Rapid, high-precision measurements of boron isotopic compositions in marine carbonates

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RATIONALE: The isotopic composition and elemental abundance of boron (B) in marine carbonates provides a powerful tool for tracking changes in seawater pH and carbonate chemistry. Progress in this field has however been hampered by the volatile nature of B, its persistent memory, and other uncertainties associated with conventional chemical extraction and mass spectrometric measurements. Here we show that for marine carbonates, these limitations can be overcome by using a simplified, low-blank, chemical extraction technique combined with robust MC-ICPMS methods.

METHODS: Samples are dissolved in dilute HNO_3 and loaded firstly onto on a cation exchange column with the major cations (Ca, Mg, Sr, Na) being quantitatively retained while the B fraction is carried in the eluent. The eluent is then passed through an anion column ensuring that any residual anions, such as SO_4^{2-}, are removed. Isotopic measurements of $^{11}B/^{10}B$ ratios are undertaken by matching both the B concentration and isotopic compositions of the samples with the bracketing standard, thereby minimising corrections for cross-contamination.

RESULTS: The veracity of the MC-ICPMS procedure is demonstrated using a gravimetrically prepared laboratory standard, UWA24.7, relative to the international reference standard NIST SRM 951 ($\delta^{11}B$ = 0 ‰). This gives values consistent with gravimetry ($\delta^{11}B$ = 24.7±0.3‰ 2sd) for solutions ranging in concentration from 50-500 ppb, equivalent to ~2-10 mg size coral samples. The overall integrity of the method for carbonate analysis is demonstrated by measurements of the international carbonate standard JCp-1 ($\delta^{11}B$ = 24.3 ±0.34‰ 2sd).

CONCLUSIONS: A streamlined, integrated approach is described here that enables rapid accurate, high precision measurements of boron isotopic compositions and elemental abundances in commonly analysed samples, such as corals, bivalves, and large benthic forams. The overall simplicity of this robust approach should greatly facilitate the wider application of boron isotope geochemistry, especially to marine carbonates.

The isotopic composition of boron ($\delta^{11}B$) incorporated into the carbonate skeleton of marine organisms is of growing interest as it provides one of the few means to determine the longer term history of seawater pH[1-6]. Understanding how the pH of the oceans is changing on both recent and longer-term timescales is important, since rapidly increasing levels of atmospheric CO_2 from anthropogenic emissions is not only causing global warming, but also driving major changes in the oceans' carbonate chemistry. Of particular concern are the still poorly understood effects of increased dissolution of CO_2 into the oceans and the associated effects of declining seawater pH, especially in surface waters[7]. This latter process, now commonly referred to as 'ocean acidification', is already causing significant perturbations to the oceans' carbonate chemistry with decreasing pH affecting, for example, the ability of many calcifying organisms to produce their calcium carbonate skeletons. The boron isotopic composition of marine carbonates thus provides one of the few means to track the longer term response of the oceans to increasing pCO_2, as well as providing an important process-based tool to investigate how declining seawater pH is affecting carbonate secreting organisms, such as corals[8, 9].

The sensitivity of the boron isotopic compositions in marine carbonates to changes in seawater pH arises because the relative abundance of the boron species in seawater, boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$) ions, is pH dependent[10]. Each boron species also has a well-defined isotopic fractionation factor[11] and importantly only the $B(OH)_4^-$ species is incorporated[1, 6], essentially quantitatively[8], into either the aragonite or calcite polymorphs. These characteristics, together with the approximately constant composition of seawater $\delta^{11}B$ on time scales $>10^6$ years, means that $\delta^{11}B$ variations preserved in marine carbonates provides a sensitive long-term proxy of seawater pH. Following standard convention the isotopic composition of boron is given as:

$$\delta^{11}B = [(^{11}B/^{10}B_{sample}/^{11}B/^{10}B_{std}) - 1]x1000\ (‰)$$

where the reference standard is NIST SRM 951[12] (NIST, Gaithersburg, MD, USA).

More recent work has shown that boron isotope systematics can also be used as a tool to study and better understand the processes of bio-mineralisation, in particular how bio-calcifiers modulate the pH of their calcifying fluid in order to form their distinctive calcium carbonate skeletons[9, 13]. Thus, the measurement of boron isotopic compositions in marine carbonates is of increasing importance, and proving to be an invaluable geochemical tool.

Existing procedures

Chemical procedures typically used for separating boron from marine carbonates (eg. corals, bivalves, forams) have mostly utilised the B-specific ion-exchange resin, Amberlite IRA-743. This resin was developed primarily to extract boron from the complex matrices encountered in the nuclear industry and subsequently for geologic samples[14]. The application of Amberlite IRA-743 resin is based on its strong adsorptive properties for B at relatively high

pH (>5). This requires careful adjustment of the sample pH, usually by addition of NH_4OH, NaOH or alternatively, by the addition of a Na acetate-acetic acid buffer[15]. Accurate adjustment of pH is necessary to ensure complete adsorption of B onto the resin as well as avoiding co-precipitation of Ca and/or Mg hydroxides which can occur at higher pH. For matrices such as seawater, in which there are also high concentrations of SO_4^{2-} and particularly NaCl, care is also required to thoroughly rinse the resin to remove Na^+ as well as Cl^- and SO_4^{2-} ions. The presence of these ions can induce matrix dependent artefacts during either thermal ionization mass spectrometry (TIMS) or multi-collector inductively couple plasma mass spectrometry (MC-ICPMS). For this reason a final cation clean-up stage is often applied after boron extraction using the IRA-743 resin (e.g. Wei et al., [3]).

Other methods have been reported for the purification of boron from aqueous samples, including solvent extraction, chelation, conversion into boron fluoride, and for –ve ion TIMS (NTIMS) micro-sublimation [16-18]. These techniques all require high yields, and often include an evaporative step[19]. Evaporation of boron solutions however requires great care, as boron is volatile in acidic solutions and therefore subject to isotopic fractionation from evaporative loss. Furthermore, during sample evaporation there is the potential risk from airborne contamination. Avoiding evaporative steps was therefore paramount in devising the new procedures described herein, and is one of the major advantages of this technique.

Boron isotopic compositions have been determined using a number of analytical approaches e.g. [19]). The earlier pioneering work was mainly based upon positive (+ve) ion TIMS (PTIMS) methods[20, 21] based on the measurement of high molecular weight species of boron. Early PTIMS studies thus analysed the $Na_2B_2O_2$ [12] or $Na_2B_4O_7$ complexes giving a precision typically within 1‰ to 2‰ (e.g. Nomura et al.,[20]). This approach was dramatically improved using the much higher atomic weight of the $CsBO_2$ complex[21, 22], whereby the boron isotopes analysed were in the form of $Cs^{10}BO_2^+$ and $Cs^{11}BO_2^+$. By operating at high mass (m/z 308 and 309), the effects of instrumental mass fractionation were reduced considerably, enabling high precision (~0.15‰ sd) analyses to be achieved. The major limitation of PTIMS, however, is that the ionisation efficiency of the $CsBO_2^+$ complex is low and hence generally microgram quantities of B are required. Like all TIMS methods, the instrumental mass fractionation is also sensitive to matrix effects thereby requiring clean chemical extraction processes as well as careful, reproducible procedures for loading samples onto TIMS filaments. Nevertheless, this approach has been successfully employed in the measurement of $^{11}B/^{10}B$ ratios in corals, which have relatively high B concentrations (30-50 ppm), and where sample size is not limiting (e.g. Wei et al.,[3]).

An alternative to conventional +ve ion mass spectrometry (PTIMS) is negative (–ve) ion mode (NTIMS) for analysing BO_2^-, which was first applied to carbonates by Duchateau and DeBievre[23] and subsequently by Vengosh et al.[24]. This method provides extremely high ionisation efficiencies for the BO_2^- complex, and therefore in marked contrast to PTIMS, NTIMS is extraordinary sensitive, enabling nanogram quantities of boron to be analysed, with deceptively small internal analytical uncertainties (<0.1‰ sd). However NTIMS is also highly sensitive to matrix effects, which together with the potential for operator bias in

filament loading and mass spectrometry, results in a substantially larger overall analytical uncertainties with respect to external reproducibility[24]. Attempts to control matrix effects by the use of additives such as boron-free seawater have met with some success[25], but generally this is most effective in higher level B samples where matrix effects are less severe. More recently[17, 18], chemical purification methods based on the sublimation of B have been employed to remove the potentially variable sample matrix. This latter approach is particularly promising; yielding a precision of ~1‰[17] for NTIMS, an ideal approach for analysing low level B samples where only modest analytical precision is required. Attempts to correct for instrumental fractionation inherent in the NTIMS approach using the BO_2^- $^{18}O/^{16}O$ complex as an internal standard have been reported[26] but have not been reproduced, probably due to the variability in the isotopic composition of the oxygen complexes combined with poorly constrained molecular-based mass fractionation processes.

More recently MC-ICPMS has become the most common approach due to the increasing availability of this instrumentation, which also has the advantage of rapid and potentially more accurate and reproducible analyses of boron isotope compositions. This is due to the intrinsic ability of MC-ICPMS instruments to better maintain a more constant level of instrumental mass bias enabling comparisons with reference standards[27]. For this purpose, standards of known composition are used to bracket samples and thereby correct for drifts in instrumental mass bias. Additional problems specific to boron MC-ICPMS analyses are its relatively volatile and persistent nature, especially when using conventional spray chambers with acidic solutions. This can result in significant memory effects and hence cross contamination between sample and standards in particular, thus requiring long wash-out times. Various approaches have been adopted to minimise this problem, such as the addition of ammonia gas to the spray chamber[28], or the use of direct injection into the plasma[29] to bypass nebulisation in a spray chamber. Both or these approaches have limitations, requiring either the handling of highly toxic ammonia gas, or in the case of direct injection special care in positioning and maintaining the direct injector[30]. Here we describe a simple alternative approach that minimises the problems of existing methods. It is based on more effective cleaning of the spray chamber together with careful matching of standard-sample concentrations and compositions. We show that, when combined with a rigorous procedure to correct for minor residual blanks, this approach provides reproducible and high precision analyses of boron isotopic compositions in marine carbonates.

EXPERIMENTAL

Laboratory facilities and reagents

The chemical dissolution and boron extraction procedures were undertaken in a newly constructed metal-free hepa-filtered (ISO 7) clean room complex recently constructed at the University of Western Australia. Sample powders were weighed using a micro-balance in a

temperature and humidity controlled balance room located within the clean room facility. The column chemistry was undertaken within hepa filtered exhaust hoods using boron-free filter material. Measurements of the boron blank due to room expose were found to be similar or lower than that in the exhausting hoods, consistent with the volatile nature of B.
Ultrapure reagents were used for the bleaching (NaClO) and Milli-Q (EMD Millipore, Corp., Billerica, MA, USA) water for the ultra-sonication stage. For sample dissolution and ion-exchange separations, concentrated HNO_3 was distilled from analytical grade stock using a Savillex (Eden Prairie, MN, USA) DST 1000 distillation unit. Acid distillations were conducted within a dedicated hepa filtered extraction hood.
The column chemistry comprised a paired cation-anion separation procedure using polypropylene Bio-Rad Bio-Spin (Bio-Rad, CA, USA) columns. The cation column (0.8 mL) was mounted immediately above a larger (1.2ml) anion column. This allows the eluent from the cation column to flow directly down into the anion column then into the collection vial (5 mL). The collection vials are suitable for direct placement into the Ar purged autosamplers, using either a Cetac 150 (Teledyne Cetac Technologies, Omaha, NE, USA) or an ESI SC2 (Elemental Scientific Inc. Omaha, NE, USA). Custom made 2-tier acrylic column holders were constructed to hold paired sets of cation-anion columns and the collection vials allowing the simultaneous extraction of either x15 or x30 samples.
For MC-ICPMS measurements, an in-house bracketing standard (UWA24.7) was prepared from a mixture of the reference standard NIST SRM 951, (i.e. $\delta^{11}B= 0$) with a ^{11}B enriched isotope (99.65%) purchased from Trace Sciences International. The UWA24.7 standard was designed to have a composition similar to that found in scleractinian corals (~25‰), with the determined value (24.7‰) being consistent within the uncertainities in the gravimetry and isotopic composition of the parent materials. An alternative approach that is now available is the use of certified standards such as the ERM-AE121 (BAM, Berlin, Germany). The international coral standard JCp-1 (Geological Survey of Japan, Tsukuba, Japan) prepared from Porites coral was also used as a reference.

Boron Extraction from carbonates

The method described here is specifically designed for the rapid, efficient extraction of boron from a relatively simple carbonate matrix with isotope analysis being undertaken with a MC-ICPMS instrument. For more complicated matrices, such as seawater or silicate-derived solutions, the more conventional [14, 31] B-specific ion-exchange resin (Amberlite IRA-743) is still recommended. The chemical extraction procedure described here has also been specifically designed to eliminate evaporative steps hence evaporation-induced isotopic fractionation of the volatile boron. Further, this simple but reliable sample processing protocol also aims to reduce the extraction time and hence the exposure of samples to aerosol and/or particulate sources of potential B contamination, thereby minimising the overall blank.
Carbonate samples are first subject to a number of selective cleaning procedures dependent on the nature and origin of the sample. Scleractinian corals, for example, are sonicated in

dilute sodium hypochlorite (~7% NaClO) bleach, either initially on cleaned slabs prior to milling, or otherwise directly on the milled coral powders. This is designed to remove organic material that may potentially retain extraneous boron and/or interfere with the chemical extraction and mass spectrometric procedures. The efficacies of the bleaching and sample pre-cleaning procedures are described elsewhere (Holcomb *et al.,*).

Following bleaching, samples are then subjected to a series of sonication and rinse steps using ultrapure Milli-Q water to remove residual bleach solution. The amount of carbonate powder processed depends on the boron concentration of the target samples and the sample volume available. Typically 10 mg of calcium carbonate is processed for aragonitic coral studies, whereas a larger sample size is initially dissolved (~50 mg) from which a sub-aliquot is used; for example in the case of annual resolution studies to ensure that the aliquots are representative.

The procedure described here is tailored for medium sized (~10 mg) samples but can also be readily modified (scaled) as required, for either smaller sized sub-samples (1-2 mg) or for larger samples that have lower boron concentration (e.g. calcitic corals). Furthermore, the protocol allows for analysis of both trace elements and boron isotopes from the same sample digestion. The powders (~10 mg) are dissolved in 0.46 mL of ~0.56N HNO_3 taking care to avoid vigorous reactions. This yields a stable solution of ~0.1 N HNO_3 with the solution having a concentration equivalent to ~9,000 ppm Ca. The sample solution is centrifuged then a small aliquot of 30 μL removed from the primary solution for trace element analysis. The trace element aliquot is then further diluted in 2% HNO_3 in two stages, firstly to yield a Ca solution of ~100 ppm and then a sub-aliquot diluted to 10 ppm Ca respectively. The 100 ppm Ca solutions are used to measure Li/Ca and B/Ca ratios, whereas the more dilute 10 ppm solution is used to analyse Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca ratios. The remaining bulk (>90%) of the primary sample solution is then processed for boron isotope analyses, as described below.

In a departure from the conventional approach using B specific resin, here we use a very simple protocol combining cation and anion chromatography. This procedure is designed to allow the direct elution of B through the columns and capture the other major constituents of the carbonate sample solution (Ca, Mg, Sr and SO_4^{2-}) on the respective resins. The first stage cation exchange column is prepared using 0.6mL of AG50W-x8 resin loaded into a small chromatography polypropylene column (0.8 mL bed volume Bio-Rad Micro Bio-Spin). Positioned immediately below the cation column is a larger anion column (1.2 mL Bio-Rad Bio-Spin) that contains 1.0 mL of AG1-x8 anion resin. The anion column is positioned to collect eluent directly from the overlying cation column. Prior to loading the sample solution, the ion exchange columns are cleaned separately using ~8 resin bed volumes of 6N HNO_3, ~12 bed volumes of Milli-Q water, followed by column preconditioning with ~1 mL of 0.075N HNO_3.

A 0.4 mL aliquot of the 0.1N HNO_3 boron containing sample solution is loaded onto the preconditioned cation column. The cation column is then eluted with 2 mL (in x4 aliquots of 0.5 mLs) of 0.075N HNO_3, with the eluent containing the boron fraction thus flowing directly

onto the underlying anion column then collected in poly-propylene vials. For coral samples, this yields a ~200 ppb boron solution suitable for immediate analyses of $\delta^{11}B$ compositions using MC-ICPMS.

As discussed, this procedure is based on the retention of the major (i.e. Ca), minor (Mg, Sr, Na), and trace (e.g. Ba, U) cations within the cation resin, whereas boron remains in the mobile liquid phase (Figure 1). The anion column that receives the eluent from the cation column, acts in a similar manner but also significantly reduces potential interferences by SO_4^{2-} anions. The effect of an anion matrix (e.g. SO_4^{2-} ions) on boron isotope analyses has been quantitatively assessed by Holcomb et al.[30] and is generally minor (i.e. < 0.5‰). However, at the relatively high precision (i.e. < 0.1‰ 2sd) obtainable using our MC-ICPMS methodology (see following), contaminants of this type can potentially limit the precision. Furthermore, the anion column requires minimal additional effort, being mainly a precautionary step to eliminate occasional high abundances of SO_4^{2-}. It is noted, however, that this cation-anion procedure does not remove Cl^- anions from the B fraction so is not recommended for seawater or other high saline waters because of likely Cl^- matrix effects.

The boron is collected in a relatively large fraction in order to ensure 100% collection efficiency, as well as to provide repeat analyses (x3) and to achieve the desired normality of HNO_3 (~0.15N) for the final boron containing solution. This is necessary since the ion exchange procedure itself changes normality of the HNO_3 from ~0.1N to ~0.15N in the final B solution. This is an important consideration since normality matching with the bracketing standard is an important factor in maintaining a constant MC-ICPMS instrument induced mass bias[32]. The chemical dissolution/extraction procedure described here can also be readily scaled for smaller (low volume) and/or larger (low level boron) samples, with the latter requiring larger columns hence resin volumes. The solution volumes are adjusted to maintain the same concentration of Ca in solution (~9,000 ppm Ca). Conversely for smaller samples (<5 mg), the boron aliquot can be extracted using columns with smaller ion exchange bed volumes, thereby maintaining a similar concentration of B in the eluent.

MC-ICPMS Measurement of Boron Isotopic Compositions

Boron isotopic compositions were analysed at the University of Western Australia's Advanced Geochemical Facility using either the Neptune Plus (Thermo Electron Corp., San Jose, CA, USA) or NU Plasma II (Nu Instruments, Wrexham, UK) multi-collector inductively couple plasma mass spectrometry (MC-ICPMS) instruments, operated with standard plasma settings (Table 1). Purified sample extracts, with a final concentration of ~0.15N HNO_3, are aspirated using a PFA nebuliser at an uptake rate of ~50 to 60 μL/minute into a quartz glass cyclonic spray chamber.

A rigorous MC-ICPMS measurement procedure is implemented that incorporates a thorough initial cleaning phase of the spray chamber, followed by ~1 hour equilibration period for both the spray chamber and MC-ICPMS prior to measurements. This is undertaken in 0.15N HNO_3 acid with repeated measurements of the laboratory reference standard to ensure stability and reproducibility. All measurements of samples as well as

standard bracketing solutions are followed by a washout period using 0.15N HNO_3 and measurement of residual blank levels and compositions. Addition of 0.01N HF to the wash solution was initially tested but found to be of only marginal benefit so was discontinued. Furthermore, separate tests undertaken by Holcomb et a.,[30] suggest that gross mis-matching between the composition and acid normality of wash versus sample solutions can cause instabilities as well as changes in instrumental mass bias thereby causing offsets in isotopic compositions.

An automated time sequence is maintained for the measurement sequence (Fig. 2) of : (1) initial blank washout of 120 ~~120~~ seconds, (2) blank measurement for 128~~0~~0 seconds, (3) uptake of sample/standard solution of 120 seconds, and (4) sample/standard solution measurements of 240 seconds. This sequence, representing a total time of 10~~9~~ minutes ~~and 20 seconds~~, is repeated with the sample bracketed by measurements of the standard (Fig. 2).

RESULTS AND DISCUSSION

A major limitation when undertaking MC-ICPMS $\delta^{11}B$ measurements is the problem of boron memory. This can be seen in Figure 2 where the residual B concentration is shown as a function of time for a standard solution of UWA24.7, which ranges in concentration from 50 ppb to 300 ppb. It can be seen that after washing with a mixture of 0.15N HNO3 for several minutes, the residual ^{11}B signal is in the range of 20mv to 30mv, equivalent to 5% (50 ppb) and ~2% (300 ppb) respectively of the total sample signal. Not surprisingly, this shows that the level of residual blank is largely determined by the concentration of the preceding sample (Fig. 2a). Importantly however, after an ~120 second washout period, the blank composition (Fig. 2b) is relatively constant enabling it to be determined within a precision of ~±1‰. This uncertainty in the blank composition translates to a maximum additional uncertainty in the blank corrected sample composition of ±<0.02‰, a small overall contribution to the analytical uncertainty. Thus, whilst a more prolonged or aggressive washout procedure could be implemented, this would have a diminishing effect on the overall blank levels with the offsetting detrimental effect of increasing the time interval between sample and standard bracketed measurements, thereby introducing greater uncertainties in correcting for instrumental drift, which is a significant uncertainty.

While accurate and reliable blank corrections are a necessary part of a robust analytical procedure, the magnitude of these corrections is also strongly dependent on the $\delta^{11}B$ composition of the samples (e.g. corals with $\delta^{11}B$ ~25‰) relative to that of the standard bracketing solutions (e.g. NIST SRM 951 $\delta^{11}B$ = 0‰). This is illustrated in Figure 3, which shows the results for an analytical session where the sample is our laboratory reference standard (UWA24.7) that is measured relative to NIST SRM 951 as a bracketing standard. In this example where similar concentrations of the 150 ppb “sample” (i.e. UWA24.7) and NIST SRM 951 standard bracketing solutions are utilised, the blank constitutes ~2% of both the sample and standard signal. Figure 3a shows that while the intensities are relatively

constant, there is also a close relationship between the blank composition and that of the preceding sample (Fig. 3b). Thus, the blank compositions measured following the introduction of our UWA24.7 sample ($\delta^{11}B$ = 24.7‰) is significantly higher than that following the NIST SRM 951 standard bracketing solutions ($\delta^{11}B$ = 0‰). Accordingly, large disparities between the $\delta^{11}B$ compositions of samples versus bracketing standards require accurate measurement of the blank compositions. Likewise, if the standards and samples have similar isotopic compositions, then the respective blank corrections to the $\delta^{11}B$ compositions of the sample and bracketing standards would also be of similar compositions and hence negligible. However, these ideal conditions cannot always be assured and hence blank corrections have been routinely implemented with a blank being measured prior to each sample (and standard).

In addition to implementing the usual thorough washout procedure, blank correction was minimised by ensuring that the bracketing standard has both a similar B concentration (and HNO_3 normality) and where possible a similar isotopic ($\delta^{11}B$) composition to that of the unknown samples. Thus for aragonitic corals, our in-house standard UWA24.7 is used as a bracketing standard, which was specifically designed to have a $\delta^{11}B$ composition of 24.7‰, similar to that of many shallow water corals measured in the laboratory Samples are corrected for instrumental drift using the relationship:

$$\delta^{11}B_{sample} = \{[2^{11}B/^{10}B_{sample}(1+ 24.7/1000)/(^{11}B/^{10}B_{std1} + {}^{11}B/^{10}B_{std2})]-1\}x1000 \quad \text{..... equation 2}$$

The results for the in-house UWA24.7 are shown in Figure 4 for concentrations of 75 ppb, 150 ppb and 500ppb. For these samples, the conventional approach of standard-sample-standard bracketing is followed with alternating measurements of the residual blank levels and composition. This illustrates that, for sample concentrations ranging from 50ppb to 300ppb, the same blank corrected compositions of $\delta^{11}B$ = 24.7 ±0.03‰ 2sd are obtained for the UWA24.7 standard, a value consistent with that calculated from the gravimetry of the parent solutions. It is noted that these results were obtained (Figure 4A) when UWA24.7 was measured relative to NBS 951, representing the extreme "worst case" in which there is the greatest disparity in $\delta^{11}B$ compositions between the standard and sample ($\delta^{11}B$ = 24.7). This demonstrates the overall veracity of our MC-ICPMS measurement and blank correction procedure. Thus, whilst blank contributions can be marginally significant they can be robustly corrected with minimal contribution to the overall analytical uncertainties when implementing a proper, systematic correction procedure.

The remaining and still major uncertainty in undertaking high precision $\delta^{11}B$ measurements is the longer-term stability of the instrumental mass fractionation during the sample-standard bracketing procedure. For the procedure shown in Figure 2, bracketing standards are measured at intervals of 24 minutes. Thus care is required to ensure maximum stability of the instrument on this time-scale and hence the need for an optimal time efficient washout procedure. In general, drift in instrumental mass bias over a 24 hour period is

minimal and generally smooth, with the deviation between bracketing standards having a typical 2sd uncertainty of from 0.03‰ to 0.3‰, depending predominantly on the signal intensity. On occasions, however, there can occasionally be rapid shifts in the mass bias reflected by relatively large variations between the values of the bracketing standards. However, non-linear shifts of this type can be readily identified by monitoring changes in the composition of the bracketing standard and are often accompanied by changes in signal intensity. The cause of these occasional shifts in mass bias is not always apparent, but experience suggests that they are probably derived from changing conditions in the spray chamber. These can be minimised by using a temperature controlled spray chamber environment, and importantly by retaining a constant chemical environment in the spray chamber. Stability of the spray chamber environment is thus essential and is best maintained by aspirating the same normality and composition acid for washing as well as sample and standard introduction. It is also important that the overall humidity or 'wetness' within the spray be maintained at a constant level as inadvertent drying of the spray chamber, for example, results in a prolonged period (~1 hour) of high boron blank. Cleaning of the spray chamber was undertaken using a DECON 90 (East Sussex UK)cleaning bath solution, then rinsed with Milli-Q H_2O and connected to the MC-ICPMS instrument. This procedure ensures that no droplets form on the inner surface of the spray chamber when solution is aspirated.

The overall veracity of both the chemical extraction and MC-ICPMS procedures are shown by a sequence of $\delta^{11}B$ measurements for the coral standards JCp-1 and our in-house NEP standard (Fig. 5). The latter is a modern carbonate coral standard (NEP) used as an in-house secondary standard to monitor the overall robustness and analytical reproducibility of our chemical MC-ICPMS procedures. Each measurement of the NEP &/or JCp-1 standards is from separate chemical processing batches and MC-ICPMS measurements, and is therefore representative of our overall reproducibility for the complete procedure. Both the JCp-1 and NEP data show similar uncertainties with a 2 standard deviation for repeat measurements of ±0.3‰. This is only slightly larger than that determined from comparisons between our UWA24.7 and NIST SRM~~NBS~~951 at 150 ppb, suggesting that the chemical processing adds negligible variability to measurements of the JCp-1 and NEP standards. Accordingly, the dominant source of error is from the inherent limitations of the MC-ICPMS procedure, i.e. sample intensity and both short and long-term instrumental stability.

As for all isotopic ratio measurements, the precision is limited by the signal to noise ratio and ultimately counting statistics. This becomes especially relevant for $\delta^{11}B$ measurements of <50 ppb B solutions. The blank correction and MC-ICPMS procedures outlined herein are also an essential pre-requisite for accurate measurements at lower intensity.

CONCLUSIONS

A streamlined integrated approach is described here that is based on a simplified rapid boron extraction procedure specifically designed for high precision MC-ICPMS measurements of boron isotopic compositions of marine carbonates such as corals, bivalves, and large benthic forams. The procedure utilises a sequential set of cation and anion exchange columns with the major cations (Ca, Mg, Sr, Na) being and anions (SO_4^{2-}) being quantitatively retained while the B fraction is carried in the eluent. The procedure is specifically designed to eliminate evaporative steps, thus minimising the potential for contamination and volatility-induced loss with the eluent being suitable for immediate MC-ICPMS analyses. In addition to this greatly simplified boron extraction procedure, we also describe a robust protocol for MC-ICPMS analyses based on matching both sample and standard concentrations and $\delta^{11}B$ compositions, which minimises blank corrections. This streamlined relatively robust approach should greatly facilitate the wider application of boron isotope geochemistry to marine carbonates.

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FIGURE CAPTIONS

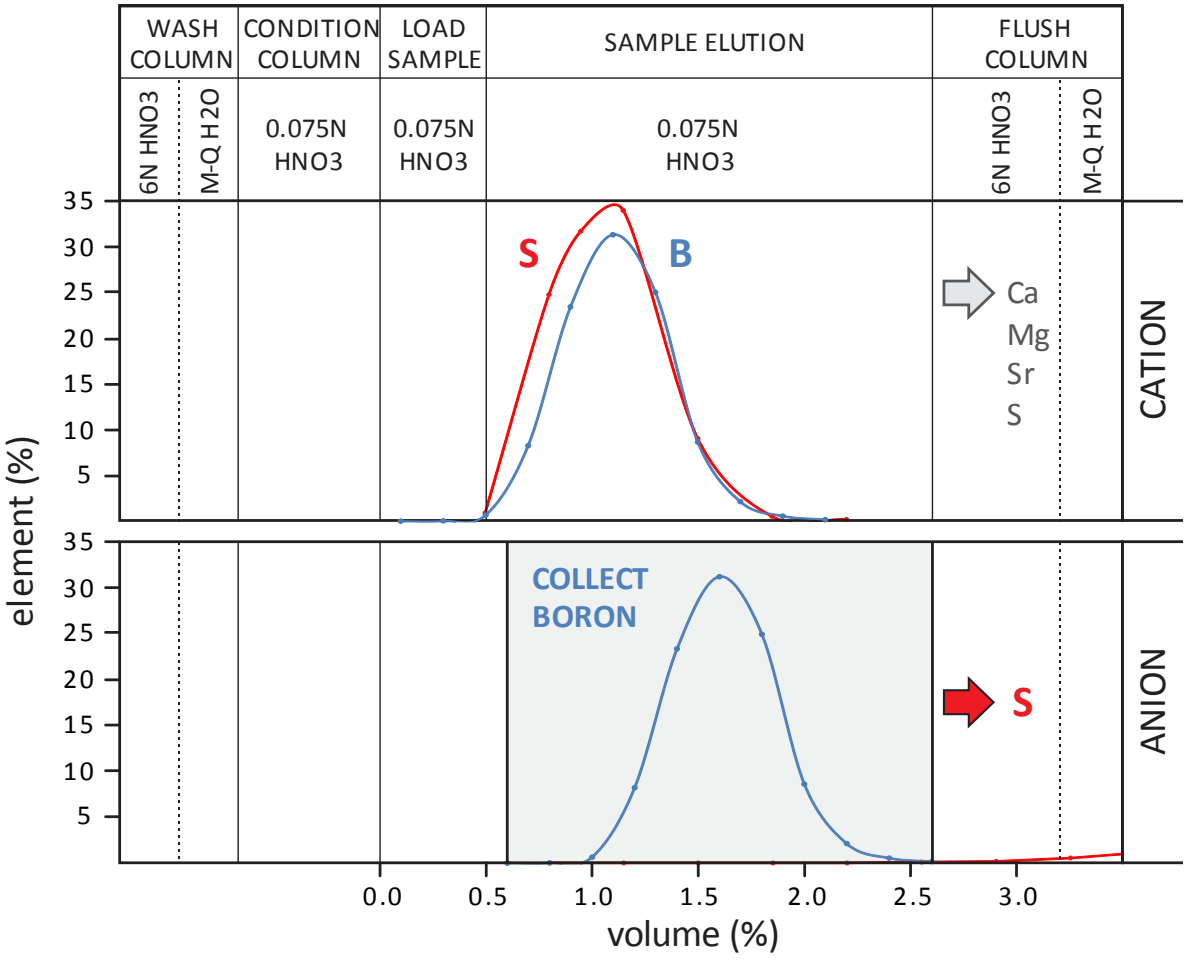


Figure 1. Ion exchange elution scheme for boron extraction using cation followed by anion exchange columns. Boron (and sulphate) is quantitatively eluted through the cation column in a total of ~2 mL of 0.075N HNO_3 with the major cations (Ca ,Mg, Sr, etc) being retained. The boron containing eluent is then passed onto an anion column which effectively retains any sulphate anions. The final boron eluent is then in ~0.15N HNO_3 suitable for MC-ICPMS analyses with the matrix-matched standard of the same normality (ie ~0.15N HNO_3).

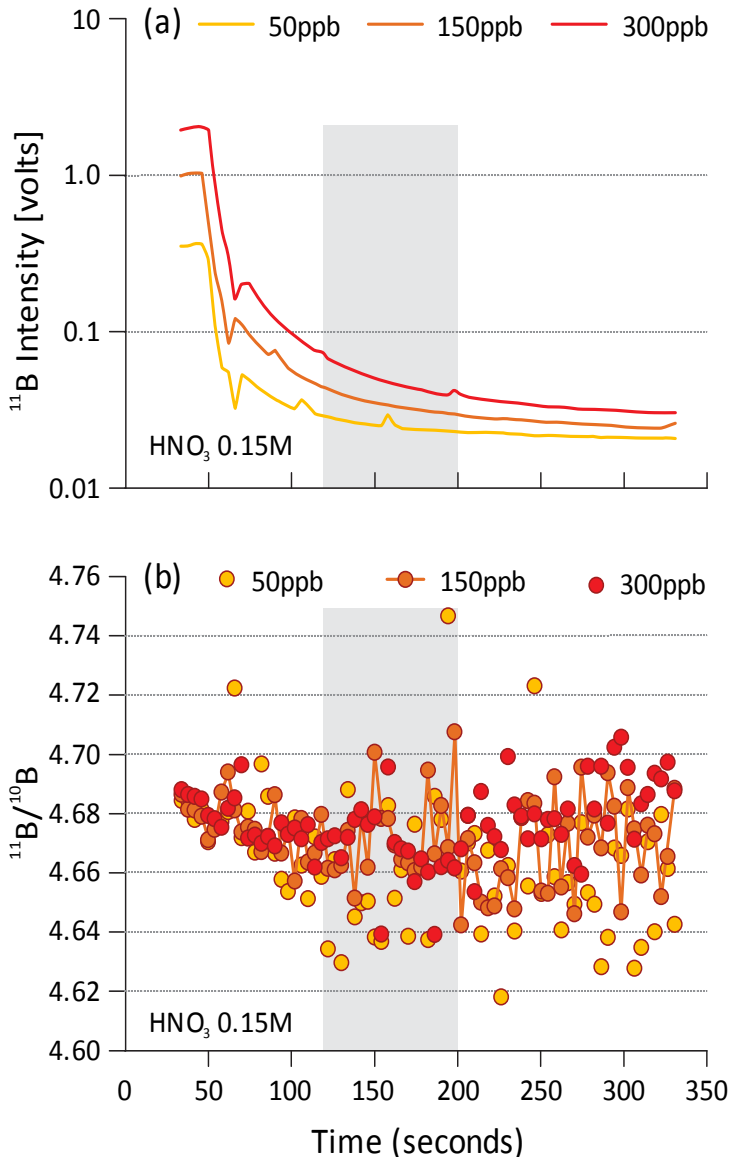


Figure 2. (a) Boron washout with 0.15N HNO_3 following introduction of 50 ppb, 150 ppb and 300 ppb B solutions into a cyclonic quartz spray chamber (b) The $^{11}B/^{10}B$ isotopic composition is shown as a function of washout duration after the measurement of the laboratory standard UWA24.7. The blank composition is measured during the interval from 120-200 seconds (shaded) and is relatively constant.

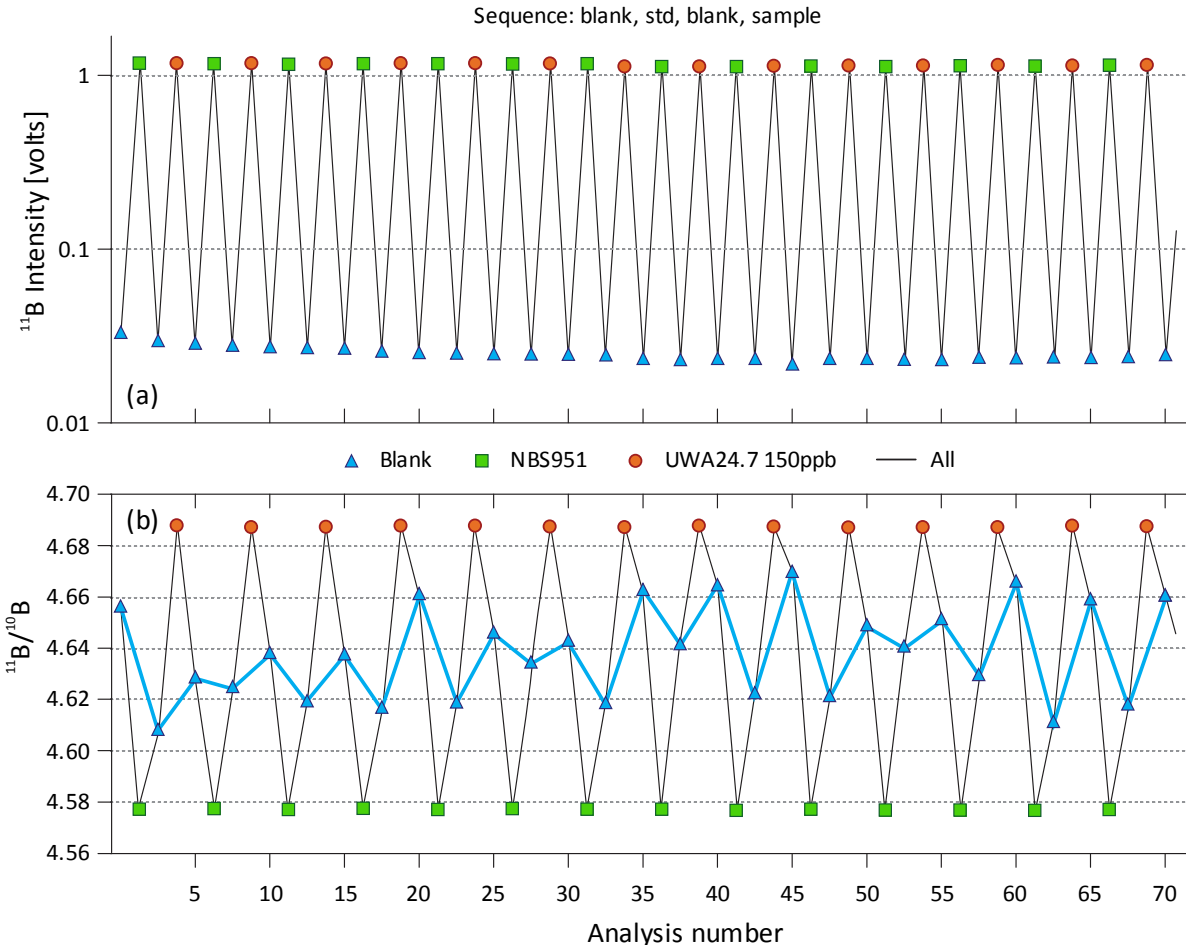
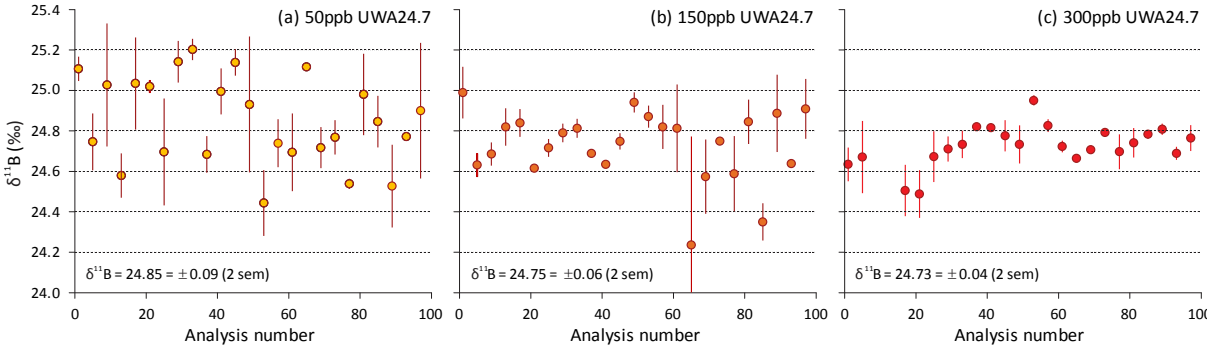


Figure 3. (a) Boron intensities for sequences of blank, standard, blank, sample, blank etc. Note the relatively stable and constant level of blank. (b) Boron $^{11}B/^{10}B$ ratios for sequences of blank, bracketing standard (NIST SRM 951, $\delta^{11}B$ = 0‰), blank and sample (UWA24.7, $\delta^{11}B$ = 24.7‰). Blank compositions are variable but show the expected systematics with those following the UWA24.7 solution having systematically higher $\delta^{11}B$ compositions than those following the NIST SRM 951 standard. The blank composition thus reflects that of the preceding samples or bracketing standards.

A



B

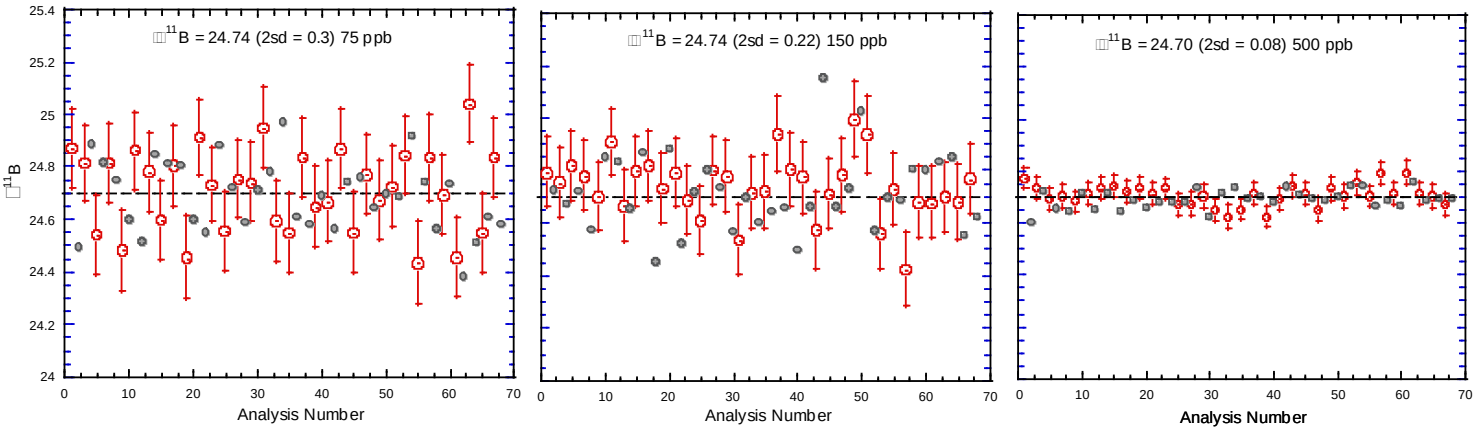


Figure 4. Boron $\delta^{11}B$ compositions for our laboratory standard UWA24.7. A) for 50 ppb, 150 ppb and 300 ppb solutions with the NIST SRM 951 used as a bracketing standard, illustrating the robustness of the blank correction procedures. B) for concentrations ranging from 75ppb, 150 ppb and 500 ppb, but with UWA24.7 used as the bracketing standard. The grey circles show the deviation of the bracketing standard (UWA24.7) used to correct samples (UWA24.7) for instrumental drift. Error bars (2sd) are the combined uncertainties from both the sample measurement as well as bracketing standards.

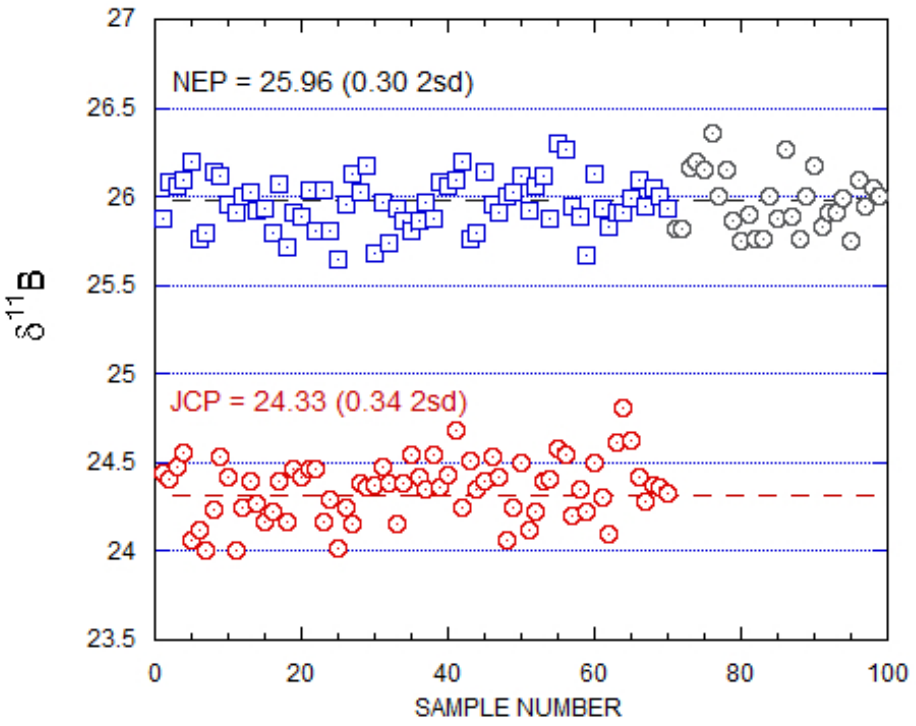


Figure 5. Plot of long-term variation $\delta^{11}B$ compositions measured for the coral carbonate standards JCp-1 ($\delta^{11}B$ = 24.33 ± 0.34‰ 2sd) and NEP ($\delta^{11}B$ = 25.96 ± 0.30‰ 2sd). For NEP the open circles are from measurements using the NEPTUNE Plus while blue squares are from measurements using the NU Plasma II, with both giving identical results. The JCp-1 standard was measured using the NU Plasma II.

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