Single laboratory comparison of MC-ICP-MS and N-TIMS boron isotope analyses in marine carbonates

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Abstract

Measurements of boron isotopes ($\delta^{11}\text{B}$) in marine carbonates are an important tool for reconstructing past ocean acidity and atmospheric carbon dioxide levels, but are challenging to obtain due to low boron concentrations and the presence of only two stable boron isotopes. Previous studies have observed differences in absolute $\delta^{11}\text{B}$ values of marine carbonates measured via negative thermal ionization mass spectrometry (N-TIMS) and multicollector inductively coupled mass spectrometry (MC-ICP-MS) that are relatively large compared to magnitudes of $\delta^{11}\text{B}$ variability in paleoceanographic studies. Here we investigate the cause of these $\delta^{11}\text{B}$ offsets and implications for paleo-pH reconstructions by performing N-TIMS and MC-ICP-MS measurements within the same laboratory on a suite of eighteen homogenized samples, including inorganic calcites grown under controlled pH conditions and Quaternary planktic foraminifera. Results show that $\delta^{11}\text{B}$ values between both measurement techniques are highly correlated ($R^2 > 0.99$), but calcite $\delta^{11}\text{B}$ values are ~ 0.5 to 2.7‰ lower when measured by MC-ICP-MS compared to N-TIMS. The $\delta^{11}\text{B}$ offset between techniques cannot be attributed to procedural blank contribution, but the magnitude of offset moderately correlates with indicators of sample chemical composition, including B/Ca, Mg/Ca and $\delta^{18}\text{O}$ ($R^2 = 0.39$ to 0.50). N-TIMS $\delta^{11}\text{B}$ does not change with calcium addition to a biogenic carbonate sample, suggesting that varying calcium abundance between samples and standards is not the reason for N-TIMS “matrix effects”. Correlation between $\delta^{18}\text{O}$ and the $\delta^{11}\text{B}$ offset is particularly apparent for calcites ($R^2 = 0.71$); the origin of this relationship is not clear, but is not likely due to ^{17}O interference. Although identifying the origin of measurement offsets requires further study, we demonstrate that such offsets do not affect the validity of $\delta^{11}\text{B}$ data: The sensitivity of $\delta^{11}\text{B}$ in inorganic calcite to pH is the same when measured by either technique, and paleo-pH reconstructed from $\delta^{11}\text{B}$ measurements in planktic foraminifera is equivalent within uncertainty when a technique-specific constant offset is applied. Our results strongly indicate that $\delta^{11}\text{B}$ measurements from both measurement techniques (N-TIMS and MC-ICP-MS) can be employed for paleo-pH reconstructions with equal confidence.

Key Words: Boron isotopes; paleo-pH; Negative thermal ionization mass spectrometry (N-TIMS); Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS); method intercomparison

1. Introduction

Naturally occurring isotopes of boron (^{11}B and ^{10}B) are fractionated between the two dominant boron compounds in seawater—boric acid and borate—by approximately 27 parts per thousand (‰, Klochko et al., 2006; Nir et al., 2015). This relatively large fractionation and the pH dependence of boron speciation in seawater comprise the theoretical basis for the boron isotope-pH proxy (Hemming and Hanson 1992). Boron isotope measurements are expressed in delta notation relative to the NIST951 boric acid standard reference material (Catanzaro et al., 1970):

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

Empirical studies show that $\delta^{11}\text{B}$ of carbonates varies as a function of the pH of the aqueous solution from which the carbonate precipitated (e.g., Sanyal et al., 1996; 2000; 2001; Hönisch et al., 2004; Rae et al., 2011; Henahan et al., 2013; Penman et al., 2013; Farmer et al., 2015). $\delta^{11}\text{B}$ in marine carbonates has been applied to reconstruct past ocean pH, from which surface ocean pCO_2 can be inferred (e.g., Hönisch and Hemming, 2005; Foster, 2008; Hönisch et al., 2009; Henahan et al., 2013).

Obtaining $\delta^{11}\text{B}$ measurements on marine carbonates with sufficient precision for paleo-pH and pCO_2 interpretation is difficult for several reasons. First, boron concentrations in marine carbonates are generally low (~5-70 ppm, Vengosh et al. 1991; Hemming and Hanson, 1992) and available sample material is often limited (typically ~0.5 to 2 mg of carbonate available for foraminifera analyses). This makes $\delta^{11}\text{B}_{\text{sample}}$ susceptible to contamination from handling and preparation blanks. In addition, the relatively large mass difference between ^{11}B and ^{10}B can result in large machine-induced isotopic fractionation during measurement. Boron lacks a third stable isotope, preventing normalization for such fractionation. Finally, typical $\delta^{11}\text{B}$ variations in marine carbonates are on the order of only a few parts per thousand. $\delta^{11}\text{B}$ measurement error is thus the principal source of uncertainty for interpretations of paleo-pH and pCO_2 (e.g., Hönisch and Hemming, 2005; Foster, 2008; Hönisch et al., 2009; Henahan et al., 2013).

The need for geochemical reconstructions of ocean acidity and atmospheric pCO_2 has fostered careful preparation and analytical techniques to obtain high $\delta^{11}\text{B}$ precision with minimal sample material. Two techniques are routinely applied for high-precision $\delta^{11}\text{B}$ measurements of small carbonate samples (< 10 ng B): negative thermal ionization mass spectrometry (N-TIMS;

Hemming and Hanson, 1994) and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS; Foster, 2008). Previous comparisons between these two approaches have found that, while boric acid solutions and seawater tend to replicate identically between N-TIMS and MC-ICP-MS techniques (Foster et al., 2013), foraminiferal carbonates tend to return lower $\delta^{11}\text{B}$ values via MC-ICP-MS than N-TIMS by ~ 1 to 2‰ (Foster, 2008; Ni et al., 2010; Rae et al., 2011; Foster et al., 2013; Henahan et al., 2013), and up to $\sim 6\text{‰}$ when distinct TIMS $\delta^{11}\text{B}$ procedures are considered (e.g., total evaporation N-TIMS, see Ni et al., 2010). As both N-TIMS and MC-ICP-MS techniques use the same standard for normalization (Equation 1), the nature of this offset and its implications for $\delta^{11}\text{B}$ proxy applications are debated. While the $\delta^{11}\text{B}$ offset between techniques appears constant for foraminiferal carbonates (Rae et al., 2011; Foster et al., 2013; Henahan et al., 2013), the underlying mechanism(s) accounting for different absolute $\delta^{11}\text{B}$ values between N-TIMS and MC-ICP-MS techniques, and implications of these differences for applications of the $\delta^{11}\text{B}$ -pH proxy, have not yet been thoroughly investigated.

Here we perform both N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ procedures on a suite of eighteen homogenized samples within a single laboratory, thus minimizing any influence from differential sample preparation procedures and handling blanks. This contribution extends beyond previous interlaboratory comparison studies (e.g., Foster et al., 2013) by assessing whether respective $\delta^{11}\text{B}$ measurement techniques affect pH translation. To test this, we measure $\delta^{11}\text{B}$ on a set of inorganic calcites precipitated from varying solution pH to compare the $\delta^{11}\text{B}$ -pH sensitivity for both techniques. We also reconstruct Quaternary surface ocean pH from downcore measurements of planktic foraminiferal $\delta^{11}\text{B}$ to assess the comparability of absolute pH reconstructions between techniques.

2. Materials and Methods

2.1 Materials used

The eighteen samples chosen for this comparison reflect several priorities: (1) A range of sample types and matrices encompassing material most commonly employed for $\delta^{11}\text{B}$ analysis in paleoceanography; (2) samples that reflect on the underlying theory of the $\delta^{11}\text{B}$ -pH proxy; and (3) consistency with previously analyzed intercalibration materials. We measured boric acid, inorganic calcite, foraminiferal ooze, and monospecific planktic foraminifera (*Globigerinoides*

sacculifer) samples previously used in the Foster et al. (2013) intercomparison study. To complement this set, we also measured inorganic calcites precipitated from NaCl-CaCl₂-B(OH)₃-Na₂CO₃ parent solutions of controlled pH and [Ca²⁺] using a seeded calcite overgrowth technique (Uchikawa et al., 2015), JCp-1 (modern *Porites sp.* coral) and JCt-1 (Holocene *Tridacna gigas* giant clam) biogenic aragonite reference materials (Inoue et al., 2004; Hathorne et al., 2013; Gutjahr et al., in prep.), and two samples of the benthic foraminifer *Cibicidoides wuellerstorfi* from Ocean Drilling Program Sites 1088 and 1264. Detailed sample information is given in Table 1.

Carbonate samples were homogenized and split into acid-cleaned 0.5 mL polypropylene vials. Inorganic calcites were rinsed ten times with boron-free MilliQ water (≥ 18.2 M Ω /cm) without additional chemical pretreatment. Biogenic carbonates were cleaned of organic matter by oxidation with 1% H₂O₂ following the procedure of Barker et al. (2003). All sample pretreatment was performed in a boron-free PTFE ultra-low particulate air (ULPA) filtered laminar flow bench at the Lamont-Doherty Earth Observatory (LDEO).

2.2. MC-ICP-MS methodology

MC-ICP-MS boron isotope analyses were performed following the methodology for boron separation and analysis given in Foster (2008) and Rae et al. (2011), with modifications for the LDEO laboratories as detailed below. For boron separation, a 2 M sodium acetate-0.5 M acetic acid solution was added to a clean 1 mL column of Amberlite IRA-743 and collected to create a boron-free buffer solution (Rae et al., 2011). Following the chemical cleaning described above, carbonate samples were dissolved in ultrapure 0.5 N HNO₃ (Fisher Optima grade, certified B blank <0.01 pg/ μ L) and buffered to pH ~ 5 by adding twice the acid volume of buffer solution (Foster, 2008). The buffered sample solution was then loaded on clean 20 μ L micro-columns of Amberlite IRA-743, the non-boron matrix washed off with eight sequential rinses of 200 μ L MilliQ water, and boron was eluted into clean 1.5 mL Savillex PFA vials with 450 μ L of ultrapure 0.5 N HNO₃ (Rae et al., 2011). An additional 90 μ L acid rinse was collected to test column recovery. Column chemistry was performed in the LDEO Ultra Clean laboratory facility in a dedicated workstation with B-free PTFE ULPA and molecular boron filters. Fall-in blanks were collected during column chemistry and yielded no more than 1-3 pg B/h.

Boron isotopes were measured on a Thermo Scientific Neptune Plus MC-ICP-MS in the LDEO ICP-MS facility. To overcome well-known boron washout problems (e.g., Al-Ammar et al., 2000), we used an Elemental Scientific Inc. 47 mm barrel-type PFA spray chamber and 50 $\mu\text{L}/\text{min}$ self-aspirating nebulizer with 5 mL/min of ammonia add gas (see Rae et al., 2011 and Foster et al., 2013), which reduced washout to 2% after 120 seconds. We used high-sensitivity ‘X’ skimmer and ‘Jet’ sample extraction cones to boost boron sensitivity (Misra et al., 2014). Although these cones also boost $^{40}\text{Ar}^{4+}$ and $^{20}\text{Ne}^{2+}$ intensity, which could potentially interfere on ^{10}B , any interference on ^{10}B is fully resolved in low-mass resolution mode (Foster, 2008; Wang et al., 2010; Misra et al., 2014). ^{11}B and ^{10}B were collected on Faraday cups with $10^{12} \Omega$ resistors in positions H4 and L4, respectively.

The sample analysis procedure includes sample-standard bracketing (SSB) with NIST 951 (Foster, 2008; Wang et al., 2010; Rae et al., 2011; Foster et al., 2013; Misra et al., 2014) and an on-peak zero rinse correction (e.g., Wei et al., 2014). A single sample analysis encompasses six measurements: Rinse-Standard-Rinse-Sample-Rinse-Standard, where rinse ^{11}B and ^{10}B are collected for ten ratios, standards are first peak-centered, then collected for thirty ratios, and finally samples are collected for thirty ratios without peak-centering. Total analysis time for a single SSB is approximately 30 minutes. Rinse ^{11}B and ^{10}B are subtracted from the following sample/standard, and then the rinse-corrected sample $^{11}\text{B}/^{10}\text{B}$ is reported as $\delta^{11}\text{B}$ relative to the bracketing, rinse-corrected standard $^{11}\text{B}/^{10}\text{B}$:

$$\delta^{11}\text{B}(\text{‰}) = \left[\frac{\frac{^{11}\text{B}_{\text{sample}} - ^{11}\text{B}_{\text{rinse}}}{^{10}\text{B}_{\text{sample}} - ^{10}\text{B}_{\text{rinse}}}}{\frac{1}{2} \sum \frac{^{11}\text{B}_{\text{NIST951}} - ^{11}\text{B}_{\text{rinse}}}{^{10}\text{B}_{\text{NIST951}} - ^{10}\text{B}_{\text{rinse}}}} - 1 \right] * 1000 \quad (2)$$

where the denominator is the average $^{11}\text{B}/^{10}\text{B}$ of the two rinse-corrected bracketing standards. All samples were first screened for sodium contamination on mass 23. Following Foster (2008), any samples with sodium concentrations greater than 10-fold blank concentration need to be discarded, which only affected two samples in this study. These two samples were discarded and reprocessed from undissolved carbonate material. In addition to sodium, sample boron concentration was screened and, when necessary, samples were adjusted to within 25% of 25 ppb B by dilution with ultrapure 0.5N HNO_3 . All bracketing standards were run at 25 ppb B ($\sim 0.5 \text{ V}$

on ^{11}B using $10^{12} \Omega$ resistors). Column recovery was tested by sample B concentration relative to B concentration in the additional rinse and always exceeded 99.7%.

Compared to the Foster (2008) and Rae et al. (2011) methodologies, we find greatest B signal intensity and stability at lower sample gas flow (0.8-0.9 L/min versus 1.2-1.3 L/min) and lower RF power (1150 W versus 1200-1400 W). Although signal intensity tends to decrease with decreasing sample gas flow and RF power, we find comparable signal intensities to previous studies (1.0 V on ^{11}B at 50 ppb, or 20 V per ppm). In the LDEO ICP-MS facility signal intensity and stability are also maximized by operating at a Z torch position of -0.3 to -0.5 mm, which may compensate for the lower sample gas flow and RF power by introducing the sample closer to the warmest core of the plasma and thus aiding ionization. With these operating conditions, sample gas tuning (Foster, 2008) is not necessary for maintaining isotope ratio stability over the course of an analysis session. Instead, tuning for maximum signal intensity and relative stability (i.e., signal intensity variations of less than 5%) provides sufficient stability for sample-standard bracketing even over extended analysis sessions (Figure A1).

$\delta^{11}\text{B}$ analytical uncertainty for our MC-ICP-MS measurements is given as two times the standard deviation (2sd) of all SSBs for each sample. Rae et al. (2011) present uncertainty as a function of sample boron intensity based on long-term standard analyses (e.g., analyses of a given standard across all tuned analytical sessions). As we match boron concentrations between samples and standards, a similar treatment of uncertainty is not given here. However, boric acid standard UMD was analyzed most frequently during our sessions ($n=63$), and its 2sd ($\pm 0.26\text{‰}$) provides a comparable measure of external reproducibility at 25 ppb (Table 1). MC-ICP-MS uncertainty is not presented as 2se (as for N-TIMS), because at least three independent $\delta^{11}\text{B}$ replicates are required to calculate standard error. An insufficient number of replicates were obtained to use 2se as the uncertainty term for about half of our MC-ICP-MS samples (Table 1).

2.3. N-TIMS methodology

The LDEO N-TIMS analysis protocol is based on Hemming and Hanson (1994)'s technique. Unlike the MC-ICP-MS procedure (Section 2.2), no boron separation or concentration is performed prior to N-TIMS analyses. This reflects three considerations: First, early N-TIMS studies that used a similar B separation procedure found excessive organic matter contamination

in samples and standards subjected to this procedure, presumably from breakdown of the ion exchange resin (Hemming and Hanson, 1994). Second, low B concentration in the column chemistry eluent requires concentrating the B through acid dry-down prior to N-TIMS analysis (Hemming and Hanson, 1994), which is undesirable due to the high potential for B volatilization and large resultant $\delta^{11}\text{B}$ variations (Ishikawa and Nakamura, 1990). Third, the HNO_3 acid matrix from the column chemistry procedure for MC-ICP-MS analysis (Foster, 2008) is incompatible with N-TIMS analyses because the addition of nitrate salts leads to large on-filament B isotope fractionation (Hemming and Hanson, 1994; Wei et al., 2014). Although conversion to an HCl acid matrix is possible through a multi-step column procedure (Wei et al., 2014), the blank from this procedure (500 ± 40 pg; Wei et al., 2014) is unacceptably large relative to the low B availability of marine carbonates.

Cleaned carbonate samples were acidified in the minimum necessary volume of ultrapure 2N HCl (Fisher Optima grade, certified B blank < 0.01 pg/ μL). The B concentration of the acidified solution varies as a function of carbonate B concentration, generally 0.4 to 1 ppm. A sufficient volume of sample analyte for 1 to 1.5 ng B (typically ~ 1 to 3 μL) was loaded onto zone-refined, outgassed Re filaments with 1 μL of a B-free seawater solution, and evaporated to a gel at an ion current of 0.5 A in a PTFE (boron-free) HEPA filtered laminar flow bench. The resulting $\delta^{11}\text{B}$ is not sensitive to the amount of B loaded above 1 ng (Foster et al., 2013). Boric acid standards were diluted to 1 ppm, and 1 μL of the diluted solution was loaded with 1 μL of boron-free seawater solution. The B-free seawater solution was prepared by passing seawater through Amberlite IRA-743 boron-specific anion exchange resin following Hemming and Hanson (1994). This solution aids sample ionization while contributing negligible B blank (~ 5 pg/ μL determined by isotope dilution). The total procedural blank including the B-free seawater solution is 10 ± 3 pg, or $< 1\%$ of sample B.

Filaments were mounted into a Thermo Scientific Triton multicollector TIMS, and boron isotopes were measured as $^{10}\text{BO}_2^-$ and $^{11}\text{BO}_2^-$ ions, i.e. masses 42 and 43. Filaments were heated under high vacuum ($< 2 \times 10^{-7}$ mbar) at 60 mA/min ion current until the filament temperature reached 980°C , at which point the ion beam was centered and focused until $^{11}\text{BO}_2^-$ ion electrical potential exceeded 100 mV. Data were acquired for 35 minutes (320 individual ion ratios). Any acquisitions exhibiting organic matter contamination (> 2000 counts per second on mass 26) or

excessive in-run isotope fractionation of $> 1\%$ were discarded. No organic matter contamination was observed in this study, while in-run fractionation affected approximately 10% of acquisitions. On average six acceptable data acquisitions were obtained for each sample, with the reported $\delta^{11}\text{B}$ the average of these acquisitions. We performed full procedural replicates for samples IC_A, IC_B, JCp-1 and JCt-1 where sample material was abundant. As the full procedural replicates for these samples were all within overlapping measurement uncertainty, we report a single $\delta^{11}\text{B}$ value for these samples that includes all replicate analyses (Table 1).

For standardization, NIST 951 boric acid is measured on a 2 ppm B solution mixed 1:1 with boron-free seawater and measured once per sample wheel, which otherwise holds 6-10 replicates of one to three carbonate samples. Because boron isotope analyses by N-TIMS are not subject to drift as in MC-ICP-MS analyses, the long-term average 43/42 ratio of this NIST 951 solution is used for normalization via Equation 1. To monitor long-term stability and external precision, we measure an in-house standard of NIST 951 precipitated in a CaCO₃ (vaterite) matrix and loaded with boron-free seawater to provide a comparable matrix to natural carbonate samples.

$\delta^{11}\text{B}$ analytical precision for N-TIMS measurements is expressed at two standard errors (2se), i.e., two times the standard deviation of individual acquisitions divided by the square root of the number of acceptable acquisitions (Hönisch and Hemming, 2005). Reproducibility of the vaterite in-house standard defines the external precision of carbonate analyses on the N-TIMS. The reported 2se for each sample is given as the larger of the internal or external precision (Foster et al., 2013).

3. Results and Discussion

All data from this study are shown in Figure 1 and Table 1. N-TIMS $\delta^{11}\text{B}$ values range from -26.89‰ (inorganic calcite sample 16B) to +24.93‰ (boric acid sample BiG-E), and MC-ICP-MS $\delta^{11}\text{B}$ values from -28.74‰ (16B) to +25.36‰ (BiG-E). N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ values for boric acids (BiG-D, -E and UMD) and biogenic aragonites (JCp-1 and JCt-1) are equivalent within analytical uncertainty (pooled average $\delta^{11}\text{B}_{\text{N-TIMS}} - \delta^{11}\text{B}_{\text{MC-ICP-MS}} = -0.02 \pm 0.32\%$, 1sd, n=5). However, N-TIMS $\delta^{11}\text{B}$ values are higher than MC-ICP-MS $\delta^{11}\text{B}$ values for all planktic and benthic foraminifer samples, inorganic calcites and the foraminiferal ooze

(pooled average $\delta^{11}\text{B}_{\text{N-TIMS}} - \delta^{11}\text{B}_{\text{MC-ICP-MS}} = 1.59 \pm 0.57\text{‰}$, 1sd, n=13). This offset extends across the calcite $\delta^{11}\text{B}$ range measured (-29 to +22‰).

York regressions (York et al., 2004) accounting for the respective reported measurement uncertainties in N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ values are shown in Table 2. It is noteworthy that $\delta^{11}\text{B}$ values are tightly correlated between approaches, despite the broad range of $\delta^{11}\text{B}$ values (-30 to +25‰, Table 1), boron concentrations (5.7 to 47 ppm, Table 1), and sample types (boric acids, inorganic calcites, foraminifers, and aragonites) in this study. The observed consistency of N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ in this study expands upon Kasemann et al. (2009), who found that $\delta^{11}\text{B}$ measured by MC-ICP-MS and N-TIMS on two corals and one inorganic calcite sample closely correlate across a $\delta^{11}\text{B}$ range of +7.5 to +25‰, with N-TIMS $\delta^{11}\text{B}$ values offset by +0.5 to +1‰ relative to MC-ICP-MS values. We note that the Kasemann et al. (2009) N-TIMS procedure differs from ours, involving higher sample B concentration, higher filament analysis temperature, and longer filament analysis durations (see Kasemann et al., 2009 for details). Additionally, MC-ICP-MS data from LDEO are one-to-one comparable to previous MC-ICP-MS data from the Bristol Isotope Group reported in Foster et al. (2013) where the sample samples were analyzed, though planktic foraminifer samples range from 0.04 to 0.48‰ lower when measured via MC-ICP-MS at LDEO (Table 2). Nonetheless, all samples agree within measurement uncertainty, which suggests that the modified MC-ICP-MS procedure at LDEO (Section 2.2) does not significantly affect absolute $\delta^{11}\text{B}$ values.

3.1 Offsets between MC-ICP-MS and N-TIMS

Although N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ data correlate strongly, the relationship is not one-to-one. As noted above, calcite samples exhibit higher $\delta^{11}\text{B}$ when analyzed by N-TIMS than MC-ICP-MS by ~0.5 to 2.5‰ (Figure 1 and Table 1), and regression y-intercepts between MC-ICP-MS and N-TIMS data are significantly less than zero when calcite samples are included (Table 2). The magnitude of these offsets is broadly consistent with previous studies showing 1 to 1.5‰ higher $\delta^{11}\text{B}$ values on benthic foraminifers (*C. wuellerstorfi*, Rae et al., 2011) and planktic foraminifers (*G. sacculifer*, Foster, 2008) when analyzed by the LDEO N-TIMS compared to MC-ICP-MS, although these analyses were not performed on the same homogenized samples.

Why does such an offset exist? The major difference between these two analytical procedures is the required removal of matrix for MC-ICP-MS analyses. Matrix variations exert much smaller effects on N-TIMS analyses and the presence of a matrix is in fact beneficial because it enhances boron ionization and reduces time-dependent fractionation, which otherwise hampers the accurate analysis of two-isotope systems by thermal ionization mass spectrometry (Section 2.3; Hemming and Hanson, 1994). One option is that MC-ICP-MS $\delta^{11}\text{B}$ values are lower due to either greater procedural blanks from the increased handling required for matrix separation, or the addition of isotopically light boron during the matrix separation (for instance, from incomplete boron removal in the buffer solution) (Foster et al., 2013). Our calcite data exhibit lower $\delta^{11}\text{B}$ when analyzed via MC-ICP-MS than via N-TIMS across the entire $\delta^{11}\text{B}$ range studied (-30 to +25‰). Importantly, the inorganic calcites analyzed here have low $\delta^{11}\text{B}$ (-24 to -29‰), yet also show lower values when analyzed via MC-ICP-MS than via N-TIMS. If MC-ICP-MS $\delta^{11}\text{B}$ values are lower because of contaminant or blank B contribution, this contribution must have an even lower $\delta^{11}\text{B}$ than the inorganic calcites (e.g., $\ll -30\text{‰}$). This is inconsistent with our measurements of total procedural blank $\delta^{11}\text{B}$ (-4 to +4‰), the $\delta^{11}\text{B}$ of boron in the buffer solution ($\sim -13\text{‰}$), and measurements of total procedural blanks at Bristol (+5‰; Rae et al., 2011). Incomplete boron recovery from the resin and associated isotope fractionation could also cause lower MC-ICP-MS values (Lemarchand et al., 2002), but can be ruled out because of near-complete boron recovery in this study (>99.7% of sample boron, Section 2.2) and previous tests of column recoveries by isotope dilution (Foster, 2008). Therefore, it seems unlikely that the required additional sample preparation artificially lowers MC-ICP-MS $\delta^{11}\text{B}$ values.

Alternatively, N-TIMS $\delta^{11}\text{B}$ values may be higher than MC-ICP-MS $\delta^{11}\text{B}$ values due to factors associated with differential ionization between samples and NIST 951 boric acid due to the presence of carbonate matrix in samples (commonly referred to as “matrix effects” after Sanyal et al., 1995). Ni et al. (2010) suggest residual, intracrystalline organic matter present in biogenic carbonate matrices after oxidative cleaning could bias N-TIMS to higher values by suppressing ionization. However, the inorganic calcites measured in this study contain no organic matter, and still exhibit higher $\delta^{11}\text{B}$ via N-TIMS than MC-ICP-MS (Figure 2a). Residual organic matter therefore cannot explain this offset, and also is unlikely to cause the similar magnitudes of offsets observed for biogenic carbonates (Figure 1).

Another option is that greater proportions of non-boron matrix could suppress ionization, leading to greater time-dependent fractionation upon thermal ionization. For instance, Foster et al. (2013) show that the difference between the LDEO N-TIMS $\delta^{11}\text{B}$ values and average $\delta^{11}\text{B}$ values from four laboratories (including LDEO N-TIMS) generally increases with decreasing sample B/Ca, which they suggest may reflect such a matrix effect on LDEO N-TIMS analyses. Similar correlations were not observed with Li/Ca, Al/Ca, or Sr/Ca (Foster et al., 2013). This B/Ca effect is uncertain, however, because the range of N-TIMS $\delta^{11}\text{B}$ offset ($\sim 1\%$) was smaller than ranges of $\delta^{11}\text{B}$ from different laboratories for the same samples (up to 4%). We assess potential relationships between sample matrix composition and the magnitude of the instrumental $\delta^{11}\text{B}$ offset for this study, where analytical differences are minimized compared to the Foster et al. (2013) study. The difference between our N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ values increases with decreasing B/Ca, although this relationship is scattered and largely driven by JCp-1 (Figure 2a; linear regression $R^2=0.50$). In addition, the difference between N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ values increases with decreasing Mg/Ca (Figure 2b; linear regression $R^2=0.39$) and decreasing carbonate $\delta^{18}\text{O}$ (Figure 2c; linear regression $R^2=0.49$). It should be noted that the Mg/Ca and $\delta^{18}\text{O}$ relationships are strongly driven by the inorganic calcites, which were precipitated from Mg-free and ^{18}O -depleted parent solutions (i.e., Mg/Ca = 0 mmol/mol, Table 1; Uchikawa et al., 2015) and generally show the greatest offset between N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ values.

As calcium is the dominant component of carbonate matrices, the increased $\delta^{11}\text{B}$ offset with both decreasing Mg/Ca and B/Ca could reflect the role of additional calcium in suppressing boron ionization for N-TIMS analyses. We tested this hypothesis by mixing a 1 ppm B solution of JCp-1 (B/Ca = 460 $\mu\text{mol/mol}$, Mg/Ca = 4.20 mmol/mol, Hathorne et al., 2013) with 1M reagent-grade (boron-free) CaCl_2 to create JCp-1 solutions with modified B/Ca of 100 and 50 $\mu\text{mol/mol}$ (corresponding to Mg/Ca of 0.91 and 0.46 mmol/mol, respectively). Addition of Cl^- ions from the CaCl_2 solution should not cause a matrix effect in N-TIMS analysis, as Cl^- is already abundant in sample solutions from using HCl for carbonate dissolution and from the boron-free seawater loading solution (Section 2.3). Figure 2d shows the results of Ca addition to JCp-1. If higher [Ca] delayed ionization, we would expect to see relatively higher $\delta^{11}\text{B}$ N-TIMS data in JCp-1 solutions with elevated [Ca] compared to the unmodified JCp-1 solutions. Specifically, the trend lines from Figure 2a and 2b would predict $\delta^{11}\text{B}$ should be $\sim 1.8\%$ higher at 50 $\mu\text{mol/mol}$ B/Ca (0.46 mmol/mol Mg/Ca), and $\sim 1.6\%$ higher at 100 $\mu\text{mol/mol}$ B/Ca (0.91 mmol/mol

Mg/Ca) relative to the unmodified JCp-1. However, we observe no significant difference between the $\delta^{11}\text{B}$ of JCp-1 at 460 $\mu\text{mol/mol B/Ca}$ ($24.17 \pm 0.29\text{‰}$), 100 $\mu\text{mol/mol B/Ca}$ ($24.03 \pm 0.21\text{‰}$), and 50 $\mu\text{mol/mol B/Ca}$ ($24.06 \pm 0.49\text{‰}$). This agrees with a previous observation that adding Ca to NIST 951 does not significantly change $\delta^{11}\text{B}$ when measured by total evaporation N-TIMS, although the low precision of these measurements prevents a detailed comparison (Foster et al., 2006). We conclude that Ca variations between samples and standards in N-TIMS measurements do not directly cause the observed $\delta^{11}\text{B}$ offsets.

Conversely, CaCl_2 addition to JCp-1 would not change $\delta^{18}\text{O}$, so this experiment does not inform on the relationship between $\delta^{18}\text{O}$ and the $\delta^{11}\text{B}$ offset (Figure 2c). One reason why $\delta^{18}\text{O}$ could correlate with the $\delta^{11}\text{B}$ offset is differential ^{17}O interference on mass 43 between samples and standards during TIMS analyses (e.g., Spivack and Edmond, 1986). For our analyses, this would occur through varying abundances of $^{10}\text{B}^{17}\text{O}^{16}\text{O}^-$ ions (of equivalent mass to $^{11}\text{B}^{16}\text{O}_2^-$) in samples versus standards. To assess this effect, $\delta^{18}\text{O}$ values are first converted to $\delta^{17}\text{O}$ assuming mass-dependent fractionation ($\delta^{17}\text{O} = 0.52 * \delta^{18}\text{O}$). The magnitude of the ^{17}O interference is then calculated by assuming NIST951 has an equivalent $^{17}\text{O}/^{16}\text{O}$ ratio as the VPDB oxygen isotope standard, such that sample $\delta^{17}\text{O}$ gives the $^{17}\text{O}/^{16}\text{O}$ deviation from NIST951. Note that knowledge of the true $^{17}\text{O}/^{16}\text{O}$ for NIST951 is not critical; rather, the total range of $\delta^{17}\text{O}$ is most important, as it defines the maximum possible $\delta^{11}\text{B}$ difference from a varying ^{17}O interference. Across the observed 23‰ $\delta^{18}\text{O}$ range ($\sim 12\text{‰}$ for $\delta^{17}\text{O}$), we calculate a total expected difference in $\delta^{11}\text{B}$ of 0.0025‰, which is inconsequential compared to analytical precision ($\sim \pm 0.25\text{‰}$). This is consistent with the small magnitude of the ^{17}O correction calculated by Spivack and Edmond (1986), who show that a 1000‰ difference in $\delta^{17}\text{O}$ would result in an interference offset of only 0.2‰ for $\delta^{11}\text{B}$. Therefore, ^{17}O interference does not likely cause the observed $\delta^{11}\text{B}$ offset- $\delta^{18}\text{O}$ relationship.

A notable feature of the $\delta^{11}\text{B}$ offset- $\delta^{18}\text{O}$ relationship is that this relationship improves dramatically if biogenic aragonites JCp-1 and JCt-1 are excluded ($R^2 = 0.71$ versus 0.49). This contrasts with excluding the aragonites from B/Ca, where the relationship greatly weakens ($R^2 = 0.19$ versus 0.50) and Mg/Ca, where the relationship slightly improves ($R^2 = 0.49$ versus 0.39). The strong negative relationship between $\delta^{18}\text{O}$ and the magnitude of the $\delta^{11}\text{B}$ offset between N-TIMS and MC-ICP-MS in calcites might reflect some causal link between isotope

systems, although we cannot currently fathom what that link may be. Additional work would be desirable to understand the underlying cause(s) of $\delta^{11}\text{B}$ differences between N-TIMS and MC-ICP-MS, and why these differences correlate to other observed isotopic and elemental properties of carbonates.

3.2 Implications for the $\delta^{11}\text{B}$ -pH proxy

Given that an offset between N-TIMS and MC-ICP-MS $\delta^{11}\text{B}$ exists, and its origin remains enigmatic, it is prudent to ask whether such an offset affects the application or interpretation of the $\delta^{11}\text{B}$ -pH proxy. An early MC-ICP-MS study suggested that different $\delta^{11}\text{B}$ values from different measurement techniques were associated with different $\delta^{11}\text{B}$ -pH sensitivities (Foster, 2008). More recently, Krief et al. (2010) and Henahan et al. (2013) refuted this prior result by showing that $\delta^{11}\text{B}$ measurements by MC-ICP-MS on corals and planktic foraminifers grown across a wide range of pH give the same $\delta^{11}\text{B}$ -pH sensitivity (defined here as the slope of the regression between $\delta^{11}\text{B}_{\text{carbonate}}$ and $\delta^{11}\text{B}$ of the borate anion in solution, which linearizes the $\delta^{11}\text{B}$ -pH relationship; see Foster et al., 2012) as previous studies that employed N-TIMS (e.g., Sanyal et al., 1996; 2001; Hönisch et al., 2004). While this is strong evidence that the $\delta^{11}\text{B}$ -pH sensitivity is independent of measurement technique, the ideal test for whether there are different $\delta^{11}\text{B}$ -pH sensitivities between N-TIMS and MC-ICP-MS would be to compare results of homogenized splits of sample material grown under controlled pH conditions.

We performed this test using three inorganic calcites precipitated from parent solutions covering a pH range of 8.37 to 8.65 (NBS scale) by Uchikawa et al. (2015). $\delta^{11}\text{B}_{\text{borate}}$ was calculated for each experiment using the $\delta^{11}\text{B}$ of experimental waters ($-12.19 \pm 0.32\text{‰}$ measured by MC-ICP-MS), the fractionation of Klochko et al. (2006), and the equilibrium constant pK_{B}^* calculated from experimental solution chemistries using PHREEQC (Parkhurst and Appelo, 2013) and the MINTEQA2 version 4 equilibrium speciation model that explicitly accounts for borate ion pairing (Allison et al., 1991). York regression lines of the form $\delta^{11}\text{B}_{\text{calcite}} = a + b \cdot \delta^{11}\text{B}_{\text{borate}}$ were fit, with b defining $\delta^{11}\text{B}$ -pH sensitivity (after Foster et al., 2012). As shown in Figure 3, there is no significant difference between the $\delta^{11}\text{B}$ -pH sensitivity on these samples measured by N-TIMS ($b = 0.69 \pm 0.14$, 2sd) or MC-ICP-MS ($b = 0.80 \pm 0.18$, 2sd) (two-tailed t-test, $\alpha = 0.05$, $p = 0.71$). Moreover, the $\delta^{11}\text{B}$ -pH sensitivity measured by both MC-ICP-MS and N-TIMS on the Uchikawa et al. (2015) pH experiment is statistically indistinguishable from a previous study of $\delta^{11}\text{B}$ in

inorganic calcite measured by N-TIMS ($b=0.72\pm0.11$, 2sd, Sanyal et al., 2000), where a two-tailed t-test for $\alpha=0.05$ yields $p=0.76$ for MC-ICP-MS versus Sanyal, and $p=0.89$ for N-TIMS versus Sanyal. However, it should be noted that the uncertainty of $\delta^{11}\text{B}_{\text{borate}}$ data in the Sanyal et al. (2000) study may not be fully captured because the details of the solution chemistries used in their experiments have not been published. In contrast, the calcite precipitation experiments of Noireaux et al. (2015), measured by MC-ICP-MS, give a lower $\delta^{11}\text{B}$ -pH sensitivity ($b=0.57\pm0.04$, 2sd) than our study or that of Sanyal et al. (2000). The Noireaux et al. (2015) data are scattered; for example, calcites from within a 0.1 pH unit experimental range show up to a 3‰ range in $\delta^{11}\text{B}$, which equates to the entire $\delta^{11}\text{B}_{\text{calcite}}$ range observed for the pH experiment of this study (Figure 3). In the Noireaux et al. (2015) study, precipitation rate and the concentrations of boron in the parent solution and calcite precipitate varied by up to four orders of magnitude between experiments ($R = 3.2\cdot10^{-6}$ to $6.7\cdot10^{-10}$ mol/m²/s, $[\text{B}]_{\text{solution}} = 0.91$ to 20.19 mM, $[\text{B}]_{\text{calcite}} = 4$ to 228 ppm). Although the effects of these variables on $\delta^{11}\text{B}_{\text{calcite}}$ have not yet been investigated in detail, it seems plausible that variations in experimental conditions may lead to the variable $\delta^{11}\text{B}_{\text{calcite}}$ results observed by Noireaux et al. (2015).

The $\delta^{11}\text{B}_{\text{calcite}}$ calibrations shown in Figure 3 confirm suggestions of previous studies (Foster et al., 2013; Henahan et al., 2013) that $\delta^{11}\text{B}$ measurements by N-TIMS and MC-ICP-MS will return the same *relative* pH change. However, *absolute* pH values are required e.g., for paleo-pCO₂ reconstruction, such that the difference in y-intercepts between the York regressions in Figure 3 needs to be taken into account when translating $\delta^{11}\text{B}$ values into paleo-pH. This technique-specific correction is critical because calibrations of $\delta^{11}\text{B}_{\text{sample}}$ to $\delta^{11}\text{B}_{\text{borate}}$ have been established by different instruments and/or techniques (e.g., Sanyal et al., 1996; 2001; Henahan et al., 2013). Provided that the technique-specific correction is soundly determined, and the instrument- or technique-specific $\delta^{11}\text{B}_{\text{sample-to-}\delta^{11}\text{B}_{\text{borate}}}$ calibrations are robust, then the absolute pH estimates derived from either instrument/technique will be identical because the relative pH change (i.e. the slope of the calibration) between instruments/techniques is the same (see above). In other words, technique-specific $\delta^{11}\text{B}$ offsets are addressed through differences in the $\delta^{11}\text{B}_{\text{sample-to-}\delta^{11}\text{B}_{\text{borate}}}$ calibration's y-intercept, as seen in Figure 3. An implication of this is that different laboratories do not need to establish laboratory-specific $\delta^{11}\text{B}_{\text{sample-to-}\delta^{11}\text{B}_{\text{borate}}}$ calibrations across a wide pH range, but can instead use the slope of published calibrations once the laboratory- and carbonate-specific $\delta^{11}\text{B}$ offset is determined.

To illustrate this concept, we present Quaternary paleo-pH reconstructions from the planktic foraminifer *G. sacculifer* in Ocean Drilling Program Site 668B samples measured here and as part of the Foster et al. (2013) study. N-TIMS $\delta^{11}\text{B}$ values are shown in Figure 4a, and MC-ICP-MS $\delta^{11}\text{B}$ values from this study and from Bristol (Foster et al., 2013) are shown in Figure 4b. Both techniques show the same temporal $\delta^{11}\text{B}$ patterns, with higher $\delta^{11}\text{B}$ during glacials (as indicated by higher planktic foraminifer $\delta^{18}\text{O}$), and lower $\delta^{11}\text{B}$ during interglacials (as indicated by lower $\delta^{18}\text{O}$), but the MC-ICP-MS $\delta^{11}\text{B}$ data are lower in absolute values than the N-TIMS $\delta^{11}\text{B}$ data. It should be noted that the Bristol MC-ICP-MS procedure has undergone greater testing and optimization for foraminiferal samples than the LDEO MC-ICP-MS procedure, and the slightly lower and more variable MC-ICP-MS values from LDEO compared to Bristol (Section 3.1) may be due to the hitherto limited MC-ICP-MS experience at LDEO. Nonetheless, MC-ICP-MS values from both laboratories do agree within overlapping measurement uncertainty.

$\delta^{11}\text{B}$ values are converted to pH using the following equation:

$$pH_{total} = pK_B^* - \log \left[\frac{\delta^{11}B_{borate} - \delta^{11}B_{sw}}{\delta^{11}B_{sw} - (\alpha_B * \delta^{11}B_{borate}) - 1000 * (\alpha_B - 1)} \right] \quad (3)$$

where pK_B^* is the equilibrium constant, which is a function of temperature and salinity (Dickson, 1990) and estimated by Hönisch et al. (2009) for ODP 668B; $\delta^{11}B_{sw} = 39.61\text{‰}$ (Foster et al., 2010), and α_B is the aqueous boron isotope fractionation factor between boric acid and borate (here from Klochko et al., 2006). These three parameters are independent of measured $\delta^{11}B_{sample}$; only $\delta^{11}B_{borate}$ depends on $\delta^{11}B_{sample}$ and is inferred using species-specific calibrations of $\delta^{11}B_{sample}$ to pH. The $\delta^{11}\text{B}$ vs. pH calibration for *G. sacculifer* was established by N-TIMS analyses of cultured specimens by Sanyal et al. (2001) and augmented by additional culture data measured on N-TIMS by Hönisch et al. (2009). When adjusted for a constant offset between cultured and coretop *G. sacculifer* specimens of the same size fraction (e.g., Hönisch and Hemming, 2005), the $\delta^{11}\text{B}$ -pH calibration for sediment core *G. sacculifer* measured on N-TIMS becomes:

$$\delta^{11}B_{borate} = (\delta^{11}B_{sacculifer \text{ N-TIMS}} - 5.72)/0.77 \quad (4)$$

Pairing this calibration based on N-TIMS with $\delta^{11}\text{B}_{\text{sacculifer}}$ values generated by MC-ICP-MS requires an additional constant (termed b) to account for the $\delta^{11}\text{B}$ offset between N-TIMS and MC-ICP-MS (i.e., MC-ICP-MS $\delta^{11}\text{B}_{\text{sacculifer}}$ values are shifted by a constant value b to align them with the N-TIMS calibration):

$$\delta^{11}\text{B}_{\text{borate}} = (\delta^{11}\text{B}_{\text{sacculifer MC-ICP-MS}} - [5.72 + b]) / 0.77 \quad (5)$$

Ideally, b should be defined by homogenized samples of the same material (in this case, *G. sacculifer*) measured by both techniques. Although samples IC₆ through IC₉ fulfill this criterion, they are also the targets of our pH reconstruction. If we used these samples to define b , we would artificially force the pH reconstructions to align. Instead, we independently define b using late Holocene *G. sacculifer* samples analyzed by Hönisch et al. (2009) on N-TIMS ($20.87 \pm 0.24\%$), and Rae et al. (2011) by MC-ICP-MS ($19.92 \pm 0.25\%$). These samples were not homogenized prior to analysis, but both measurements were performed on the same size fraction (e.g., Hönisch and Hemming, 2004). This gives a b value of -0.95, and Equation 5 thus becomes:

$$\delta^{11}\text{B}_{\text{borate}} = (\delta^{11}\text{B}_{\text{sacculifer MC-ICP-MS}} - 4.77) / 0.77 \quad (6)$$

The resultant pH reconstruction from application of Equations 3, 4, and 6 is shown in Figure 4c. There are no systematic differences from absolute pH for these four samples between the three measurements ($\text{pH}_{\text{N-TIMS}} - \text{pH}_{\text{LDEO MC-ICP-MS}} = 0.00 \pm 0.03$; $\text{pH}_{\text{N-TIMS}} - \text{pH}_{\text{Bristol MC-ICP-MS}} = -0.02 \pm 0.02$; $\text{pH}_{\text{LDEO MC-ICP-MS}} - \text{pH}_{\text{Bristol MC-ICP-MS}} = -0.02 \pm 0.02$, all errors 1sd). Past surface ocean pH agrees on average within 0.03 units for each glacial and interglacial interval between the three measurements. For comparison, the average glacial-interglacial pH change for the two glacial-interglacial cycles studied here is 0.12 units, and pH uncertainty arising from the $\delta^{11}\text{B}$ measurement uncertainty averages ± 0.03 units. Figure 4c shows that adjusting the $\delta^{11}\text{B}_{\text{borate}}$ calibration's y-intercept for analytical technique-specific offset gives comparable reconstructions of *absolute* ocean pH.

5. Conclusions

This single-laboratory comparison of N-TIMS and MC-ICP-MS boron isotope measurements demonstrates a high degree of reproducibility between techniques on homogenized boric acid, inorganic calcite, and biogenic calcite and aragonite sample materials. However, our results

show that calcite $\delta^{11}\text{B}$ is 0.5 to 2.5‰ higher when measured by N-TIMS than MC-ICP-MS. The cause of this $\delta^{11}\text{B}$ measurement offset remains unclear, but is unlikely due to either the increased sample processing necessary for MC-ICP-MS analyses, nor to the varying ratio of calcium matrix to boron (“matrix effects”) in N-TIMS analyses. Intriguingly, the $\delta^{11}\text{B}$ offset between N-TIMS and MC-ICP-MS measurements correlates to $\delta^{18}\text{O}$ in calcites. The origin of this correlation is unclear from the samples in this study, but additional studies of this relationship may inform on the cause of N-TIMS matrix effects. Measurements of inorganic calcites precipitated from parent solutions of varying pH confirm that both techniques return the same pH sensitivity of calcite $\delta^{11}\text{B}$ within uncertainty. This result supports the notion that relative $\delta^{11}\text{B}$ changes are directly comparable between MC-ICP-MS and N-TIMS. We show that the same absolute pH changes are reconstructed from both MC-ICP-MS and N-TIMS when the magnitude of measurement $\delta^{11}\text{B}$ offset for a given sample material is accounted for by technique-specific calibrations of sample $\delta^{11}\text{B}$ to $\delta^{11}\text{B}$ of borate ion (and hence pH). These results strongly support the validity and comparability of $\delta^{11}\text{B}$ -pH proxy applications generated from both N-TIMS and MC-ICP-MS measurement techniques.

6. Acknowledgements

We are indebted to Louise Bolge for her tireless support with operating the LDEO Neptune MC-ICP-MS, Emmanuel Ponzevera for assistance in initial setup of the boron isotope method on LDEO’s Neptune, Nina Ruprecht for assistance in establishing column chemistry procedures, and helpful discussions with Thomas Chalk, Michael Henehan, Joseph Stewart and Gavin Foster. JRF acknowledges support from the National Science Foundation Graduate Research Fellowship Program (DGE-11-44155). JU acknowledges support from NSF grant OCE-13-33357 for producing inorganic calcite samples. This research was funded by NSF OCE-10-41133 to BH.

7. References

- Al-Ammar, A.S., Gupta, R.K., and Barnes, R.M., 2000. Elimination of boron memory effect in inductively coupled plasma-mass spectrometry by ammonia gas injection into the spray chamber during analysis. *Spectrochim. Acta B*, 55, 629-635.
- Allison, J.D., Brown, D.S. and Kevin, J., 1991. *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual* (p. 117). Athens, GA:

Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency.

Barker, S., Greaves, M. and Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochemistry, Geophysics, Geosystems*, 4, doi:10.1029/2003GC000559.

Bell, D.B., Jung, S.J.A., Kroon, D., Lourens, L.J. and Hodell, D.A., 2014. Local and regional trends in Plio-Pleistocene $\delta^{18}\text{O}$ records from benthic foraminifera. *Geochemistry Geophysics Geosystems*, 15, 3304-3321, doi:10.1002/2014GC005297.

Catanzaro, E., Champion, C., Garner, E., Marinenko, G., Sappenfield, K. and Shields, W., 1970. Boric acid: isotopic and assay standard reference materials. *National Bureau of Standards (USA) Special Publication 260*, pp. 1-70.

Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Research Part A*, 37, 755-766.

Farmer, J.R., Hönisch, B., Robinson, L.F. and Hill, T.M., 2015. Effects of seawater-pH and biomineralization on the boron isotopic composition of deep-sea bamboo corals. *Geochimica et Cosmochimica Acta*, 155, 86-106, doi:10.1016/j.gca.2015.01.018.

Foster, G.L., 2008. Seawater pH, pCO_2 and $[\text{CO}_2^{3-}]$ variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271, 254-266, doi:10.1016/j.epsl.2008.04.015.

Foster, G.L., Ni, Y., Haley, B. and Elliott, T., 2006. Accurate and precise isotopic measurement of sub-nanogram sized samples of foraminiferal hosted boron by total evaporation NTIMS. *Chemical Geology*, 230, 161-174, doi:10.1016/j.chemgeo.2005.12.006.

Foster, G.L., Pogge von Strandmann, P.A.E. and Rae, J.W.B., 2010. Boron and magnesium isotopic composition of seawater. *Geochemistry Geophysics Geosystems*, 11, Q08015, doi:10.1029/2010GC003201.

Foster, G.L., Lear, C.H. and Rae, J.W., 2012. The evolution of pCO₂, ice volume and climate during the middle Miocene. *Earth and Planetary Science Letters*, 341, 243-254, doi:10.1016/j.epsl.2012.06.007.

Foster, G.L., Hönisch, B., Paris, G., Dwyer, G.S., Rae, J.W.B., Elliott, T., Gaillardet, J., Hemming, N.G., Louvat, P., and Vengosh, A., 2013. Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine CaCO₃ by MC-ICPM and NTIMS. *Chemical Geology*, 358, 1-14, doi:10.1016/j.chemgeo.2013.08.027.

Gutjahr, M., Bordier, L., Douville, E., Farmer, J., Foster, G., Hathorne, E., Hönisch, B., Lemarchand, D., Louvat, P., McCulloch, M., Noireaux, J., Pallavicini, N., Rae, J., Rodushkin, I., Roux, P., Steward, J.A., Thil, F., and You, C.-F. In prep. Boron Isotope Intercomparison Project (BIIP): Latest assessment of $\delta^{11}\text{B}$ interlaboratory comparability for standard carbonates JCp-1 and JCt-1. To be submitted to *Geostandards and Geoanalytical Research*.

Hathorne, E.C., Gagnon, A., Felis, T., Adkins, J., Asami, R., Boer, W., Caillon, N., Case, D., Cobb, K.M., Douville, E. and deMenocal, P., 2013. Interlaboratory study for coral Sr/Ca and other element/Ca ratio measurements. *Geochemistry, Geophysics, Geosystems*, 14(9), 3730-3750, doi:10.1002/ggg3.20230.

Hemming, N.G. and Hanson, G.N., 1992. Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta*, 56, 537-543.

Hemming, N.G. and Hanson, G.N., 1994. A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chemical Geology*, 114, 147-156.

Henehan, M.J., Rae, J.W., Foster, G.L., Erez, J., Prentice, K.C., Kucera, M., Bostock, H.C., Martínez-Botí, M.A., Milton, J.A., Wilson, P.A. and Marshall, B.J., 2013. Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo-CO₂ reconstruction. *Earth and Planetary Science Letters*, 364, 111-122, doi:10.1016/j.epsl.2012.12.029.

Hodell, D.A., Venz, K.A., Charles, C.D. and Ninneman, U.S., 2003. Pleistocene vertical carbon isotope and carbonate gradients in the South Atlantic sector of the Southern Ocean. *Geochemistry Geophysics Geosystems*, 4, 1004, doi:10.1029/2002GC000367.

Hönisch, B., and Hemming, N.G., 2004. Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: Partial dissolution and shell size effects. *Paleoceanography*, 19, PA4010, doi:10.1029/2004PA001026.

Hönisch, B. and Hemming, N.G., 2005. Surface ocean pH response to variations in pCO₂ through two full glacial cycles. *Earth and Planetary Science Letters*, 236, 305-314, doi:10.1016/j.epsl.2005.04.027.

Hönisch, B., Hemming, N., Grottoli, A.G., Amat, A., Hanson, G.N. and Bijma, J., 2004. Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects. *Geochimica et Cosmochimica Acta*, 68, 3675-3685, doi:10.1016/j.gca.2004.03.002.

Hönisch, B., Hemming, N.G., Archer, D., Siddall, M. and McManus, J.F., 2009. Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. *Science*, 324, 1551-1554, doi: 10.1126/science.1171477.

Inoue, M., Nohara, M., Okai, T., Suzuki, A. and Kawahata, H., 2004. Concentrations of trace elements in carbonate reference materials coral JCp-1 and giant clam JCt-1 by inductively coupled plasma-mass spectrometry. *Geostandards and Geoanalytical Research*, 28, 411-416.

Ishikawa, T., and Nakamura, E., 1990. Suppression of boron volatilization from a hydrofluoric acid solution using a boron-mannitol complex. *Anal. Chem.*, 62(23), 2612-2616.

Kasemann, S.A., Schmidt, D.N., Bijma, J., and Foster, G.L., 2009. *In situ* boron isotope analysis in marine carbonates and its application for foraminifera and palaeo-pH. *Chemical Geology*, 260, 138-147, doi:10.1016/j.chemgeo.2008.12.015.

Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H. and Tossell, J.A., 2006. Experimental measurement of boron isotope fractionation in seawater. *Earth and Planetary Science Letters*, 248, 276-285, doi:10.1016/j.epsl.2006.05.034.

Krief, S., Hendy, E.J., Fine, M., Yam, R. Meibom, A., Foster, G.L., and Shemesh, A., 2010. Physiological and isotopic responses of scleractinian corals to ocean acidification, *Geochimica et Cosmochimica Acta*, 74, 4988-5001, doi:10.1016/j.gca.2010.05.023.

Lemarchand, D., Gaillardet, J., Lewin, E., Allegre, C.J., 2002. Boron isotope systematics in large rivers: Implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chemical Geology*, 190, 123-140.

Misra, S., Owen, R., Kerr, J., Greaves, M. and Elderfield, H., 2014. Determination of $\delta^{11}\text{B}$ by HR-ICP-MS from mass limited samples: Application to natural carbonates and water samples. *Geochimica et Cosmochimica Acta*, 140, 531-552, doi:10.1016/j.gca.2014.05.047.

Ni, Y., Foster, G.L. and Elliott, T., 2010. The accuracy of $\delta^{11}\text{B}$ measurements of foraminifers. *Chemical Geology*, 274, 187-195, doi:10.1016/j.chemgeo.2010.04.008.

Nir, O., Vengosh, A., Harkness, J.S., Dwyer, G.S. and Lahav, O., 2015. Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH. *Earth and Planetary Science Letters*, 414, 1-5, doi:10.1016/j.epsl.2015.01.006.

Noireaux, J., Mavromatis, V., Gaillardet, J., Schott, J., Montouillout, V., Louvat, P., Rollion-Bard, C., and Neuville, D.R., 2015. Crystallographic control on the boron isotope paleo-pH proxy, *Earth and Planetary Science Letters*, 430, 398-407, doi:10.1016/j.epsl.2015.07.063.

Parkhurst, D.L. and Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at <http://pubs.usgs.gov/tm/06/a43/>.

Penman, D.E., Hönisch, B., Rasbury, E.T., Hemming, N.G. and Spero, H.J., 2013. Boron, carbon, and oxygen isotopic composition of brachiopod shells: Intra-shell variability, controls, and potential as a paleo-pH recorder. *Chemical Geology*, 340, 32-39, doi:10.1016/j.chemgeo.2012.11.016.

Rae, J.W., Foster, G.L., Schmidt, D.N. and Elliott, T., 2011. Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth and Planetary Science Letters*, 302, 403-413, doi:10.1016/j.epsl.2010.12.034.

Ravelo, A.C. and Fairbanks, R.G., 1992. Oxygen isotopic composition of multiple species of planktonic foraminifera: Recorders of the modern photic zone temperature gradient.

Paleoceanography, 7, 815-831.

Sanyal, A., Hemming, N.G., Hanson, G.N. and Broecker, W.S., 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature*, 373, 234-236.

Sanyal, A., Hemming, N.G., Broecker, W.S., Lea, D.W., Spero, H.J. and Hanson, G.N., 1996. Oceanic pH control on the boron isotopic composition of foraminifera: evidence from culture experiments. *Paleoceanography*, 11, 513-517.

Sanyal, A., Nugent, M., Reeder, R.J. and Bijma, J., 2000. Seawater pH control on the boron isotopic composition of calcite: evidence from inorganic calcite precipitation experiments.

Geochimica et Cosmochimica Acta, 64, 1551-1555.

Sanyal, A., Bijma, J., Spero, H. and Lea, D.W., 2001. Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*: Implications for the boron isotope paleo-pH proxy. *Paleoceanography*, 16, 515-519.

Spivack, A.J. and Edmond, J.M., 1986. Determination of Boron Isotope Ratios by Thermal Ionization Mass Spectrometry of the Dicesium Metaborate Cation. *Anal. Chem.*, 58, 31-35.

Uchikawa, J., Penman, D.E., Zachos, J.C. and Zeebe, R.E., 2015. Experimental evidence for kinetic effects on B/Ca in synthetic calcite: Implications for potential B(OH)_4^- and B(OH)_3 incorporation. *Geochimica et Cosmochimica Acta*, 150, 171-191, doi:10.1016/j.gca.2014.11.022.

Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A.R. and McCulloch, M.T., 1991.

Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochimica et Cosmochimica Acta*, 55, 2901-2910.

Wang, B.S., You, C.F., Huang, K.F., Wu, S.F., Aggarwal, S.K., Chung, C.H. and Lin, P.Y., 2010. Direct separation of boron from Na-and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS. *Talanta*, 82, 1378-1384, doi:10.1016/j.talanta.2010.07.010.

Wei, H.-Z., Jiang, S.-Y., Hemming, N.G., Yang, J.-H., Yang, T., Wu, H.-P., Yang, T.-L., Yan, X., and Pu, W., 2014. An improved procedure for separation/purification of boron from complex

matrices and high-precision measurement of boron isotopes by positive thermal ionization and multicollector inductively coupled plasma mass spectrometry. *Talanta*, 123, 151-160, doi:10.1016/j.talanta.2014.02.009.

York, D., Evensen, N.M., Martinez, M.L. and Delgado, J.D.B., 2004. Unified equations for the slope, intercept, and standard errors of the best straight line. *American Journal of Physics*, 72, 367-375.

Zeebe, R.E. and Wolf-Gladrow, D.A., 2001. *CO₂ in seawater: equilibrium, kinetics, isotopes*. Elsevier Oceanography Series, 65, Elsevier (Amsterdam).

Figures.

Figure 1. (a) N-TIMS $\delta^{11}\text{B}$ versus MC-ICP-MS $\delta^{11}\text{B}$ for all samples in this study. (b) and (c) are close-up view of the data from +7 to +27‰ and from -30 to -10‰, respectively. Black line in all panels is the 1:1 relationship. Error bars are 2se for N-TIMS and 2sd for MC-ICP-MS, and are smaller than symbols when not visible. Individual carbonate species are defined by colored symbols as described in the legend in (a). Black lines are 1:1 lines describing perfect agreement between the two methods.

Figure 2. (a) Difference between N-TIMS $\delta^{11}\text{B}$ and MC-ICP-MS $\delta^{11}\text{B}$ versus carbonate B/Ca ratios (Table 1). Individual carbonate species are defined by colored symbols as described in the legend in (a). Error bars are calculated from quadratic addition of measurement errors. Black solid line indicates least-squares regression. (b) Difference between N-TIMS $\delta^{11}\text{B}$ and MC-ICP-MS $\delta^{11}\text{B}$ versus carbonate Mg/Ca ratios. Black dash-dot line indicates least-squares regression. (c) Difference between N-TIMS $\delta^{11}\text{B}$ and MC-ICP-MS $\delta^{11}\text{B}$ versus carbonate $\delta^{18}\text{O}$ ratios (bottom axis), and $\delta^{17}\text{O}$ ratios (top axis) assuming mass-dependent fractionation ($\delta^{17}\text{O}=0.52*\delta^{18}\text{O}$). Black dashed line indicates least-squares regression. Solid blue line indicates the change in $\delta^{11}\text{B}$ resulting from interference of $^{10}\text{B}^{17}\text{O}^{16}\text{O}^-$ ions on $^{11}\text{B}^{16}\text{O}_2^-$ ions after Spivack and Edmond (1986). (d) Calcium addition experiment to JCp-1 measured via N-TIMS. Y-axis gives the difference between the measured $\delta^{11}\text{B}$ of JCp-1 after Ca addition at modified B/Ca as well as Mg/Ca, and the $\delta^{11}\text{B}$ of JCp-1 at original solution (B/Ca = 460 $\mu\text{mol/mol}$ and Mg/Ca = 4.20 mmol/mol). Linear regressions from (a, solid line) and (b, dashed line) are shown for comparison.

Figure 3. Calcite $\delta^{11}\text{B}$ versus $\delta^{11}\text{B}$ of borate anion in the parent solution for inorganic calcites grown at various pH by Uchikawa et al. (2015) (squares), Sanyal et al. (2000) (black circles), and Noireaux et al. (2015) (gray circles). All data are normalized to $\delta^{11}\text{B}$ of seawater (39.61‰, Foster et al., 2010) using the following equation: $\delta^{11}\text{B}_{\text{corrected}} = \delta^{11}\text{B}_{\text{measured}} * \alpha + 1000 * (\alpha - 1)$, where α is the fractionation factor between natural and experimental seawater given by $(\delta^{11}\text{B}_{\text{seawater}} + 1000) / (\delta^{11}\text{B}_{\text{solution}} + 1000)$ (see Zeebe and Wolf-Gladrow, 2001). Black dashed line describes the 1:1 line between $\delta^{11}\text{B}_{\text{borate}}$ and $\delta^{11}\text{B}_{\text{calcite}}$. The legend defines the respective study and analytical technique behind each dataset and gives the $\delta^{11}\text{B}_{\text{borate}}$ vs. $\delta^{11}\text{B}_{\text{calcite}}$ York regressions, including the 2 sigma errors for the slopes and intercepts.

Figure 4. Glacial-interglacial $\delta^{11}\text{B}$ of planktic foraminifer *G. sacculifer* at ODP 668B from (a) N-TIMS (red, Foster et al., 2013) and (b) MC-ICP-MS (blue filled: this study; blue outlined: Foster et al., 2013). The $\delta^{11}\text{B}$ axis is shifted by -1‰ in (b) compared to (a), but the $\delta^{11}\text{B}$ axes cover the same 2.5‰ range in both panels. (c) Surface ocean pH reconstructed from $\delta^{11}\text{B}$ using N-TIMS and MC-ICP-MS specific calibrations (see text for details). Gray line in each plot is the *G. ruber* oxygen isotope stratigraphy for ODP 668B from Hönisch et al. (2009).

Auxiliary Material

Figure A1. Stability of boric acid standards and carbonates across an MC-ICP-MS analysis session without sample gas tuning. All data are from December 4th, 2015 and cover an eight-hour analytical session. While the absolute $^{11}\text{B}/^{10}\text{B}$ of NIST 951 does change over time (blue diamonds), the timescale of this change is long relative to bracketing standards, such that there is no significant difference in the sample-standard bracketed $\delta^{11}\text{B}$ of either boric acid standard UMD (red diamonds) or biogenic aragonite JCp-1 (yellow squares) over the course of this session. All values obtained are within 2sd of the long-term sample average $\delta^{11}\text{B}$ defined from analyses of UMD and JCp-1 across all analysis sessions (red diamond with red error bars and yellow square with yellow error bars on bottom panel axes; values in manuscript Table 1).

Figure 2

Figure 3

Figure 4

● N-TIMS LDEO

¹¹B/¹⁰B NIST 951

¹¹B/¹⁰B UMD¹¹B/¹⁰B NIST 951 $^{11}\text{B}/^{10}\text{B}$ JCP- $\delta^{11}\text{B}$ (‰ vs. NIST 951)

Session: $-13.05 \pm 0.19\text{‰}$ (2sd)
Long-term: $-13.12 \pm 0.26\text{‰}$ (2sd)

Session: $24.07 \pm 0.20\text{‰}$ (2sd)
Long-term: $24.36 \pm 0.43\text{‰}$ (2sd)

 $\delta^{11}\text{B}$ (‰ vs. NIST 951)

Table 1. Samples used for N-TIMS and MC-ICPMS $\delta^{11}\text{B}$ comparison

Sample Type	Identifier	Mineralogy	B (ppm)	B/Ca ($\mu\text{mol/mol}$)	Mg/Ca (mmol/mol)	Source
Boric Acid	BiG-D	--	--	--		1
	BiG-E	--	--	--		1
	UMD	--	--	--		1
Inorganic CaCO_3	15A	Calcite	5.7	53	0	2
	9B	Calcite	9.0	83	0	2
	10A	Calcite	16.9	157	0	2
	17B	Calcite	7.9	73	0	2
	16B	Calcite	10.9	101	0	2
	IC _B	Calcite	13.0	121	1.97	1
Foraminifera Ooze	IC _A	Calcite	7.0	65	3.88	1
Planktic foraminifera	IC ₆	Calcite	11.0	98	4.24	1
	IC ₇	Calcite	10.0	95	3.59	1
	IC ₈	Calcite	9.0	88	4.1	1
	IC ₉	Calcite	11.0	100	3.51	1
Benthic foraminifera	Cw ₁	Calcite	24.0	222	1.61	3
	Cw ₂	Calcite	22.9	212	1.365	3
Coral	JCp-1	Aragonite	47.7	460	4.199	4,5
Giant Clam	JCt-1	Aragonite	19.4	191	1.289	4,5

Sample B/Ca, Mg/Ca and $\delta^{18}\text{O}$ sources:¹Foster et al. (2013)²Uchikawa et al. (2015)³This study⁴Gutjahr et al. (in prep.)⁵Metal/Ca from Hathorne et al. (2013)⁶Uchikawa and Penman (unpublished)⁷This study, using methodology of Farmer et al. (2015)⁸*G. ruber* values from Hönisch et al. (2009) assuming no offset (e.g., Ravelo and Fairbanks, 19⁹Hodell et al. (2003)¹⁰Bell et al. (2014)

Table 2

Table 2. York regressions ($Y = a + b \cdot X$) and regression parameter uncertainties

Samples Used	n	X	Y	b	2σ
All	18	N-TIMS	MC-ICPMS	1.028	0.005
Calcites only	13	N-TIMS	MC-ICPMS	1.024	0.006
Boric acids & Aragonites	5	N-TIMS	MC-ICPMS	1.013	0.020
ICs: Foster et al. (2013)	9	N-TIMS	MC-ICPMS	0.994	0.019
ICs: Foster et al. (2013)	9	N-TIMS	MC-ICPMS (Bristol)	0.996	0.019
ICs: Foster et al. (2013)	9	MC-ICPMS	MC-ICPMS (Bristol)	0.999	0.012

Note: Italicized values correspond to intercept values significantly offset from zero