Determination of B/Ca of natural carbonates by HR-ICP-MS

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Abstract We report a new method for HR-ICP-MS based accurate and precise B/Ca determination from low mass natural carbonates ($\leq$5 μg CaCO3), utilizing a mixed acid matrix (0.1 M HNO3 and 0.3 M HF) and accurate matrix matching technique. Our procedural B/Ca blank of 2.0 $\pm$ 1.0 μmol/mol, internal precision $\leq$1.0%, average within run external precision $\leq$4.0% (2σ), and rapid sample analysis (60 samples/day) make the method well suited for routine measurements. Established methods of B/Ca determination require $\geq$65 μg CaCO3 to achieve a comparable external precision of 3.5% (2σ). We report a B/Ca detection limit of 2 μmol/mol compared to $\geq$10 μmol/mol for previous methods, a fivefold improvement. The method presented here can determine a wide range of B/Ca (9.0–250 μmol/mol) in mass limited samples with considerable tolerance for matrix matching efficiency ($\leq$$\pm$30%). The long-term reproducibility of B/Ca measured on Cambridge in-house consistency standards containing <20, ~85, and ~200 μmol/mol of B/Ca are $\pm$3.7% (2σ, n = 100), $\pm$3.9% (2σ, n = 150), and $\pm$3.2% (2 s, n =180), respectively. A host of other trace element to Ca ratios can also be determined at comparable external precision from samples containing $\leq$5 μg CaCO3. This method is suitable for trace element analysis of single foraminifera shells.

1. Introduction

The variety of paleoclimatic applications of calcite bound boron, both concentrations (B/Ca) and isotope ratio (δ^{11}B), has rendered them highly interesting proxies. The deep ocean carbon reservoir, the largest surface carbon reservoir of the planet, plays a critical role in modulating atmospheric pCO2 variations at the glacial-interglacial timescale. B/Ca of benthic foraminifera has the potential to reconstruct the carbonate ion (ΔCO$_3^{2-}$) history of their habitat [*Yu and Elderfield*, 2007; *Yu et al.*, 2010] unraveling past changes in oceanic circulation and surface productivity patterns and better constraining processes responsible for atmospheric pCO2 variations. Although the sensitivity of B/Ca of epibenthic species to carbonate ion saturation is now well documented, the situation for infaunal species is less certain. Pore waters are saturated with respect to carbonate ion concentrations [*Martin and Sayles*, 1996] suggesting that differences exist between shallow and deeper infaunal species that are in part related to decreased bottom water oxygenation. Low B/Ca of ~20 μmol/mol has been reported for *Uvigerina* spp. [*Yu and Elderfield*, 2007]. However, more precise data below the detection limits of current methods are required to identify any potential carbonate ion effect on infaunal species. Additionally, B/Ca of planktonic foraminifera has the potential to reconstruct pH and [CO$_3^{2-}$] [*Yu et al.*, 2007a; *Foster*, 2008; *Allen et al.*, 2011] with certain limitations [*Allen and Honisch*, 2012]. Despite these important applications, the coupled effects of limited sample availability and multiple analytical challenges have limited the widespread application of B/Ca as a paleoceanographic tool.

The traditional methods of B/Ca analysis on foraminifera by ICP-MS are limited in their application by relatively high calcite mass consumption and instrumental boron blanks [*Yu et al.*, 2005]. Analyses at low concentrations of total dissolved calcite suffer from blank related issues. Increasing the calcite concentration in solution overcomes the boron blank; however, this measure exacerbates the problem of boron memory effects [*Al-Ammar et al.*, 1999, 2000]. These two factors are responsible for the relatively high calcite mass requirement for B/Ca measurements. The established B/Ca determination methods are optimized for comparatively large sample size of $\geq$65 μg calcite with detection limits $\geq$15 μmol/mol [*Yu et al.*, 2005, 2007a; *Rae et al.*, 2011]. As a result, the determination of B/Ca in a host of marine carbonates with B/Ca $\leq$20 μmol/mol (e.g., infaunal benthic foraminifera) and sample size $\leq$50 μg calcite is beyond the analytical capacity of the existing methods.

High fidelity temporal records of B/Ca, reconstructed from down-core benthic foraminifera samples, require analysis of species-specific samples from well-defined size fractions [*Yu and Elderfield*, 2007]. This approach greatly limits the mass of calcite available for analysis, thereby necessitating a B/Ca determination method capable of analyzing small masses of calcite (5–10 μg), including single foraminifera specimens.

Mass spectrometric methods for determination of boron concentrations suffer from multiple analytical challenges. The two most critical problems associated with ICP-MS boron measurements are: (i) low analyte sensitivity of boron due to its high first ionization potential (B-IP1 = 8.3 eV), which results in poor ionization efficiency of boron in the plasma and (ii) long washout time between samples due to strong surface affinity, which leads to a strong memory effect [*Al-Ammar et al.*, 1999, 2000]. The presence of boron in standard HEPA filters and laboratory glassware coupled with its volatile nature results in large instrument and laboratory blanks [*Rosner et al.*, 2005; *Foster et al.*, 2006]. Analysis of foraminifera samples with low boron abundances ([B]$_{Carbonate}$ ~ 2–20 ppm) and in a calcium ion dominated solution is further complicated by matrix effect induced ionization suppression of boron [*Yu et al.*, 2005]. Efforts to boost the boron signal using large carbonate samples (≥250 μg CaCO$_3$) are not only limited by sample availability but also by the nonlinear boron sensitivity response for sample matrices with high total dissolved solid (TDS) [*Yu et al.*, 2005]. Also, the volatile nature of boron in an acid matrix leads to a strong memory effect, hindering accurate boron concentration measurements by traditional ICP-MS methods [*Al-Ammar et al.*, 1999, 2000]. The combination of low ionization efficiency in the plasma, very large instrumental blanks, and long wash out time places a lower limit on both the minimum B/Ca of calcite that can be accurately measured and on the minimum carbonate sample size required to give sufficient accuracy and precision.

We minimized boron memory effect in the sample introduction system by using a mixture of nitric and hydrofluoric acid (0.1 M HNO$_3$ and 0.3 M HF) as our sample matrix. The use of mineral acid HF limits surface adsorption of boron in the sample introduction system, thereby reducing instrumental boron blanks by more than an order of magnitude and significantly improving boron washout efficiency [*Makishima et al.*, 1997]. Utilizing this rapid quantitative washout of boron in HF matrix, we developed a method for accurate and precise B/Ca determination in low mass marine carbonates.

Our new ICP-MS method with low boron blanks and extremely high instrumental sensitivity has lowered the total carbonate mass consumption per analysis by more than an order of magnitude, allowing the determination of B/Ca ratios ≤10 μmol/mol in ≤5 μg carbonate samples. In summary, we report an improved method for B/Ca determination from natural carbonates using HR-ICP-MS and a mixed acid matrix containing HF and HNO$_3$. Our mass spectrometric method is characterized by low blanks, high sensitivity, rapid boron washout, and high precision. This method can be used to generate species and size fraction specific down-core B/Ca records from marine sediments with limited carbonate samples.

2. Materials and Methods

2.1. Acids and Labware
All acids and standards were prepared under boron free Class 100 clean laboratory conditions to minimize boron, sodium, potassium, magnesium, and calcium blanks [*Foster et al.*, 2006]. Pre-cleaned Nalgene® Teflon® bottles (boiled in ~7 M HNO$_3$) were used for solution storage. Savillex® Teflon® beakers and ICP-MS vials (boiled in ~7 M HNO$_3$) were used for standard preparation and analysis. All acids, ICP-MS standards and samples were prepared using 18.3 Mega-Ohm MQ water and Seastar® Optima® (Fisher®) grade HF and HNO$_3$. Eppendorf® snap cap vials (0.5 mL) were used for sample cleaning and analysis. The Eppendorf® vials were boiled in 10% v/v HCl, rigorously rinsed, and then boiled in MQ water to neutralize pH.

2.2. B/Ca Standard Preparation
A series of standards of fixed Ca concentration and variable Li, B, Na, Mg, Al, P, Mn, Fe, Zn, Sr, Cd, Ba, and U were prepared for foraminiferal trace element analysis following the protocol outlined in *Yu et al.* [2005] (supporting information Table S1). All ICP-MS standards were gravimetrically prepared using high purity single element standards. A high concentration (10,000 ppm) Ca standard was prepared by gravimetrically dissolving 99.997% pure CaCO$_3$ (Sigma-Aldrich) to serve as the fixed calcium concentration matrix. Concentrated stock solutions of individual standards with 1000 ppm calcium were prepared by mixing individual single element standards. Each contributing single element standard was analyzed for all other

Table 1. ICP-MS Settings for Boron Isotopes and Me/Ca Determinations

Parameter	Trace Element Mode
Plasma RF power	1250 W
Nebulizer	ESI™—50 μL
Spray chamber	Teflon Scott type (single pass)[a]
Injector	ESI™ platinum (1.8 mm I.D.)
Sample cone	Pt-normal
Skimmer cone	Pt-H
Extraction voltage	−2000 V
Sample matrix	0.1 M HNO_3 + 0.3 M HF
Uptake time	70 s
Analysis time	100 s
Washout time	120 s
Mass resolution	Low and medium
Magnet mass	Variable
Runs	3 (LR), 3 (MR)
Passes	15 (LR), 3 (MR)
Detection mode	Dual (fixed for each analyte)

[a]Assembled from Savillex® PFA parts for column components.

elements of interest to determine their background equivalent concentration, which was incorporated into the mixed stock standard solutions. Our 100 ppm Ca working standards were prepared gravimetrically. The calibration standards for ICP-MS analysis, usually at 10 ppm calcium concentration, were volumetrically prepared from the working standards on the day of analysis using the same batch of acid used for sample preparation.

We prepared four in-house consistency standards for Me/Ca analysis by combining concentrated fractions of cleaned foraminifera samples. The four standards were prepared to cover the wide range (∼20 to 200 μmol/mol) of B/Ca expected in down-core samples as follows: one of *C. wuellerstorfi* (B/Ca$_{wuellerstorfi}$ ∼ 200 μmol/mol), two of *Uvigerina* spp. (B/Ca$_{Uvig-1}$ and B/Ca$_{Uvig-2}$ ∼ 20 μmol/mol), and a synthetic mixture of *C. wuellerstorfi* and *Uvigerina* spp. (B/Ca$_{Mix}$ ∼ 80 μmol/mol). The concentrates (∼100 ppm Ca) of the in-house consistency standards were diluted on the day of analysis using the same batch of acid used for sample and calibration standard preparation.

2.3. Mass Spectrometry

Boron and other elements of interest were analyzed at the University of Cambridge on a Thermo® Element XR, a single collector sector field high resolution inductively coupled plasma mass spectrometer, fitted with a high sensitivity interface pump (Jet pump). Instrumental settings for isotope and trace element analyses are listed in Table 1. In order to analyze B/Ca in a mixed acid matrix (0.1 M HNO_3 and 0.3 M HF), a Teflon® Scott type (single pass) spray chamber was constructed. Additionally, we used a platinum injector (1.8 mm I.D.) to significantly reduce the instrumental boron blanks (Table 2). Time resolved analyses of boron uptake and washout in different acid matrices, along with the evaluation of boron blanks were carried out to determine the best matrix for isotope and B/Ca analysis (supporting information Figure S1).

2.3.1. B/Ca and Metal/Ca

Trace elements to Ca ratio (Me/Ca) determinations by Element XR were carried out using a set of external calibration standards (supporting information Table S1). Samples were analyzed at fixed calcium concentration. Samples and standards were concentration matched within ±5%. Samples were analyzed at a matrix calcium concentration ([Ca]$_{Matrix}$) of 10 ppm when normal ion extraction cones were used, or at a

Table 2. Boron Blanks and Sensitivity in Different Acid Matrices[a]

Spray Chamber		Injector Material	[HNO$_3$] (M)	[HF] (M)	^{11}B Blank (cps)	1 ppb ^{11}B (cps)	^{11}B-S/N	^{115}In Blank (cps)	1 ppb ^{115}In (cps)	^{115}In-S/N
Material	Type									
Quartz	Cyclonic	Quartz	0.1		16,953	19,3140	11	4611	2,028,881	440
Quartz	Cyclonic	Platinum	0.1		11,623	214,302	18	2102	2,497,732	1188
Quartz	Cyclonic	Platinum	0.4		5422	118,875	22	5851	1,557,314	266
Teflon	Scott	Platinum	0.1		7708	302,183	39	19,105	4,357,595	228
Teflon	Scott	Platinum	0.2		19,663	299,794	15	14,594	4,176,358	286
Teflon	Scott	Platinum	0.4		19,750	286,104	14	11,152	3,904,246	350
Teflon	Scott	Platinum	0.1	0.15	4970	288,935	58			
Teflon	Scott	Platinum	0.2	0.15	6456	265,298	41			
Teflon	Scott	Platinum	0.4	0.15	3587	250,590	70			
Teflon	Scott	Platinum	0.1	0.3	2011	315,428	157			
Teflon	Scott	Platinum	0.2	0.3	2286	285,282	125			
Teflon	Scott	Platinum	0.4	0.3	3312	264,047	80			

[a]All measurements were performed with normal sample and skimmer cones. S/N is defined as signal-to-noise (blank) ratio where the "Signal" is the sensitivity in counts per second (cps) of the isotope of an analyte for a 1 ppb solution and the "Noise" is defined as the matrix blank in cps.

**Table 3.** ICP-MS Method for Me/Ca Determination

Isotope	Mass Resolution	Mass Window	Sample Time	Samples Per Peak	Integration Window	Detection Mode	Integration Type	Runs	Passes
7Li	Low	15	0.005	50	10	Counting	Average	3	15
11B	Low	15	0.005	100	10	Counting	Average	3	15
25Mg	Low	10	0.01	50	5	Analog	Average	3	15
27Al	Low	10	0.01	50	5	Analog	Average	3	15
43Ca	Low	10	0.02	50	5	Analog	Average	3	15
87Sr	Low	10	0.04	50	5	Analog	Average	3	15
111Cd	Low	15	0.02	100	10	Counting	Average	3	15
137Ba	Low	10	0.02	50	5	Counting	Average	3	15
238U	Low	10	0.05	100	5	Counting	Average	3	15
23Na	Medium	100	0.02	25	50	Analog	Average	3	5
43Ca	Medium	100	0.01	25	50	Analog	Average	3	5
55Mn	Medium	100	0.01	25	50	Counting	Average	3	5
56Fe	Medium	100	0.05	25	50	Counting	Average	3	5
66Zn	Medium	100	0.01	25	50	Counting	Average	3	5

$[Ca]_{Matrix}$ of 5 ppm using the Jet and X cones. Prior to ICP-MS Me/Ca analysis, samples were analyzed by ICP-AES (Varian® VISTA) to determine their calcium concentration and then appropriately diluted [*de Villiers et al.*, 2002]. The sensitivity of the ICP-MS was optimized in low mass resolution ($\Delta m/m = 300$) mode on ^{11}B, ^{115}In, and ^{175}Lu using a 1 ppb/analyte multielement tune solution. Minimum sensitivities of 250,000 cps/ppb on ^{11}B, 2,500,000 cps/ppb on ^{115}In, and 2,000,000 cps/ppb on ^{175}Lu were set as operational criteria. For medium resolution ($\Delta m/m = 4000$) tuning, the instrument was optimized on ^{56}Fe to achieve a mass resolution of ≥ 4000. Before sample analysis, mass bias determination was carried out using a foraminiferal matrix matched solution. Detector cross calibration between pulse and analog modes was performed daily. Samples were analyzed in blocks of seven with a pair of acid blanks and internal consistency standards (Standard 3 of calibration) bracketing each block. At low calcium concentrations ($[Ca]_{Matrix} \leq 20$ ppm), minimal instrumental sensitivity drift and rapid wash out time allowed for analysis of 10 samples/h.

The concentrations of foraminiferal trace elements of interest (Li, B, Na, Mg, Al, Mn, Fe, Zn, Sr, Cd, Ba, and U) span a large range, from nmol/mol for U/Ca to mmol/mol for Mg/Ca. Each isotope of the analytes was measured at a fixed detection mode to avoid detection mode switch (pulse to analog) during analysis. Calcium was measured in both low and medium resolution to maintain accuracy of Me/Ca ratios obtained from the two mass resolution modes (Table 3).

### 2.4. Foraminifera Sample Preparation
Species and size fraction specific foraminifera shells were handpicked under an optical microscope to select samples with minimal or no signs of diagenetic alteration or authigenic mineral deposits. One to two milligrams of *Orbulina universa*, *Globoratalia inflata*, *Globigerinoides bulloides*, and *Globigerinoides sacculifer* specimens of size fraction 300–355 μm were picked. Samples were chemically cleaned in batches of 1 mg or less; this required that the larger samples were split into equal weight fractions during cleaning and recombined before dissolution. Foraminifera shells were gently cracked open, fragmented shells were ultrasonicated in MQ water (three times), methanol (two times), and again in MQ water (two times) to remove clay materials. After clay removal shells were either *reductively* (ammonia—ammonium acetate buffer and hydrazine) and/or *oxidatively* (sodium hydroxide and hydrogen peroxide) cleaned [*Boyle and Keigwin*, 1985; *Rosenthal et al.*, 1997; *Barker et al.*, 2003; *Yu et al.*, 2007]. To evaluate the effect of the sample cleaning method on calcite bound boron, the species-specific core-top foraminifera samples were split into three fractions and cleaned following one of a reductive-oxidative-reductive (hydrazine-H_2O_2-hydrazine), reductive-oxidative (hydrazine-H_2O_2), and oxidative only (H_2O_2) sequence of cleaning steps. Postchemical cleaning, the samples were leached with very dilute ultra clean HNO_3 (0.001 M) to release any chemisorbed elements from the surface of the calcite. Leached samples were dissolved in a minimum volume of 1 M HNO_3 (40–60 μL), centrifuged for 2 min at 10,000 rpm and the supernatant was used for Me/Ca analysis. A 5 μL aliquot of the supernatant was diluted with 200 μL of 0.1 M HNO_3 to prepare a sample stock solution for Me/Ca analysis. The remainder (~50 μL) of the supernatant was retained for isotope analysis. A 50 μL aliquot of the Me/Ca stock solution was further fivefold diluted with 0.1 M HNO_3 for calcium
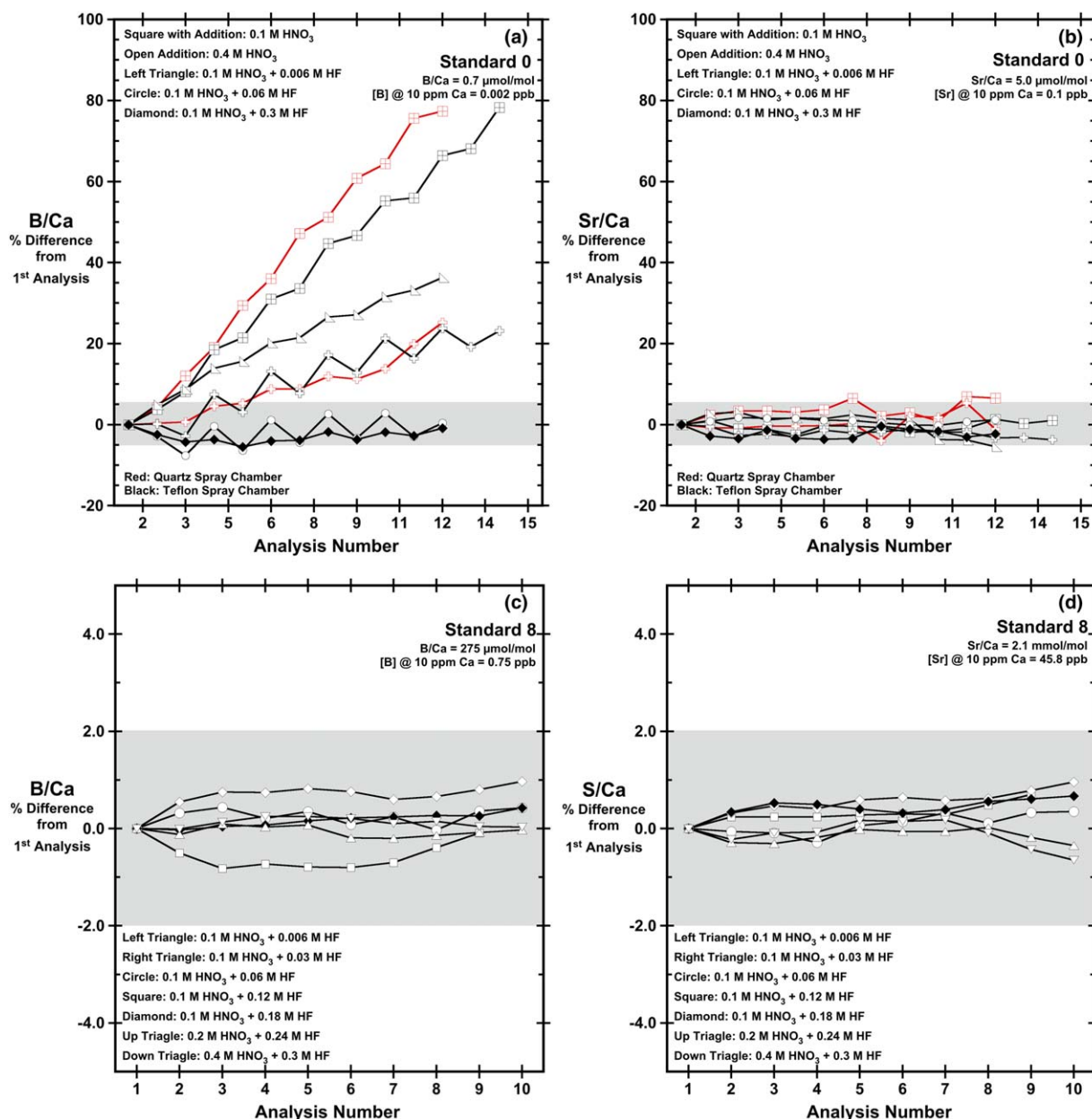
Figure 1. Matrix dependent B/Ca washout. Comparison of B/Ca and Sr/Ca memory effects in different acid matrices. Figures 1(a) and 1(b) represent back to back analyses of the lowest concentration Me/Ca calibration standard (Standard 0) and an intermediate concentration standard (Standard 3) both bracketed by acid blanks (supporting information Table S1 and Figure S2)—the data for Standard 0 are shown here. The complimentary plots of B/Ca and Sr/Ca comparison of Standard 3 analyses from the first scheme of ICP analyses are shown in supporting information Figure S2. Figures 1(c) and 1(d) represent consecutive analyses of the highest concentration Me/Ca standard (Standard 8) bracketed by acid blanks. These figures represent percent difference between the first analysis and subsequent analyses for both B/Ca and Sr/Ca. All analyses were performed at 10 ppm $[Ca]_{Matrix}$ with $[B]_{Standard}$ of 0.002, 0.17, and 0.75 ppb in Standard 0, Standard 3, and Standard 8, respectively. The $[Sr]_{Standard}$ for the same standards were 0.1, 22.4, and 45.8 ppb. The B/Ca and Sr/Ca data in all the figures are acid blank corrected; however, none of the data is corrected for instrumental drift. The gray area in Figures 1(a) and 1(b) represents $\pm5\%$ variation from the first analysis and in Figures 1(c) and 1(d) represent $\pm2\%$ variation. In Figures 1(a) and 1(b), the red symbols represent analyses performed with a quartz cyclonic spray chamber. All other analyses were performed with a Teflon® Scott type spray chamber—black symbols. The symbols are as follows: 0.1 M HNO_3—squares with addition symbols; 0.4 M HNO_3—open addition symbols; 0.1 M HNO_3 + 0.006 M HF—left triangles; 0.1 M HNO_3 + 0.03 M HF—right triangles; 0.1 M HNO_3 + 0.06 M HF—circles; 0.1 M HNO_3 + 0.12 M HF—squares; 0.1 M HNO_3 + 0.18 M HF—diamonds; 0.1 M HNO_3 + 0.24 M HF—up triangles; and 0.1 M HNO_3 + 0.3 M HF—down triangles.

concentration analysis on the ICP-AES. Prior to ICP-MS analysis of Me/Ca, samples were diluted to fixed calcium concentrations ($[Ca]_{Matrix} \leq 10$ ppm) using 0.1 M HNO_3 and 0.3 M HF mix acid matrix. The acid matrix containing HF was used only in the final dilution step.
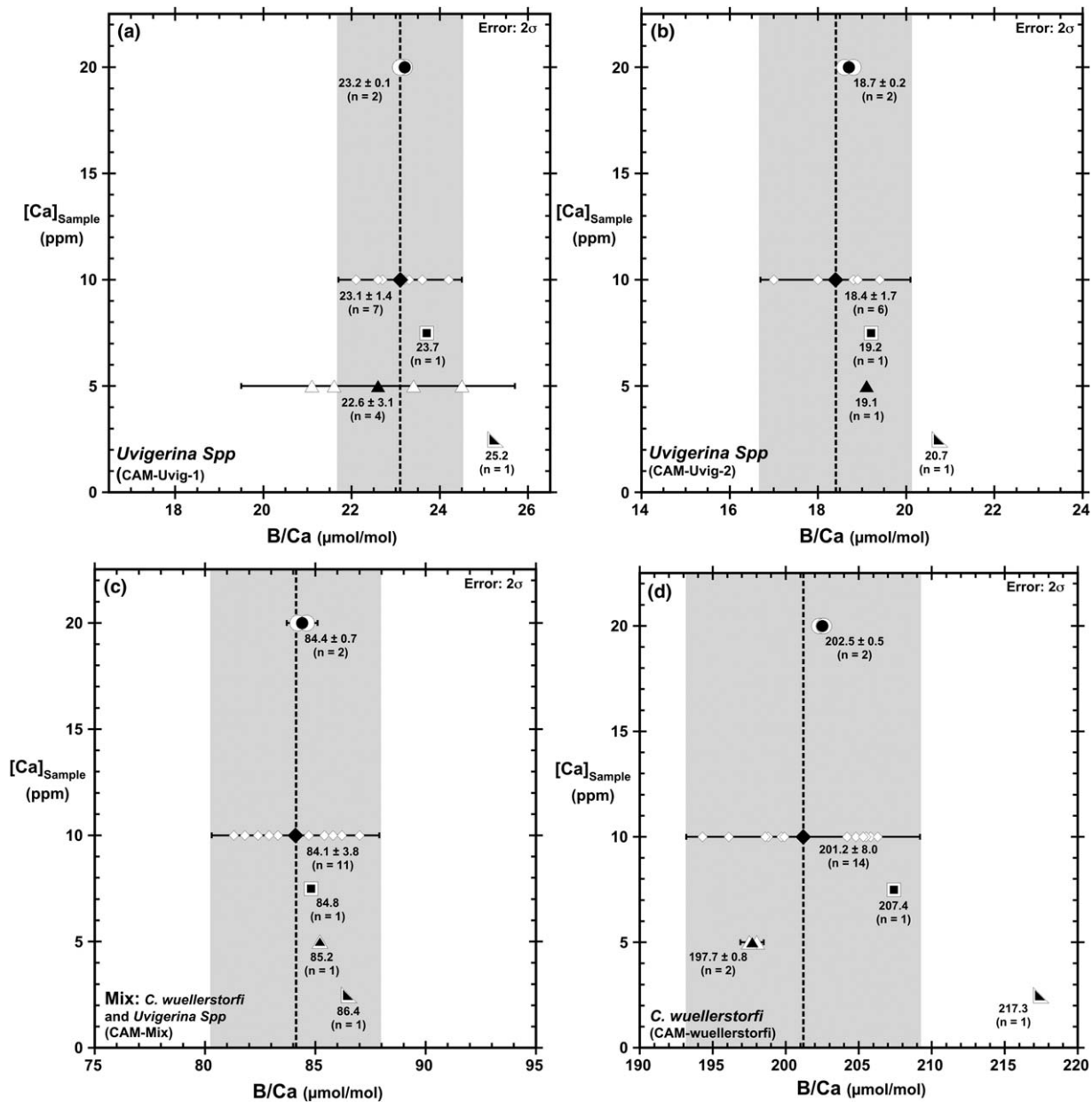
Figure 2. (a–d) Accuracy of B/Ca determination at different degrees of sample dilution. The four Cambridge consistency standards, two of *Uvigerina* spp. (CAM-Uvig-1 and CAM-Uvig-2); one of *C. wuellerstorfi* (CAM-wuellerstorfi); and a synthetic mixture of *C. wuellerstorfi* and *Uvigerina* spp. (CAM-Mix) were analyzed at $[Ca]_{Matrix}$ of 2.5, 5.0, 7.5, 10.0, and 20.0 ppm (Table 4). External calibration standards were accurately ($\pm 1\%$) $[Ca]_{Matrix}$ matched with the consistency standards during analyses at different $[Ca]_{Matrix}$. Open symbols represent an average of 10 measurements acquired during a single instrument session. The solid symbols represent the average of the open symbols with 2σ analytical uncertainty. Samples analyzed at 2.5 ppm $[Ca]_{Matrix}$ are represented by left triangles, at 5.0 ppm $[Ca]_{Matrix}$ by up triangles, at 7.5 ppm $[Ca]_{Matrix}$ by squares, at 10.0 ppm $[Ca]_{Matrix}$ by diamonds, and at 20.0 ppm by circles. In each figure, the dotted line represents the average of all B/Ca analyses performed at 10.0 ppm $[Ca]_{Matrix}$, the preferred $[Ca]_{Matrix}$ of analyses and the gray area represents the 2σ spread in the B/Ca measured at 10 ppm $[Ca]_{Matrix}$.

3. Results and Discussion

3.1. B/Ca Determination by ICP-MS

Determination of the cationic composition of foraminifera (Me/Ca: trace element to Ca ratio) by ICP-MS requires the analyses of elements from the lightest to the heaviest end of the periodic table ([7]Li to [238]U), spanning more than seven orders of magnitude in concentration (Ca >> Mg >> U). As 99.9% of the dissolved foraminifera matrix is calcium, for precise Me/Ca measurements, closely matching the calcium

Table 4. External Precision on Me/Ca Determinations of Cambridge Consistency Standards

Consistency Standard	Number of Analyses	Li/Ca μmol/ mol (±2σ)	B/Ca μmol/ mol (±2σ)	Mg/Ca mmol/ mol (±2σ)	Sr/Ca mmol/ mol (±2σ)	Cd/Ca μmol/ mol (±2σ)	Ba/Ca μmol/ mol (±2σ)	U/Ca nmol/ mol (±2σ)	Na/Ca mmol/ mol (±2σ)	Mn/Ca μmol/ mol (±2σ)
CAM-wuellerstorfi	180	16.4 ± 0.8	201.7 ± 6.5	1.225 ± 0.055	1.299 ± 0.016	0.287 ± 0.023	4.80 ± 0.20	44.0 ± 1.7	5.85 ± 0.23	71.27 ± 1.56
CAM-Mix	150	15.3 ± 0.8	84.3 ± 3.3	1.443 ± 0.078	1.297 ± 0.011	0.211 ± 0.014	3.26 ± 0.14	65.2 ± 2.4	4.53 ± 0.16	26.25 ± 0.81
CAM-Uvig-1	130	15.2 ± 0.7	23.2 ± 1.6	1.435 ± 0.053	1.173 ± 0.017	0.167 ± 0.010	3.57 ± 0.15	48.6 ± 1.7	4.23 ± 0.09	30.85 ± 0.94
CAM-Uvig-2	100	13.7 ± 0.6	18.9 ± 0.7	1.455 ± 0.065	1.178 ± 0.011	0.163 ± 0.008	3.20 ± 0.06	51.6 ± 1.7	3.54 ± 0.08	30.61 ± 0.52

concentrations of the standards and the samples is sufficient for high internal precision. However, the accuracy of the Me/Ca determination method is dictated by the choice of isotope and mode (mass resolution) of determination for each analyte element. Isobaric interference from the plasma and matrix based cations can potentially produce internally precise yet inaccurate estimates of Me/Ca [*Yu et al.*, 2005; *Marchitto*, 2006].

Determination of B/Ca by ICP-MS is limited by the comparatively low abundance of boron in foraminiferal calcite, poor ionization of boron in the plasma, high blanks, and the extremely long washout time between samples [*Al-Ammar et al.*, 1999, 2000; *Yu et al.*, 2005]. Additionally, postmass spectrometric analysis requires rigorous processing of the raw data to eliminate the effects of instrumental drift [*Yu et al.*, 2005]. During B/Ca determination in nitric acid matrix boron shows a strong memory effect (Figures 1a and 2b). This cumulative effect is marginally more severe for quartz spray chambers than for Teflon spray chambers. An increase in matrix acid molarity facilitates boron washout; however, a quantitative washout is not achievable with nitric acid. At $[Ca]_{Matrix}$ of 10 ppm a boron memory effect of ~0.4 pg results in an increase of 1 μmol/mol in the measured B/Ca ratio (supporting information Text S1). The observed increase in the measured B/Ca ratios of Standard 0 (0.5 μmol/mol) and Standard 3 (12 μmol/mol) when using nitric acid matrix, equates to a total boron blank of 0.2 pg and 5.1 pg respectively. If using established methods of B/Ca determination at $[Ca]_{Matrix} \geq 100$ ppm, for samples with B/Ca ~20 μmol/mol, a similar boron blank of ~5 pg will lead to >6% increase in measured B/Ca ratios (Total $B_{Analyte} > 80$ pg at 150 μL sample volume). Other elements of interest, such as Li, Al, Mg, Sr, Cd, Ba, and U, do not suffer from similar washout related problems (Figure 1c). Adoption of a mineral acid based matrix resolves the boron washout problem without affecting the ionization or washout behaviors of other elements of interest (Figure 1d). A mixed acid matrix of 0.1 M HNO_3 and 0.3 M HF was used in the present study. Presence of HF in the matrix can lead to precipitation of CaF_2 from highly concentrated solutions of calcium. To avoid CaF_2 precipitation only the final dilution of samples, just prior to ICP-MS analysis, were carried out with the HF based matrix. The preferred calcium concentration of analyte, based on signal stability and calcium accumulation on sampling cones, was found to be ≤25 ppm in our choice of matrix. However, higher concentrations of calcium can be analyzed in HF based matrix by increasing the nitric acid concentration to prevent CaF_2 precipitation.

Routine trace element determinations by ICP-MS were carried out at $[Ca]_{Matrix}$ of 10 ppm. A list of elements and their choice of isotope are tabulated in Table 3. The detection mode for each element was kept fixed through the entire run to avoid detection mode switch induced changes in sensitivity. Sample dilutions were carefully schemed to ensure that the intensities (cps) of low abundance elements (viz. Li, B, Cd, and U) that are measured in counting mode remained below the threshold for counting to analog detection mode switch. Instrumental sensitivity was optimized on ^{11}B, ^{115}In, and ^{175}Lu, with a typical sensitivity of ~2.5 × 10^6 cps/ppb on ^{115}In (see section 2.3.). The instrument was conditioned with a 10

Table 5. Summary of B/Ca Method[a]

| Parameter	Matrix	Extraction Cones		Vol_{Smpl} (μL)	[Ca] (μg/mL)	B/Ca_{Smpl} (μmol/mol)	[B] (ng/mL)	$^{11}B_{Smpl}$ (cps)	$^{11}B_{Blank}$ (cps)	B_{Total} (ng)
		Sample	Skimmer							
B/Ca_{High}	HNO_3 + HF	Pt-H	Pt-Normal	150	10	200	0.55	≥2 × 10^5	≤2000	0.08
B/Ca_{Low}	HNO_3 + HF	Pt-H	Pt-Normal	150	10	20	0.05	≥2 × 10^4	≤2000	0.008

[a]During a typical analytical session (60 samples/10 h) the average matrix blank is 6450 ± 199 cps (2σ, n = 15); average sensitivity for consistency standard C. wuellerstorfi (CAM-wuellerstorfi, B/Ca = 201.7 ± 6.5 μmol/mol) is 352,442 ± 4666 cps (2σ, n = 10); and for consistency standard *Uvigerina* spp. – 1 (CAM-Uvig-1, B/Ca = 23.2 ± 1.6 μmol/mol) is 35,879 ± 716 cps (2σ, n = 10).
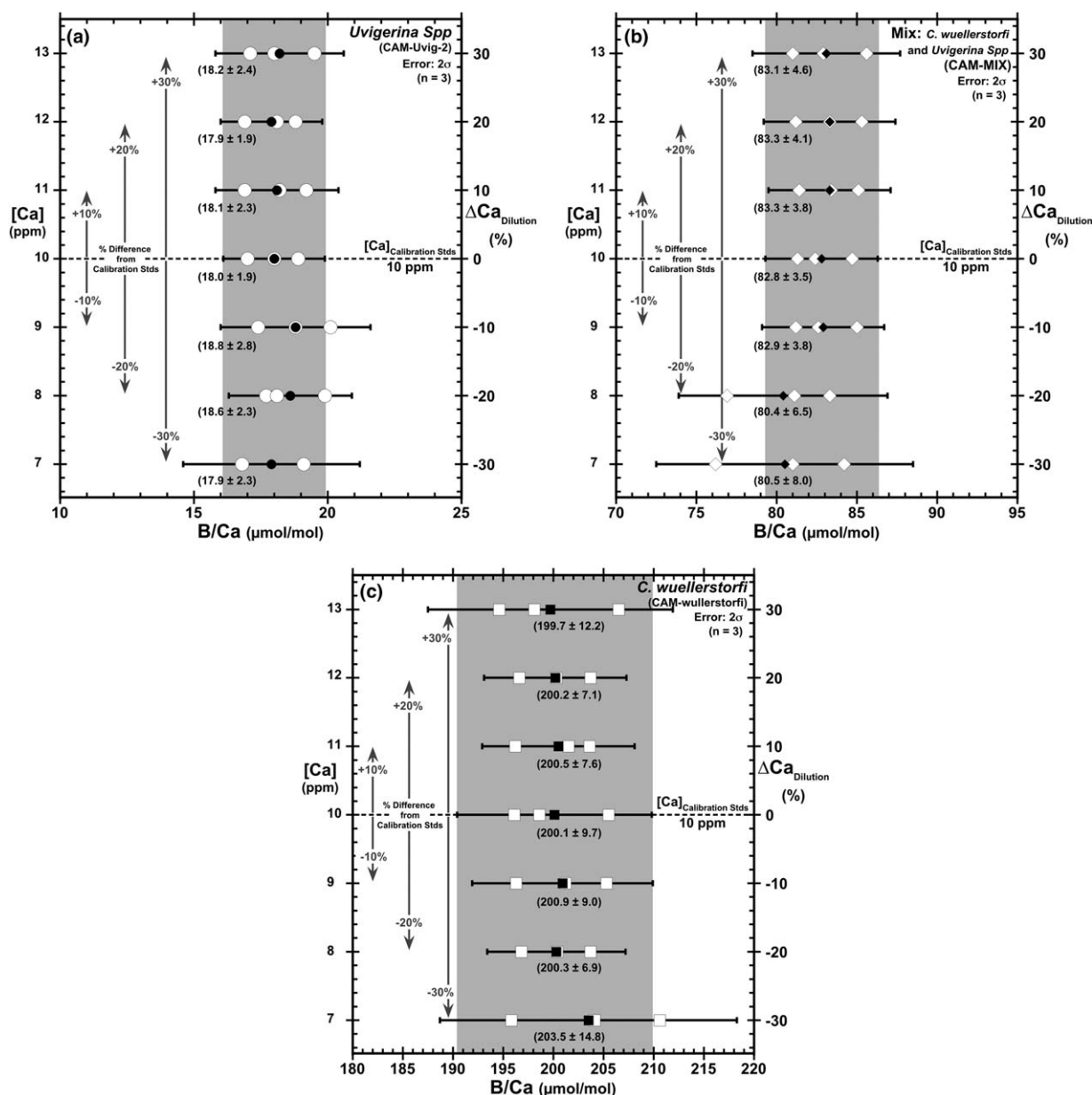
Figure 3. (a–c) Effect of matrix matching efficiency on B/Ca measurements. Three of the Cambridge consistency standards CAM-Uvig-2, CAM-wuellerstorfi, and CAM-Mix were analyzed at ±0%, ±10%, ±20%, ±30% [Ca]$_{Matrix}$ dilution difference from the external calibration standards at [Ca]$_{Matrix}$ of 10 ppm (Table 4). The left-hand Y axis represents the [Ca]$_{Matrix}$ of the consistency standards and the right-hand Y axis represents percentage difference dilution of the consistency standards from the calibration standards. The consistency standards were analyzed over three analytical sessions. In each session, there were five measurements made, and the open symbols represent the average of those five measurements. The solid symbols represent the average of the three open symbols, which is a total of (5 × 3) 15 measurements, with 2σ analytical uncertainty. The external calibration standards were analyzed at [Ca]$_{Matrix}$ of 10 ppm for every instrument session. In each figure, the dotted horizontal line represents the average of B/Ca analyses performed at exact dilution, and the vertical gray area represents the 2σ spread in the B/Ca of the consistency standard measured at the same concentration as calibration standards (10 ppm [Ca]$_{Matrix}$), the preferred [Ca]$_{Matrix}$ of analyses.

ppm calcium solution (Standard 0) for a minimum of 30 min prior to sample analysis. External calibration standards were measured at the beginning and end of each day. Samples were analyzed in blocks of seven, bracketed by a pair of acid blanks and a pair of bracketing standards to correct for instrumental drift. The use of platinum cones and analysis of solutions containing low total dissolved solids at [Ca]$_{Matrix}$ of 10 ppm ensured the instrumental sensitivity drift over periods of 12 or more hours was <±5%.
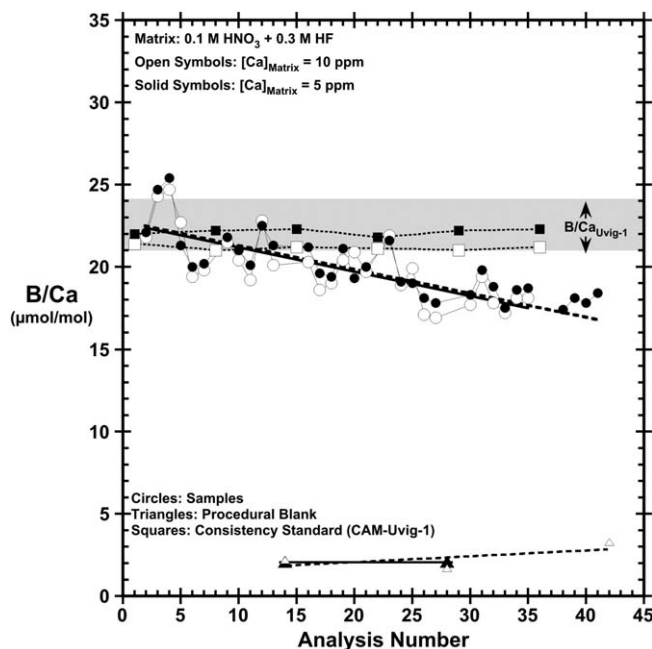
Figure 4. Analytical precision of B/Ca determination at variable [Ca]$_{Matrix}$. A series of down-core *Uvigerina peregrina* samples (circles), spanning a glacial-interglacial cycle, were analyzed in HNO$_3$-HF matrix at [Ca]$_{Matrix}$ of 5 and 10 ppm. For the two sets of analyses calibration standards, consistency standards, samples, and procedural blanks were diluted from the same concentrated stock solution. The same standard-sample analyses scheme was replicated for the two sets of analyses. The down-core samples are plotted against their analysis number in the sequence, not against age or depth in the core. The data on the plots show blank corrected, drift corrected, normalized B/Ca from each run. The down-core *Uvigerina peregrina* samples are represented by circles, procedural blanks by triangles, and the consistency standards (CAM-Uvig-1) by squares. The observed decreasing trend is real variation from sample to sample spanning a glacial-interglacial cycle—not an instrumental artifact. Analyses at 5 ppm [Ca]$_{Matrix}$ are represented by open symbols and at 10 ppm [Ca]$_{Matrix}$ by solid symbols. The gray shaded area represents the mean measured B/Ca of the CAM-Uvig-1 (B/Ca$_{Uvig-1}$ = 23.2 ± 1.6 μmol/mol, 2σ, n = 130). The solid lines and dashed lines represent the linear fits through the samples and blanks analyzed at 5 and 10 ppm [Ca]$_{Matrix}$, respectively.
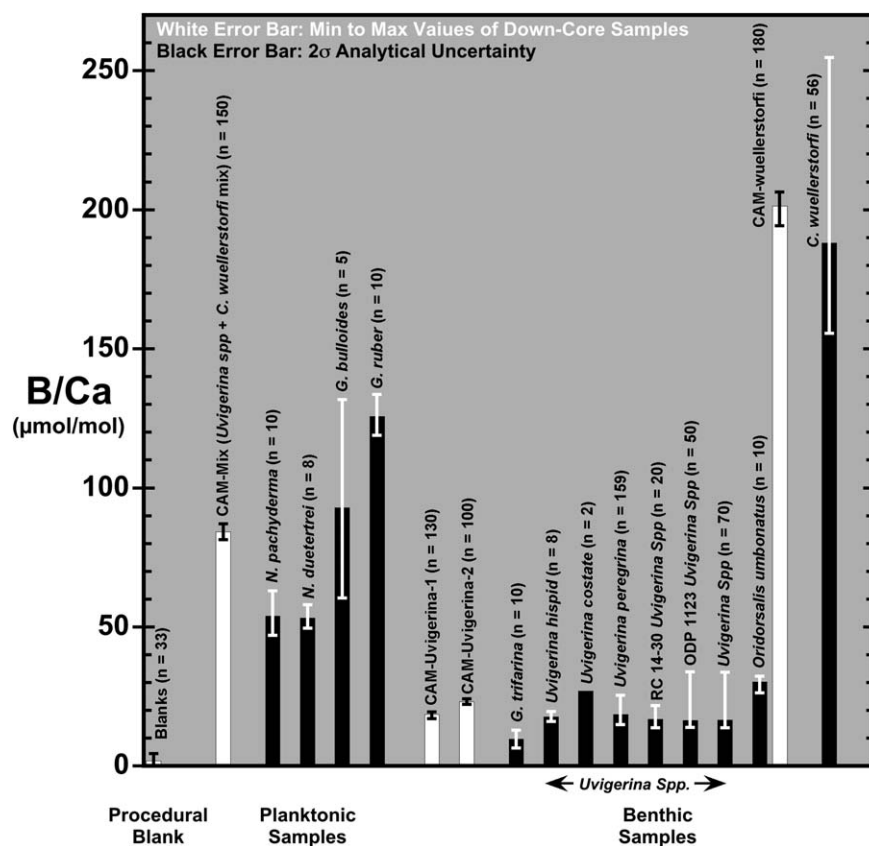
3.2. B/Ca of Foraminifera and In-House Consistency Standards

The analytical merit of our B/Ca method was evaluated by analyzing the four internal consistency standards described previously. We measured B/Ca$_{wuellerstorfi}$ = 201.7 ± 6.5 μmol/mol (n = 180), B/Ca$_{Uvig-1}$ = 23.2 ± 1.6 μmol/mol (n = 130), B/Ca$_{Uvig-2}$ = 18.9 ± 0.7 μmol/mol (n = 100), and B/Ca$_{Mix}$ = 84.3 ± 3.3 μmol/mol (n = 150) during multiple instrument sessions that spread over 8 months (Table 4—External precision on Me/Ca on different consistency standards).

We analyzed these four standards over a range of matrix calcium concentrations to determine the minimum calcite mass required for accurate measurements by our new method. External calibration standards and the four consistency standards were appropriately diluted from the same concentrated stock solutions to 2.5, 5.0, 7.5, 10.0, and 20.0 ppm [Ca]$_{Matrix}$ for B/Ca analyses (Figures 2a–2d). Measured B/Ca of all four standards, covering an analyte

B/Ca of 20 to 200 μmol/mol, are indistinguishable from each other in the dilution range of 5–20 ppm [Ca]$_{Matrix}$. The B/Ca measurement at 2.5 ppm [Ca]$_{Matrix}$ is usually higher, except for the CAM-Mix standard, than those at [Ca]$_{Matrix}$ ≥ 5 ppm. At 2.5 ppm [Ca]$_{Matrix}$, the total amount of boron analyzed for a B/Ca of 20 and 200 μmol/mol is ∼8 and 80 pg, respectively (sample volume = 150 μL) (Table 5). At this low level of boron mass consumption for 2.5 ppm [Ca]$_{Matrix}$, a ±5% offset from true B/Ca can arise from 0.4 to 4 pg of boron contamination for B/Ca 20 and 200 μmol/mol, respectively. In summary, the B/Ca estimates from analyses at [Ca]$_{Matrix}$ ≥ 5 ppm, for four different standards and across a B/Ca range of ∼20 to 200 μmol/mol, are in good agreement for each internal standard. With a typical calcite mass consumption of ∼4 μg per ICP-MS analysis ([Ca]$_{Matrix}$ = 10 ppm), this present method enables measurement of B/Ca on a single foraminifera shell.

Accurate analysis of foraminifera B/Ca (and Me/Ca) requires closely matching the [Ca]$_{Matrix}$ of the samples to that of the standards. A key advantage of the present method, performing Me/Ca analyses at low [Ca]$_{Matrix}$, is that the requirement for closely matching the calcium concentrations is relaxed (Figures 3a–3c). Three of the Cambridge consistency standards (CAM-wuellerstorfi, Mix, and Uvig-2) were analyzed, in triplicate, at ±10% (9 and 11 ppm Ca), ±20% (8 and 12 ppm Ca), and ±30% (7 and 13 ppm Ca) dilution difference from the calibration standards at [Ca]$_{Matrix}$ 10 ppm. Measured B/Ca of all three CAM consistency standards, analyzed over this [Ca]$_{Matrix}$ spread of 7–13 ppm, is consistent (≤2.0%, 2σ) with analyses carried out at exact [Ca]$_{Matrix}$ concentration matching at 10 ppm. The consistency standards analyzed at 7 and 13 ppm [Ca]$_{Matrix}$ have >40% difference in their boron mass consumption per analysis. Over this [Ca]$_{Matrix}$ range, the

Figure 5. A summary of all B/Ca measurements in 0.1 M HNO_3 and 0.3 M HF acid matrix at $[Ca]_{Matrix} \geq 5$ ppm in planktonic and benthic foraminifera. Samples are sorted according to species type, with the Cambridge consistency standards including procedural blanks in white and the down-core samples in black. The different species of planktonic and benthic foraminifera (the black bars) plotted here are down-core samples that span one or more glacial-interglacial cycles. The white error bars for down-core samples represent the range of minimum and maximum B/Ca measured, and the black error bars for the consistency standards are $\pm 2\sigma$ analytical uncertainty (Table 4). All down-core foraminifera samples represented in this plot were cleaned by oxidative (H_2O_2) method only. The type of foraminifera and the numbers of analyses are displayed in parentheses.

observed analytical uncertainty in B/Ca of CAM-wuellerstorfi, Mix, and Uvig-2 are 3.8, 3.0, and 0.9 μmol/mol, respectively (Figure 3). This spread in B/Ca, for all of the consistency standards lies within the analytical precision of the present method and does not exhibit bias based on absolute B/Ca of the standard or the $[Ca]_{Matrix}$ of the analyte. For example, at the two ends of the spectrum, the mass of boron consumed per analysis for CAM-wuellerstorfi at 13 ppm $[Ca]_{Matrix}$ is ~50 pg and for Uvig-2 at 7 ppm $[Ca]_{Matrix}$ is ~3 pg. Hence, there is approximately 47 pg difference in boron mass consumption per analyses for the CAM consistency standards at different dilution efficiencies (difference in $[Ca]_{Matrix}$ of analyte from calibration standards analyzed at 10 ppm). If there was a boron memory effect from incomplete washout or the samples were contaminated (~100 s of fg-B), B/Ca measurements would not be internally consistent for different $[Ca]_{Matrix}$. This effect would be most severe at low $[Ca]_{Matrix}$ for samples like CAM-Uvig-2 with ~3 to 4.5 pg-B mass consumption per analysis. Hence, the internal consistency of the B/Ca measurements, irrespective of total boron mass consumption, highlights both the quantitative washout out of boron from the sample introduction system and the absence of sample-to-sample boron carry over effect.

Similar external precisions were observed for other elements of interest (Table 4). Analyses of a series of down-core *Uvigerina peregrina* samples with average B/Ca of <20 μmol/mol, interspaced with CAM-Uvig-2 consistency standards, at $[Ca]_{Matrix}$ of 5 and 10 ppm generates identical results (Figure 4). This confirms that accurate measurements of B/Ca in carbonates with low boron abundance can be performed at a calcite mass consumption of <2 μg/sample (B_{Mass} = 2 pg) and that a consistent down-core record for low B/Ca benthic foraminifera was obtained. A comprehensive summary of the different species of down-core foraminifera analyzed for B/Ca by the present method is presented in Figure 5.

Table 6. B/Ca of Chemically Cleaned Planktonic Foraminifera[a]

Species	Cleaning Protocol	B/Ca$_{Average}$ (μmol/mol) ($\pm 2\sigma$)	Numer of Analyses	B/Ca$_{Min}$ (μmol/mol)	B/Ca$_{Max}$ (μmol/mol)
North Atlantic Core-Top					
O. universa	Ox	75.2 ± 3.1	4	73.4	76.7
O. universa	Red-Ox	73.4 ± 1.6	4	72.3	74.2
O. universa	Red-Ox-Red	75.5 ± 5.7	4	71.8	78.6
O. universa	All	74.7 ± 4.0	12	71.8	78.6
G. inflata	Ox	81.6 ± 9.4	4	77.2	87.2
G. inflata	Red-Ox	77.0 ± 3.6	4	74.8	78.5
G. inflata	Red-Ox-Red	79.9 ± 4.8	4	76.4	81.6
G. inflata	All	79.5 ± 7.1	12	74.8	87.2
G. bulloides	Ox	52.0 ± 3.1	4	49.7	53.0
G. bulloides	Red-Ox	54.1 ± 1.9	4	52.8	55.0
G. bulloides	Red-Ox-Red	56.6 ± 15.9	4	48.7	64.8
G. bulloides	All	54.2 ± 9.4	12	48.7	64.8
Core 2					
G. bulloides	Ox	46.6 ± 19.3	12	36.6	69.4
G. bulloides	Red-Ox	42.4 + 7.0	12	37.8	49.9
G. bulloides	All	44.5 ± 14.8	24	36.6	69.4
Central Indian					
G. sacculifer	Ox	98.8 ± 10.4	9	90.5	106.5

[a]B/Ca measured at [Ca]$_{Matrix}$ = 25 ppm in 0.1 M HNO_3 acid.

3.3. Effect of Chemical Cleaning on Foraminiferal B/Ca

The faithfulness of the foraminiferal archive as a recorder of paleo-seawater chemical composition is subject to complexities arising from postdepositional alteration of the shells. The processes affecting foraminifera shells in sediments are: diagenesis of the carbonate tests, secondary calcite deposition from pore waters, and preferential dissolution of the heterogeneous primary calcite—mostly high magnesium calcite [*Boyle*, 1983; *Delaney and Boyle*, 1986; *Brown and Elderfield*, 1996, *Barker et al.*, 2003; *Yu et al.*, 2007b]. Diagenetic alteration of shells (dissolution and recrystallization) and presence of authigenic mineral phases (iron-manganese oxides, marine clays) can offset the true calcite bound trace element concentrations in unprocessed/uncleaned foraminifera samples. This is a major problem for benthic foraminifera samples with relatively high Mn/Ca ($\geq$100 μmol/mol). Oxides of manganese and iron preferentially uptake significant amounts of boron from their ambient solution (pore waters) and at seawater pH the partition coefficient between adsorbed and aqueous boron (K_d) ranges from 34 to 39 [*Lemarchand et al.*, 2007]. As a result, samples with high ($\geq$100 μmol/mol) Fe/Ca or Mn/Ca are prone to contamination from boron adsorbed on Fe/Mn-oxide surfaces. Chemical cleaning of foraminifera shells is, especially with hydrazine, designed to remove postdepositional materials from calcite in order to minimize the effect of these secondary phases on the analytes of interest [*Boyle*, 1983; *Boyle and Keigwin*, 1985; *Rosenthal et al.*, 1997]. For accurate calcite bound boron concentration determination, benthic foraminifera samples with high Mn/Ca ($\geq$400 μmol/mol) require double reductive cleaning whereas, samples with Mn/Ca $\leq$50 μmol/mol do not require any hydrazine treatment [*Misra and Froelich*, 2009]. However, preferential leaching of the high magnesium calcite during chemical cleaning can bias the measure composition toward the composition of the more dissolution resistant phases [*Barker et al.*, 2003]. The impact of foraminifera chemical cleaning on calcite bound boron concentration was evaluated by processing core-top samples of similar weight (>2 mg) and size fraction (>300 μg) with hydrazine-H_2O_2-hydrazine, hydrazine-H_2O_2, and H_2O_2 only cleaning protocols. Species-specific samples of *Orbulina universa* and *Globoratalia inflata*, and *Globigerinoides bulloides* were cleaned following the different cleaning protocols (Table 6). Calcite bound boron concentration showed no dependence on foraminifera chemical cleaning protocol in agreement with *Yu et al.* [2007b].

4. Conclusions

We report a method for B/Ca determination by HR-ICP-MS with extremely low instrumental blanks and low detection limits. Our new method requires $\leq$5 μg of calcite per analysis, and can be applied to single shell samples. The long-term precision of this method, as estimated on four consistency standards, is

independent of the boron content of the calcite shell. This low mass consumption B/Ca method opens the possibility of analyzing B/Ca when sample availability is limited.

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