to openly distribute samples to the entire isotope geochemistry community. This decision was motivated by the possibility that these earlier studies were too wide-ranging to accurately determine the likely drivers of the observed variability. Instead, here we distributed samples to four laboratories whose principal analyst has a specific interest and history of marine carbonate boron isotope analysis (Vengosh et al., 1991; Hemming and Hanson, 1992; Gaillardet and Allegre, 1995; Foster, 2008; Hönisch et al., 2009; Paris et al., 2010; Louvat et al., 2011; Rae et al., 2011). These samples comprise 15 different samples of CaCO₃, ranging from inorganic calcite to aragonitic corals (Table 1), and 3 samples of boric acid. Each laboratory used somewhat different analytical methods (Table 2), and we only asked that each laboratory followed its usual analytical protocol. Although this may somewhat limit easy comparison between laboratories (which may, for instance, report different numbers of replicate measurements), these different approaches are all in active use. This study is therefore a preliminary investigation into the interlaboratory biases that may currently exist in the boron isotope measurement of marine carbonates and is a first attempt at pinpointing the likely cause of any variations we observe.

Table 2
Analytical techniques used by each laboratory.

Laboratory	Measurement technique	Chromatographic pre-concentration of B	Key reference
Bristol Isotope Group (BIG)	MC-ICPMS	Yes	Foster (2008)
Lamont-Doherty Earth Observatory (LDEO)	NTIMS	No	Hemming and Hanson (1994)
IPGP	Direct injection MC-ICPMS	Yes	Louvat et al. (2011)
Duke University	NTIMS	Yes	Dwyer and Vengosh (in prep.)

MC-ICPMS: multicollector inductively coupled plasma mass spectrometry.

NTIMS: negative ion thermal ionisation mass spectrometry.

2. Intercomparison materials

In order to compare $\delta^{11}\text{B}$ results of marine carbonates among laboratories, it was first necessary to determine if any systematic analytical biases existed. This is best achieved by using boric acid solutions that require no chemical treatment prior to analysis, other than dilution. Each laboratory was supplied with three boric acid solutions for this purpose: BIG-D, BIG-E and UMD. These are either commercially purchased boric acid powders (UMD) or enriched boric acids (BIG-D and BIG-E) made at the Bristol Isotope Group (BIG) by G. Foster by mixing NIST SRM 951 boric acid (80.17% ^{11}B) with a ^{11}B -enriched boric acid (99.27% ^{11}B). The gravimetrically determined $\delta^{11}\text{B}$ for BIG-D and BIG-E are $15.54 \pm 0.2\%$ and $25.6 \pm 0.3\%$. The uncertainty in the isotopic composition of these mixtures is estimated by assuming a $\pm 1\%$ weighing error alone and no attempt has been made to propagate the uncertainty in the isotopic composition of the ^{11}B -enriched boric acid. Between 0.5 and 1 l of stock solution of these boric acids was made at boron concentrations of ~ 7 ppm (BIG-D and BIG-E) and ~ 15 ppm (UMD), and aliquots of ~ 5 ml were distributed to each laboratory in acid-cleaned screw top Teflon vials.

Calcium carbonate samples were distributed in two batches. Intercomparison (IC) samples 1–11 were prepared by B. Hönisch at the Lamont Doherty Earth Observatory (LDEO) and IC samples A–D were prepared by G. Foster at the BIG.

IC_{1–5} are scleractinian corals *Porites cylindrica* (IC₁ & IC₃) and *Acropora nobilis* (IC₂, IC₄ & IC₅), which were grown under controlled laboratory conditions over a range of pH (Hönisch et al., 2004). Fine to medium-coarse powders of several specimens grown in the same tank and under the same pH were combined and homogenized. A total of ~ 15 mg of sample material was bleached overnight with NaOCl to oxidise organic material, followed by 10 \times rinsing and ultrasonication in boron-purified MilliQ water to ensure complete removal of NaOCl. IC_{6–9} are planktic foraminifers of the species *Globigerinoides sacculifer* (>500 μm sieve size), selected from extreme glacial/interglacial sediment samples of ODP 668B in the eastern equatorial Atlantic (Hönisch and Hemming, 2005). Foraminifer shells were crushed between two glass slides under a microscope, transferred to 1.5 ml plastic vials, then rinsed and ultrasonicated 30 times to remove adhering clays, followed by the full trace metal cleaning procedure for planktic foraminifers after Barker et al. (2003). IC₁₀ and IC₁₁ are brachiopods of the species *Terebratalia transversa*, which were obtained from the collection of the American Museum of Natural History in New York (Penman et al., 2013). Brachiopods were cut lengthwise (along their axis of symmetry, perpendicular to the hinge), then fixed to a glass slide with epoxy resin and cut again to obtain a ~ 2 mm thick section. Sections were polished with 50 μm grit on a polishing wheel and ~ 5 mg samples were drilled at the widest part of the shell, approximately halfway along the length and halfway through the width of the shell, using a 0.5 mm diamond tipped dental burr. This sampling strategy results in fine powders that were then transferred to 1.5 ml plastic vials and cleaned similar to the coral powders described above. For distribution, approximately 3 mg splits of each cleaned coral and foraminifer sample, and ~ 1 mg of brachiopod sample were transferred into 1.5 ml acid cleaned vials, using micro-pipette tips and boron-purified MilliQ water as a transfer agent. All sample cleaning and transfers were done in a PTFE (boron free) filtered laminar flow bench at LDEO.

IC_A to IC_D are a Miocene-aged deep ocean carbonate (IC_A), an inorganic calcite (IC_B), a calcitic scleraxonian octocoral (IC_C), and an aragonitic coral belonging to the genus *Porites* (IC_D). For these samples between 0.3 and 0.4 g of solid CaCO_3 was hand crushed to a powder using an agate mortar and pestle in the B-free clean laboratory at the BIG by G. Foster. The resulting powders were transferred to a glass vial before weighing the powder on weighing-paper and transferring aliquots to acid cleaned 2 ml plastic vials for distribution. Each laboratory was sent approximately the same amount of CaCO_3 (between 70 and 100 mg; Table 2). In contrast to IC_{1–11} these samples were not cleaned

Table 3

Trace element ratios of calcium carbonate samples determined using ICPMS.

Sample	Li/Ca (mmol/mol)	B/Ca (mmol/mol)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)
IC _A	11.3	65	3.88	1.35
IC _B	0.03	121	1.97	0.36
IC _C	40.4	198	82.5	2.78
IC _D	5.1	376	4.35	8.57
IC ₁	6.3	490	4.09	8.76
IC ₂	6.8	522	4.34	8.96
IC ₃	6.6	484	4.86	8.62
IC ₄	7.2	483	4.87	8.92
IC ₅	7.2	480	4.73	8.93
IC ₆	12.1	98	4.24	1.31
IC ₇	14.8	95	3.59	1.31
IC ₈	12.6	88	4.10	1.26
IC ₉	14.1	100	3.51	1.31
IC ₁₀	19.2	200	9.14	1.15
IC ₁₁	31.0	225	5.24	1.10

prior to distribution and each laboratory followed a slightly different cleaning protocol (detailed in Section 3).

Trace element concentrations for all carbonate samples were determined on an aliquot of each sample dissolved at the BIG using a Thermo Scientific Element 2 and protocols detailed elsewhere (e.g., Ni et al., 2007; Foster, 2008). The variation in these trace element ratios reflects the different types of CaCO_3 (i.e. inorganic CaCO_3 to Miocene-aged deep sea carbonate ooze) and covers a large part of the natural range in composition for marine CaCO_3 . Of particular relevance are the B/Ca ratios of these samples, which range from 65 to 522 $\mu\text{mol/mol}$ (Table 3).

In addition to these materials, data are also presented on the boron isotopic composition of seawater. The residence time of boron in seawater is around 15 million years (Lemarchand et al., 2002a), which is sufficiently long compared to the mixing time of the oceans that boron has a homogeneous concentration (~ 432.6 $\mu\text{mol/kg}$ \times salinity/35; Lee et al., 2010) and a homogeneous isotope ratio (Spivack and Edmond, 1987; Foster et al., 2010). Consequently, seawater tends to be a common in-house reference material, and no seawater sample was distributed; rather here each laboratory reports the $\delta^{11}\text{B}$ values measured for its own in-house seawater reference material.

3. Measurement techniques used

3.1. MC-ICPMS at Bristol

The analytical protocols for measuring boron isotopes by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) at Bristol are described in detail elsewhere (Foster, 2008; Rae et al., 2011) but for comparative purposes they are summarised here.

Sample sub-set IC_A–IC_D was cleaned with an oxidative cleaning approach closely following Barker et al. (2003). They were first rinsed 2–3 times in MilliQ > 18.2 M Ω /cm water with multiple short (~ 30 s) ultrasonications. Organic matter was oxidised using 1% hydrogen peroxide (buffered with 0.1 M ammonium hydroxide) in a water bath at 80 $^\circ\text{C}$. This oxidative solution was removed with MilliQ rinses and samples were treated with 0.0005 M HNO_3 to remove adsorbed contaminants. Dissolution was achieved in 500–2000 μl of 0.5 M HNO_3 (depending on sample size). Oxidative cleaning was carried out in plastic vials and samples were transferred to 1.5 ml Teflon centrifuge tubes for dissolution. Following dissolution the samples were centrifuged and transferred to Teflon screw top vials for storage, leaving around 10 μl in the centrifuge tube containing any undissolved residue. Those samples supplied already cleaned (IC₁–IC₁₁) were transferred to acid-cleaned plastic centrifuge tubes, rinsed three times in MilliQ water. Following dissolution in 0.075 M HNO_3 in Teflon centrifuge tubes, they were centrifuged and transferred to screw-top Teflon vials for storage, leaving the last 10 μl . All reagents are either Teflon-distilled, with HNO_3 distilled

with manitol, or are made from RoMil ultrapure reagents (H_2O_2) with certified low boron blanks (<100 ppt; pg/g). All dissolution, cleaning, sample handling, and column chemistry were carried out in a dedicated over-pressured flow hood within a class 100 clean lab at the BIG fitted with boron-free HEPA filters throughout. Blank tests indicate that vials accumulate boron at the rate of ~4 pg/h when left open in the over-pressured flow hood. At every stage efforts are made to ensure sample exposure to the laboratory air is minimised.

A small aliquot (<5%) of each dissolved sample is analysed for a suite of trace elements (Ca, Mg, B, Al, Mn, Fe, Ba, Sr, Li, Na, Cd, U, Nd) on a Thermo Finnigan Element 2 ICP-MS, matching sample and standard Ca concentration (1–4 mmol/l) and using ammonia add-gas to improve boron washout (Al-Ammar et al., 2000). This step is necessary to ensure that the correct amount of boron is used for each analysis. For carbonate samples this also provides an indication of cleaning efficiency (in terms of Al/Ca ratio; Rae et al., 2011). External reproducibility of these trace element measurements is 2–5% (2sd) based on long-term replicates of in-house consistency standards (see Ni et al., 2007).

Prior to boron isotope analysis, boron is separated from sample matrix using boron-specific anionic exchange resin Amberlite IRA-743 (Kiss, 1988) in a 20 μl micro-column. Samples are buffered to pH 5 using a 2 M sodium acetate–0.5 M acetic acid buffer and loaded onto freshly cleaned columns. This pH was chosen to avoid the risk of precipitation of Ca (plus trace elements) prior to column chemistry. The buffer and carbonate matrix of the sample is washed off using MilliQ water and the boron is eluted in 450 μl of 0.5 M HNO_3 . Column yields assessed by isotope dilution are >95% (Foster, 2008) and elution tails of every sample are checked with an extra 90 μl acid rinse. In all cases this tail represents less than 1% (on average around 0.2%) of the boron loaded. Typically, the majority of matrix loaded is Na derived from the buffer (~10 mg compared to 1–2 mg Ca from the sample). Boron concentrations of each sample are checked prior to analysis using a small aliquot, and Na concentrations are also monitored in this aliquot in order to check for complete removal of sample matrix. Elemental analysis by ICPMS of Na contaminated samples revealed that even in carbonate samples ^{23}Na was the major cation contaminant, likely indicative of incomplete removal of the 2 M sodium acetate–0.5 M acetic acid buffer (Foster, 2008). Typically <5% of samples are influenced by sample matrix in this way and these samples can show anomalous mass fractionation behaviour and are therefore rejected.

A significant potential source of inaccuracy for approaches that require matrix removal (e.g., MC-ICPMS) is isotope fractionation resulting from incomplete recovery of boron from the Amberlite IRA-743 resin (Lemarchand et al., 2002b). One way this phenomenon can be examined is by processing NIST SRM 951 and other boric acid samples through the entire chemical procedure and comparing the measured isotope ratios with that of the untreated boric acid. As detailed by Foster (2008), for NIST SRM 951 and an enriched boric acid (JA-A = JABA of Aggarwal et al., 2009; $\delta^{11}\text{B} = 10.8\text{‰}$) this chemical treatment does not result in any significant fractionation. Notably, even for these tests involving boric acids, a significant amount of matrix is loaded onto the columns in the form of the buffer. In order to better approximate a marine carbonate matrix, Foster (2008) added boron free (<100 ppt; pg/g) mixed element calcium solution (24 mmol/l Ca plus Mg, Sr, Na, Mn, Li, Ba, Cd, U, Al, Cu, Fe, Nd, and Zn in typical foraminiferal proportions) to NIST SRM 951 prior to column chemistry, and again there was no detectable fractionation. Tipper et al. (2008) noted that although measurement of such synthetic samples provides a valuable indicator of reliability of a separation procedure, not all of the potential matrix problems of a complex natural sample are necessarily envisaged. To further demonstrate the robustness of the protocol followed here, Ni et al. (2010) followed the example of Lemarchand et al. (2002b) and Tipper et al. (2008) and performed a standard addition experiment using sample IC_B (called 871std in Ni et al., 2010). In detail, aliquots of dissolved IC_B were mixed with variable amounts of NIST SRM 951 prior to column chemistry. The mixtures were made such that the

amount of carbonate was kept constant and at a value typical of foraminiferal analyses by this method. The results of this standard addition experiment confirm that any residual sample matrix does not have a significant influence on the $\delta^{11}\text{B}$ measured in calcium carbonate samples using the method outlined here (Ni et al., 2010).

Depending on available sample size, between 1 and 5 mg of CaCO_3 was typically dissolved for isotope analysis and between 3 and 24 ng of boron was loaded for each column separation (determined prior to loading using ICPMS). Sample handling and airborne contamination were reduced by following the procedures outlined above and at no time were samples dried down. Total procedural blanks (TPB) were determined by ICPMS for every column batch and averaged ~100 pg (~1% of sample size) with a $\delta^{11}\text{B}$ of ~5‰. A TPB correction was made using the B concentration of the TPB for each column batch and the average TPB isotope composition (5‰). These corrections were typically small (~0.1‰) but need to be monitored and applied to optimise accuracy. An additional source of blank contamination arises from airborne contamination during analysis on the MC-ICPMS. It was found that such exposure in the autosampler prior to analysis results in a “fall-in” blank of ~10 pg/h. This effect is corrected using blanks determined on aliquots of 0.5 M HNO_3 of the same volume of the samples, which are analysed every second sample.

All boron isotope analyses by MC-ICPMS at Bristol were carried out on a Thermo Scientific Neptune housed in the Bristol Isotope Group. Typical operating conditions are summarised in Foster (2008). The well documented wash-out problems of boron during ICPMS analysis (e.g., Al-Ammar et al., 2000) were overcome using a PFA spray chamber from Elemental Scientific Inc. (ESI) with 2–3 ml/min of ammonia add gas, ported in immediately after the ESI PFA 50 $\mu\text{l}/\text{min}$ self aspirating nebuliser (Foster, 2008). This ammonia add gas ensures that the spray chamber volume remains basic despite samples, standards and washes being introduced in 0.5 M HNO_3 . At high pH boron exists predominantly as borate ion in solution and is not volatile, so wash out occurs in an acceptable amount of time (down to ~2% in 120 s; Foster, 2008). Potential interferences include Ar^{4+} or Ne^{2+} on mass 10 (Wang et al., 2010) and $^{10}\text{BH}^+$ on mass 11 (Foster, 2008). The former is fully resolved at low-mass resolution and high-resolution mass scans revealed that the latter interference is not present in significant proportions on the Neptune (Foster, 2008; Wang et al., 2010).

Instrumental mass bias was corrected using a sample-standard bracketing technique using 50 ppb (ng/g) NIST SRM 951 in 0.5 M HNO_3 . It was found that it was not necessary to intensity match samples and standards within the typical measured range of 5–50 ppb (Foster, 2008; Rae et al., 2011) and samples were run at concentrations of 20 to 50 ppb (yielding around ~3–8 pA of ^{11}B). As a consequence of this measurement procedure, boron isotope ratios are determined as delta values without further normalisation. Each analysis consisted of a 2 minute simultaneous collection of masses 11 and 10 on Faraday cups H3 and L3. Background corrections (accounting for acid blank and instrumental baseline) were carried out using “on-peak zeros”. The analytical routine used allows the analysis, background and mass bias correction of 2 unknowns in 30 min. Each sample was analysed in duplicate in a single analytical session and the average value is used. To obtain two independent measurements we ensure that these duplicate analyses do not share a bracketing standard. Mass fractionation in MC-ICPMS analyses is large, ~15%/amu for boron, but, given careful tuning to optimise for mass bias stability (see Foster, 2008; Wang et al., 2010), this level of fractionation was typically constant or slowly drifted through an analytical session (with a range of $\sim\pm 0.5\text{‰}$) and is accurately corrected using the sample-standard bracketing routine (Foster, 2008). Peak centres are performed approximately every 30 min.

The reported $\delta^{11}\text{B}$ represents the average of two analyses, several hours apart, during a given analytical session. Reproducibility using this method has been assessed by repeat analysis of in-house boric acid, seawater and coral standards at a range of concentrations (see

Rae et al., 2011). It was found that the external reproducibility (at 2 standard deviations) of total procedural replicates varied with measured ^{11}B intensity as described by:

$$2\text{sd} = 1.7 \times \exp^{-29[^{11}\text{B}]} + 0.31 \times \exp^{-0.75[^{11}\text{B}]} \quad (2)$$

This equation is used to estimate appropriate external reproducibility for samples of different sizes (reflected by their ^{11}B intensity [^{11}B]) and is typically around 0.23‰ for a 20 ng and 0.33‰ for 4 ng of B at 95% confidence. An in-house coral standard is run with each chemistry batch of 8 samples as a further monitor of reproducibility, which was $\pm 0.23\%$ (2sd) for the duration of this study.

For the boric acids (BIG-D, BIG-E and UMD) no chemical pre-treatment was necessary and stock solutions were simply diluted to 50 ppb [B] using 0.5 M HNO_3 for analysis by MC-ICPMS. In this case the reported $\delta^{11}\text{B}$ in Table 4 are simply the reproducibility (2sd) of a number of analyses during multiple analytical sessions. Foster et al. (2010) report the results of a detailed study of seawater $\delta^{11}\text{B}$. This study involved the analysis of 28 samples of seawater from a range of locations and depths. The analytical techniques used for these seawater analyses closely follow that described above (see Foster et al., 2010 for full details).

3.2. MC-ICPMS at Paris

The analytical protocols for measuring boron isotopes on the Thermo Scientific Neptune multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) using demountable-Direct Injection High Efficiency Nebulisation (d-DIHEN) in Paris (IPGP) are described in detail elsewhere (Louvat et al., 2011). Description of the points relevant to the present discussion are summarised hereafter.

Prior to dissolution, all carbonate samples were rinsed three times in distilled water and no further cleaning procedure applied. Samples were then directly dissolved in 2 M distilled (Teflon sub-boiled) HNO_3 and this solution was loaded onto 300 μl of clean Dowex AG50X8 cationic resin to remove Ca. The resin was then rinsed using $6 \times 150 \mu\text{l}$ of 0.1 M HNO_3 to ensure complete boron recovery. Afterwards, the boron separation protocol is similar to that developed by Lemarchand et al. (2002b), except that in order to avoid matrix effects from Cl, HCl was replaced by HNO_3 and NaNO_3 was used in place of NaCl (Paris et al., 2010). The Ca-free boron solution is then concentrated and purified on a micro-column containing 50 μl of Amberlite IRA 743 resin. The resin is first washed with 100 ml of 0.5 M HNO_3 and conditioned with 250 μl of MilliQ H_2O . The pH of the sample solution is increased to 9 using distilled ammonia, as the K_d value between the IRA 743 resin and the boron in solution is at a maximum for this pH (Lemarchand et al., 2002b). After sample introduction, the resin is washed with $2 \times 50 \mu\text{l}$ of H_2O , 50 μl of NaNO_3 0.6 M (at pH 9), and 50 μl of H_2O is added to elute the remaining cations and anions. Boron is then eluted using successively 50 μl of 0.5 M HNO_3 and $5 \times 100 \mu\text{l}$ of 0.1 M HNO_3 . The final elution volume is 550 μl , which is then diluted with H_2O to reach 1.3 ml of 0.05 M HNO_3 . The extraction yields are tested by running a boric acid of known concentration and isotope

composition through this chemical procedure and are typically >99%. Matrix effects were checked by passing the same boric acid added to a boron depleted seawater and with standard addition experiments on the seawater standard NASS5 (Louvat et al., 2011). The total boron blank of this procedure is lower than 1 ng with a boron isotopic composition of roughly 0‰. Because the boron isotopic composition of the blank is not known precisely, no attempt to correct the measured isotopic composition was made. The influence of blank propagation on $\delta^{11}\text{B}$ is less than 0.1‰, which is smaller than the analytical reproducibility (0.25‰ 2sd; Louvat et al., 2011).

For the boric acids (BIG-D, BIG-E and UMD) no chemical pre-treatment was necessary and stock solutions were simply diluted to 200 ppb [B] using 0.05 M HNO_3 for analysis by MC-ICPMS.

Boron isotopes were measured with a Thermo Scientific MC-ICPMS Neptune using a d-DIHEN as the sample introduction device (Louvat et al., 2011). Direct injection nebulisation introduces the aspirated sample-aerosol directly into the plasma, the nebuliser (a long Meinhard-like nebuliser) being introduced into the ICP-MS torch in place of the injector used in traditional injection devices. One advantage of the d-DIHEN (demountable version of the DIHEN) as described by Westphal et al. (2004) is that the spray is adjustable and both needle and capillary can be changed individually. Direct injection gives higher sensitivities than a standard spray chamber for most elements from Li to U (Louvat et al., 2011), with d-DIHEN sensitivities similar or lower to those with desolvating systems (e.g., APEX from ESI), except for volatile elements, which are lost during desolvation, such as boron. Optimised operating settings of the Neptune MC-ICP-MS with the d-DIHEN device are described in Louvat et al. (2011). For a 100 ppb B solution, sensitivity using the d-DIHEN is about 30 to 40 pA of ^{11}B with X-cones. The d-DIHEN method induces a significant instrumental fractionation that evolves with time. Boron isotopic compositions are thus measured by sample-standard bracketing, using NIST SRM 951 (0‰ by definition) as a bracketing solution, with identical concentration (within 5%) for the standard solution and the sample. Samples and standards are measured using the same method. The instrumental baseline is measured by defocusing the signal for 10 s, and then ^{11}B and ^{10}B are simultaneously collected over a period of 2 min. A peak centre is performed every hour and no “on-peak zero” is subtracted.

The main advantage of the d-DIHEN device is to reduce wash-times compared to other introduction systems. This is particularly true for “sticky” elements, such as boron. With d-DIHEN, 100 s of 0.5 M HNO_3 wash is sufficient to reach a ^{11}B signal as low as 1% of the previous sample or standard signal (e.g., 2 mV after a standard of 3 V). Because our measurement method was not originally developed for analysis of samples such as foraminifera, which contain relatively small amounts of B, a blank correction routine has not been developed. For solutions at a concentration higher than 50 ppb, the machine blank is about 1‰ of the sample/standard signal and is not significant compared to the external reproducibility. For samples with B concentrations lower than 50 ppb, blank issues might result in lowering the measured ratios (with increasing blank effect for decreasing concentration). At concentrations lower than 50 ppb, internal and external reproducibilities also worsen.

Given the necessary wash and uptake times, a standard-sample sequence lasts for 10 to 12 min, with a time lapse of 5 to 6 min between

Table 4
Boron isotope data for interlaboratory comparison samples—boric acids and seawater.

Sample ^a	BIG			LDEO			IPGP			DUKE			Overall	
	$\delta^{11}\text{B}$ (‰)	2 σ^b	n	$\delta^{11}\text{B}$ (‰)	2 σ^b	n	$\delta^{11}\text{B}$ (‰)	2 σ^b	n	$\delta^{11}\text{B}$ (‰)	2 σ^b	n	$\delta^{11}\text{B}$ (‰)	2sd
Boric acid														
BIG-D	14.76	0.30	45	14.71	0.52	4	14.65	0.26	15	14.10	0.80	3	14.56	0.61
BIG-E	25.11	0.18	8	24.93	0.42	6	25.04	0.25	15	24.75	0.44	4	24.96	0.31
UMD	−12.92	0.28	4	−12.84	0.60	3	−13.03	0.25	15	−12.68	0.44	2	−12.87	0.29
Seawater	39.61	0.20		39.70	0.34		39.89	0.24		39.40	0.40		39.65	0.41

^a Seawater value reported by each laboratory in the literature (see text for details), except for Duke.

^b Uncertainty at 95% confidence including uncertainty relating to measurement of NIST SRM 951 as discussed in text.

Table 5Boron isotope data for interlaboratory comparison of calcium carbonate samples IC_A to IC_D.

Sample ^a	Bristol					LDEO								IPGP					DUKE				Overall						
	1	2	3	Mean	2 σ ^b	1	2	3	4	5	6	7	8	Mean	2 σ ^b	1	2	3	4	5	Mean	2 σ ^b	1	2	Mean	2 σ ^b	Mean	2sd	
IC _{A-1a}	15.59	15.62	15.52	15.58		16.53	16.88	16.94	17.08	16.89				16.86		16.21	16.23				16.22		15.33	14.90	15.11				
IC _{A-1b}	15.81	15.74		15.78																									
IC _{A-1c}	15.62	15.63		15.63																									
IC _{A-2}	15.59	15.66		15.63		17.00	17.12	16.73	15.46	16.92				16.94		16.33	16.15				16.24								
IC _{A-3}						17.18	16.82	16.87	16.69					16.89															
IC _{A-4}						16.77	16.77	16.60						16.71															
IC_A mean				15.65	0.23									16.85	0.35						16.23	0.25			15.11	0.39	15.96	1.50	
IC _{B-1a}	8.12	8.05	8.10	8.09		10.62	10.63	10.47						10.57		9.10	8.96	8.79			8.95		8.94	8.09	8.51				
IC _{B-1b}	8.58	8.37		8.48																									
IC _{B-2}	8.56	8.40		8.48		10.29	9.75	9.69	10.33	10.19	9.60			9.97		8.97	8.95	8.76			8.89								
IC _{B-3}						10.24	9.97	10.16	10.34	10.16	7.90			10.17															
IC _{B-4}						9.66	9.65	10.04	10.42					9.94															
IC_B mean				8.35	0.45									10.17	0.58						8.92	0.25			8.51	0.39	8.99	1.64	
IC _{C-1a}	15.50	15.59	15.46	15.52		16.22	15.40	16.57	16.32	16.23				16.15		16.23	16.19	16.21			16.21		15.58	15.90	15.74				
IC _{C-1b}	15.55	15.60		15.58																									
IC _{C-2}						16.49	16.95	16.23	16.69	17.02	16.96	16.79	16.59	16.71		15.87	15.87	15.84			15.86								
IC _{C-3}						16.35	15.73	15.83						15.97		16.19	16.12	15.87			16.06								
IC_C mean				15.55	0.23									16.28	0.78						16.04	0.35			15.74	0.39	15.90	0.65	
IC _{D-1a}	24.96	24.98	24.94	24.96		25.87	26.23	25.32						25.81		25.02	24.94	24.98	25.24	25.32	25.10		25.06	25.26	25.16				
IC _{D-1b}	25.07	25.08		25.07																									
IC _{D-2}	25.03	24.95		24.99		25.66	25.52	26.02						25.73		25.06	25.04	25.13	25.22	25.18	25.13								
IC _{D-3}						24.87	25.12	24.87	25.65	25.66	26.04	26.00		25.46		24.80	24.58	24.74	24.95	24.92	24.80								
IC _{D-4}						25.75	25.96	25.96	26.00	25.75				25.88		25.07	25.15	25.05	24.98	24.93	25.04								
IC_D mean				25.01	0.23									25.72	0.37						25.01	0.30			25.16	0.39	25.23	0.67	

^a Full procedural replicates of samples are labelled with consecutive numbers, repeat chemical processing of the same dissolved sample is labelled with consecutive letters.^b Uncertainty at the 95% confidence level, either reproducibility of the values presented or the external precision (whichever is larger).

Table 6
Boron isotope data for interlaboratory comparison calcium carbonate samples IC₁ to IC₁₁.

Sample ^a	BIG		LDEO ^b								IPGP					DUKE					Overall				
	1	2	Mean	2 σ^c	1	2	3	4	5	6	7	8	Mean	2 σ^c	1	2	3	Mean	2 σ^c	Mean	2sd				
IC _{1-A}	25.02	25.02	25.02	0.23	25.29	25.02	25.22	25.24	23.86	24.93	0.35	25.39	25.20	25.30	25.37	25.10	25.27	0.25	24.36	23.76	24.59	24.24	0.48	24.86	0.89
IC _{2-A}	24.41	24.42	24.41	0.23	24.47	23.86	24.75	24.06	24.19	24.27	0.31	24.60	24.79	24.81	24.79	24.64	24.73	0.25	22.44	22.91	22.74	22.70	0.39	24.03	1.81
IC _{3-A}	24.15	24.13	24.14	0.23	23.46	24.26	24.00	23.40	24.03	23.79	0.42	24.67	24.48	24.58	24.69	24.62	24.61	0.25	22.44	23.14	23.01	22.86	0.42	23.75	1.35
IC _{3-B}					23.23	22.98	22.91	23.66	23.93	23.34	0.39														
IC _{4-A}	23.28	23.27	23.27	0.23	22.16	22.33	21.99	23.39	22.46	22.64	0.53	22.93	22.75	22.79	22.89	22.76	22.82	0.25	21.84	22.44	22.19	22.16	0.39	22.72	0.92
IC _{5-A}	22.43	22.39	22.41	0.23	20.72	20.77	19.26	21.47	21.30	21.06	0.31	22.40	22.63	22.75	22.61	22.56	22.59	0.25	22.12	22.22	22.02	22.12	0.39	22.04	1.37
IC _{6-A}	20.10	20.28	20.19	0.23	20.35	21.05	20.53	20.71	19.56	20.69	0.28	21.19	21.21	21.34	21.17	21.01	21.18	0.25	18.67	19.47	17.55	18.56	0.95	20.16	2.27
IC _{7-A}	20.54	20.94	20.74	0.27	21.58	21.91	21.51	21.67	21.98	22.14	0.22	21.97	20.81	20.87	20.96	20.92	20.92	0.25	20.14	19.92	19.52	19.86	0.39	20.87	1.73
IC _{8-A}	19.89	20.08	19.99	0.23	21.14	20.56	20.84			20.85	0.40	20.65	20.74	20.82	20.63	20.75	20.72	0.25	18.17	18.82	18.25	18.41	0.40	19.99	2.24
IC _{9-A}	21.12	21.05	21.08	0.24	22.34	22.44	21.73	21.25	22.39	22.14	0.31	19.17	19.21	19.87	19.94	20.35	19.71	1.01	19.99	19.57	20.97	20.18	0.81	20.78	2.15
IC _{10-A}	17.67	17.95	17.81	0.27	18.53	18.51	18.55	18.47	17.79	18.52	0.31	16.01	15.52	16.09	15.72	16.09	15.84	0.53	16.10	15.20	15.63	15.64	0.51	16.95	2.86
IC _{11-A}	15.67	15.87	15.77	0.33	15.82	16.44	16.38	16.59		16.31	0.35	14.87	14.38	14.56	14.93	15.42	14.83	0.79	14.88	14.33	14.60	14.60	0.39	15.38	1.60

^a Repeat dissolutions of samples are labelled with consecutive letters.

^b Data in italics are rejected as outliers.

^c Uncertainty at the 95% confidence level, either reproducibility of the values presented or the external precision (whichever is larger).

each measured standard solution on which the variation of instrumental mass fractionation is typically small (0.1‰ on average) and is considered linear. Samples are added to the rack at the time of analysis, so minimal aerial contamination occurs. Samples IC_D and IC₁ to IC₁₁ were measured three times in succession according to the following sequence: standard₁–sample₁–standard₂–sample₂–standard₃–sample₃–standard₄. Such a sequence yields five successive $\delta^{11}\text{B}$ values (see Tipper et al., 2008). If, during the course of the run, two consecutive ratios measured for the bracketing standard solution deviate by >0.2‰, the sample value is rejected.

The day to day consistency of $\delta^{11}\text{B}$ measurements was checked by measuring a ¹⁰B enriched standard (SE43) and seawater NASS-5 processed through chemistry every 10 samples. Long term reproducibilities for these in-house reference materials are $39.85 \pm 0.24\text{‰}$ for seawater NASS5 (2sd, n = 61) and $-43.15 \pm 0.25\text{‰}$ for SE43 (2sd, n = 74) (Louvat et al., 2011). Accuracy has been assessed using two sets of gravimetric mixtures of boric acid standards NBS951 and NBS952, and of NBS951 and boron extracted from seawater NASS5, with $\delta^{11}\text{B}$ between -90‰ and $+40\text{‰}$, and between -2.0 and $+2.5\text{‰}$ respectively (Louvat et al., 2011). By doing so, we showed that, despite external reproducibilities of $\pm 0.25\text{‰}$ (2sd), d-DIHEN measurements clearly discriminate boron isotope compositions distinct by only 0.25‰ (Louvat et al., 2011). Corals already analysed by Gaillardet and Allegre (1995) by positive ion TIMS were run with this method and yielded identical $\delta^{11}\text{B}$ values (Louvat et al., 2011).

Samples IC_D and IC₁ to IC₁₁ are measured three times in a row and average and standard deviation were evaluated out of the 5 values issued from the 3 bracketing standards (see Tipper et al., 2008). The 2sd values reported in Tables 4 to 6 are calculated from at least 3 measurements (except for IC_A and IC_B) of the same solution. Chemical purification duplicates or triplicates were performed for samples IC_A to IC_D.

3.3. NTIMS at LDEO

At LDEO, boron isotopes are measured as BO_2^- ions on masses 43 and 42, using a Thermo Scientific Triton multi-collector TIMS. Sample preparation for isotope analysis includes oxidative treatment of crushed carbonate samples with NaOCl or hot buffered H_2O_2 to remove organic matter, and dissolution of the cleaned carbonate in 2 M suprapure HCl (Fisher Optima, <100 ppt B; pg/g). Samples are dissolved immediately before they are loaded for analysis, and they are centrifuged to separate any insoluble residue. One microliter of boron free seawater, prepared with Amberlite IRA-743 anion exchange resin, is first loaded onto outgassed zone refined rhenium filaments, followed by a 1–2 μl aliquot of sample solution containing a total of ~1.5 ng of boron. For this study, precise boron concentrations of individual samples were provided by G. Foster (Table 1) and the acid addition was determined accordingly, however, typically we measure boron concentrations for a few exemplary samples and use the lowest concentration as a guideline for how much acid to add. As long as at least 1 ng of B is loaded onto each filament, the accuracy of this approach is not very important, as loading tests of sample solutions containing 1 to 2 ng of boron yield the same $\delta^{11}\text{B}$ within analytical uncertainty. The loaded solutions are then evaporated at an ion current of 0.5 A until the load is reduced to a gel, and subsequently mounted into the mass spectrometer. Sample cleaning and loading are done in PTFE (boron free) filtered laminar flow benches and the total blank (including the blank of the B-free seawater) of these analyses (determined by ID-TIMS) is 10 ± 3 pg, or ~1% of the boron in the sample.

Isotope analyses by TIMS are subject to time-dependent in-run mass fractionation. Mass fractionation therefore has to be kept minimal and a strict analytical protocol has been developed for data collection and acceptance. Mass fractionation can be minimised by heating the sample slowly over a period of 25 min until the analysis temperature of 980 °C is reached. The signal intensity is then optimised by repeated

ion beam focusing, until a minimum signal intensity of 100 mV is reached and the signal intensity is stable or slowly rising. This can take 5–10 min, and in few cases the temperature has to be increased further (up to 1020 °C) to yield 100 mV, however, in all cases some aliquots are successfully measured at 980 °C and comparison of carbonate data shows no systematic difference in aliquots measured across this temperature range. Data collection starts immediately upon achieving the 100 mV signal. Data are acquired for a minimum of 25 min giving 240 ion ratios, and up to 45 min and 400 ratios for small signal intensities. In-run fractionation is considered excessive and unacceptable if the 43/42 ratio of an analysis increases by >0.004 (i.e. 1‰ in $\delta^{11}\text{B}$) over the data collection period (25–45 min), and such analyses are excluded from further consideration. In addition to mass fractionation, it has also been suggested that organic matter can form CNO^- molecules, which could interfere on mass 42 and bias the boron isotope ratio (Hemming and Hanson, 1994). At the beginning of each analysis, the presence of potential organic matter interference is monitored by scanning for CN^- on mass 26, using an electron multiplier, and analyses with elevated (>2000 counts/s) mass 26 counts are rejected. Data rejection based on this second criterion is extremely rare, as the signal on mass 26 is typically very low (60–200 counts/s).

Given the large number of isotope ratios (240–400) measured on each individual aliquot, the 2σ internal precision of NTIMS analyses is consistently better than 0.1‰, significantly lower than external reproducibility. The long-term instrumental mass bias of TIMS measurements is stable and not subject to drift. This is confirmed by repeat measurements of standards, which follow a normal distribution in $^{11}\text{B}/^{10}\text{B}$. The long-term average 43/42 ratio of SRM NIST 951 (used for normalisation of all samples) is 4.0026, with 2sd of 0.0043 (1.1‰, $n = 133$); given comparable mass fractionation on samples and standards the uncertainty on normalisation is thus 0.0004 (2se; equivalent to $\pm 0.09\%$). The repeatability of carbonate samples is estimated as 2se ($2\text{sd}/\sqrt{n}$) of repeat measurements of the same sample solution, where a minimum of 3 acceptable analyses is required. As described above, only those analyses are considered acceptable that neither fractionate excessively, nor display significant signal on mass 26. These are quantitative criteria and are not subject to operator bias or interpretation. In practice, the data population for a sample often includes 4–8 acceptable analyses but occasionally an analysis that meets the fractionation and interference criteria deviates by >2sd from the median of all acceptable analyses of a sample solution (where 2sd is calculated including this outlier). Such a deviation from the median is indicative of an analytical artefact and such an analysis is therefore excluded from the sample average as an analytical outlier. Data are finally reported as the average of the acceptable data population (excluding outliers) and 2se of this population is reported.

In addition to seawater and NIST SRM 951 boric acid standard we also routinely measure an in-house carbonate standard, which is NIST SRM 951 precipitated in CaCO_3 (vaterite) and loaded with boron free seawater, similar to carbonate samples and NIST SRM 951. The reproducibility of this in-house standard provides a measure for the external reproducibility of carbonate analyses by NTIMS. 2sd of 60 (out of 73 total) acceptable individual analyses of this standard measured over the study period is 0.62‰. As we average together individual sample analyses, reproducibility is given at 2se = 0.36‰ ($n = 3$), 0.31‰ ($n = 4$), 0.28‰ ($n = 5$), 0.25‰ ($n = 6$), 0.23‰ ($n = 7$) and 0.22‰ for $n = 8$ acceptable analyses. The reported uncertainty is either the 2se estimated from repeat analyses of a particular sample, or the 2se external reproducibility of the in-house carbonate standard for the respective number of repeat analyses, whichever is larger.

Similar to the MC-ICPMS studies described above, boric acids (BIG-D, BIG-E and UMD) do not require any chemical pre-treatment and stock solutions were diluted with boron-free MilliQ to 1 ppm [B], and 1 μl aliquots were loaded onto outgassed zone refined Re filaments with 1 μl boron free seawater. These boric acids are measured at the same temperature as the carbonate samples but it was found that the boric

acids ionise excessively at 980 °C compared to the carbonates, leading to somewhat greater in-run fractionation, the 2se reproducibility of 3 boric acid measurements ($\pm 0.60\%$) is not as good as that of 3 measurements of a carbonate sample ($\pm 0.36\%$) and the external reproducibility for boric acid analyses is therefore reported as either the value estimated from repeat sample analysis, or that of an equal number of analyses of the NIST SRM 951 standard, whichever is larger.

3.4. NTIMS at Duke

Boron isotopes in CaCO_3 were measured by negative thermal ionisation mass spectrometry at Duke University following an alternative procedure currently under development (Dwyer and Vengosh, in prep.), which is briefly described here. The principal difference of this alternative procedure from the more traditional NTIMS approach (e.g., see Section 3.3) is that Ca and other cations are removed from digested calcium carbonate samples prior to analysis via column-method or batch-method cation exchange. In addition, rather than the commonly used boron-free seawater, this alternative NTIMS procedure uses a filament loading solution prepared from ICP-MS-grade single-element solutions of sodium, magnesium, calcium, and potassium with final concentrations of approximately 8000 ppm, 1300 ppm, 500 ppm, and 400 ppm, respectively with a resultant certified boron blank of <30 ppt (pg/g). The advantages of this alternative procedure are: (1) the load solution requires only simple mixing of off-the-shelf solutions, thereby reducing preparation steps, minimising potential contamination by boron-blank, and avoiding possible inadvertent introduction of CNO^- molecular interference that may be derived from the boron-specific resin (e.g., Hemming and Hanson, 1994; Foster et al., 2006) used in preparing the more traditional filament load solution, boron-free seawater; and (2) the removal of Ca from samples results in a boric acid solution that much better approximates the NIST SRM 951 boric acid standard solution used for boron isotopic normalisation. Results thus far indicate that samples (and standards) prepared and analysed using the alternative procedure ionise at ~ 900 °C and typically display negligible molecular interference (typically less than 500 cps for CN^-) and minimal mass dependent fractionation (typically 0.2 to 0.5‰ for 60 min of analysis). Furthermore, samples pre-heat and ionise in a similar and predictable pattern, thus allowing fully-automated heating and analysis, thereby reducing analyst labour, increasing sample throughput, and reducing potential analytical inconsistencies associated with operator-controlled heating and analysis. One disadvantage of the alternative procedure is that it is not yet well-designed for small CaCO_3 samples, such as samples IC_{1–11} analysed in this study, which were 2 to 20 times smaller than typically preferred thus far with this method. Such small samples are challenging because the cation exchange procedure leads to dilution of sample boron from exchange-resin preconditioning acid and from the practical limits on liquid volumes that can easily be handled. Thus, the dilution effects increase as the sample size decreases. These factors in turn limit the amount of boron that can be effectively loaded onto a filament, potentially decreasing the signal-to-noise ratio, increasing the possible influence of isobaric molecular interferences, and, perhaps most importantly, increasing the potential influence of any blank contamination. While the filament loading blank has been measured to be less than 15 pg B, characterizing a total procedural boron blank is complicated because of a number of difficulties in properly mimicking the processes that take place during cation exchange of a dissolved CaCO_3 sample, and in effectively measuring the isotopic composition of such a small amount of boron due to inherently low signal-to-noise ratio and possible increased influence of isobaric interference from CNO^- . A preliminary total procedural blank analysis (filament loading blank plus an aliquot of acid solution passed through a 200 μl batch-method cation-exchange sequence) yielded a blank of around 20 pg with a $\delta^{11}\text{B}$ of approximately -12% . The accuracy of this isotopic composition is quite uncertain, but the measured $\delta^{11}\text{B}$ may be artificially low as the relative influence

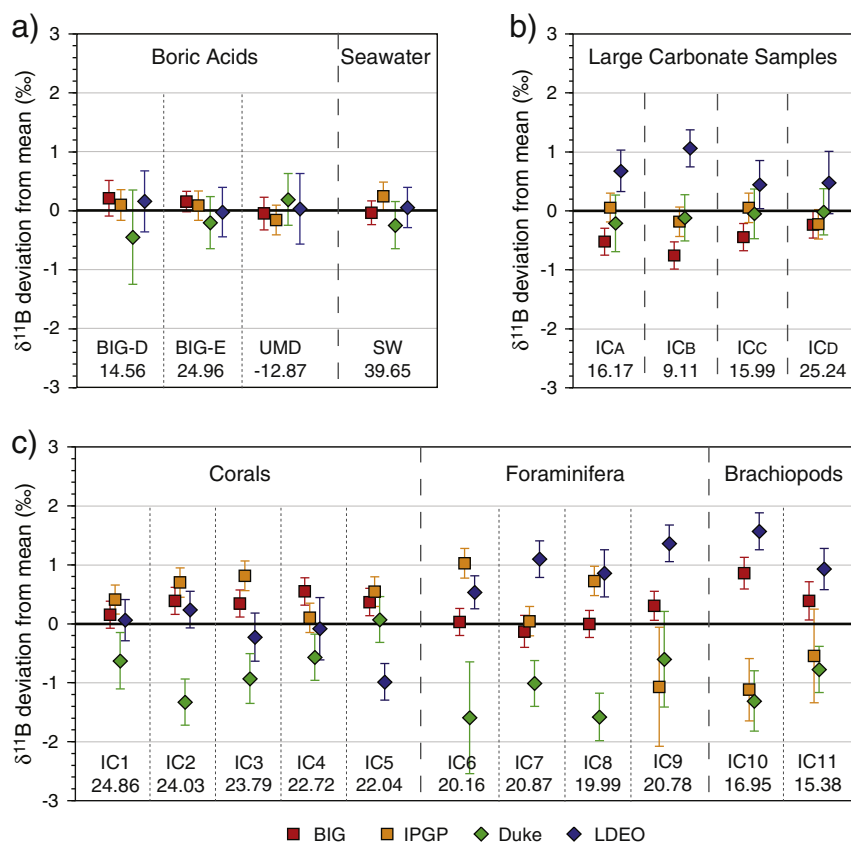


Fig. 1. Centred boron isotope ratios, calculated by subtracting the interlaboratory mean for each sample from the individual $\delta^{11}\text{B}$ value reported for that sample by each laboratory. a) Boric acids BIG-D, BIG-E and UMD, and seawater. b) Carbonate samples $\text{IC}_{\text{A-D}}$, where 700–3000 ng B was available for analysis. c) Carbonate samples IC_{1-11} where <200 ng of B was available for analysis. Different samples are separated by dotted lines, and different sample matrices are separated by dashed lines. The interlaboratory mean $\delta^{11}\text{B}$ for each sample is indicated (in ‰) under each sample name. Lab abbreviations are: Bristol Isotope Group (BIG), Lamont Doherty Earth Observatory (LDEO), Institut de Physique du Globe de Paris (IPGP), Duke University (DUKE). Error bars are at 95% confidence as discussed in the text.

of CNO^- appears to be ~1000 times greater than observed in typical sample runs. Blanks were measured via NTIMS isotope dilution using spike solution prepared from NIST SRM 952. The prepared NIST SRM 952 spike solution was verified by measuring the boron concentration of NIST SRM 1643e water standard with certified boron concentration. Due to the uncertainties surrounding the character of the blank, no correction has been made to any of the data reported here. For our typical preferred sample size, in which 3–10 ng of boron is loaded onto the filament, blank contribution appears to be negligible based on preliminary results of analysis of reference materials across a wide range of boron isotopic compositions ($\delta^{11}\text{B}$ ~+ 40‰ to -21‰), including groundwater IAEA B3, coral JGS JcP-1, both of which underwent cation exchange, and ERM boric acids (AE120, AE121, AE122) which were diluted and analysed using the alternative load solution described above. Respectively, measured $\delta^{11}\text{B}$ values for B3, JcP-1, and AE120, AE122, AE122 were: -21.47‰ (se = 0.46, n = 3), +24.33‰ (se = 0.11, n = 8), -20.10‰ (se = 0.14, n = 5), +19.64‰ (se = 0.23, n = 11), +39.56‰ (se = 0.17, n = 6), all within 2se error of published values (JcP-1, Wang et al., 2010; B3, Gonfiantini et al., 2003; AE120-122, Vogl and Rosner, 2012). For smaller amounts of boron, blank may indeed have an impact. In addition to potential blank issues with small samples, the alternative procedure may promote, as yet un-quantified, fractionation during the dry down and loading of relatively large volume, and hence dilute, sample solutions (e.g., Xiao et al., 1997).

Prior to analysis, the CaCO_3 samples in this study were digested in 40 to 400 μl (depending on sample size) of quartz-distilled 2 M HCl and subjected to cation exchange using AG50W-X8 resin to remove calcium and other cations. The resin was preconditioned with quartz-distilled

H_2O , 6 M HCl, and finally 2 M HCl. Samples $\text{IC}_{\text{A-D}}$ were transferred to acid-washed PFA vials prior to digestion whereas samples IC_1 – IC_{11} were digested in the original polypropylene micro-centrifuge tubes received. The IC CaCO_3 samples received no cleaning or additional pretreatment at Duke prior to digestion. Following digestion and cation exchange, samples were reacted for a minimum of 24 h with ultra-pure H_2O_2 (Fisher Optima) at a ratio of approximately 1:10 (v/v) to oxidise any remaining organic matter. Two to twelve microliters of sample solution was loaded onto single rhenium filaments in an attempt to achieve an estimated minimum load of at least 1 ng of B. The exact amount of boron loaded is not known as the boron concentration of the final sample solutions was not measured due in part to limited sample. Prior to loading the sample, 2 μl of load solution was loaded onto the filament and the combined solution was dried and final-heated at 0.5A and 0.8 A, respectively. NIST SRM 951 standard solution with a concentration of ~5 ng/ μl was loaded and analysed in a similar fashion. Samples and standards were then analysed in negative-ion mode on a Thermo Scientific Triton at Duke University. Further details of the alternative NTIMS procedure will be described elsewhere (Dwyer and Vengosh, in prep.).

External reproducibility of this approach, assessed through repeat measurements of an in-house *Porites* coral standard, is $\pm 0.38\%$ (2sd; n = 15). Analyses of NIST SRM 951 during the analytical period gave a $^{11}\text{B}/^{10}\text{B} = 4.0065 \pm 0.0003$ ($\pm 0.1\%$ 2se; n = 38). A quadratic addition of this uncertainty with the external reproducibility gives an external precision of this approach, at 95% confidence, of $\pm 0.39\%$. Quoted precisions for $\text{IC}_{\text{A-D}}$ and IC_1 – IC_{11} are the larger of either this external precision or the observed reproducibility (2se) of repeat measurements of

samples (including the quadratic addition of uncertainty in the $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951; Tables 4 to 6).

4. Results and discussion

Boron isotope data for seawater, boric acids and intercomparison calcium carbonate samples $\text{IC}_A\text{--IC}_D$ and $\text{IC}_1\text{--IC}_{11}$ are presented in Tables 4 to 6. To allow different samples to be easily compared, Fig. 1 shows the offset of each laboratory's reported $\delta^{11}\text{B}$ value for a given sample from the overall interlaboratory mean for that sample. We refer to samples treated in this way as being "centred".

4.1. Boric acids and seawater

The $\delta^{11}\text{B}$ values reported for the three boric acids (BIG-D, BIG-E and UMD) show a very good agreement between the four laboratories (Table 4 and Fig. 1a), with overall means and 2sd of: $14.56 \pm 0.61\%$, $24.96 \pm 0.31\%$ and $-12.87 \pm 0.29\%$ for BIG-D, BIG-E and UMD, respectively. Each laboratory's centred $\delta^{11}\text{B}$ value is within its reported measurement uncertainty of the interlaboratory mean. Although the interlaboratory average $\delta^{11}\text{B}$ values for BIG-D and BIG-E are slightly offset from the gravimetric values ($\pm 1\%$ weighing error) of $15.4^{+0.2}_{-0.3}\%$ and $25.6^{+0.3}_{-0.8}\%$, probably due to larger than accounted for weighing errors or incorrect end-member $^{11}\text{B}/^{10}\text{B}$ values, regardless this level of interlaboratory agreement is very encouraging. This agreement also confirms the observations of Aggarwal et al. (2004) that there are inherently no analytical biases between the different analytical techniques used here, provided strict analytical protocols are followed. Also, our

results are in stark contrast to the study of Aggarwal et al. (2009) where a number of laboratories using similar analytical techniques to those used here exhibited a range of $\sim 4\%$ for a similar study of boric acid solutions.

The $\delta^{11}\text{B}$ reported for the seawater by the four laboratories, like the boric acids, is in very good agreement with an overall mean $\delta^{11}\text{B} = 39.65 \pm 0.41\%$ (2sd). The centred $\delta^{11}\text{B}$ values of each laboratory are also within measurement uncertainty of this interlaboratory mean (Fig. 1 and Table 4). These data imply that a seawater matrix does not induce any significant discrepancy among laboratories either during mass spectrometric measurement or during boron purification. Earlier interlaboratory studies also analysed seawater samples (IAEA-B1; Gonfiantini et al., 2003) and, although similar $\delta^{11}\text{B}$ values were reported by most laboratories, the range in values was considerably higher (around 2%).

4.2. Calcium carbonates

The $\delta^{11}\text{B}$ of the calcium carbonate samples used for the intercomparison varies from $\sim 9\%$ to $\sim 25\%$ and so largely spans the range of $\delta^{11}\text{B}$ typical of marine carbonates (e.g., Vengosh et al., 1991; Hemming and Hanson, 1992; Fig. 1b & c and Tables 5 and 6). The variability in the $\delta^{11}\text{B}$ reported for each sample (reflected by the 2sd of the 4 values) ranges from 0.65 to 2.86%, with a pooled 2sd of $\pm 1.46\%$ for the whole sample set. This is larger than reported measurement uncertainties, and is also larger than the 2sd of the boric acid and seawater samples (pooled 2sd of 0.38%; Table 4 and Fig. 1). While this variability is a concern, it is important to note that it is significantly lower than that reported for a Miocene marine limestone sample in previous interlaboratory comparisons, which had a range of around $\pm 7\%$ (IAEA-B7; Gonfiantini et al., 2003). Since we see no significant interlaboratory bias in $\delta^{11}\text{B}$ for boric acids and seawater (Fig. 1 and Table 4), this increased variability must relate in some way to the CaCO_3 sample matrix.

4.3. The potential causes of interlaboratory variation in $\delta^{11}\text{B}$ of CaCO_3

The observed variations in $\delta^{11}\text{B}$ for samples with a CaCO_3 matrix may arise for a variety of reasons depending on the analytical technique, but there are several common factors. These include: (i) sample matrix, or residual matrix after purification, which can cause differential ionisation of samples compared to the normalising NIST SRM 951 standard. In all cases this will result in inaccurate $\delta^{11}\text{B}$. (ii) For those techniques where matrix is removed, isotopic fractionation can occur during the purification on Amberlite IRA 743 anionic exchange resin as the initial column eluants are enriched in ^{11}B and the final eluants are depleted in ^{11}B (e.g., Lemarchand et al., 2002b). (iii) Laboratory blank can influence the measured $\delta^{11}\text{B}$ of the CaCO_3 samples more so than boric acid and seawater, as for all techniques the analysis of CaCO_3 requires more handling and treatment (see Section 3). (iv) The different cleaning techniques practised by each laboratory (see Section 3) may have influenced the measured isotope ratio. (v) All samples were prepared and split by hand and part of the increased level of disagreement may be related to the heterogeneity of the sample powders analysed given the $\delta^{11}\text{B}$ heterogeneity that can exist in some organic calcium carbonates (e.g., Blamart et al., 2007).

Given that the overall mean reproducibility of sample set $\text{IC}_1\text{--IC}_{11}$ (pooled 2sd of $\pm 1.62\%$), which was all cleaned in one laboratory (at LDEO; Section 3), is actually larger than that of $\text{IC}_A\text{--IC}_D$ (pooled 2sd of $\pm 0.93\%$), which was cleaned in a number of different ways (see Section 3), it is unlikely that the different cleaning protocols followed by each laboratory play a significant role in generating the observed variability. Despite the efforts taken to ensure sample homogenisation, sample heterogeneity (i.e. nugget effects) may be a compounding factor, particularly for the smaller samples in set $\text{IC}_1\text{--IC}_{11}$. However in three laboratories, several completely separate aliquots of sample set

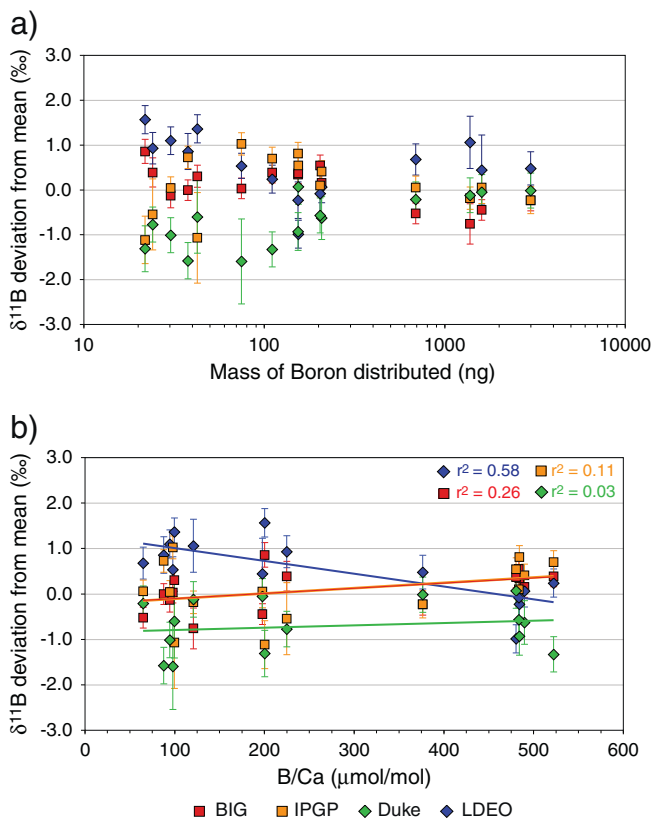


Fig. 2. Plot of centred data vs. total amount of B distributed to each lab (a) and sample B/Ca ratio (b). Note that, as each point represents the difference from the mean interlaboratory value, a strong trend in one dataset in one direction will produce slight trends in the opposite direction in the other datasets. With this caveat in mind, we note that: (i) in (a) for small samples there is a correlation with sample amount in the labs where blank was not closely controlled (i.e. IPGP and DUKE); (ii) in (b) there is a correlation with B/Ca in the LDEO analyses where matrix was not removed. Abbreviations and other details as discussed in the caption for Fig. 1.

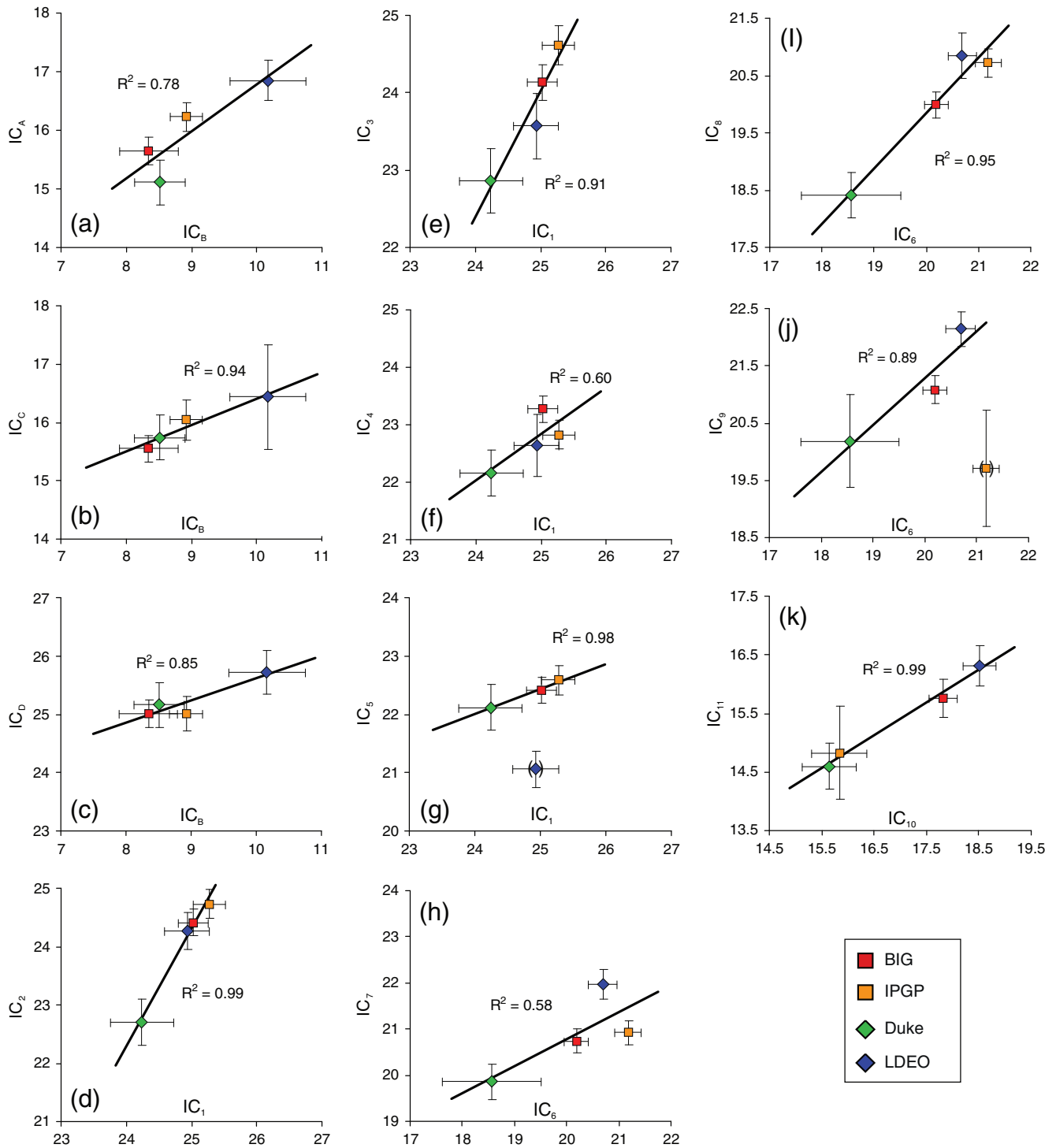


Fig. 3. Cross plots of reported $\delta^{11}\text{B}$ for each sub-set of samples: IC_A – IC_D (a–c), IC_1 – IC_5 (d–g), IC_6 – IC_9 (h–j) and IC_{10} – IC_{11} (k). Error bars are at 95% confidence as discussed in the text. Best fit lines and associated R^2 are also shown. Where obvious outliers have been identified (highlighted by parentheses), best fit lines have been drawn from the remaining laboratories only.

IC_A – IC_D were processed, and typically yielded values within uncertainty (Table 5). This suggests that, for this sample set at least, sample heterogeneity is unlikely to be a major cause of the observed $\delta^{11}\text{B}$ variability.

A comparison of the mass of boron distributed with centred $\delta^{11}\text{B}$, shows that the extent of interlaboratory variability for CaCO_3 samples roughly increases as sample size decreases (Fig. 2a). For sample set IC_A – IC_D , where between 700 and 3000 ng of B was available, the data have a pooled 2sd of 0.93%, but for sample set IC_1 – IC_{11} variations of up to $\pm 2.9\%$ are observed, with a pooled 2sd of 1.62%. Although

analytical uncertainty may increase with smaller sample size (due to counting statistics and increased influence of Johnson noise), this cannot explain the increase in scatter here, which is much larger than reported measurement uncertainties.

A comparison between the B/Ca ratio of the measured CaCO_3 with centred $\delta^{11}\text{B}$ shows very little correlation for all laboratories except LDEO, where there appears to be an increasing deviation from the interlaboratory mean with decreasing B/Ca ratio (Fig. 2b). We note that, in this treatment, the trend of an individual laboratory may be influenced by trends in the other laboratories. However the trends

Table 7
Correlation matrix for interlaboratory CaCO₃ samples showing R² of cross plots of δ¹¹B reported by each laboratory.

	IC-A	IC-B	IC-C	IC-D
IC-A		0.78	0.76	0.45
IC-B	0.78		0.94	0.85
IC-C	0.76	0.94		0.68
IC-D	0.45	0.85	0.68	

	IC-1	IC-2	IC-3	IC-4	IC-5
IC-1		0.99	0.91	0.60	0.98
IC-2	0.99		0.85	0.65	0.98
IC-3	0.91	0.85		0.61	0.99
IC-4	0.60	0.65	0.61		0.49
IC-5	0.98	0.98	0.99	0.49	

	IC-6	IC-7	IC-8	IC-9
IC-6		0.58	0.95	0.89
IC-7	0.58		0.79	1.00
IC-8	0.95	0.79		0.96
IC-9	0.89	1.00	0.96	

	IC-10	IC-11
IC-10		0.99
IC-11	0.99	

Numbers in italics have one outlier removed identified in Fig. 3.

described above are robust to any such effects, as systematic removal of each laboratory in turn does not change these overall patterns.

Given the range of techniques and the variable number of analyses performed by each laboratory, it is hard to systematically constrain the exact cause of these relationships. We encourage future studies to examine these effects in detail. However, it is likely that two plausible mechanisms may at least in part influence this behaviour: (i) contamination by laboratory blank during sample handling; and (ii) matrix effects during analysis. These issues represent the different consequences of contrasting strategies for addressing the same analytical problem. Sample matrix can be removed by chemical separation, but this increase in handling results in an increase in blank contribution. If matrix is not removed, however, samples with different matrices will inevitably behave differently, to some extent, during analysis. We examine in turn how each of these processes might influence the data produced in this study.

Smaller samples, with lower amounts of boron are more susceptible to the influence of blank. Increased interlaboratory variation in δ¹¹B for the samples with lower amounts of boron should be evident if there is a

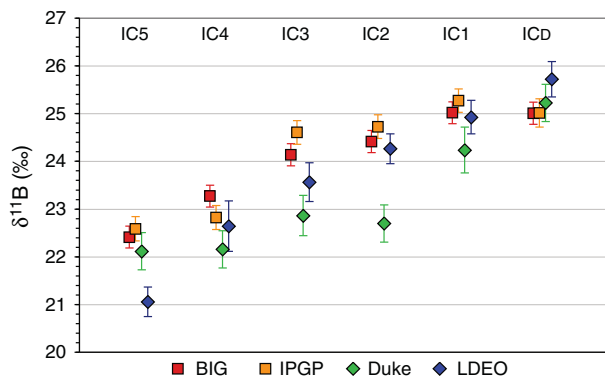


Fig. 4. Coral δ¹¹B (samples IC₁₋₅ and IC_D) reported by each laboratory. Relative differences in δ¹¹B for this sample set are reproduced with 2sd of 1.09%.

significant but different blank in the participating labs. This may be the case for the sample set IC₁₋₁₁, where the small amounts of each sample distributed replicated scenarios where samples are limited, such as for hand separated foraminifera. Given that some laboratories had not optimised their procedures for such small samples, a blank influence is not unexpected for this sample set. As discussed in Section 3, it was known that the blank for the procedure under development at Duke might be problematic for small samples. Notably in the Duke analyses, δ¹¹B is often offset below the overall mean for samples IC₁₋₁₁ (Fig. 2a). This is consistent with some contribution of laboratory blank, which is typically isotopically light (e.g. Rae et al., 2011). Those samples where more B was available for analysis show less variability (Fig. 2a). Indeed, this may at least partially explain the good agreement observed for seawater, as less processing is required for this matrix for all techniques and seawater samples tend to be of a larger volume and so contain more boron in total. Unfortunately, insufficient information was recorded to make quantitative assessments of the influence of the blank in all cases, although this is something that can be readily done in future studies.

However, it is important to note that blank cannot explain all of the observed interlaboratory bias, as samples with >200 ng B available for analysis still show significantly more variability (pooled 2sd of ± 0.88‰) than boric acids and seawater (pooled sd of ± 0.38‰). All reported procedural blanks will have a <0.1% influence on the δ¹¹B of a sample with 200 ng of boron. Blank should also only be a minor concern in the samples IC_{A-D}, for which abundant material (>700 ng B) was available for analysis, yet there is still an interlaboratory variability of up to ± 0.8‰ (Fig. 2a; Table 4). A matrix effect is therefore more likely to be the cause in this case. This should generate a contrast between the three labs where matrix is removed and the LDEO NTIMS analyses, where samples are loaded onto filaments in their dissolved CaCO₃ matrix. The ratio of boron to matrix loaded carbonate will vary with changing B/Ca in these NTIMS analyses, potentially inducing a systematic bias. Indeed the LDEO measurements are heavier than the analyses from the other labs in which matrix has been removed and with a magnitude somewhat dependent on sample B/Ca (Fig. 2b). However, it is difficult at this stage, and with this sample set, to pinpoint the respective source of any matrix effect in each method. Moreover, for many applications, it is not the reported δ¹¹B that is of importance but the relative differences between samples of similar matrix and we investigate this further in the following section.

4.4. Relative differences of δ¹¹B of CaCO₃ samples

Whatever the exact reason for the observed interlaboratory range in absolute δ¹¹B, the variation is largely systematic, as illustrated in a representative cross-plot in Fig. 3. Correlation coefficients (R²) for linear regression of reported δ¹¹B for particular pairs of samples are all greater than 0.45 with an average of 0.81 (Table 7), confirming the highly systematic nature of the interlaboratory variation we observe for each sample sub-set that shares a common matrix (IC₁ to IC₅, IC₆ to IC₉, and IC₁₀ to IC₁₁) and similar total B (IC_A to IC_D, IC₁ to IC₅, IC₆ to IC₉, and IC₁₀ to IC₁₁). This is further illustrated by comparison of δ¹¹B variations for the coral samples (IC₁₋₅ and IC_D) (Fig. 4). This systematic variation is important because, although accurate δ¹¹B values are desirable, for many palaeoceanographic and palaeoclimate applications, relative differences in δ¹¹B can be used without unduly compromising palaeoclimate or palaeoceanographic interpretations.

5. Concluding remarks and recommendations

The results of this study indicate that there is no significant difference between the various analytical techniques used by the four laboratories involved in this study when samples with simple matrices such as boric acids are measured. Such an agreement is in contrast with previous interlaboratory comparisons (e.g., Aggarwal et al., 2009). A similarly good

agreement exists for analyses of seawater ($\delta^{11}\text{B} = 39.65 \pm 0.41\%$, 2sd), and again this is a significant improvement on earlier interlaboratory comparison exercises (e.g., $37.67 \pm 2.09\%$, 2sd; Gonfiantini et al., 2003). However, consistent with the study of Gonfiantini et al. (2003), we find that for samples with a CaCO_3 matrix significant variation in reported $\delta^{11}\text{B}$ exists, but in our case these are often smaller (pooled 2sd of 1.46%) and largely systematic. We also present evidence suggesting that the interlaboratory variations observed in $\delta^{11}\text{B}$ are related in some way to the size of the sample (in terms of total B available) and/or the B/Ca (i.e. boron to matrix ratio) of the analysed samples, although the exact mechanism responsible is not yet clear at this stage.

This study is far from an exhaustive investigation but does point to ways in which interlaboratory variation in absolute $\delta^{11}\text{B}$ can be reduced and should serve as a guide to other laboratories interested in analysing $\delta^{11}\text{B}$ in marine carbonates. Specifically, and in light of the relationships between interlaboratory variation and sample size we observe, we suggest that interlaboratory variation in absolute $\delta^{11}\text{B}$ for CaCO_3 samples may be reduced by:

- (i) Minimising and quantifying the extent of boron contamination during every step of sample processing.
- (ii) Assessing the effect of sample size on measured $\delta^{11}\text{B}$ and external reproducibility.
- (iii) Understanding and minimising the causes of “matrix” effects specific to each particular sample type and analytical protocol.

For palaeoceanographic applications relative differences in $\delta^{11}\text{B}$ can be useful. The four laboratories investigated here are largely able to reproduce relative changes in $\delta^{11}\text{B}$, for a sample set of similar [B], B/Ca ratio and matrix (e.g., coral, foraminifera, brachiopod). However, despite this encouraging agreement, these results clearly demonstrate the need for a suite of well-characterised marine carbonate reference materials for boron isotope analysis. This would allow for a much better comparison between laboratories and provide the materials necessary for future studies to investigate and minimise interlaboratory variations in absolute $\delta^{11}\text{B}$. The Japanese Geological Survey coral (JcT-1) and giant clam (JcP-1) reference materials are clearly steps in this direction (e.g., Wang et al., 2010). However more effort is needed by the boron isotope community to make, characterise and distribute secondary reference materials to ensure the most accurate $\delta^{11}\text{B}$ data are produced.

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