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Accurate and precise isotopic measurement of sub-nanogram sized samples of foraminiferal hosted boron by total evaporation NTIMS

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Abstract

We report a total evaporation negative ion thermal mass spectrometry (TE-NTIMS) technique that enables precise and accurate (±0.7‰; 2 s.d.) measurements of boron isotope ratios. The fundamental advantage of TE-NTIMS is that the effect of instrumental mass fractionation is minimised and sample signal maximised by analysing samples to exhaustion. We can analyse as little as 300 pg of B, which enables repeat analyses of dissolutions of small numbers of foraminifera (as little as 0.1 mg or ~10 individual foraminfera). This represents a several fold reduction in the number of tests required compared to previous NTIMS studies and brings the amount of sample into line with other commonly used paleo-proxies. Standard addition experiments indicate that the $^{11}B/^{10}B$ ratio of the NIST SRM 951 standard is not biased by differing amounts of seawater or carbonate matrix and yield an $^{11}B/^{10}B$ within error of the certified value. We also show that our sample preparation induces no additional variations (e.g. blank contribution) beyond our analytical uncertainty. We obtain $^{11}B/^{10}B$ ratios for seawater within error of values obtained using plasma ionisation, positive and negative thermal ionisation mass-spectrometry. Our measurements of core-top *G. sacculifer* from three ocean basins yield $\delta^{11}B$ within analytical error (23.3–24.3‰) and fall within the range of published values. This study, however, further highlights significant interlaboratory biases in isotopic compositions of core-top foraminifera. Significantly, we show that our approach is not influenced by processing blank nor systematic differences in mass bias between measurements of sample and standard, which has yet to be documented for some other laboratories.

Keywords: Boron isotopes; Total evaporation; NTIMS; Foraminifera; Paleo-ocean pH

1. Introduction

Seawater pH is a fundamental variable in the oceanic carbonate system, not least in that it is strongly influenced by the atmospheric concentration of CO_2 (pCO_2; e.g. Zeebe and Wolf-Gladow, 2001). The boron isotopic composition of marine carbonates, such as formanifera tests, have been shown to reflect oceanic pH (Vengosh et al., 1991; Hemming and Hanson, 1992; Sanyal et al., 1996). Thus, boron isotopic measurements of ancient carbonate material potentially allows a reconstruction of paleo-ocean pH, and ultimately provides constraints on past pCO_2 — a critical control on past climate. Despite a number of important contributions (e.g. Vengosh et al., 1991; Spivack et al., 1993; Hemming and Hanson, 1992; Sanyal et al., 1995, 1996; Palmer et al., 1998; Pearson and Palmer, 2000), the full potential of boron isotopes as a paleo-pH meter

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has yet to be realised, in part as a result of analytical difficulties. With only two naturally occurring isotopes, ^{11}B and ^{10}B (that comprise ~80% and ~20% of total boron, respectively), accurate instrumental mass fractionation correction is a major challenge. At the same time a successful technique requires high ionisation efficiency and a good control of ubiquitous boron blank contributions.

Paleoceanographic applications require an accuracy and precision of less than 1‰ (equivalent to ~0.1 pH units at a typical oceanic pH) using less than a few nanograms of B (typically equivalent to <100 hand-picked foramiferal tests). Larger sample loads need more time consuming sample preparation and potentially limit 'down-core' temporal resolution or suitable core localities. Fig. 1 is a comparison of the commonly applied methods of boron isotopic analysis, and it is clear that only negative-ion thermal ionisation mass spectrometry (NTIMS) can provide sufficiently high ionisation efficiency to run the required amounts of B.

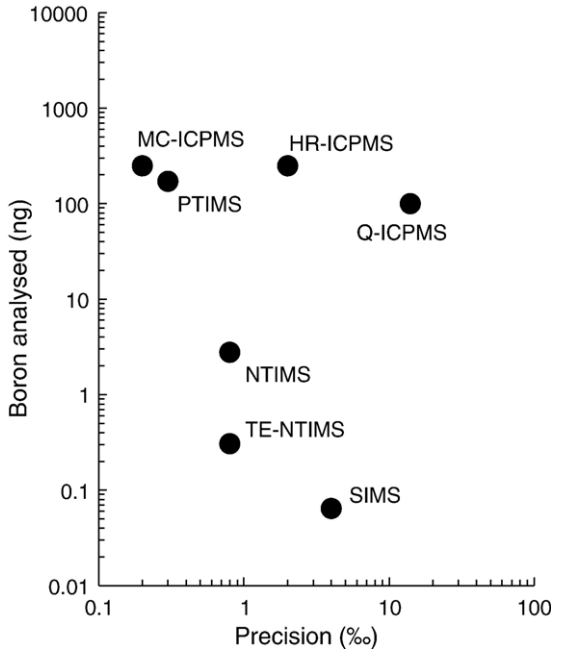

Fig. 1. A comparison of the approximate precision and required amount of boron for various methods available to measure the isotopic composition of boron. Modified from Aggarwal et al. (2003), TE-NTIMS is from this study. The following abbreviations have been used: PTIMS — positive ion thermal mass spectrometry; MC-ICPMS — multicollector inductively coupled plasma mass spectrometry; HR-ICPMS — high resolution inductively coupled plasma mass spectrometry; Q-ICPMS — quadrapole inductively coupled plasma mass spectrometry; NTIMS — negative ion thermal mass spectrometry; TE-NTIMS — total evaporation negative ion thermal mass spectrometry; SIMS — secondary ion mass spectrometry.

NTIMS uses natural matrices (e.g. seawater or calcium carbonate shells) as activators to produce BO_2^- beams with an ionisation efficiency reaching several percent. This approach also obviates the need to separate B from its host. Instrumental mass fractionation of the dominant $^{10}B^{16}O_2^-$ and $^{11}B^{16}O_2^-$ species is typically greater than for heavier meta-borate molecular ions (e.g. $Cs_2BO_2^+$) commonly analysed by positive ionisation TIMS and this typically results in poorer reproducibility for NTIMS, specifically 0.6‰ to 2.0‰; 2 s.d. (e.g. Vengosh et al., 1991; Spivack et al., 1993; Hemming and Hanson, 1992; Sanyal et al., 1995; Hönisch and Hemming, 2004) compared to <0.4‰ for PTIMS (Spivack and Edmond, 1987; Lemarchand et al., 2002). In the traditional NTIMS approach, it is assumed that mass fractionation is standardised by running samples at similar temperatures (~900 to 1050 °C) and duration to the reference NIST SRM 951 standard. Samples can then be reported in delta notation ($\delta^{11}B$) as parts per thousand variation from the measured NIST SRM 951.

A high level of operator skill and strict analytical protocols are required in order to achieve good reproducibility using NTIMS (e.g. Pearson and Palmer, 1999; Hönisch and Hemming, 2004). For example, samples that show unusual fractionation behaviour during analysis are rejected in some approaches (e.g. Hönisch and Hemming, 2004) and triplicate analyses are required in order to have confidence in the generated data (Hönisch and Hemming, 2004). As a result, the standard NTIMS approach requires relatively large amounts of calcite — if each sample is run in triplicate and each analysis consumes 1–2 ng of boron, a total of 3–6 mg of calcite or 75 to 150 individual tests (at 40 μg per 400 μm diameter test) is needed for each sample. Although this represents much less material than required by PTIMS, it does prevent smaller size fractions and rarer foraminiferal species being analysed. For example, single species of benthic formanifera cannot be easily analysed using the current NTIMS protocols.

Some authors have noted variable, matrix related fractionations (Hemming and Hanson, 1994) due to the differing ionisation characteristics and efficiencies of different materials (e.g. due to increased ionisation efficiency, complex salts appear to fractionate less over a given time period than simple salt matrices). Since NIST SRM 951 boric acid standard cannot be run efficiently without a loading matrix, most laboratories run it in a boron-free seawater matrix, made by passing seawater through boron specific resin (Hemming and Hanson, 1994). Boron-free seawater is also added in similar amounts to carbonate samples (dissolved in HCl), in order to closely match the matrices between

sample and standard and to enhance the ionisation efficiency of the carbonate. The absolute accuracy of the traditional NTIMS approach depends critically on the degrees of fractionation being the same in sample and standard, but evidence to support this assumption is rarely documented.

Most laboratories quote a long-term mean in-house seawater standard value (global seawater is isotopically homogenous; Spivack and Edmond, 1987) but no interlaboratory foraminiferal carbonate standard exists to allow accuracy to be assessed for different loading matrices. Furthermore, a recent interlaboratory comparison of calcium carbonate (a limestone) and water samples run by a range of methods found that results varied by about a factor of ten more than the quoted precision of each laboratory (Gonfiantini et al., 2003). Despite relatively large *absolute* variations (~2‰) between laboratories that have run the same carbonate solution by NTIMS (see Hönisch et al., 2003), it has been demonstrated that the relative *difference* between carbonate samples is similar between laboratories (Hönisch et al., 2003). Whilst the difference in boron isotope ratios between samples is the dominant control on calculated seawater pH, the absolute $\delta^{11}B$ also influences inferred pH and so its accurate determination is of significance.

It is clearly important that isotopic measurements are accurate, and we have attempted to address some of these issues by employing the significantly different approach of total evaporation (TE). TE-NTIMS dramatically diminishes the effect of instrumental mass fractionation since the sample is analysed to exhaustion. This method also enables the analysis of smaller sample loads, provided that the inherently large ambient boron blank can be mitigated. Once the blank limitation is overcome, it is possible to perform multiple analyses of foraminferal samples of less than 0.5 mg in size (equivalent to 10 tests 400 μm in diameter), bringing the sample requirements for boron isotope analysis in line with other, more conventional paleoceanographic foraminiferal proxies (e.g. trace metal/Ca, $\delta^{18}O$, $\delta^{13}C$).

2. Instrumentation and analytical methodology

2.1. Sample preparation, blanks and sample loading

All sample manipulation and preparation was carried out in the HEPA filtered class 1000 clean room suite at the Department of Earth Sciences, University of Bristol. Since standard HEPA filters are ~10 wt.% borosilicate, it was initially found that laboratory air was a significant contributor to boron blank. This problem was overcome by replacing the standard HEPA filters with boron-free, PTFE membrane filters (MegaCell™ from AAF International). Special care was also necessary to avoid boron contamination from the analyst, and all sample handling was carried out in an overpressured glove box. Total procedural blanks were further minimised by using Telfon vials at all stages of sample preparation and dissolution, and by using 18.2 MΩ MilliQ water (Millipore, UK) and RoMil (Cambridge, UK) ultrapure reagents. Exposure of samples to laboratory air was strictly minimised.

Foraminiferal samples (10–50 tests, 425–700 μm in diameter) were crushed between two pre-cleaned glass plates, transferred to an acid-leached 2 ml Teflon centrifuge tube, rinsed and ultra-sonicated several times to ensure complete clay removal. Organic material was oxidised by bleaching the samples in sodium hypochlorite (NaClO; 5% Cl; Fisher Scientific) for 24 h. The sample was then centrifuged and the NaClO was extracted with a pipette. The bleached forams were then repeatedly rinsed and briefly (30 s) ultra-sonicated to ensure complete removal of NaClO and any soluble salts (15–20 times were sufficient). The cleaned foraminferal calcite was then transferred to a clean 5 ml Telfon vial and dissolved in 2 M HCl. The amount of 2 M HCl added was controlled by dropwise titration until carbonate dissolution was complete. This minimises excess H^+ ions and results in final solutions with similar boron concentration (~800 ng/g assuming [B] in the forams = 10 μg/g; Hemming and Hanson, 1992). A more accurate estimate of the solution strength was obtained by measurement of calcium concentration on a ThermoFinnigan ELEMENT 2 ICP-MS. 1–0.5 μl of the dissolved sample was diluted to 400 μl in 2 N HNO_3 and run against gravimetric standard solutions in a procedure following Rosenthal et al. (1999). In this procedure we also monitor levels of other metals (e.g. Mn, Al) that give an indication of the efficiency of the cleaning process in removing secondary precipitates and clays, respectively. The seawater samples analysed were filtered prior to analysis using pre-cleaned 0.45 μm Millipore PTFE filters and then acidified to pH 2 with RoMil ultrapure HNO_3. A Sclerosponge sample, CE-95, was supplied by Florian Böhm (GEOMAR) as a powder and was treated in a similar fashion to a crushed foram sample.

The NIST SRM 951 boric acid standard (certified value of $^{11}B/^{10}B = 4.0437 \pm 0.0033$; Catanzaro et al., 1970) was analysed so that our data can be reported in the standard $\delta^{11}B$ terminology. In order to be comparable to our carbonate samples, a loading matrix of boron-free foraminifera was prepared by separating

boron from a dissolved, milligram-sized, mixed-species foram concentrate (cleaned as described above). The batch separation technique of Lecuyer et al. (2002) was used with Amberlite 743 resin. A number of solutions were prepared but for most the calcium concentrations were ~80 mmol/l — significantly less than that of our unknown foraminiferal solutions. In order to examine whether the amount of loading matrix affects the measured $^{11}B/^{10}B$ ratio, a B-free solution with ~880 mmol/l Ca, comparable to the concentrations of our unknowns, was also prepared. For all the boron-free matrices, the boron blank was 2–20 pg with an $^{11}B/^{10}B$ ratio=4.02–4.06. Note, however, that it is very difficult to separate out a blank component that is uniquely attributable to a loading matrix since this estimate also includes the loading blank and is a maximum value. Reagent blanks are similarly difficult to determine, particularly since drying down a solution results in significant boron contamination. However, all reagents used are supplied certified with boron concentrations <100 ppt, and no significant blank contribution from reagents was determined when they were analysed in concentrated form.

To determine the long-term reproducibility of the TE-NTIMS method, as well as the day-to-day machine performance, we use an in-house, mixed foraminiferal carbonate standard ('871std'; 582 ppb B as determined by isotope dilution from a gravimetrically prepared solution of NIST SRM 952 $^{11}B/^{10}B$=0.05319; Catanzaro et al., 1970). This foraminiferal standard was prepared in a similar fashion to foraminiferal samples described above. In order to investigate fully the effect of loading matrix on the measured $^{11}B/^{10}B$ of NIST SRM 951, two standard additions were performed; one with 871std and the other seawater both variably mixed with NIST SRM 951.

Samples and standards were loaded onto zone refined Re single filaments, previously washed in weakly acidified MilliQ water and outgassed at 4.8 A for 2 h. Loading solutions were evaporated to dryness with a filament current of 0.8 A and then further heated with a current of 1.2 A for 30 s. For standard measurements, NIST SRM 951 was diluted using 2M HCl to 150, 400 or 800 ppb and 1 μl was loaded on to 1–0.2 μl of boron-free foram matrix. We attempted to run the same amount of boron for all samples and standards. For the carbonate samples, the amount of sample solution required was calculated from the measured Ca concentration, assuming the sample was stoichiometric calcite with a boron concentration of 10 μg/g (typical of modern foraminifera; Hemming and Hanson, 1992). Typically we loaded 1–2 μl using 0–1 and 0–0.5 μl Hamilton syringe pipettes with pre-cleaned and rinsed Teflon tubing for accurate and clean solution delivery. No additional loading matrix was added to carbonate samples. Prior to sample loading, filaments were left for 7 to 9 days sealed in plastic boxes. This aging of the filament surface makes it easier to load the sample in a small spot that remains centrally located on the filament. Notably, variations in the measured isotope ratios were found if the optimal focus position occurred close to the extremes of the sample magazine focus which can result from loading a sample close to the edge of the filament.

When loading within a laminar flow hood with a standard HEPA filter, we found loading blanks were erratic and varied from 10 to 40 pg, which results in a ~1.5‰ lowering of $^{11}B/^{10}B$ for a 400 pg sample. We employed a number of strategies to minimise loading blank. Initially loading was carried out in a stream of air cleaned by bubbling through a 2–5 wt.% solution of mannitol (the 'mannitol trap'). The filament was loaded within 2 cm of the ~5 cm diameter exhaust pipe of the mannitol trap in a steam of air travelling at ~1 m/s. This method ensured that loading blank was consistently 5–15 pg (calculated from the measured $^{11}B/^{10}B$ in a small, 60 pg, load of 871std relative to a larger load, 600 pg, and assuming a blank $^{11}B/^{10}B$=4.02). Later it was found that loading within a stream of N_2 has a similar effect but the higher flow rates achievable resulted in lowering the blank to <5 pg. This approach leads to an insignificant blank correction (0.2‰) on sample loads of 400 pg. Indeed the lower limit on the amount of sample loaded is set by our loading blank — small sample loads are desirable both from a sample use point of view but also because the time required to make an analysis by total evaporation. As our loading blank decreased during this study our typical sample loads also changed from 800 to 400 pg.

Despite these precautions it was impossible to reduce the loading blank further, presumably because boron is a contaminant within the zone refined Re. Loading blank were assessed several times during each analytical session by measuring the $^{11}B/^{10}B$ of 60 pg of 871std compared to 600 pg of the same standard. If elevated loading blanks were detected, samples analysed during that analytical session are treated as suspect, although this was rarely the case once the protocol was established. After loading, filaments were immediately placed in the mass spectrometer and pumped down to vacuum. An adequate source vacuum of 4×10^{-7} bar can be achieved in the source in 3 to 4 h, but generally the mass spectrometer was left overnight to pump down.

2.2. Mass spectrometry

All the data presented in this contribution were collected on a ThermoFinnigan Triton multicollecter thermal ionisation mass spectrometer at the University of Bristol. The mass spectrometer was operated in negative ion mode with an accelerating voltage of 10 kV. Boron isotopes were analysed simultaneously in Faraday cups as $^{11}BO_2^-$ (mass 43) and $^{10}BO_2^-$ (mass 42) species (axial and L1 cup, respectively). Filaments are initially heated at 300 mA/min until 1200 mA (860–960 °C). During this period an electronic baseline measurement is made. Since all samples were loaded in HCl, at this point there is a ^{35}Cl signal that can be focussed. A secondary electron multiplier (SEM) measurement of potential organic interference at mass 26 ($^{12}C^{14}N$) is also made. A sample with a high level of organics (>5000 cps) at this stage is treated as suspect (see Hemming and Hanson, 1994). The filament current is then raised with continual focussing and centering until an $^{11}BO_2^-$ ion beam of 20 mV (all Faraday cups with 10^{11} Ω amplifiers) is reached (~1350–1450 mA, 950–1050 °C). The automated total evaporation analysis routine is then started. The filament current is raised at 120 mA/min for 1 min until a $^{10}BO_2^-$ intensity of 3.2 V ($^{11}BO_2^-$ 12–14 V) is reached. Filament current is continuously raised throughout the run to maintain this level of signal, thereby minimising analysis time. In the negative ion mode of the Triton, the maximum beam intensity that can be accurately measured is 15.5 V and the filament current is managed to ensure this value is not exceeded. Collection continues until the $^{10}BO_2^-$ ion beam decays to less than 5 mV. For a 400 pg boron carbonate load this normally takes less than 2 h and results in a total of 300–800 8-s integrations. Fig. 2 shows the signal intensity, filament current and $^{11}B/^{10}B$ ratio of a typical analysis. The $^{11}B/^{10}B_{TE}$ is calculated by rationing the summed beam intensities measured at masses 43 and 42 and then subtracting 0.00079 to correct for the $^{10}B^{17}O^{16}O$ contribution to the peak at mass 43. Collecting and measuring all the boron ionised in this way minimises the effect of instrumental mass fractionation. This approach should be effective for techniques with high ionisation efficiencies and small variability of neutral species emitted (see Kanno, 1971). Using this method, however, internal precision cannot be calculated and each analysis is assigned an error derived from the (2 s.d.) external reproducibility of 871std.

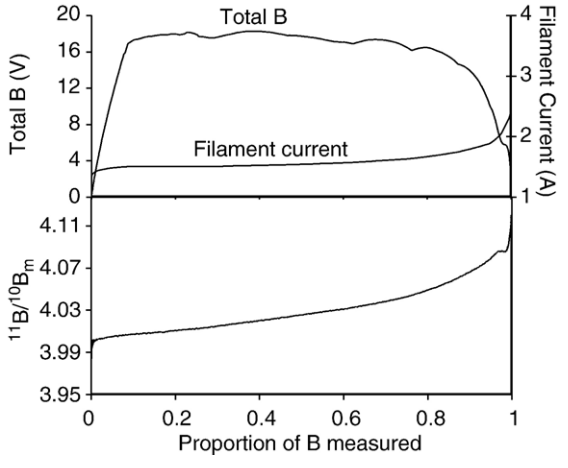

Fig. 2. A typical total evaporation measurement of NIST SRM 951 in a boron-free carbonate matrix. Total boron refers to the sum of the ^{11}B and ^{10}B intensities of each integration.

3. Results and discussion

3.1. Analysis of boron by TE-NTIMS in a boron-free carbonate matrix

Over 1 year, 29 analyses of 400 and 150 pg loads of NIST SRM 951 in a boron-free foraminiferal matrix (Ca concentration of 80 mmol/l) gave a $^{11}B/^{10}B_{TE}$= 4.0354±0.0061 (1.5‰; 2 s.d.; Fig. 3a and Table 1). This is within error of the certified value (Catanzaro et al., 1970). Boron ion yields vary between analyses and the average ionisation efficiency is ~8%, varying between 1% and 12%. Fig. 3b shows there is little correlation between measured $^{11}B/^{10}B_{TE}$ ratio and boron yield. Since the loading blank has an $^{11}B/^{10}B$ ratio that is similar to NIST SRM 951, loading blank is not significant in these analyses.

In order to examine the effect of the amount of loading matrix on measured $^{11}B/^{10}B_{TE}$ a boron-free foram solution was prepared with ~880 mmol/l calcium (a similar concentration to foram samples). This was loaded in progressively smaller amounts of 1, 0.5 and 0.2 µl (35, 18 and 7 µg of Ca, respectively). As Fig. 3c shows, there is no detectable difference in the measured $^{11}B/^{10}B_{TE}$ ratio (Table 1). Note, however, that individually these analyses reproduce poorly (up to ~3‰; 2 s.d.). Fig. 3c also shows that the reproducibility becomes worse at higher calcium concentrations, suggesting it is a consequence of either the high calcium concentration and/or organic contaminants in the loading matrix acquired during boron removal (see below). This poor reproducibility may mask any systematic variations caused by changing the amount of loading matrix loaded. For these analyses of NIST SRM 951, boron ion yield varied considerably from 1% to 60% (Table 1). Again

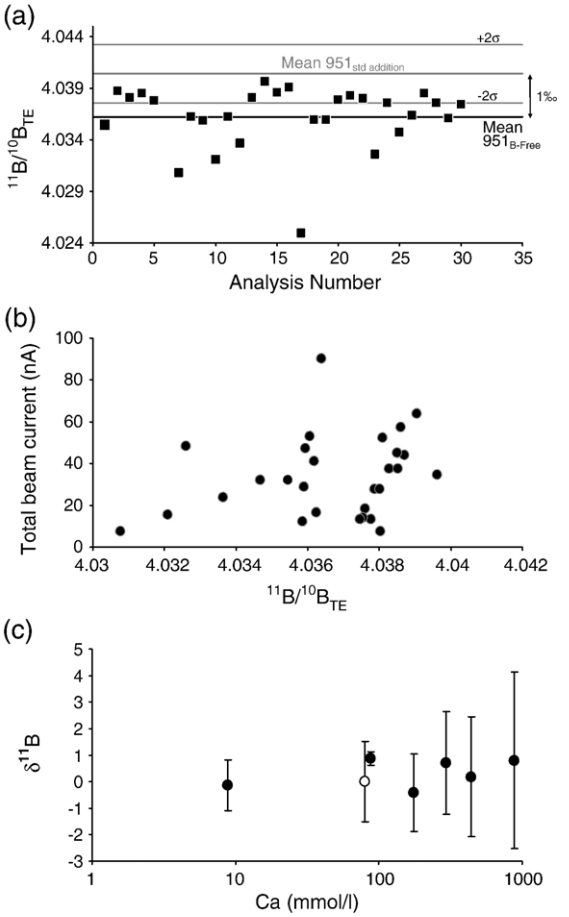

Fig. 3. (a) Repeat analyses of NIST SRM 951 boric acid standard, measured using a boron-free foraminiferal loading matrix over a 1 year period. The mean value is 4.0354±0.0061 (2 s.d.; black line). The horizontal grey lines mark the mean and standard deviation of NIST SRM 951 determined by standard addition with 871std (4.0396± 0.0028 2σ). Note that the mean value for NIST SRM 951 in B-free matrix is around 1‰ lighter than the value determined by standard addition (see Fig. 6). (b) Measured $^{11}B/^{10}B_{TE}$ variation with boron yield in total volts of boron measured. (c) Measured $\delta^{11}B$ of NIST SRM 951 (plotted as permil deviation from the long-term mean — open circle) in different concentrations of foraminferal matrix.

there is no clear correlation between the yield and the measured $^{11}B/^{10}B_{TE}$ ratio (not shown). This lack of correlation is surprising but indicates that, although ionisation is retarded, the resulting fractionation is not systematically influenced, such that poor ionisation does not result in biasing the resulting $^{11}B/^{10}B$ in any particular direction. We tentatively attribute poor ion yields to ionisation suppression as a result of 'organics', in this case probably derived from the resin during preparation of the B-free loading matrix (see Hemming and Hanson, 1994). We can speculate that isobaric interferences (see below) and changes in fractionaton roughly counter-balance each other to result in no net difference in measured ratio.

It has been demonstrated that organic material present on the filament can result in the generation of CN^- (mass 26) and CNO^- (mass 42) molecular ions (Hemming and Hanson, 1994). $^{12}C^{14}N^{16}O^-$ ions can interfere with $^{10}B^{16}O_2^-$ at mass 42, thereby lowering the measured 43/42 ratio and hence the inferred $^{11}B/^{10}B$. The presence of organic contamination is therefore a potentially serious problem for NTIMS analysis of boron isotopes. By monitoring CN^- at the beginning and end of a run, samples can be screened. Accepting only runs with $CN^- < 5000$ cps should ensure negligible organic influence on mass 42 (Hemming and Hanson, 1994). The approach followed by Kasemann et al. (2001) is to wait for the organics to burn off. In the TE-NTIMS approach, after the BO_2^- beam is initially found the temperature of the filament is constantly raised and data collected, leading to the possibility of organic contamination throughout the analysis. Although organics on the filament seem to burn off at low temperature (Kasemann et al., 2001), the heating and ionisation of organics previously condensed on the slit plate immediately adjacent to the heated filament may occur as the filament temperature is raised. Mass 26 can only be monitored (from the confines of the hardware) at the low temperature beginning and high temperature end of the run. The effect of organic interferences can be inferred on some runs, and is particularly apparent when small amounts of boron are analysed. Fig. 4 shows the analysis of a B-free loading matrix (880 mmol/l Ca) with no additional boron added, i.e. it is just an analysis of the loading blank (at the time of this analysis this was ~20 pg). The decrease in measured ratio, starting after ~60% of boron has been released (see Fig. 4) suggests that the organic interference has become significant and is decreasing the measured ratio faster than it increases due to fractionation (c.f. Fig. 2). When this analysis was started, only ~200 cps were detected at mass 26, suggesting the level of organics at that point was not significant. At the end of the analysis the level of organics had risen to ~8000 cps. We suspect the contamination of boron-free matrices by organic material, derived from the resin used to remove boron (see Hemming and Hanson, 1994), is responsible for the poor reproducibility and relatively low and variable yield (in comparison to natural carbonates, see below) of these analyses of NIST SRM 951.

A number of attempts were made to reduce the level of organics imparted to the boron-free matrices although none were successful. Approaches included treatment with H_2O_2, resin pre-treatment, and UV irradiation after

Table 1
Summary of TE-NTIMS analyses of 951 in a carbonate matrix

[Ca] mmol/l[a]	[B] pg[b]	$^{11}B/^{10}B_{TE}$	Total B (V)	[Ca] mmol/l[a]	[B] pg[b]	$^{11}B/^{10}B_{TE}$	Total B (V)
80	400	4.0347	3207	880	800	4.03572	2982
80	400	4.0379	4400	880	800	4.03080	1907
80	400	4.0372	754	880	400	4.03549	742
80	400	4.0377	4516	880	400	4.04392	2780
80	400	4.0370	1319	880	320	4.04518	7865
80	400	4.0300	752	880	400	4.04770	6964
80	400	4.0355	1661				
80	400	4.0351	1213	440	800	4.03683	7691
80	400	4.0313	1570	440	800	4.03295	2556
80	400	4.0354	4113	440	800	4.04207	6551
80	400	4.0329	2369				
80	400	4.0373	5230	293	400	4.04477	15537
80	400	4.0388	3475	293	400	4.03567	2125
80	400	4.0378	5735	293	400	4.03761	8842
80	400	4.0383	6389	293	400	4.03958	3476
80	400	4.0241	1705				
80	400	4.0351	2902	176	800	4.03543	27218
80	400	4.0352	4733	176	800	4.03273	4355
80	400	4.0371	2794	176	800	4.03250	1870
80	400	4.0375	3750	176	800	4.03885	17076
80	400	4.0372	2796				
80	400	4.0318	4832	88	400	4.03962	20664
80	400	4.0368	1853	88	160	4.03995	8000
80	400	4.0339	3199	88	400	4.04065	17807
80	400	4.0356	9008				
80	150	4.0377	3772	9	400	4.03464	2996
80	150	4.0368	1416	9	400	4.03738	3578
80	150	4.0353	5299				
80	150	4.0367	1334				
Mean		4.0354					
2 s.d. abs		0.0061					
2 s.d. permil		1.5					

[a] Calcium concentration of boron-free loading matrix in millimole per liter.
[b] Amount of boron analysed.

boron removal. It thus seems that for TE-NTIMS analysis, at least, it is not possible to analyse NIST SRM 951 in boron-free matrices due to the unavoidable organic contamination of the matrix during boron removal. Artificial matrices, such as artificial seawater, also cannot be used since these cannot be produced with a sufficiently low boron concentration.

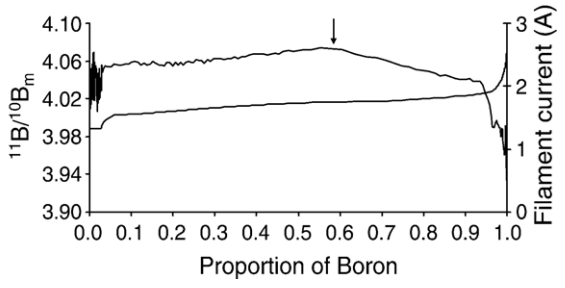

Fig. 4. A total evaporation measurement of ~22 pg of boron hosted in a boron-free carbonate matrix. Note how the $^{11}B/^{10}B$ ratio begins to decrease after around 60% of the boron has been released (indicated by arrow). This decrease is most likely due to organic contamination and interference occurring throughout the analysis.

3.2. Analysis of boron by TE-NTIMS in natural matrices

Repeat analysis ($n=65$) of 300–600 pg of 871std foraminferal solution (Ca concentration = 800 mmol/l) over 30 analytical sessions and over 5 months gave a $^{11}B/^{10}B_{TE} = 4.1124 \pm 0.0030$ (0.7‰; 2 s.d.; Fig. 5a and Table 2). Loading blank over this period was estimated to be <10 pg and as such the blank contribution is insignificant (Fig. 5b). The ionisation efficiency for 600 pg of this solution is ~18%, and varies from 5% to 22%. Again there is no relationship between the $^{11}B/^{10}B_{TE}$ and the ion yield (not shown). Smaller amounts of

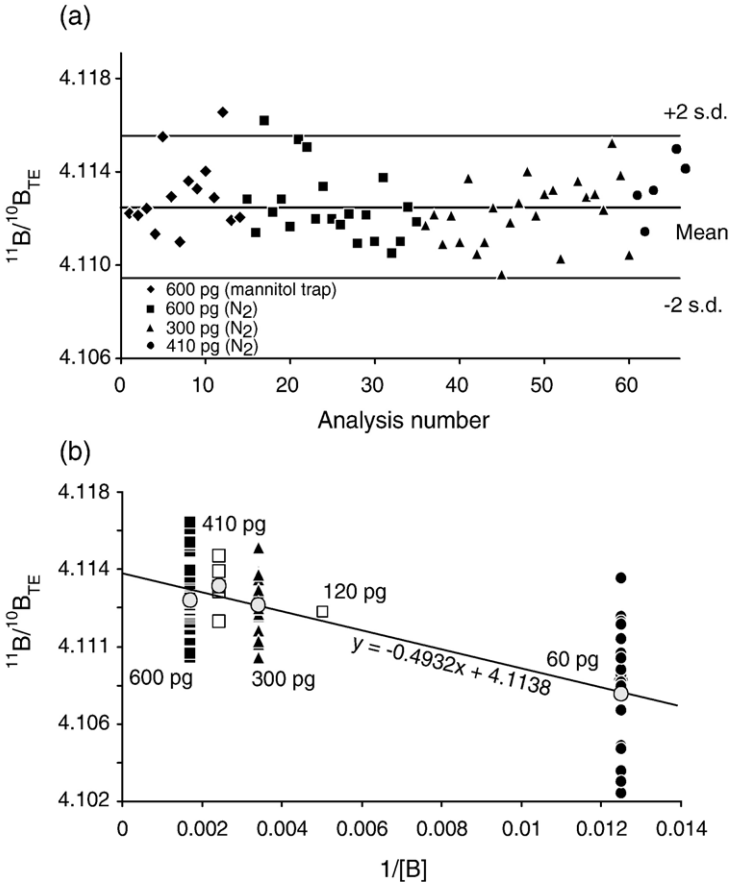

Fig. 5. (a) Repeat analyses of 300–600 pg of in-house foraminferal carbonate standard 871std. Mean measured $^{11}B/^{10}B_{TE}=4.1124\pm0.0030$ (±0.7‰; 2 s.d.). Analyses are split into groups based upon the amount of boron loaded and the method in which they were loaded. Mannitol trap denotes those samples loaded in a stream of air filtered through a solution of 2 wt.% Mannitol. All other samples were loaded in a stream of N_2. (b) Measured $^{11}B/^{10}B_{TE}$ of 871std plotted against the inverse of the boron concentration loaded. Sixty picogram loads clearly show the effect of loading blank, increasing the scatter in the data and reducing the average value. For all other concentrations the measured values are within error of the blank free value indicated by the intercept with the *y*-axis (at infinite boron concentration).

solution ionise better, for example, 60 pg of 871std give an average ionisation efficiency of ~25%, suggesting that the absolute amount of boron or calcium loaded on the filament, rather than the B/Ca ratio may control ionisation. The lack of organic contaminants in this standard is inferred from its good reproducibility, enhanced ionisation efficiency and lack of a measurable 26 signal at the beginning and end of the analysis.

Similar levels of reproducibility and ionisation efficiency can also be achieved when analysing boron hosted in an aragonite matrix (Sclerosponge *Ceratoporella nicholsoni*; CE-95 supplied by F. Böhm) and in seawater (Bransfield Strait, Southern Ocean — 62°26′S, 59°24′W and B1 Mediterranean supplied by S. Tonarini). Four repeat analyses of ~50 μg of CE-95 (~800 pg of boron) over two analytical sessions gave an $^{11}B/^{10}B_{TE}=4.1179\pm0.0038$ (0.9‰; 2 s.d.). Four analyses, each of 250 μg (0.25 μl) of Bransfield Strait seawater (~1 ng of boron) over two analytical sessions gave an $^{11}B/^{10}B_{TE}=4.1918\pm0.0049$ (1.2‰; 2 s.d.), three analyses of 250 μg (0.25 μl) Mediterranean seawater (~1 ng of boron) gave an $^{11}B/^{10}B_{TE}=4.1978\pm0.0034$ (0.8‰; 2 s.d.). The poorer reproducibility of Bransfield Strait seawater possibly results from a small blank effect. Since seawater is isotopically very heavy ($^{11}B/^{10}B$ ~4.2) compared to our blank $^{11}B/^{10}B$ ratio (~4.02) it is particularly susceptible to blank contamination, despite our precautions to minimise loading blank.

3.3. Standard addition experiments

Owing to the unacceptable 'organic' contamination, it is not possible to examine the effects of different B-free matrices on the measured $^{11}B/^{10}B_{TE}$

Table 2
Summary of TE-NTIMS analyses of 871 foram standard

[B] pg[a]	$^{11}B/^{10}B_{TE}$	[B] pg[a]	$^{11}B/^{10}B_{TE}$	[B] pg[a]	$^{11}B/^{10}B_{TE}$	[B] pg[a]	$^{11}B/^{10}B_{TE}$
585	4.1095	293	4.1095	59	4.1025	120	4.1119
585	4.1097	293	4.1102	59	4.1025		
585	4.1104	293	4.1103	59	4.1030	410	4.1113
585	4.1108	293	4.1104	59	4.1031	410	4.1129
585	4.1109	293	4.1108	59	4.1031	410	4.1131
585	4.1109	293	4.1109	59	4.1036	410	4.1139
585	4.1109	293	4.1109	59	4.1048	410	4.1147
585	4.1113	293	4.1116	59	4.1049		
585	4.1113	293	4.1117	59	4.1067		
585	4.1115	293	4.1120	59	4.1078		
585	4.1116	293	4.1121	59	4.1080		
585	4.1117	293	4.1121	59	4.1080		
585	4.1118	293	4.1123	59	4.1081		
585	4.1119	293	4.1124	59	4.1081		
585	4.1119	293	4.1126	59	4.1082		
585	4.1120	293	4.1129	59	4.1082		
585	4.1121	293	4.1130	59	4.1082		
585	4.1121	293	4.1130	59	4.1083		
585	4.1121	293	4.1131	59	4.1086		
585	4.1121	293	4.1135	59	4.1089		
585	4.1122	293	4.1136	59	4.1094		
585	4.1123	293	4.1138	59	4.1097		
585	4.1124	293	4.1139	59	4.1097		
585	4.1127	293	4.1152	59	4.1097		
585	4.1127			59	4.1104		
585	4.1128			59	4.1112		
585	4.1128			59	4.1113		
585	4.1132			59	4.1116		
585	4.1133			59	4.1136		
585	4.1135						
585	4.1136						
585	4.1140						
585	4.1150						
585	4.1153						
585	4.1154						
585	4.1161						
585	4.1165						
Mean	4.1124	Mean	4.1122	Mean	4.1076	Mean	4.1132
2 s.d. abs	0.0033	2 s.d. abs	0.0028	2 s.d. abs	0.0060	2 s.d. abs	0.0026
2 s.d. permil	0.80	2 s.d. permil	0.68	2 s.d. permil	1.46	2 s.d. permil	0.62

[a] Amount of boron analysed.

of NIST SRM 951. A different approach is thus required to assess the accuracy of isotope ratios relative to the NIST SRM 951 (i.e. using the standard delta-notation). One method that allows the recovery of both the NIST SRM 951 $^{11}B/^{10}B_{TE}$ and an assessment of the effect of loading matrix is standard addition.

One standard addition experiment was performed with various mixtures of our 871std and NIST SRM 951 (100%, 60%, 38% and 17% 871std). The mixtures were made to ensure the boron concentration in each mixture was similar (~0.8 ppm). Since only 871std contained calcium, the Ca concentration of the mixtures varied from 480 to 136 mmol/l. The results are listed in Table 3 and, despite the large variations in the matrix load, all the mixtures fall on a mixing line between the end members (Fig. 6). These results can be used in two ways. Firstly they indicate that the amount of carbonate matrix has no effect on the measured $^{11}B/^{10}B_{TE}$ ratio, as this would cause the results to deviate from a straight line. Secondly, the lower intercept of this mixing line can be used to obtain the value of NIST SRM 951 in a carbonate loading matrix, avoiding the effects of organics in a B-free carbonate loading matrix. Using a York regression (York, 1969), assuming a 0.5% error on

Table 3
Standard addition experiments

Proportion of sample	$^{11}B/^{10}B_{TE}$					Average	1 s.e.
	1	2	3	4	5		
871std							
1	4.1124[a]					4.1124	0.0002[b]
0.602	4.08182	4.08392				4.0829	0.0010
0.379	4.06112	4.06872				4.0649	0.0038
0.168	4.05371	4.05091	4.05381	4.0464	4.0538	4.0512	0.0014
Seawater							
1	4.1913	4.1953	4.1895	4.1913		4.1918	0.0012
0.834	4.1701					4.1701	
0.556	4.1273					4.1273	
0.358	4.0977	4.0979				4.0979	0.0001

[a] Long-term mean, see Fig. 5 and Table 2.
[b] Long-term standard deviation/$65^{0.5}$.

the mixing proportions and calculating standard errors for the $^{11}B/^{10}B$ of each mixture from repeat analyses, we calculate an intercept $^{11}B/^{10}B$ ratio of 4.0396± 0.0028 (0.7‰; 2σ), with an MSWD=0.1. Note that this very low MSDW may either be fortuitous or may indicate that the estimated errors on each analysis are too high, therefore the error associated with this intercept may be a maximum. The $^{11}B/^{10}B$ ratio of the intercept is within error of the certified value, but at the upper end of the analyses of NIST SRM 951 run with a boron-free matrix (Fig. 3a). The lower value of the latter is consistent with the hypothesis that it is contaminated with organics that interfere with $^{10}BO_2^-$ at mass 42.

A second standard addition was performed with various mixtures of Bransfield Strait seawater and NIST SRM 951 (100%, 83%, 56%, and 36% seawater). The results are also shown in Fig. 6 and Table 3. Not all these samples were run in duplicate and as such, reproducibilities and hence a York (1969) regression could not be calculated. We have however fitted a least squares regression line (R^2=0.9994) and calculated a lower intercept $^{11}B/^{10}B$ ratio of 4.045 for NIST SRM 951 in a seawater matrix. Given the likely error associated with this estimate (~0.7‰ from comparison with the 871 standard addition experiment above), NIST SRM 951 analysed in a seawater or carbonate matrix gives identical results. These data suggest that there is no systematic bias in the measured $^{11}B/^{10}B_{TE}$ related to the nature of either the loading matrix or the amount of matrix loaded.

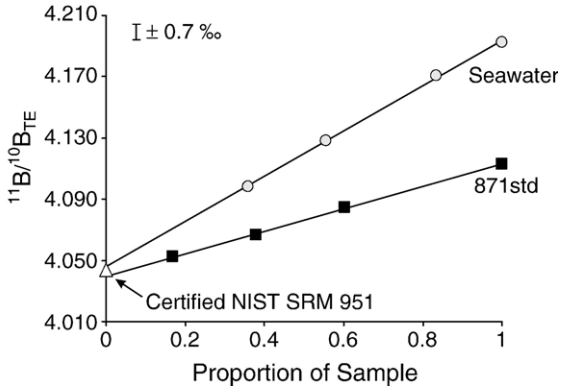

Fig. 6. Standard addition experiments for seawater (circles) and 871std (squares). In each regression the unforced intercept is equal to the NIST SRM 951 value in that particular matrix as determined by total evaporation. For the 871std experiment analyses are means multiple analyses with error bars smaller than the plotted symbols. The difference between the intercept determined by both experiments is not considered significant (see text).

3.4. Foraminiferal analyses

The data presented in the previous section clearly demonstrate that the total evaporation method is capable of yielding precise boron isotopic analyses of 200–1000 pg of boron hosted in carbonate and seawater matrices. A true estimate of the precision of the technique with regard to foraminferal analyses, however, can only be assessed once the reproducibility of the preparation of real samples has been quantified. Thus the blank associated with sample preparation, dissolution and handling needs to be assessed. To achieve this, 140 foraminifera (*G. sacculifer* — with the final gametogenic chamber) were picked from the ERDC-92 box core (supplied by P. Pearson) from the Western Pacific (2°13.5′S, 156°59.9′E, water depth 1598 m). The samples were from a depth of 13–14 m, an age of 9.6 ka (Palmer and Pearson, 2003) and were all hand picked from the 355 to 425 μm size fraction. Prior to crushing, the 140 tests were split into two sets of 50 and two sets of 20 tests. Each set was crushed,

Table 4
Compilation of foraminiferal samples analysed by total evaporation NTIMS

Sample	Species	n[a]	[Ca] μg[b]	Size (μm)	$^{11}B/^{10}B_{TE}$ measured			$^{11}B/^{10}B_{TE}$	$\delta^{11}B$[c] mean
					1	2	3		
9.6 ka ERDC-92 (2°13.5′S, 156°59.9′E, water depth 1598 m, Pacific Ocean)									
20a	*G.sacculifer*	20	99	355–425	4.1209	4.1222	4.1215	4.1215	20.3
20b	*G.sacculifer*	20	100	355–425	4.1170	4.1209		4.1189	19.6
20c	*G.sacculifer*	20	113	355–425	4.1225			4.1225	20.5
50a	*G.sacculifer*	50	312	355–425	4.1203			4.1203	20.0
50b	*G.sacculifer*	50	405	355–425	4.1216			4.1216	20.3
Core-top ODP 806 (0°19.1′N, 159°21.7′E, water depth 2520 m, Pacific Ocean)									
806-13	*G.sacculifer*	10	115	600–710	4.1385	4.1360		4.1372	24.2
806-11	*G.sacculifer*	25	482	500–600	4.1353			4.1353	23.7
806-12	*G.sacculifer*	25	352	500–600	4.1383	4.1378		4.1381	24.4
Core-top ODP 664 (°6.4′N, 23°13.7′W, water depth 3806 m, Atlantic Ocean)									
664-001	*G.sacculifer*	16	387	600–710	4.1358	4.1387	4.1368	4.1371	24.1
664-B40	*O. Universa*	45	365	500–600	4.1214	4.1249	4.1259	4.1241	20.9
RC 14–37PC (1.5°N, 90.2°E, water depth 2230 m, Indian Ocean)									
RC14–37	*G.sacculifer*	20	519	515–865	4.1347	4.1326		4.1337	23.3

[a] Number of tests picked, pre-cleaning.
[b] Amount of calcium in micrograms.
[c] Permil deviation from NIST SRM 951, $^{11}B/^{10}BTE=4.0396$.

cleaned and dissolved separately. The results of this study are shown in Table 4. Given the variable amounts of sample and hence B in the splits, it is expected that any processing blank would affect the sample splits with fewer foraminifera to a greater degree than the larger ones. It is evident from Table 4 that despite four times more B (assuming a constant B/Ca ratio) in the larger sample splits, the $^{11}B/^{10}B$ is similar for all four samples (averaging at $^{11}B/^{10}B_{TE}=4.1209\pm0.7‰$; 2 s.d.). These results suggest that preparation blank is insignificant.

A further demonstration of the reproducibility of the approach is also shown in Table 4. Three repeat dissolutions of 10–25 tests of *G. Sacculifer* (with final gametogenic chamber) from the core-top of ODP 806 (0°19.1′N, 159°21.7′E, water depth 2520 m) in the Western Pacific, from the 600–710 μm and 500–600 size fraction, reproduce at $^{11}B/^{10}B_{TE}=4.1369\pm0.7‰$ (2 s.d.; see Table 2). We also analysed core-top *G. sacculifer* from the 90° E ridge in the Indian Ocean (RC14–37PC; 1.5° N, 90.2° E, 2230 m water depth; supplied by B. Hönisch) and Equatorial Atlantic (ODP 664; 0°6.4′N, 23°13.7′W, water depth 3806 m). Ten tests from the 600–710 μm size fraction for each site were analysed and for ODP 664 we obtained a mean $^{11}B/^{10}B_{TE}=4.1371$ and for RC 14–37PC $^{11}B/^{10}{}_{TE}=4.1337$. Given our long-term reproducibility of 871std (0.7‰), these data are within error of each other and with the *G. sacculifer* of similar size analysed from the equatorial Pacific. We note that the 9.6 ka samples analysed from the Pacific (discussed previously, Table 4) were picked from a smaller size fraction (355–425 μm) and have lower $^{11}B/^{10}B$ ratios ($^{11}B/^{10}B_{TE}=4.1209$). We suggest that this is consistent with decreasing boron isotope ratio with foraminiferal test size, recently documented by Hönisch and Hemming (2004).

It is commonly observed that the $^{11}B/^{10}B$ ratio of *G. sacculifer* is around 2–3‰ higher than that of co-existing *O. universa* species (Sanyal et al., 1996; Sanyal et al., 1997; Hönisch et al., 2003). In order to see if this offset also exists for our TE-NTIMS technique we analysed 45 tests of *O. universa* from the 500–600 μm size fraction from ODP 664. We obtain a mean $^{11}B/^{10}B_{TE}=4.1241$, which is 3.1‰ lower than the *G. sacculifer* core-top and so is consistent with published observations.

3.5. Accuracy of TE-NTIMS boron isotope analysis

Judging the accuracy of any boron isotope analytical methodology is complicated by the lack of suitable interlaboratory comparison materials. The carbonate and seawater samples analysed here, however, allow comparison of the results of TE-NTIMS compared and other analytical methodologies. Of particular use in this regard is sample B1 (Mediterranean seawater) that is a sample that was distributed to 27 laboratories as part of the interlaboratory comparison study of Gonfiantini et al. (2003). In order to allow a comparison, measurements must be converted into delta notation using the boron isotope composition of NIST SRM 951 ($^{11}B/^{10}B_{TE}=4.0396$).

The most precise technique for measuring boron isotope analysis is currently considered to be positive ion TIMS using $Cs_2BO_2^+$ (Gonfiantini et al., 2003). Sample B1 was analysed by PTIMS in five laboratories, our TE-NTIMS value of $\delta^{11}B = 39.2 \pm 0.8‰$ (2 s.d.) agrees well with those workers who routinely measure boron isotopes in aqueous samples (e.g. J. Gaillardet and D. Lemarchand — $\delta^{11}B = 38.8 \pm 0.4‰$; 2 s.d.) and is well within the range of all five laboratories ($\delta^{11}B = 38.6 \pm 1.7‰$; 2 s.d.). Our TE-NTIMS measurement is also very similar to the results for this sample reported from 2 laboratories using the standard NTIMS approach ($\delta^{11}B = 39.1 \pm 0.35$; Gonfiantini et al., 2003). Aggarwal et al. (2004) made a recent compilation of estimates (using several analytical techniques: NTIMS, PTIMS and MCICPMS) of the boron isotopic composition of global seawater (owing to the long residence time of B in the oceans, the $^{11}B/^{10}B$ of open ocean seawater is expected to be uniform worldwide). The mean $\delta^{11}B$ value of these estimates is 39.5±0.6‰ (2. s.d.). Our measurements of Mediterranean and Southern Ocean water (39.2±0.8‰ and 37.7±1.2‰) are within error of this value. However, note that our Southern Ocean water may be biased to slightly lower values by a small blank or organic contamination problem (see above).

Although not an interlaboratory standard, sample CE-95 has been multiply analysed previously at GEOMAR by F. Böhm using the standard NTIMS technique as an in-house standard. The average $\delta^{11}B$ value obtained at GEOMAR laboratory is 20.4±0.6‰ (2 s.d.; $n = 16$; F. Böhm personal communication). We have analysed CE-95 four times and obtain a $\delta^{11}B = 19.4 \pm 0.9‰$ (2 s.d.), which is within error of the value measured at GEOMAR.

In principle, it should be possible to assess the accuracy of recent foraminifera analyses simply from a knowledge of the pH of seawater in which they grew. Unfortunately, the uncertainties inherent in the boron isotope proxy for pH, especially the equilibrium isotope fractionation factor, the nature of boron incorporation in carbonate and potential "vital" effects of biologically mediated $CaCO_3$ growth (see Pagani et al., 2005 for a review) limit the success of such an approach. It is important however to check the consistency of our $^{11}B/^{10}B$ measurements of recent (core-top) foraminifera with other studies of core-top (Sanyal et al., 1995; Palmer and Pearson, 2003; Hönisch and Hemming, 2004) and cultured forams (Sanyal et al., 1996; Sanyal et al., 2001) of similar species. Core-top samples represent an average of foraminifera that have grown during the last few thousand years, largely prior to ocean acidification over the last ~100 years as a result of the anthropogenic rise in atmospheric CO_2 (Feely et al., 2004). To compare these samples to those grown under controlled culture conditions it is first necessary to infer an ocean pH in which they grew. Due to the nature of the carbonate system, knowledge of two carbonate parameters is required in order to calculate ocean pH. Using a "pre-industrial" atmospheric pCO_2 concentration of 280 ppm (Petit et al., 1999) and assuming alkalinity, salinity, and surface ocean temperature have remained constant (values taken from the nearest WOCE site to the sample site) it is possible to calculate "pre-industrial" ocean pH using the equations in Zeebe and Wolf-Gladow (2001). Fig. 7 shows the core-top *G. sacculifer* data collected here plotted against their "pre-industrial" pH. On this figure we have also plotted other published estimates of the $\delta^{11}B$ of core-top *G. sacculifer* (Sanyal et al., 1995; Palmer and Pearson, 2003; Hönisch and Hemming, 2004) and the cultured *G. sacculifer* of Sanyal et al. (2001).

It is clear from Fig. 7 that there is an offset between the theoretical curve based on the commonly used equilibrium isotope fractionation factor of Kakihana et al. (1977) and the $\delta^{11}B$ measured in cultured forams,

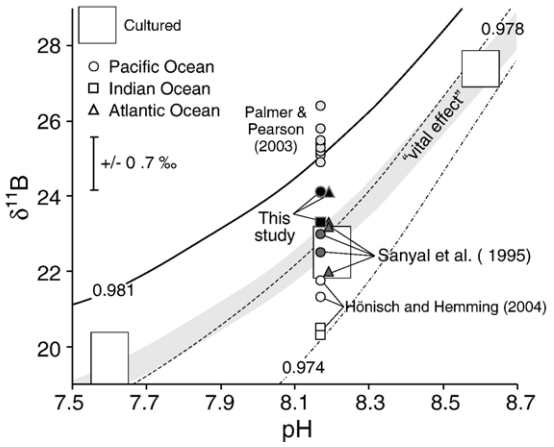

Fig. 7. Boron isotope composition (at 25 °C) of $B(OH)_4^-$ given various isotopic fractionation factors (α). Alpha values are taken from Kakihana et al. (1977; 0.981), Pagani et al. (2005; 0.974) and our own best fit (0.9775) to the *G. sacculifer* culture data of Sanyal et al. (2001). The thick grey line is calculated using a $\alpha = 0.981$ and a ~2‰ vital effect (i.e. constant 2‰ biologically induced fractionation). Also shown are our data for core-top forams from the Indian (black triangle), Atlantic (black square) and Pacific (black circle) oceans, in addition to the cultured *G. sacculifer* of Sanyal et al. (2001; large white squares describing both the error in pH and $\delta^{11}B$), and published core-top *G. sacculifer* of Sanyal et al. (1995; dark grey), Palmer and Pearson (2003; light grey) and Hönisch and Hemming (2004; white).

and in most of the measured core-top forams. Not only have there been a number of divergent reassessments of alpha (1.024 to >1.030; Pagani et al., 2005; Zeebe, 2005; Liu and Tossell, 2005) but there are several other poorly known parameters involved in predicting the $\delta^{11}B$ of foraminifera from inorganic equilibria constraints (see recent review Pagani et al., 2005). The potential importance of "vital effects", for example, has been discussed in several previous studies (Sanyal et al., 2001; Zeebe et al., 2003; Hönisch et al., 2003). Our core-top data lie between, but formally within error of, the cultured and core-top samples measured by Sanyal et al. (1995, 2001) and Holocene Pacific *G. sacculifer* analysed by Palmer and Pearson (2003; $\delta^{11}B = 24.9$ to 26‰). Our core-top *G. sacculifer* from the Pacific, and analyses on splits of the same samples from the Indian Ocean are significantly heavier than those of Hönisch and Hemming (2004). The cause of this large inter-laboratory variability (20.3‰ to 26‰, a range of ~6‰) is at present unknown. Notably, all these forams are roughly the same size, so size fraction effects (Hönisch and Hemming, 2004) cannot be invoked to explain these differences. Since all these laboratories report a similar $\delta^{11}B$ values for seawater (~39.5‰; Palmer et al., 1998; Sanyal et al., 2001; Hönisch et al., 2003), it is likely that the variability stems from either fractionations induced by sample preparation (including foram cleaning and blank contamination) or variations in analytical protocol leading to shifts in NIST SRM 951 relative to carbonate samples. In this study, we extensively document experiments that have investigated the influence of different loading matrices and preparation blank and we believe that is important for similar information to be reported on other measurement procedures. It is important to reiterate, however, that the relative variations between foraminiferal samples are reproducible between laboratories and this information can still provide an important record of past oceanic pH change. For example, it has been shown by several workers, and replicated here, that core-top and cultured *O. universa* are consistently ~3‰ lighter than *G. sacculifer* grown under similar conditions.

4. Conclusions

In this contribution we have shown that by analysing boron isotopes by total evaporation it is possible to reduce the required sample size by a more than a factor of 6 times (3–6 mg compared to <0.5 mg), bringing the sample requirements in-line with other foraminiferal paleoceanographic proxies (e.g. trace metal/Ca). For such sample sizes, blank contamination is a problem. This can, however, be overcome provided strict laboratory protocols are followed, ultraclean reagents are used throughout, and filaments are loaded in a stream of pure nitrogen gas. This reduction in sample requirements comes with no loss in analytical precision (±0.7‰). It is hard to assess the accuracy of any N-TIMS B isotope measurements of foraminifera. Nevertheless, our total evaporation technique yields measurements of NIST SRM 951 within error of the certified value using both seawater and carbonate matrices. We also document an absence of significant blank contribution during sample preparation. We thus believe that our new technique provides a robust means to determine the boron isotopic composition of foraminifera, which is a critical pre-requisite for the application of the boron isotope paleo-pH proxy.

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