In situ boron isotope analysis in marine carbonates and its application for foraminifera and palaeo-pH

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ABSTRACT

The boron isotope composition of marine carbonates such as foraminiferal tests and coral skeletons is increasingly being used to reconstruct seawater pH values and atmospheric pCO$_2$ concentrations spanning hundreds of thousands or even millions of years. However, inter specific and small scale (microns) intra specific isotopic variation, either due to life processes of an organism or patchy recrystallisation and dissolution in fossilised material, can limit the use of the boron isotope ratio as palaeo-pH recorder. One approach to address this problem is the combined use of *in situ* and high spatial resolution mass spectrometry and high precision bulk analytical techniques. While much effort has been invested to establish reference material for silicates little attention has been devoted towards characterizing and using carbonate material allowing direct isotopic comparisons between B isotope data produced on carbonates by different techniques and laboratories. Hence, here we present data on the boron isotope composition of carbonate material determined by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), thermal ionization mass spectrometry (TIMS), and secondary ionization mass spectrometry (SIMS). The new reference material permits the B isotope analysis of single foraminiferal chambers using SIMS and to empirically relate between seawater pH, the B isotope composition of *O. universa* and the predicted foraminiferal vital effect.

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1. Introduction

Chemical signatures of the ambient seawater incorporated in marine carbonates are used to reconstruct past environment and climate conditions. A key challenge for palaeoclimate reconstructions and models is the level of atmospheric carbon dioxide (DeConto and Pollard, 2003). More recently, the impact of rising CO$_2$ in the atmosphere on ocean pH has been the focus of increasing concern (e.g. Raven et al., 2005). Changes of the alkalinity of the oceans will have important implications on many marine carbonate producers with calcification being impeded progressively as the seawater becomes more acidic. Facing the current anthropogenic increase in CO$_2$, the capability to faithfully reconstruct the past pH condition of the ocean has become an increasingly important research topic.

Over the last decade a number of studies have demonstrated the great potential of boron as a proxy to study seawater pH variation and atmospheric CO$_2$ concentrations (e.g. Spivack and Edmond, 1987; Hemming and Hanson, 1992; Sanyal et al., 1995; Pearson and Palmer, 2000). The speciation of boron and the distribution of the two different isotopes between the different species are sensitive to pH variations which can produce significant and traceable changes in the isotopic composition of carbonates (Vengosh et al., 1991; Hemming and Hanson, 1992). However, there is debate and concern on how robust and reliable boron isotopes are as a pH and potential pCO$_2$ proxy (e.g. Pagani et al., 2005; Hönisch et al., 2007).

One substantial uncertainty on the boron isotope based pH reconstruction can be caused by the isotope fractionation factor used to construct the theoretical δ^{11}B–pH curve (Pagani et al., 2005; Klochko et al., 2006). However, even with a better established fractionation factor, some of the ocean pH reconstructions over the Cenozoic using foraminiferal test are unrealistic high and inaccurate for the Quaternary. This could be due to foraminiferal vital effect considerations and assumptions in total dissolved inorganic carbon (DIC) or alkalinity in seawater (see Pagani et al., 2005 for discussion). In addition, poor levels of agreement between different laboratories of the boron isotope composition reported for the same foraminiferal species from similar localities are reported (Foster et al., 2006). One source for the disagreement in the boron isotope composition in marine carbonates

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is due to analytical difficulties. Despite the increase in boron isotope studies and laboratories performing the analyses, the accurate determination of boron isotope compositions in geological materials is still not routine and requires significant analytical skills and a rigorous analytical protocol as demonstrated in the intercomparison work described by Gonfiantini et al. (2003) and Tonarini et al. (2003). In fact, the worst agreement among laboratories was observed for the marine limestone sample.

Another obstacle specifically for the analysis of carbonates is the lack of a suitable certified reference material. So far, the only certified reference material universally used and available for bulk boron isotope analysis is the boric acid NIST SRM 915. Additional reference materials are either seawater or essential silica based materials such as microanalytical glasses, minerals and volcanic rocks all of which are potentially imposing a matrix effect on the analysis depending on the sample preparation (e.g. Kasemann et al., 2001; Tonarini et al., 2003; Rosner and Meixner, 2004).

Further significant uncertainties are caused by vital effects on the boron isotope composition of biogenic carbonates. Foraminiferal tests, coral skeletons and bivalve shells are key components of marine carbonates and an important archive of palaeoclimatic data. As such the B isotopic composition of the biogenic calcite preserved in marine sediments provides an archive for the pH of the ocean and is the main target for reconstructions of past atmospheric CO_2 concentrations (e.g. Spivack et al., 1993; Sanyal et al., 1995; Palmer et al., 1998; Pearson and Palmer, 2000; Sanyal et al., 2001; Palmer and Pearson, 2003; Hönisch and Hemming, 2004; Ni et al., 2007; Foster, 2008). However, physiological processes, such as respiration, photosynthesis and calcification can modify the micro-environmental pH in the calcifying region of the organism (e.g. Rink et al., 1998; Wolf-Gladrow et al., 1999; Zeebe et al., 2003) and thus change the B-isotope composition of the carbonate (Rollion-Bard et al., 2003; Zeebe et al., 2003; Blamart et al., 2007) . Yet, vital effects do not necessarily compromise the use of $\delta^{11}B$ as a palaeo-pH indicator as modelled by Zeebe et al. (2003).

Boron isotope records from corals and bivalves restricted to near shore environments are often not in equilibrium with the atmosphere and hence do not allow to reconstruct atmospheric CO_2. The main carbonate producers in the open ocean waters used in palaeoceanographic reconstructions are shallow (mixed layer) dwelling planktic foraminifers. Foraminiferal carbonates provide an additional complication with regards to palaeoenvironmental reconstructions. Depending on the species, ontogenetic depth migration can range from a few tens to several hundreds of meters (Hemleben et al., 1989). Consequently, chambers formed at different water depths, and hence pH conditions, are likely to have different B isotope ratios. In addition to this "ontogenetic" calcification, some species secrete an additional layer of so called gametogenic calcite just prior to reproduction (e.g. Bé, 1980; Hamilton et al., 2008). Similar to the Mg/Ca (Nürnberg et al., 1996) and Ca isotope ratio (Kasemann et al., 2008), it can not be excluded that these different modes of calcification might also fractionate boron isotopes differently, even under identical environmental conditions. In addition to biological controls on the boron isotope composition in biogenic carbonate, post-depositional processes such as partial dissolution and diagenetic alteration via e.g. exchange with pore water can also alter the original signal (e.g. Vengosh et al., 1991; Ishikawa and Nakamura, 1993; Spivack and You, 1997; Wara et al., 2003).

To make full use of the proxy and to asses the robustness of boron isotope analyses and the precision of the pH and pCO_2 reconstructions we need to better understand the factors that influence the incorporation of boron into biogenic carbonates e.g. thoroughly evaluate the biological aspects of boron isotope incorporation. To tackle these questions a combination of bulk analytical and in situ microanalytical techniques is necessary. Bulk analytical techniques such as thermal ionization mass spectrometry (TIMS) and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) provide a high sample

throughput and high precision boron isotope data. Generally, these techniques require considerable amounts of sample material for analysis e.g. more than 100 planktic foraminiferal specimens of the same species from ideally a narrow size fraction or pieces of corals (~3 mg) (e.g. Hemming and Hanson, 1992; Hönisch et al., 2004; Foster, 2008). In contrast, microanalytical in situ techniques such as secondary ionization mass spectrometry (SIMS) offer the spatial micron scale resolution necessary to target individual organism as well as analyse selected chambers and calcite layers in foraminiferal test, specific annual and even diurnal growth bands in corals and bivalves (Rollion-Bard et al., 2003; Blamart et al., 2007; Kasemann et al., 2008).

In situ boron isotope analyses of biogenic carbonates are still in its infancy, but preliminary studies in coral skeletons and foraminiferal tests revealed significant and systematic B isotopic variations potentially induced by pH variations at the sites of calcification (Rollion-Bard et al., 2003; Schmidt and Kasemann 2006; Blamart et al., 2007). Such large variations have never been reported using conventional bulk and micro-drill sampling techniques. In addition, preliminary in situ studies on the lithium, carbon, oxygen and calcium isotope composition of biogenic carbonates (Rollion-Bard et al., 2003; Rollion-Bard et al., 2007; Vigier et al., 2007; Kasemann et al., 2008) demonstrate the need and capability of high spatial resolution SIMS to determine the internal isotopic variability and the influence of growth rates, habitat and symbionts on the isotopic composition.

To make full use of in situ boron isotope analyses and its potential to evaluate the nature and extent of boron isotope variation in marine carbonates, we document analytical conditions that offer the necessary spatial resolution but also provide a sufficient analytical uncertainty. We present the boron isotope composition of biogenic and inorganic carbonates that have been measured using bulk analyses (MC-ICP-MS, TIMS) and in situ techniques (SIMS) to allow inter-laboratory and -analytical comparison. Since this material is not commercially available reference material, we also analysed synthetic, silica-rich glass reference materials from the National Institute of Standards and Technology (NIST) for direct comparison. Finally, we apply SIMS to analyse the boron isotope composition of cultured samples of the foraminifer Orbulina universa whose final chamber was completely built in a pH controlled medium (Sanyal et al., 1996, 2001).

2. Materials and methods

2.1. Samples

The carbonate samples in this study consist of one marine bivalve (KW-T6), two corals (M93-TB-FC-1; PS69/318-1), 2 planktic foraminifers (O. universa) and one inorganic calcite (UWC-1). Sample KW-T6 is a shell fragment of Tridacna gigas from Huon Peninsula, Papua New Guinea, showing diurnal growth increments between 10 and 30 μm (night and day respectively; M. Elliot pers. comm. 2008). Sample M93-TB-FC-1 is a piece of massive Porites (sp) coral microatoll from the north coast of Papua New Guinea. The sample has been U-series dated to 2.5±0.4 ka BP and analysed for oxygen isotopes (Tudhope et al., 2000, 2001). The cold water coral Desmophyllum (sp) PS69/318-1 is from the Pacific sector of the Southern Ocean (69°08.64′S and 123°13.35′W), dredged by R.V. "Polarstern" operated by the Alfred Wegener Institute for Polar and Marine Research in 2005 from a water depth between 1480 and 1788 m. O. universa were collected by scuba divers about 11 km south of La Parguera (Puerto Rico) and cultured at seawater conditions of pH 8.2 and 8.6, and 10 times artificially enhanced (~50 μg g^{-1}) boron concentration (Sanyal et al., 2001). The inorganic calcite sample UWC-1 (University of Wisconsin Calcite standard; Graham et al., 1998) is a piece from a 10 cm cleavage rhomb of sky blue marble from the Valentine Wollastonite Mine in the Adirondacks (sample #88-V-1; Gerdes and Valley, 1994). The metamorphic grade is upper amphibolite facies and the calcite has common inclusions of coarse flakes of graphite.

Table 1
Major element composition of carbonate standards and certified reference glasses

Oxide wt.%	KW-T6[a] Tridacna gigas	M93-TB-FC-1[b] Porites (sp)	PS69/318-1[a] Desmophyllum (sp)	UWC-1[b] Marble	OKA[b] Carbonatite	SRM 610[c] Synthetic reference glasses	SRM 612[c]
SiO_2		0.000(7)		0.005(11)	0.000	69.06	71.79
TiO_2					0.001	0.07	0.008
Al_2O_3						1.92	1.99
Fe_2O_{3tot}						0.07	0.008
FeO		0.00(1)		0.00(1)	0.069		
MnO		0.001(8)	0.00003(1)	0.012(12)	0.291	0.06	0.005
MgO	0.06(3)	0.221(27)	3.7(18)	0.090(13)	0.114	0.08	0.013
CaO	56.0(58)	52.66(45)	56.0(60)	55.66(17)	55.98	11.39	11.85
Na_2O		0.607(5)		0.00(3)		13.76	14.02
K_2O		0.009(5)		0.002(6)		0.059	0.008
P_2O_5						0.078	0.013
CO_2		45.09(43)		44.13(16)			
SrO	0.093(3)	0.927(19)	0.29(1)	0.046(48)	1.42		
SO_3		0.438(33)		0.012(20)			

The indicated uncertainties for the carbonate reference material are valid for the last digits (1σ).
[a] Element concentration is based on SIMS analyses.
[b] Element concentration is based on electron microprobe analyses.
[c] Compilation of element concentration for the matrix of the NIST Glasses (Hinton, 1999) and selected doped elements (Pearce et al., 1997).

In addition to carbonates, we also analysed the B isotope composition of NIST Standard Reference Materials SRMs 610 and 612; synthetic Si–Na–Ca–Al oxide glasses which were produced for NIST (see Table 1 for major element compositions). The boron concentration and isotope composition of the glasses have been well characterized (e.g. Kasemann et al., 2001) and these glasses are widely distributed and commercially available.

2.2. Sample preparation

For (MC-ICP-MS) analyses the carbonate samples were crushed, cleaned and dissolved in 100–300 µL distilled 0.5 M HNO_3 following the cleaning technique described in Foster (2008). Before (MC-ICP-MS) analysis, boron was separated from the dissolved carbonate samples by a one-step anion exchange procedure. The buffered sample solution (pH ~ 5) containing ~ 30 ng of boron was loaded on small 25 µL-columns filled with crushed and sieved (to 63–120 µm) boron specific Amberlite IRA 743 resin. The matrix was eluted using repeat rinses of Milli-Q water and the boron then collected using 0.5 HNO_3 as the eluent. The total procedural blanks typically ranged from 70–100 pg and the column yield for this procedure is ~ 95% (Foster, 2008).

For TIMS analyses 10 mg of cleaned carbonate samples (coral and bivalve) were dissolved in 1 M HCl, mixed with mannitol (1 mg B : 20 mg mannitol), evaporated to dryness and re-dissolved in suprapure H_2O for loading. The total boron blank for this procedure was less than 1 ng (see Kasemann et al., 2005). In preparation for microanalysis, the carbonate samples and reference glasses were embedded in epoxy and polished.

2.3. Multi-collector inductively coupled plasma-mass spectrometry

Boron isotope analyses were carried out on a Thermo-Finnigan Neptune MC-ICP-MS at the University of Bristol following the method outlined in Foster (2008). A PFA spray chamber with a ~ 3 mL/min add gas of ammonia, ported in immediately after the ESI PFA 50 µL/min nebuliser, was used for sample introduction. This approach ensures that the spray chamber volume remains basic despite samples, standards and washes being introduced in 0.5 M HNO_3 and a fast sample wash-out time. Solution concentrations were typically 30–50 ng mL^{-1} boron which equates to 3–7 pA of [11]B. Boron isotopes were determined by 2 min simultaneous collection of [11]B^+ and [10]B^+ using Faraday cups. Including blank correction and a measurement of bracketing standards, a complete measurement of a single sample

takes ~ 30 min and each sample is analysed at least twice and an average value is used. Instrumental mass bias was corrected by using the average value of bracketing, intensity-matched NIST SRM 951 boric acid reference material. The boron isotope values of the samples are given relative to NIST SRM 951 in the conventional δ-notation with an uncertainty of the fully processed reference material of 0.2‰ (2σ). For further analytical information see Foster (2008).

2.4. Thermal ionisation mass spectrometry

Boron isotope ratios measurements were made on a multi-collector Finnigan TRITON mass spectrometer, following the method of Kasemann et al. (2001). From each sample solution, ~ 3 ng B together with 0.5 µL B-free seawater was loaded on a Re single filament, dried at 0.7 and then heated at 1.2 A for 30 s. Analyses were carried out at filament temperatures of about 1000 to 1050 °C. Boron isotopes were measured as BO_2^- complexes on masses 42 and 43. Ion beam intensities on mass 43 were typically ~ 10 pA and ion counting was started at intensities of about 2 pA. A complete measurement of a single sample involves 80 blocks of 12 cycles each, taking about 2 h of data acquisition. In each analytical session, the $n(^{11}B)/n(^{10}B)$ ratio of our certified reference material NIST SRM 951 was reproduced within 0.8‰ (2σ, $n=6$). The boron isotope values are given relative to NIST SRM 951 in the conventional δ-notation. Each sample solution was run in full duplicate, while two different fragments were analysed for M93-TB-FC-1, and the uncertainty of the reference material was propagated into the uncertainty on the isotope ratio of the sample (2σ_{mean} or σ_f).

2.5. Secondary ionization mass spectrometry (SIMS)

All samples were analysed for boron concentration and isotope ratios using the single collector, secondary ionization mass spectro-meter Cameca ims 4f at the NERC Ion Microprobe Facility at the University of Edinburgh. A primary ion beam of $^{16}O^-$ and net 15 keV with a beam current range between 10 and 40 nA was used to produce positive secondary ions of $^{10}B^+$ and $^{11}B^+$. The secondary ions were analysed with an energy window of 52 eV, a 150 µm image field using the 450 µm contrast and 1800 µm field apertures. Secondary ions were counted by peak jumping on an ETP electron multiplier and the isotope ratio was measured for 200 cycles, each cycle consisting of 5 and 3 s integrations of $^{10}B^+$ and $^{11}B^+$ respectively. Initial measurements on samples with high boron concentration (e.g. corals, bivalves and

Table 2
Boron concentration and isotope composition of carbonate reference materials by SIMS, MC-ICP-MS and TIMS

Material	B [µg g^{-1}] SIMS ims-4f ±2σ	B [µg g^{-1}] LA-ICP-MS ±2σ	δ^{11}B [‰]$^{\Delta M \sim 2400}$ SIMS $_{ims-1270}$ ±1σ_{mean}	δ^{11}B [‰]$^{\Delta M \sim 1600}$ SIMS $_{ims-4f}$ ±1σ_{mean}	δ^{11}B [‰]$^{\Delta M \sim 500}$ SIMS $_{ims-4f}$ ±1σ_{mean}	δ^{11}B [‰] MC-ICP-MS ±2σ_{mean}	δ^{11}B [‰] TIMS ±2σ_{mean}
M93-TB-FC-1	±2.0	39.3(36)	±0.7	±0.5	±0.7	24.6(1)	25.0(30)
UWC-1	12.6(6)	12.9(28)	7.7(19)	7.8(12)	8.8(16)	7.5(2)	8.6(8)
PS69/318-1	25.4(40)				16.8(10)	15.5(1)	15.9(7)
KW-T6	29.5(37)			15.3(11)	15.9(12)	15.4(1)	

The indicated uncertainties are valid for the last digits. LA-ICP-MS data are referenced to NIST SRM 612. Note that the TIMS and MC-ICP-MS isotope data are referenced to NIST SRM 951, while the SIMS data are referenced to M93-TB-FC-1.

reference glasses; see Table 2) were performed using a mass resolution of ~1600, sufficient to resolve mass interferences of ^{9}Be^{1}H$^+$ ($\Delta M = 1400$), ^{10}B^{1}H$^+$ ($\Delta M = 900$) and ^{30}Si^{3+} ($\Delta M = 460$). However, to increase the count rate and improve the uncertainty, analytical sessions of foraminifers were run using a mass resolution of ~500. While the molecular species ^{9}Be^{1}H$^+$ was undetectable in the carbonate samples, the ^{10}B^{1}H$^+$ interference on ^{11}B is ~0.3‰ and hence insignificant (~0.1‰) within the range of the analysed isotope ratios and our analytical uncertainty. Mass spectrometric results for NIST SRMs 610 and 612 under different analytical conditions are reported in Table 3.

Additional boron isotope ratio measurements were made on the Cameca ims 1270 multicollector secondary ionization mass spectrometer (SIMS) at the University of Edinburgh. Here, positive secondary ions were produced by a 5 nA, 22 keV, ^{16}O$^-$ primary beam focused to a 15 µm spot size. The secondary ions were analysed with a mass resolution (ΔM) of ~2400 using an energy window of 50 eV, a 60 µm image field, a 400 µm contrast and a 3000 µm field aperture. Prior to each analysis, the samples were pre-sputtered for 1 min to remove surface contamination. Boron isotopes were measured for 60 cycles, each cycle consisting of 5 and 3 s count times on ^{10}B$^+$ and ^{11}B$^+$, respectively, on the single electron multiplier. Analyses of M93-TB-FC-1 showed an internal uncertainty of 1.7‰ (1σ_{mean}) for a single-point analysis and an external uncertainty of 2.9‰ (1σ $n = 17$) (see Table 4).

In each analytical SIMS session the homogeneous reference glasses NIST SRM 610 and 612 were run to check the instrumental mass fractionation (IMF) and analytical uncertainty. Within a 6 day analytical session, the instrumental mass fractionation (IMF) for B was stable at the per mil level (1$\sigma = 0.7$‰, $n = 18$ NIST SRM 610). Boron isotope data are reported in the conventional δ^{11}B ‰ notation relative to NIST SRM 951 (Catanzaro et al., 1970). Calibration to the reference

material was through the Porites coral M93-TB-FC-1 using δ^{11}B$_{M93} = 24.8 \pm 0.4$‰, (2σ_{mean}) as determined by our TIMS and MC-ICP-MS measurements (Table 2). The accuracy for M93-TB-FC-1 as measured by SIMS under the different analytical conditions was better than 2.9‰ at one standard deviation (1σ, see Table 4 for details).

$$\delta^{11}B_{SIMS} = \left(\left(\left({}^{11}B/{}^{10}B_{Sample} / {}^{11}B/{}^{10}B_{M93-TB-FC-1} \right)_{SIMS} - 1 \right) * 1000 \right) + \delta^{11}B_{M93-TB-FC-1}$$

Trace element concentrations were measured applying a 10 nA, 15 keV, ^{16}O$^-$ primary beam and using the Cameca ims 4f. Secondary ions of ^{11}B (8-s), ^{26}Mg (3-s), ^{27}Al (2-s), ^{30}Si (4-s), ^{44}Ca (2-s), ^{55}Mn (5-s) and ^{88}Sr (3-s) were analysed with an energy window of 40 eV, an energy offset of 75 eV, a 25 µm image field using a 150 µm contrast and 750 µm field aperture, and counted by peak jumping on an ETP electron multiplier for 15 cycles. The element count rates were normalised to Ca and the relative ion yields were obtained from the internal lab carbonate standards NCC (Swart 1990; Norman Cross Calcite, supplied by A.E. Dickson, University of Cambridge) and OKA (Carbonatite Complex in the Monteregian Hills, Quebec, Canada, supplied by J. Blundy, University of Bristol: Mg = 688 µg g^{-1}, Ca = 400439 µg g^{-1}, Mn = 2250 µg g^{-1} and Sr = 11967 µg g^{-1}; see Allison et al. (2007) and Table 1), coral M93-TB-FC-1 (B = 39.6 µg g^{-1}), and the reference material NIST SRM 610 (Li, Al and Si, see Pearce et al., 1997). Note that the B concentration for M93-TB-FC-1 was taken from laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) analysis performed at the Australian National University using an Agilent 7500 series mass spectrometer. Laser optics, ablation cell geometry, and signal smoothing devices are described in Eggins et al. (2003). Ca was used as an internal standard and NIST SRM 612 (Pearce et al., 1997) was

Table 3
Mass spectrometric results of this study for the reference material NIST SRM 610 and NIST SRM 612 determined by SIMS under different analytical conditions

	Cameca 1270 (ΔM) ~2400				Cameca 4f (ΔM) ~1600				Cameca 4f (ΔM) ~500			
	SRM 610		SRM 612		SRM 610		SRM 612		SRM 610		SRM 612	
	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}	$n(^{11}$B$)/n(^{10}$B$)$	1σ_{mean}
	3.886	0.002	3.879	0.003	3.899	0.007	3.880	0.004	3.893	0.001	3.885	0.003
	3.884	0.002	3.885	0.003	3.886	0.002	3.883	0.004	3.886	0.001	3.886	0.003
	3.898	0.001	3.875	0.003	3.888	0.001	3.889	0.005	3.887	0.001	3.880	0.003
	3.895	0.002	3.882	0.003	3.887	0.003	3.885	0.005	3.888	0.001	3.870	0.003
	3.892	0.001	3.881	0.003	3.892	0.003	3.883	0.005	3.885	0.001	3.879	0.004
					3.891	0.004			3.885	0.001		
					3.894	0.002			3.886	0.001		
					3.890	0.002			3.884	0.001		
					3.892	0.002			3.879	0.001		
					3.885	0.002			3.882	0.001		
Average	3.891		3.881		3.891		3.884		3.885		3.880	
1σ, ‰	1.5		1.0		1.1		0.9		1.0		1.7	
1σ_{mean}, ‰	0.7		0.5		0.4		0.5		0.3		0.8	
$\Delta_{610/612}$	0.010				0.006				0.005			

Each data set represent one analytical day/session.

Tale 4

Mass spectrometric results of this study for the coral reference material determined by SIMS under different analytical conditions

	Cameca 1270 (ΔM) ~2400		Cameca 4f (ΔM) ~1600		Cameca 4f (ΔM) ~500			
	M93-TB-FC-1		M93-TB-FC-1		M93-TB-FC-1		PS69/318-1	
	$n(^{11}B)/n(^{10}B)$	$1\sigma_{mean}$	$n(^{11}B)/n(^{10}B)$	$1\sigma_{mean}$	$n(^{11}B)/n(^{10}B)$	$1\sigma_{mean}$	$n(^{11}B)/n(^{10}B)$	$1\sigma_{mean}$
	3.795	0.007	3.762	0.005	3.793	0.005	3.744	0.006
	3.807	0.005	3.767	0.005	3.771	0.005	3.752	0.006
	3.796	0.007	3.792	0.005	3.776	0.005	3.769	0.006
	3.793	0.006	3.769	0.005	3.777	0.005	3.767	0.006
	3.805	0.006	3.774	0.005	3.761	0.005	3.764	0.006
	3.789	0.007	3.768	0.004	3.787	0.005	3.764	0.007
	3.802	0.007	3.773	0.004	3.791	0.005	3.757	0.007
	3.787	0.005	3.776	0.004	3.779	0.005	3.759	0.005
	3.784	0.007	3.772	0.004	3.778	0.005	3.731	0.006
	3.775	0.007	3.764	0.003	3.774	0.005	3.732	0.006
	3.764	0.006	3.766	0.003	3.780	0.005	3.739	0.006
	3.787	0.007	3.778	0.003	3.788	0.005	3.737	0.006
	3.779	0.007			3.766	0.005	3.732	0.007
	3.792	0.006			3.795	0.005	3.758	0.007
	3.788	0.006			3.779	0.005		
	3.779	0.006			3.799	0.005		
	3.793	0.008						
Average	3.789		3.772		3.781		3.750	
1σ, ‰	2.9		2.1		2.8		3.7	
$1\sigma_{mean}$, ‰	0.7		0.5		0.7		1.0	
$2\sigma_{mean}$, ‰	1.4		0.9		1.4		2.0	

Each data set represent one analytical day/session.

used for calibration. The analytical uncertainties for element concentration determinations were less than 10% ($2\sigma_r$).

3. Results and discussion

3.1. Boron isotopic composition

Table 2 represents the boron isotope composition of the carbonate materials investigated by SIMS, TIMS and (MC-ICP-MS). All isotope data are listed in the conventional $\delta^{11}B$ (‰) notation relative to the reference material NIST SRM 951. The uncertainties of the SIMS Cameca 4f (ΔM~500) data are given as ($1\sigma_{mean}$) based on 5 analytical sessions, each involving between 3 to 6 analytical days and 63 single analyses on M93-TB-FC-1, 28 on PS69/318-1 and 9 on UWC-1 as well as 6 analyses on KW-T6 in one analytical day. One analytical session on the Cameca ims 1270 (ΔM~2400) included 5 analyses for UWC-1 and 14 for M93-TB-FC-1. One session on the Cameca ims 4f (ΔM~1600) covered 6 consecutive analyses for KW-T6 and UWC-1, and 12 for M93-TB-FC-1. The uncertainties on the TIMS and (MC-ICP-MS) data are given as 2σ based on at least two analyses of the same sample solution. Also provided in Table 2 are the boron concentration data for the carbonate samples.

3.2. Bulk analytical techniques

The boron isotope data obtained by TIMS and (MC-ICP-MS) on the carbonate material agree to within 1.1‰ (Table 2, Fig. 1a). This is quite an encouraging result given the different factors that govern uncertainties in these two different methods. While (MC-ICP-MS) involves column chemistry to separate B from the matrix and corrects for instrumental bias by rapid sample standard bracketing, TIMS has to face slightly different matrices and can control instrumental mass bias only by meticulous loading and running protocols. Clearly, the level of agreement (which is close to analytical uncertainty) suggests that there are no systematic biases between the two approaches.

3.3. Microanalytical techniques

The bulk samples and SIMS data on the carbonate materials agree to within 1.3‰, independent on the boron concentration or carbonate

matrix (Table 2, Fig. 1a). To check the isotopic homogeneity of all carbonate samples, SIMS profiles have been performed on either different sample fragments or along growth axis. For the inorganic calcite UWC-1 within and between crystal heterogeneities of ~3.2‰ (1σ) have been found. Ion profiles across the biogenic samples demonstrate isotopic variations (1σ) of 2.9‰ ($n=17$) for M93-TB-FC-1, 3.2‰ ($n=10$) for KW-T6 and 3.7‰ ($n=14$) for PS69/318-1.

To investigate possible analytical effects on the B isotope data produced by SIMS using a low mass resolution of ΔM~500, additional isotope ratio measurements on high B concentrated samples were made on the Cameca ims 1270 and ims 4f using a mass resolution of ΔM~2400 and 1600, respectively. Good agreement between the data (<1.0‰, Table 2) supports the reliability of the data sets.

The trace element concentration in carbonates, such as iron, magnesium and strontium, can vary significantly (Table 1) potentially influencing the relative ion yield of the analysed elements and imposing a potential matrix dependent IMF on the isotope measurements (R. Hinton pers. comm. 2008) as already documented for silicates (e.g. Steele et al., 1981). While the Sr amount content is quite variable in corals (e.g. Allison et al., 2001), it is rather constant and homogeneous in foraminifera (see Schmidt et al., 2008 for discussion). In contrast, the Mg amount content in foraminiferal calcite tests can vary not only between different species but also between different chambers and calcite layers in individual foraminifers (e.g. Eggins et al., 2004; Schmidt et al., 2008). Hence, the influence of Mg and Sr on the IMF has to be assessed. The carbonate reference material used in this study have different MgO and SrO amount contents ranging from 0.06% to 3.7% and 0.05% to 1.4%, respectively and cover the overall compositional range for most corals and foraminifers (e.g. Allison et al., 2001; Schmidt et al., 2008). In addition the calcium carbonate reference material includes the polymorphs aragonite (e.g. *T. gigas, Porites*) and calcite (e.g. *Desmophyllum*), which allows us to check the influence of the crystal structure on the IMF. For the four carbonate reference materials (M93-TB-FC-1, PS69/318-1, UWC-1, KW-T6), we obtained the same IMF within each analytical session. This suggests that within the compositional range of the analysed material neither the Mg and Sr amount content nor the crystal structure affect the IMF. This confirms that the B isotope data obtained for the reference carbonates by SIMS are sufficiently accurate and demonstrate that the ion microprobe technique can be used for the *in situ* analyses of boron isotopic variations in carbonates of
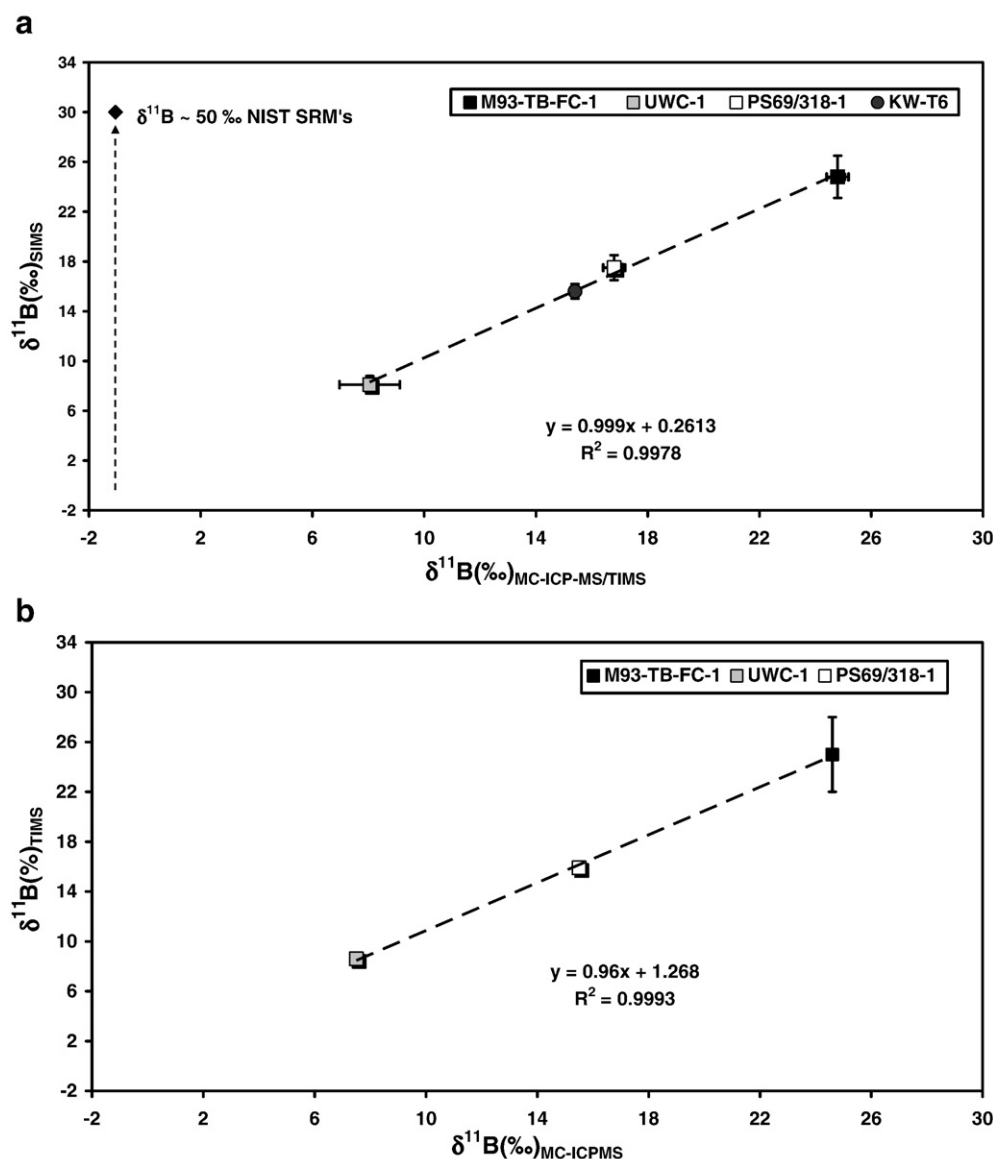
Fig. 1. (a) Comparison of the boron isotope values obtained by TIMS and (MC-ICP-MS) for carbonate reference material demonstrating the good agreement of the data measured by the two techniques. The uncertainties are $2\sigma_{mean}$. (b) B isotope values obtained by SIMS (calibrated to NIST SRM 951 via M93-TB-FC-1) vs. the B isotope data obtained by (MC-ICP-MS) for carbonate reference material. The B isotope data for the carbonates measured by the different techniques, fall on a single calibration line. The uncertainty for the SIMS data is given as $1\sigma_{mean}$.

similar composition. To increase the range in sample matrices and to check if the carbonate reference material can also be used as reference for samples with matrices far beyond such non-silicates, we examined the silicate glass reference materials from NIST that have matrices with high Si–Na–Ca–Al-element concentrations.

SIMS profiles across the NIST SRM glass wafers demonstrate an overall boron isotope homogeneity to better than 0.8‰ ($1\sigma_{mean}$) (see Table 3). However, the SIMS B isotope data of the two NIST glasses are considerable different (off by ~50‰) from the published values (Kasemann et al., 2001) when calibrated relative to M93-TB-FC-1 (see Fig. 1). This demonstrates a considerable matrix effect on the boron isotope composition and excludes the NIST reference material with its silicate framework and unusual element composition as a reference material for carbonate. However, given the good isotopic homogeneity of the NIST glasses compared to the carbonates materials (see chapter 2.5.), each analytical session combined carbonate and silicate reference

analyses to monitor instrumental stability, mass fractionation and analytical uncertainty.

3.4. Microanalysis of foraminiferal tests: pH and vital effect

The ultimate application for *in situ* boron isotope analysis using SIMS is on foraminiferal tests, since the constraint on the applicability of foraminifers as an archive for environmental information is the heterogeneity on the internal and inter-individual scale rather than the analytical precision (Boyle, 1988). These heterogeneities can result from the calcification process itself or from differences in the carbonate chemistry at the site of calcification induced by symbiont photosynthesis or host/symbiont respiration. In addition, differences in depth habitat, seasonality, changes in the microhabitat, bioturbation as well as post-depositional alteration can add inter- as well as intra-individual heterogeneity. To avoid these problems we analysed

Table 5
Summary of analytical results of cultured *O. universa* and chemical composition of seawater used for culture experiments

Sample	pH	B [μg g^{-1}]	Total Alkalinity μeq kg^{-1}	CO$_3$$^{2-}$ μmol kg^{-1}	Seawater δ^{11}B [‰] ±1σ$_{mean}$	Foraminifera δ^{11}B [‰] ±1σ$_{mean}$	pH Calculated $^{11-10}K_B$=1.0194 ±1σ$_{mean}$	pH Calculated $^{11-10}K_B$=1.0272 ±1σ$_{mean}$	ΔpH $^{11-10}K_B$=1.0194	ΔpH $^{11-10}K_B$=1.0272	Vital effect $^{11-10}K_B$=1.0194	Vital effect $^{11-10}K_B$=1.0272
BS 10	8.19	50.8	3333	232	−6.9(6)	−22.9(7)	7.99(12)	8.44(5)	−0.23	−0.26	1.9	−3.6
BS 23	8.67	50.4	4769	571	−6.3(5)	−17.1(10)	8.52(10)	8.78(7)	−0.16	−0.11	1.8	−1.7

The indicated uncertainties are valid for the last digits.
SIMS boron isotope data are given relative to NIST SRM 951 and are referenced to M93-TB-FC-1.

samples of *O. universa* whose ultimate chambers were completely build in a controlled culture medium (Sanyal et al., 1995, 2001).

We applied the *in situ* B isotope measurement technique developed on our carbonate reference material and described above on 2 specimens of *O. universa*. The planktic foraminifers were collected by scuba divers and maintained in culture analogous to published experiments of *Globigerinoides sacculifer* by Sanyal et al. (2001). The aim of the cultures was to establish an empirical relationship between pH and the boron isotope compositions. The principal seawater chemistry is given in Table 5 while the details of the experiment i.e. collection and culturing are described in Sanyal et al. (2001). Essentially, the seawater was artificially enriched to 10 times boron with a known δ^{11}B and the pH was adjusted to a target value of ca. 7.6, 8.2 or 8.6. The final culture water δ^{11}B and pH for the two experiments BS10 and BS23 were −6.9±0.6‰ and 8.19±0.05 and −6.3±0.5‰ and 8.67±0.05, respectively. The boron isotope composition of the two specimens from experiment BS10 and BS23 is −22.9±0.7‰ (1σ$_{mean}$, *n*=7) and −17.1±1.0‰ (1σ$_{mean}$, *n*=6), respectively (Table 5) and based on multiple single spot analysis along the spherical chamber. Specimens maintained at lower pH as well as those cultured at seawater boron concentration, produced thin spherical chambers that did not allow for sufficient δ^{11}B analyses to be included in the isotope compilation.

To compare the measured δ^{11}B values with the given pH conditions of the modified seawater, the foraminiferal δ^{11}B values were converted to pH by

$$\text{pH} = pK_B - \log((\delta^{11}B_{seawater} - \delta^{11}B_{sample} - a)/(\delta^{11}B_{seawater} - {}^{11-10}K_B *$$
$$(\delta^{11}B_{sample} + a) - 1000*({}^{11-10}K_B - 1)))$$

where the equilibrium constant pK$_B$ is 8.574 for the experimental temperature of 27 °C (Lewis and Wallace, 1998), *a* is the species specific vital effect and $^{11-10}K_B$ the boron isotope equilibrium constant of either 1.0272±0.0006 (Klochko et al., 2006) or 1.0194 (Kakihana et al., 1977). Note that this equation is an approximation and accurately applicable only in natural seawater conditions. The use of δ^{11}B values distinctive to normal marine values e.g. negative δ^{11}B values can result in inaccurate pH calculations. Hence, we converted our δ^{11}B data relative to modern seawater values prior to their translation into pH values.

Until recently, most δ^{11}B-based pH reconstructions applied the theoretical $^{11-10}K_B$=1.0194 (25 °C) of Kakihana et al. (1977), yet foraminiferal culture experiments and diffusion-reaction models calculating the micro-environmental pH of the foraminifer suggested that the calculated value of the thermodynamic fractionation must
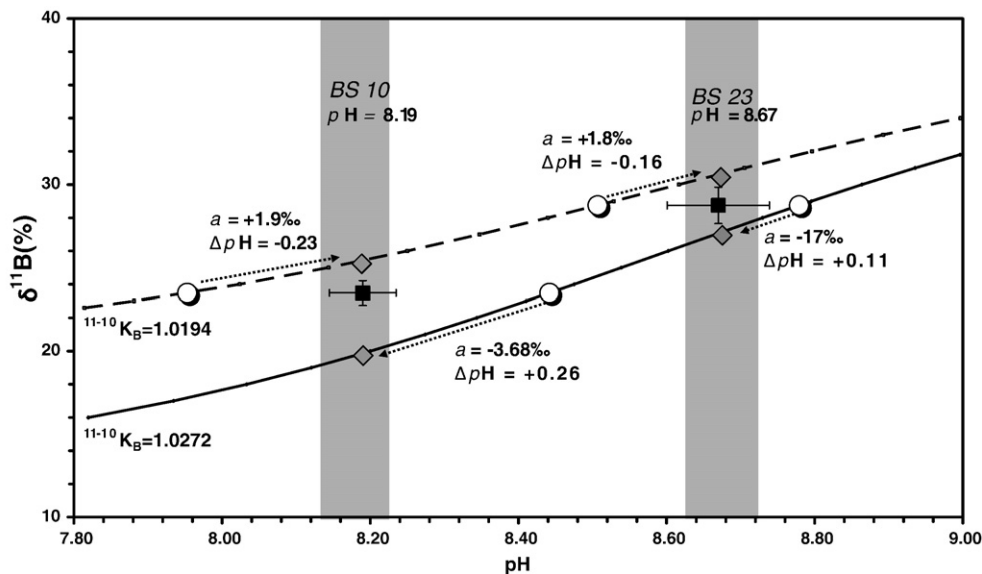

Fig. 2. Boron isotope composition of cultured *O. universa* and seawater pH relationship using the theoretical $^{11-10}K_B$=1.0194 from Kakihana et al. (1977) and empirical $^{11-10}K_B$=1.0272 from Klochko et al. (2006). Black squares indicate the measured B isotope composition of the cultured O. universa for the given ambient seawater pH (grey are marks the uncertainty on the pH). The open circles represent the calculated pH value from the measured boron isotope composition of the foraminifers. The grey diamonds identify the expected boron isotopic composition for the given pH. ΔpH denotes the offset in the pH and *a* gives the calculated vital effect. Note that the measured B isotope data for the culture seawater and O. universa are converted relative to modern seawater (δ^{11}B$_{Seawater}$ is taken to be 39.5‰) to allow for accurate pH calculations (see text).

have been larger than 20‰ (Zeebe et al., 2003). In a recent evaluation of the $\delta^{11}B$–pH proxy, Pagani et al. (2005) estimated a $^{11-10}K_B$ from inorganic carbonate precipitation experiments (Sanyal et al., 2000) of 1.0267 (22 °C). This higher value has since then been supported in an experimental study of B-isotope fractionation in seawater by Klochko et al. (2006), presenting an empirical $^{11-10}K_B$ of 1.0272±0.0006 ($2\sigma_{mean}$; 25 °C). Here, we discuss our B isotope data using both the recently published (Klochko et al., 2006) as well as the traditionally in palaeo-reconstructions used fractionation factor (Kakihana et al., 1977).

In a direct $\delta^{11}B$ to pH conversion, *O. universa* (BS10) cultured at pH 8.19 has a $\delta^{11}B$ value of −22.9‰ resulting in a pH of 8.44±0.5 using $^{11-10}K_B$=1.0272 and a pH of 7.99±0.12 while using $^{11-10}K_B$=1.0194. Similarly, at pH 8.67 (BS23) the cultured *O. universa* has a $\delta^{11}B$ of −17.1‰ which implies a pH of 8.78±0.7 using $^{11-10}K_B$=1.0272 and 8.52±0.1 using $^{11-10}K_B$=1.0194 (Fig. 2, Table 5). Hence, by applying the $\delta^{11}B_{Borate}$–pH relationship of Kakihana et al. (1977) to our $\delta^{11}B$ results on *O. universa*, the recorded pH values are 0.16 (BS23) and 0.23 (BS10) pH units lower than the artificial seawater. This translates to lower $\delta^{11}B$ values of 1.8 respectively 1.9‰. The general negative offset between the given and calculated pH values using the fractionation factor from Kakihana et al. (1977) is consistent with results from Sanyal et al. (1996) and Zeebe et al. (2003). In contrast, applying the theoretical $\delta^{11}B$–pH curve of Klochko et al. (2006), there is an offset to higher pH values of 1.1 to 2.6 units, respectively $\delta^{11}B$ of 1.7 and 3.6‰. Consequently, this results in contrasting "vital effects" of $a \approx +1.9$ for $^{11-10}K_B$=1.0194 and $a \approx −2.6$ for $^{11-10}K_B$=1.0272 (see Fig. 2 and Table 5).

While the boron isotope composition of foraminifers has been established as an empirical palaeo-pH proxy (e.g. Spivack et al., 1993; Sanyal et al., 1995; Palmer et al., 1998; Pearson and Palmer, 2000; Hönisch and Hemming, 2004; Zeebe et al., 2008) it was questioned whether foraminifers record the pH of the seawater or the pH of the microenvironment (see Zeebe et al., 2003 for discussion). Vital effects such as symbiont activity, respiration and calcification alter the pH of the ambient water in which the foraminifer lives, forming a microenvironment with different pH around the test (Jørgensen et al., 1985; Rink et al., 1998; Wolf-Gladrow et al., 1999; Zeebe et al., 2003). Respiration, i.e. production of CO_2, results in lower pH, while photosynthesis, i.e. consumption of CO_2 and/or HCO_3^- creates more alkaline conditions. In case of *O. universa*, pH microsensor studies (Rink et al., 1998) as well as modelled pH profiles (Wolf-Gladrow et al., 1999) of the foraminiferal microenvironment demonstrated that the pH at the shell surface dropped about 0.4 pH units in darkness, i.e. without photosymbiotic activity and solely with respiration, and increased between 0.25 and up to 0.5 pH units above ambient seawater during symbiont photosynthesis. Assuming a ratio of dark: light calcification in *O. universa* about 1:3 (Lea et al., 1995), the pH of the microenvironment should be between 0.1 and 0.37 pH units higher than the seawater. An experimental study by Zeebe et al. (2001) also predicted that the $\delta^{11}B$ of *O. universa* should be about 1.6‰ (Zeebe et al., 2003) and up to 3.7‰ higher than the $\delta^{11}B$ of inorganic calcite depending on the assumed pH profile and photosynthetic rate (Rink et al., 1998, Wolf-Gladrow et al., 1999), as well as the applied fractionation factor. In comparisons, the average $\delta^{11}B$ of the calcite test from *G. sacculifer* should be ~3.2‰ heavier than the $\delta^{11}B$ of the bulk seawater (Zeebe et al., 2003).

In addition, Zeebe et al. (2003) also calculated the effect of the 10-fold boron enrichment to result in smaller pH differences and hence in smaller $\delta^{11}B$ offsets in the foraminiferal carbonate compared to specimens grown in normal seawater due to the buffer capacity of the boric acid/borate buffer. Hence, regardless of the chosen pH profile and chemical composition of the seawater, the pH recorded in the calcite test should be always above bulk seawater. Consequently, the relative offset towards lower pH values (~0.2 pH units) and the positive vital effect (~1.9) using the theoretical thermodynamic fractionation factor by Kakihana et al. (1977) are significantly lower

than could be explained by any biological process. This paradox and the challenge it is posing on the traditionally in palaeo-reconstructions used fractionation factor has already been described by Zeebe et al. (2003). In contrast, the positive pH (~0.19 pH units) and negative vital (~−1.9) offset using the fractionation factor by Klochko et al. (2006) fits the theoretical calculations including the ecological considerations very well. A similar observation has been made by Foster (2008) on a core top calibration of planktic and benthic foraminiferal species. By using the $\delta^{11}B_{Borate}$–pH relationship of Klochko et al. (2006), the study revealed a strong agreement between the measured boron isotopic composition of the foraminifers, the $\delta^{11}B_{Borate}$ of the seawater and the vital effect. However, it should be noted that the empirical calibrations that have been produced to date using the theoretical thermodynamic fractionation factor by Kakihana et al. (1977), remain equally valid as long as they are applied to pH calculations restricted to small overall variations and pH values similar those of the modern ocean.

4. Conclusions

We determined boron concentrations and isotope data for a suite of biogenic and inorganic carbonates, which are currently distributed between several laboratories to increase the amount of B isotope analysis and to provide a new set of microanalytical and bulk analytical calibration materials. We also measured boron isotope ratio for the NIST standard reference materials SRM 610 and SRM 612. These glasses are commonly used as microanalytical calibration and reference materials for various *in situ* methods. The B isotope data for all carbonates samples determined by MC-ICP-MS and TIMS agree within analytical uncertainty. This is reassuring given the very different controlling parameters of the two techniques. The bulk analytical and SIMS data agree to within 1.3‰, independent of the boron concentration and carbonate matrix. The limiting factor on the uncertainty is generally the internal heterogeneity of the carbonate samples rather than the analytical precision. This confirms that the B isotope data on the carbonate samples, obtained by SIMS, are sufficiently accurate to be used for geochemical applications. It also demonstrates that this technique is a useful tool for the *in situ* analysis of B isotope ratios in carbonate materials to distinguish between the biological and environmental control on the B isotope composition in biogenic carbonates and to improve our current understanding of biological influences on the boron isotope fractionation. In addition, the high-spatial resolution capacity would allow analysing the B isotope composition of carbonate material e.g. single foraminifers or partially dissolved and recrystallised material from past ocean acidification events previously inaccessible using bulk analytical techniques. The good agreement between the $\delta^{11}B_{Borate}$ of the seawater and the proposed vital effect of *O. universa* and other planktic and benthic foraminiferal species clearly favours and supports the application of the recent experimental determination of $^{11-10}K_B$=1.0272 in future studies of boron isotopes as a pH proxy.

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