



# Simultaneous determination of $\delta^{11}\text{B}$ and B/Ca ratio in marine biogenic carbonates at nanogram level



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## ABSTRACT

In this study we introduce a new in situ technique which allows the determination of the boron isotopic composition and B/Ca ratios simultaneously at the nanogram level using a combination of optical emission spectroscopy and multiple ion counting MC ICP-MS with laser ablation. This technique offers a new application in the paleo-field of oceanography and climatology since small samples like e.g. single foraminiferal shells can be analyzed. The simultaneous determination of the boron isotopic composition and B/Ca ratios provides two independent proxies which allow the reconstruction of the full carbonate system. To test the new technique we performed measurements on the cultured, benthic foraminifer *Amphistegina lessonii*. Our results yielded an average boron isotopic composition  $\delta^{11}\text{B} = 18.0 \pm 0.83\text{‰}$  (SD) with an average internal precision of 0.52‰ (RSE). The boron concentration was  $53 \pm 7 \mu\text{g/g}$  (SD). These results agree with the range reported in the literature. The reconstructed mean pH value is in excellent agreement with the measured pH of the seawater in which the foraminifers grew.

The analysis of a foraminifer consumed approximately 1200 ng calcium carbonate containing ca. 0.06 ng boron. Compared to bulk analytical methods, this new technique requires less material and reduces the time for sample preparation.

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## 1. Introduction

Element signatures of biogenic marine calcium carbonates ( $\text{CaCO}_3$ ) are powerful tools to reconstruct the physico-chemical conditions of the environment. The incorporation of boron (B) into biogenic  $\text{CaCO}_3$  such as the skeletons of corals or tests (shells) of foraminifers is of particular interest because its concentration and isotopic composition records information about the marine carbonate system which in turn allows the calculation of atmospheric  $\text{CO}_2$  concentration.

In seawater B mainly exists as boric acid ( $\text{BOH}_3$ ) and borate ( $\text{BOH}_4^-$ ) whose species distribution and isotopic composition is strongly pH dependent (Dickson, 1990). The B isotopic composition of coral and foraminiferal  $\text{CaCO}_3$  provided strong evidence that only borate is incorporated into  $\text{CaCO}_3$  (Hemming and Hanson, 1992). Hence, the B isotopic composition of  $\text{CaCO}_3$  reflects the B isotopic composition of borate in seawater. Based on this relationship, the B isotopic composition of several foraminiferal species was used to reconstruct past seawater pH (Sanyal et al, 1995; Hönisch and Hemming, 2005; Yu et al., 2010). The second B based proxy is rooted in the observed linearity between B/Ca

ratios determined in foraminifers and  $\text{CO}_3^{2-}$  concentration in seawater (Yu and Elderfield, 2007; Yu et al., 2010; Brown et al., 2011).

Several analytical techniques are used to measure the B isotopic composition in marine carbonates:

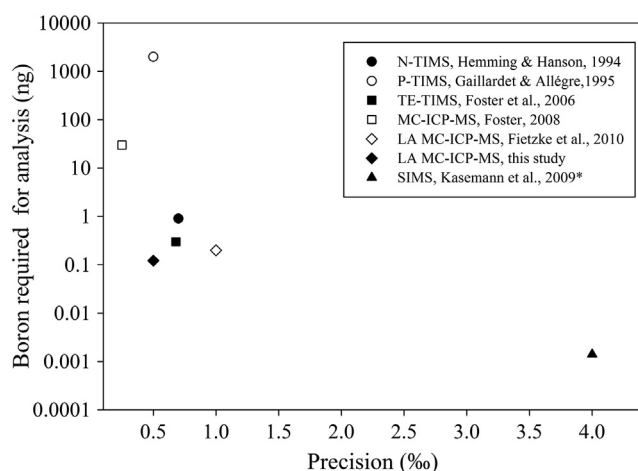
- 1) thermal ionization mass spectrometry (TIMS) (N-TIMS (e.g. Hemming and Hanson, 1994; Sanyal et al., 1996), P-TIMS (e.g. Gaillardet and Allègre, 1995), TE-TIMS (Foster et al., 2006))
- 2) multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS (e.g. Lécuyer et al., 2002; Foster, 2008; Louvat et al., 2010))
- 3) secondary ion mass spectrometry (SIMS (e.g. Kasemann et al., 2009; Rollion-Bard and Erez, 2010))
- 4) laser ablation (LA) MC-ICP-MS (Fietzke et al., 2010).

For TIMS and MC-ICP-MS samples have to be dissolved. For the latter an additional matrix separation of B is needed. SIMS requires a flat sample surface whereas for LA MC-ICP-MS no sample preparation is required.

While TIMS and MC-ICP-MS represent bulk analytical techniques, SIMS and LA MC-ICP-MS are in situ techniques which allow determining the isotope ratios and elemental concentrations (but not simultaneously) with high spatial resolution. This needs far less material than bulk analytical techniques which allows performing measurements on

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**Fig. 1.** Precision and amount of required boron for various analytical techniques for boron isotope analysis in carbonate matrices (corals and foraminifers (TE-TIMS)). \*Required B amount was calculated assuming a sputter rate of  $0.0066 \mu\text{m}^3/\text{nAs}$ .

e.g. single specimens of foraminifers. Furthermore, it is possible to resolve the spatial variation in the B isotopic composition and B concentration observed in most biogenic carbonates on the  $\mu\text{m}$  scale. This can help to develop a process based understanding of B incorporation into foraminifer  $\text{CaCO}_3$ , a process which is still not fully understood but fundamental for the use of B as a paleo-proxy. However, due to the inhomogeneity of B distribution the question arises how many measurements are required to reach a precision comparable to that of bulk analytical techniques.

For a pH reconstruction with a resolution of  $\sim 0.1$  pH unit using boron isotopes a precision better than 1‰ (2 SD) is required (Foster et al., 2006). A comparison of the precision of a variety of analytical techniques for B isotope determination of carbonate matrices is shown in Fig. 1. The highest amount of total B is needed for P-TIMS (2000 ng) to achieve a precision (2 SD) of 0.5%. Far less material (30 ng B) is consumed using MC-ICP-MS giving the highest precision of 0.25%. For the N-TIMS and TE-TIMS approach about three times less B is required resulting in a precision of  $\sim 0.7\%$ . Techniques with the lowest demand of B are LA MC-ICP-MS (0.2; 0.03 ng) and SIMS (0.0014 ng). While the latter suffers from the worst precision (4%) LA MC-ICP-MS achieves a precision ranging between 0.5 and 1%. Using LA MC-ICP-MS in combination with ion counters instead of faraday cups, the required B amount can be reduced by almost a factor of ten.

## 2. Material and methods

### 2.1. Simultaneous determination of B isotopic composition and B concentration

The measured B intensity of a reference material corresponds to its known B concentration. Based on this relationship the unknown B concentration of a sample can be calculated. However, in our case measurements of the reference material (SRMNIST 610) and samples have not been performed at the same laser repetition rate (see Section 2.5) hence their B ratio is not proportional. The correction for different laser repetition rates e.g. for the amount of material ablated and transported to the ICP can be realized using an optical spectrometer by the collection of Ca counts on the two high intensity first order emission lines of Ca II at 393.48 and 396.86 nm. This is required as B isotope measurements are performed in static mode of the mass spectrometer. Peak jumping would result in significant loss of time resolution. The detection of Ca cps of SRMNIST 610 and samples (whose Ca concentrations are known: [Ca] of SRMNIST 610 is 8.45%, [Ca] of  $\text{CaCO}_3$  is 40%) allows to correct for different laser repetition rates (Longerich et al., 1996). For simultaneous determination of B isotopic composition and B concentration a Fiber Optics Spectrometer (Maya2000 Pro, Ocean Optics) was connected to the torch of a Thermo Finnigan Neptune multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Leibniz University of Hannover. Laser ablation on reference material and samples was performed by an in-house build UV-femtosecond laser ablation system based on a regenerative one box femtosecond laser (Solstice Newport/Spectra Physics).

### 2.2. Optical emission analysis

Ocean Optics Maya2000 Pro is a high-sensitivity fiber optical spectrometer. It exhibits a measuring range of 250 to 460 nm with a resolution of 0.11 nm covering the first order emission lines of Mg, Ca, Sr and Ba. It is equipped with a back-thinned 2D FFT-CCD detector, and a grating with a

Plasma source instruments suffer from instrumental discrimination caused by the space charge effect typically being in the range of several %. In contrast, instrumental bias induced by TIMS is a few ‰. Although MC-ICP-MS shows a higher instrumental mass bias compared to NTIMS the results obtained by Aggarwal et al. (2004) indicate that mass bias has no significant impact on  $\delta^{11}\text{B}$  accuracy and precision. Since boron has only two natural isotopes, it is impossible to perform isotope labeling experiments with known isotopic signatures to assess the amount of fractionation during sample preparation and TIMS measurements. To correct for mass bias during TIMS measurements, sample runs are only accepted if the fractionation is less than 1‰ over an acquisition time of at least 20 min (Hönisch and Hemming, 2004). The temporal drift and the machine induced fractionation in case of MC-ICP-MS can be corrected using the sample standard bracketing procedure.

Several laser ablation studies on B isotopes have been carried out but these studies focused on samples with a silica matrix (le Roux et al., 2004; Tiepolo et al., 2006; Hou et al., 2010; Mikova et al., 2014). The limitation of B measurements on carbonate samples using laser ablation is the absence of a solid matrix matched standard. However, Fietzke et al. (2010) recently carried out B isotopic measurements using LA MC-ICP-MS on silicate glass standards as reference material and showed that no matrix dependent offsets between silicate and carbonate matrices exist suggesting that silicate glass standards may serve as adequate reference material.

Several studies determined  $\delta^{11}\text{B}$  and B/Ca on the same set of samples (Wara et al., 2003; Ni et al., 2007; Yu et al., 2010). For these studies the sample requirement was large since the B isotope signature and B concentration were determined separately.

In this study we present a new analytical approach which allows the simultaneous determination of the B isotopic composition and B/Ca ratios in biogenic marine carbonates using LA MC-ICP-MS in combination with ICP-OES and a silicate glass standard. The new approach offers the possibility to obtain two independent parameters of the carbonate system from the same sample which allows to fully constrain the carbonate chemistry. Since biogenic carbonates are known to be inhomogeneous on the  $\mu\text{m}$  scale it is of great importance to be able to directly relate the B isotopic composition obtained at one position with the B concentration at the same position.

This technique can be applied on single foraminiferal tests and no sample preparation is required. We determined the  $\delta^{11}\text{B}$  and B/Ca ratios of cultured, benthic foraminifers (*Amphistegina lessonii*) and a natural grown coral sample (*Porites lutea*).

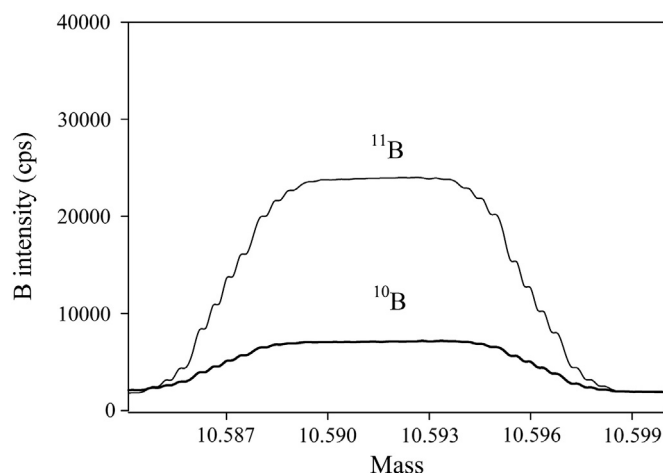


Fig. 2. Peak shape of  $^{10}\text{B}$  and  $^{11}\text{B}$  in low resolution mode. No interferences with  $\text{Ne}^{2+}$  and  $\text{Ar}^{4+}$  were observed.

groove density of 1200 lines/mm. More technical information about Maya2000 Pro can be found on <http://www.oceanoptics.com/products/maya.asp>. The optical fiber used is 2 m long (attenuation of the photon flux is length dependent) connecting the spectrometer through a fiber optics coupler (including an adjustable focusing lens) at the end of the plasma torch of the MC-ICP-MS. Ca II ion lines were measured at a wavelength of 393.48 nm and 396.86 nm. At these wavelengths the Ca spectra shows no detectable interferences for the matrices used. In order to keep the count rate in the linear range for the detector the integration time was adjusted accordingly. The acquisition parameters of the foraminifer's measurement session were set to acquire 220 cycles per analysis with an integration time of 1 s for each cycle, the integration time of the coral measurement session was 0.25 s for each cycle acquiring 880 cycles. Because of the stable background (BG) signal detected for the first 40 cycles BG correction was done by subtracting its intensity from the intensity of the reference material and samples. Off peak zeros did not result in improvements of the acquired data.

Average count rates of B and Ca of the samples and the reference material are given in Table 1 together with laser efficiencies.

### 2.3. Pre-tests

In order to examine whether the coupling between the Thermo Finnigan Neptune MC-ICP-MS and Maya2000 Pro represents a reliable method of simultaneous determination of B isotopic composition and B concentration two pre-tests were conducted.

As a first step it was verified whether the B concentration in several reference materials with a variable B concentration shows a linearity if measured simultaneously using Maya2000 Pro and a conventional HR-ICP-MS. For that purpose Maya2000 Pro was connected with an optic fiber to the coupling lens at the end of the plasma torch of a ThermoScientific Element XR which has the same plasma source as the Thermo Finnigan Neptune MC-ICP-MS. Simultaneous collection of B counts (Element XR) and Ca counts (Maya2000 Pro) was performed on a variety of reference materials. The Ca data obtained from Maya2000 Pro was used to calculate the B concentration of these materials according to the method described in Section 2.1.

Next, we tested the possibility of simultaneous acquisition of B isotopes and Ca intensities. For that purpose Maya2000 Pro was connected to the torch of a Thermo Finnigan Neptune MC-ICP-MS. We chose SRMNIST 610 ([B] 351  $\mu\text{g/g}$ , [Ca] 8.45%) and SRMNIST 612 ([B] 37  $\mu\text{g/g}$ , [Ca] 8.52%) as analytes. Matching of B intensities between the analytes was achieved by changing the laser repetition rate. The Ca intensity obtained from Maya2000 Pro was used in order to correct for different repetition rates, allowing to calculate the B concentration of SRMNIST 612 as described in Section 2.1.

### 2.4. Laser ablation

The in-house built laser ablation system (Solstice Newport/Spectra Physics) is based on a 100 femtosecond Ti-sapphire regenerative amplifier system operating at a fundamental wavelength of 777 nm in the infrared spectrum. Subsequent harmonic generations produce the wavelengths 389 nm in the second, 259 nm in the third and 194 nm in the fourth harmonic. The pulse energies measured with a pyroelectric sensor (Molelectron, USA) are 3.2 mJ/pulse at 777 nm, 0.7 mJ/pulse at 259 nm, and 0.085 mJ/pulse at 194 nm. After the fourth harmonic generation stage the 194 nm beam is steered by eight dichroic mirrors into an 8 $\times$  objective (NewWave-Research, USA) and focussed onto the sample. Spot size was set to 50  $\mu\text{m}$  for standard and samples. Within this spot an energy density of 2 J/cm<sup>2</sup> is maintained. Information about the sample introduction system and ablation chamber is given in Horn et al. (2006). The only change is that the ablation cell is made from Plexiglas.

Table 1

Average intensities for Ca and B isotopes counts yielded at different laser ablation rates. The background counts are subtracted.

	Ca (cps)	$^{11}\text{B}$ (cps)	$^{10}\text{B}$ (cps)	Laser efficiency (Hz)
Benthic foraminifers	24,000	313,000	68,500	20
NIST 610	840	306,000	68,000	8
Coral	41,600	555,000	120,000	20
NIST 610	1750	590,000	130,000	10

**Table 2**  
Instrumental operating conditions for the Neptune MC-ICP-MS and LA.

	Benthic foraminifers	Coral
Cool gas [l/min]:	14.6	14.6
Aux gas [l/min]:	1.2	0.6
Sample gas [l/min]:	1.3	1.5
Add Gas [l/min]:	0.3	0.4
Operation power [W]:	1269	1269
Guard electrode:	On	Off
Wavelength [nm]:	194	194
Pulse energy [J/cm <sup>2</sup> ]:	2	2
Pulse width [fs]:	~200	~200
Spot size [μm]:	50	50

## 2.5. MC-ICP-MS

All measurements are carried out in low mass resolution ( $\Delta m/m = 350$ ). Compact discrete dynode multipliers (CDD, Thermo) are attached to faraday cups at the low site on L4 and the high site on H4. The low resolution mode is sufficient enough to resolve potential interferences from doubly charged ions due to the intrinsic high resolution in the low mass region. Possible interferences are the clusters of  $^{40}\text{Ar}^{4+}$  or  $^{20}\text{Ne}^{2+}$  (le Roux et al., 2004) which are well resolved to the background level. Typically obtained peak shapes are shown in Fig. 2 for the background signals for both B isotopes. Working with ion counters necessitates to determine the detector dead time, especially for isotope ratios with large isotope abundance differences. The dead time corrections have been performed by measuring the  $^{238}\text{U}/^{235}\text{U}$  ratio using SRM 981 in a multidynamic measuring sequence. Subsequently, the dead time has been checked prior to every analytical session by analyzing SRMNIST 610 using different repetition rates of the laser resulting in a counting range between 300,000 and 1,000,000 cps. Prior to each analytical session the instrument was tuned for optimal peak shape. The standard operating parameters are summarized in Table 2. All measurements were performed at plateau voltage of the CDDs which was checked prior to every analytical session. Before the beginning of sample analysis measurements of SRMNIST 610 were continued until instrumental drift due to warm-up was less than 300 ppm over a bracketing sequence duration of 12 min. Boron signal intensities of SRMNIST 610 and samples were matched within 10% in signal intensity by adapting the laser repetition rate. For analysis we adopt the standard sample bracketing procedure using SRMNIST 610 as reference material containing 351 μg/g B and 8.45% Ca. The application of this external calibration technique is required for any stable isotope system and allows the correction of the instrumental mass discrimination and its temporal drift by using a reference material of known isotopic composition prior and after the analysis of the samples. The acquisition parameters in static mode for analysis of SRMNIST 610 and samples were set to acquire 200 cycles of 1 s integrations each. During the first 40 cycles the BG signal was acquired whereas the remaining cycles represent the sum of the BG and reference material, or BG and sample signals. A complete measurement consisting of 200 cycles of a single reference material/sample takes 4 min before the next sample can be introduced. Data evaluation was performed using a modified spreadsheet macro 'LamTool' initially created for different radiogenic isotope system by Jan Košler. We modified the macro for B isotope analysis. The B isotopic composition is reported using the delta notation:

$$\delta^{11}\text{B}_{\text{sample}}(\text{‰}) = \left[ \frac{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{sample}}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{NIST 610}}} - 1 \right] \times 1000. \quad (1)$$

The  $^{11/10}\text{B}$  ratio of NIST 610 represents a mean value calculated from the NIST 610 measurements performed before and after the sample.

## 2.6. MC-ICP-MS – background correction

The BG is a signal noise whose isotopic B ratio (~2.4) differs strongly from that of the reference material and samples (~4). Therefore a BG correction is essential, especially when dealing with constantly decaying background signals. In order to perform a BG correction the signal of the BG for both isotopes was detected during each measurement in the first 40 cycles by keeping the laser shutter closed and opening for the analysis of the reference material and samples, respectively. Then, the mean value of detected BG intensity was subtracted from the intensity of the reference material/sample for each individual measurement cycle.

## 2.7. Uncertainties for boron isotopes and concentration

The delta notation ( $\delta^{11}\text{B}$ ) representing the B isotopic composition of a sample is not a quantity which can be measured directly but depends on two measured quantities ( $^{11/10}\text{B}$  of SRMNIST 610 and  $^{11/10}\text{B}$  of sample) and their uncertainties (SE). The error of  $\delta^{11}\text{B}$  is therefore calculated by error propagation of the ratio  $\text{SE}/^{11/10}\text{B}$  according to the standard bracketing method. It represents an external and relative error and is expressed as 2 RSE:

$$2 \text{ RSE } \delta^{11}\text{B} (\text{‰}) = \sqrt{\left( \frac{\text{SE}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{NIST}-1}} \right)^2 + \left( \frac{\text{SE}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{sample}}} \right)^2 + \left( \frac{\text{SE}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{NIST}+1}} \right)^2} \times 1000 \times 2 \quad (2)$$

where NIST – 1 and NIST + 1 represent measurements performed before and after the sample, respectively.

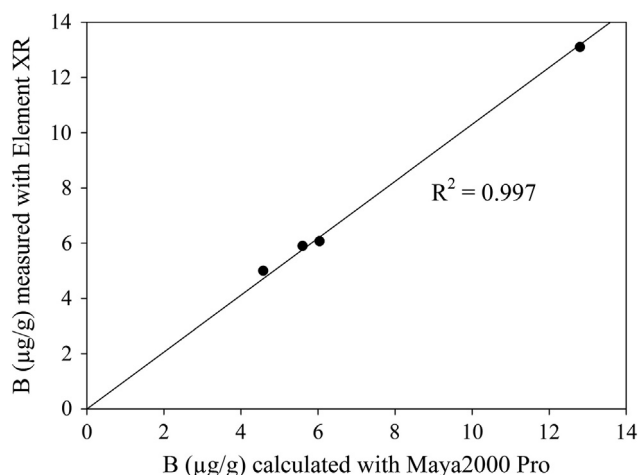


Fig. 3. Boron concentration of several reference materials measured by Element XR and calculated based on the emission line of Ca II at 393.48 nm measured by Maya2000 Pro.

For the determination of the relative error of the B concentration and B/Ca we considered the B and Ca concentrations of SRM NIST 610 and their uncertainties known from literature (lit) and the intensities of B and Ca and their uncertainties measured (m) in this study where B cps were normalized to Ca cps:

$$\text{RSD (\%)} = \sqrt{\frac{\left(\frac{\text{SD B conc}_{\text{NIST}}}{\text{B conc}_{\text{NIST}}}\right)_{\text{lit}}^2 + \left(\frac{\text{SD Ca conc}_{\text{NIST}}}{\text{Ca conc}_{\text{NIST}}}\right)_{\text{lit}}^2 + \left(\frac{\text{SD B cps}_{\text{NIST}}}{\text{B cps}_{\text{NIST}}}\right)_{\text{m}}^2 + \left(\frac{\text{SD Ca cps}_{\text{NIST}}}{\text{Ca cps}_{\text{NIST}}}\right)_{\text{m}}^2}{\left(\frac{\text{SD B cps}_{\text{sample}}}{\text{B cps}_{\text{sample}}}\right)_{\text{m}}^2 + \left(\frac{\text{SD Ca cps}_{\text{sample}}}{\text{Ca cps}_{\text{sample}}}\right)_{\text{m}}^2}} \times 100. \quad (3)$$

The analytical uncertainty and external reproducibility is given best by repeated measurements of a homogenous material such as NIST 610. Delta  $^{11}\text{B}$  values of NIST 610 were calculated by:

$$\delta^{11}\text{B}(\text{‰}) = \left[ \frac{^{11/10}\text{B}_0}{(^{11/10}\text{B}_{-1} + ^{11/10}\text{B}_{+1})/2} - 1 \right] \times 1000 \quad (4)$$

where the measurements of the  $(^{11/10}\text{B})_{-1}$  and  $(^{11/10}\text{B})_{+1}$  ratios of NIST 610 were performed before and after the measurement of  $(^{11/10}\text{B})_0$ , respectively. For the determination of the analytical uncertainty and external reproducibility all measurements of NIST 610 performed between each sample measurement were taken into account.

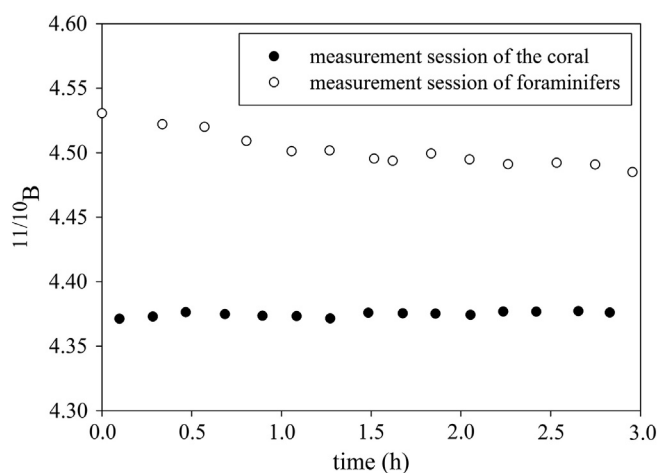
## 2.8. Samples

### 2.8.1. Benthic foraminifers

Live specimens of the benthic symbiont-bearing foraminifer *A. lessonii* were obtained from a coral reef aquarium at the Burgers Zoo (Arnhem, The Netherlands). SCUBA divers collected approximately 0.5 kg of sediment containing different species of foraminifera (Ernst et al., 2011). The sediment was transported to the Alfred Wegener Institute – Helmholtz Centre for Polar and Marine Research (Bremerhaven, Germany) immediately. About 30 specimens of *A. lessonii* were transferred to well plates containing North Sea seawater (NSW) and placed in a temperature controlled room at 25 °C. After two weeks ~40% of the specimens had reproduced asexually, yielding 10–30 juveniles per specimen. Subsequently, juvenile foraminifers were transferred into petri dishes containing NSW (pH 8.08 total scale) and placed in a transparent and gas tight plastic box. Every third day the NSW was replaced by using a freshly opened aliquot from the corresponding batch of NSW. Each time when NSW was replaced foraminifers were fed with concentrated and sterilized algae *Dunaliella salina*. Before feeding algae were centrifuged to minimize dilution of NSW and exposed to 90 °C for 20 min after centrifugation in order to reduce bacterial activity. In order to avoid evaporation of NSW in the petri dishes the air flushing into the plastic box was saturated with water by bubbling it through a fritted wash bottle filled with de-ionized water. A day/night cycle of 12 h light/dark was applied. Light intensity was 100–150  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ . Foraminifers grew for two months. Afterwards specimens were harvested,

Table 3  
B concentrations ( $\mu\text{g/g}$ ) for several reference materials (as listed in GeoReM) and measurements performed using Element XR and Maya2000 Pro.

Reference material	GeoReM	Element XR (HR ICP-MS)	$\pm$	Maya2000 Pro	$\pm$	n (this study)
T1-G (diorite glass)	2.24–5.05	6.07	0.38	6.04	0.31	10
StHs6/80 (andesite glass)	10.6–14.6	13.1	0.62	12.8	0.58	10
Atho-G (rhyolite glass)	5–12	5.9	–	5.6	–	1
BHVO-2G (basalt)	4.6–6.84	5	–	4.58	–	1



**Fig. 4.** Isotope ratio  $^{11/10}\text{B}$  of SRM NIST 610 representing the instrumental drift during the foraminifer and coral sessions illustrating that the standard sample bracketing is adequately correcting for instrumental drift.

bleached in diluted NaOCl (1:3, active chlorine 4.6%) for 6 h, rinsed four times using de-ionized water, and dried for 12 h at 50 °C. For laser ablation analysis specimens were mounted on a glass slide using double sided sticky tape. We performed raster measurements with a spot size of 50  $\mu\text{m}$  and 20 Hz on the spiral side of the shell. The size of the raster varied depending on the size of the foraminifer. However, the ablated area always covered parts of several chambers and the “knob”, a massive calcium carbonate part of the test with less pores. Each foraminifer had been measured once. Reference material measurements were performed in raster mode (100  $\mu\text{m} \times 100 \mu\text{m}$ ) with a spot size of 50  $\mu\text{m}$  at 10 Hz.

### 2.8.2. Coral sample

The coral sample (*P. lutea*) was collected in the Andaman Sea (Indian Ocean) near the island Miang from a water depth of 15 m in December 2010. The pH of the seawater was 8.01 (total scale). The coral belonged to a previous project performed at the Geomar in Kiel, and was embedded in Araldite, and cut with a diamond blade using a Buehler IsoMet 1000 precision saw. It should be noted that for the B analysis performed in this study embedding would not have been necessary. We performed raster measurements with a spot size of 50  $\mu\text{m}$  at 20 Hz and different raster sizes (raster size was adapted to measure solid structures showing no pores). One raster was ablated three to four times. Altogether five rasters were measured. Measurements of the reference material were performed in raster mode (100  $\mu\text{m} \times 100 \mu\text{m}$ ) with a spot size of 50  $\mu\text{m}$  at 10 Hz.

## 3. Results and discussion

### 3.1. Results of pre-tests

Table 3 shows the B concentration of the measured reference materials obtained from the Element XR, Maya2000 Pro, and data from the Geological and Environmental Reference Material (GeoReM) website. Boron data from GeoReM represents a concentration range

based on B concentration values determined from several publications. For more information about these publications the reader is referred to the GeoReM website. The B results of our analysis match the concentration range reported in GeoReM. In addition, the B concentration obtained from Maya2000 Pro and Element XR are linearly related (Fig. 3). This confirms our approach of using the optical emission signal for Ca analysis allowing the calculation of B concentration.

**Table 4**

Results of the B analysis of the foraminifers. Details on errors see Section 2.7.

Single measurements of foraminifers							
$\delta^{11}\text{B}$ (‰)	2 RSE $\delta^{11}\text{B}$ (‰)	RSE $^{11/10}\text{B}$ (‰)	B ( $\mu\text{g/g}$ )	RSD B (%)	B/Ca (mmol/mol)	pH reconstructed	
19.33	1.01	0.28	32	5.52	0.370	8.14	
17.11	1.41	0.53	52	4.39	0.593	7.93	
18.83	1.51	0.59	59	3.09	0.666	8.10	
19.46	1.41	0.52	60	4.06	0.677	8.15	
18.47	1.36	0.46	48	3.43	0.546	8.07	
17.79	1.49	0.52	61	3.14	0.690	8.00	
17.07	1.36	0.46	53	3.21	0.600	7.93	
16.98	1.47	0.56	55	4.03	0.621	7.92	
18.56	1.55	0.58	62	3.21	0.709	8.08	
17.36	1.70	0.64	54	4.31	0.611	7.96	
18.10	1.60	0.55	54	3.68	0.648	8.03	
17.28	1.21	0.31	51	3.35	0.470	7.95	
17.67	1.25	0.41	49	4.15	0.440	7.99	
Mean values							
$\delta^{11}\text{B}$ (‰)	SD <sup>a</sup> $\delta^{11}\text{B}$ (‰)	B ( $\mu\text{g/g}$ )	SD <sup>a</sup> B ( $\mu\text{g/g}$ )	B/Ca (mmol/mol)	pH reconstructed	SD <sup>a</sup> pH reconstructed	pH seawater measured
18.01	0.83	53	7	0.588	8.02	0.08	8.08 $\pm$ 0.05

<sup>a</sup> SD is calculated using single values.

**Table 5**  
B analysis of the coral. Details on errors see Section 2.7.

Single measurements of the coral						
$\delta^{11}\text{B}$ (‰)	2 RSE $\delta^{11}\text{B}$ (‰)	RSE $^{11}/^{10}\text{B}$ (‰)	B ( $\mu\text{g/g}$ )	RSD B (%)	B/Ca (mmol/mol)	
21.32	0.51	0.32	60	3.73	0.55	
21.64	0.45	0.33	61	3.62	0.56	
21.29	0.48	0.23	62	3.35	0.57	
21.67	0.45	0.27	65	2.89	0.60	
21.83	0.49	0.33	65	2.94	0.60	
20.81	0.50	0.31	60	3.22	0.56	
20.74	0.48	0.27	57	2.93	0.53	
20.36	0.48	0.36	55	3.12	0.51	
21.72	0.46	0.24	62	2.63	0.58	
21.92	0.50	0.29	65	3.04	0.60	
20.19	0.46	0.35	62	3.11	0.57	
20.23	0.44	0.28	60	3.01	0.55	
20.13	0.47	0.28	59	2.85	0.55	
Mean values						
$\delta^{11}\text{B}$ (‰)	SD <sup>a</sup> $\delta^{11}\text{B}$ (‰)	B ( $\mu\text{g/g}$ )	SD <sup>a</sup> B ( $\mu\text{g/g}$ )	B/Ca (mmol/mol)	SD <sup>a</sup> B/Ca (mmol/mol)	
21.07	0.65	61	3	0.564	0.026	

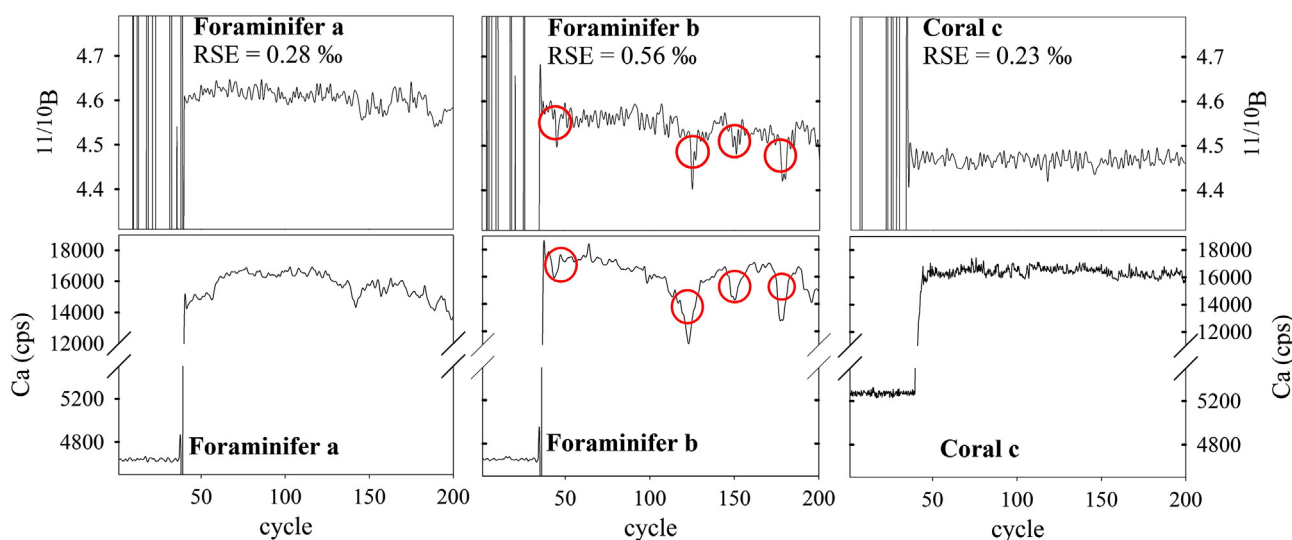
<sup>a</sup> SD calculated using single values.

The B isotopic composition and B concentration of SRMNIST 612 using SRMNIST 610 as reference material is  $-1.46 \pm 0.35\%$  (SD) and  $39 \pm 0.7 \mu\text{g/g}$  (SD). To our knowledge, SRMNIST 610 and SRMNIST 612 have never been measured against each other so far. However, several publications report the B isotopic composition of SRMNIST 610 and SRMNIST 612 measured against SRM 951 as reference material, respectively. The B isotopic composition of SRMNIST 610 and SRMNIST 612 using SRM 951 as reference material shows a range from  $-1.31$  to  $-0.16\%$  for NIST 610 and from  $-1.07$  to  $-0.29\%$  for NIST 612 (Kasemann et al., 2001; le Roux et al., 2004; Fietzke et al., 2010). The comparison between SRMNIST 610 and SRMNIST 612 shows that, within errors, both standards are isotopically equal. The B isotopic composition of the two standards measured in this study lies, within errors, within the range reported in literature. The B concentration of SRMNIST 612 reported in literature ranges from 34 to 39  $\mu\text{g/g}$  (Tiepolo et al., 2005; Jacob, 2006; Liu et al., 2008; Hu et al., 2009; Deschamps et al., 2010; Lazarov et al., 2012). This result is in agreement with the B concentration of SRMNIST 612 determined in this study. Therefore, the coupling between the Thermo Finnigan Neptune MC-ICP-MS and

Maya2000 Pro represents a reliable opportunity for simultaneous determination of B isotopic composition and B concentration.

### 3.2. SRMNIST 610 – accuracy, precision, and reproducibility

The analysis of the foraminifers and the coral was performed on two different days. The mean internal precision (RSE) of SRMNIST 610 for the foraminifer session was 0.33‰. For the coral session we obtained a better RSE of 0.24‰. The difference in RSE might be caused by the heavily ablated surface of SRMNIST 610 due to previous measurements. After identification of this problem, the surface of SRMNIST 610 was polished prior to the analysis of the coral resulting in a lower RSE by almost 0.1‰ during the coral session. A mean RSE of 0.24‰ represents a sufficient homogeneity of B isotopes distribution and makes SRMNIST 610 a suitable standard for LA MC ICP-MS. For the foraminifer session an external reproducibility of NIST 610 of  $0.45 \pm 0.74\%$  (2 SD) was achieved. For the coral session we obtained on average  $0.26 \pm 0.44\%$  (2 SD). The  $^{11}/^{10}\text{B}$  ratios of SRMNIST 610 reported during both sessions are shown in Fig. 4. For the foraminifer session we clearly observe an



**Fig. 5.** Graphs showing the ratio  $^{11}/^{10}\text{B}$  (above) and Ca counts (below) of two foraminifers (a + b) and one coral (c). The graph of the foraminifer b shows four holes (marked by circles) in the test as the laser penetrated the chamber wall. Additionally, a zoning in  $^{11}/^{10}\text{B}$  during the measurement can be seen. Both conditions lead to a worse RSE than for foraminifer a.

**Table 6**  
Size, estimated ablated calcite mass, and total B mass of ablated material.

Foraminifer #	Size ( $\mu\text{m}$ )	Calcite mass ablated (ng)	Total B corresponding to ablated mass (ng)
1	490	734	0.0235
2	460	1296	0.0674
3	450	1058	0.0624
4	430	1026	0.0616
5	400	1539	0.0739
6	400	1193	0.0728
7	450	1296	0.0687
8	380	1134	0.0624
9	380	1037	0.0643
10	470	1285	0.0694
11	460	1210	0.0653
12	510	1377	0.0702
13	520	1555	0.0762

instrumental drift giving approximately a decrease in  $^{11/10}\text{B}$  of 1% by the end of the session. However, the standard sample bracketing procedure accounts for this type of drift. For the coral session the instrument was stable throughout the analysis.

### 3.3. Samples

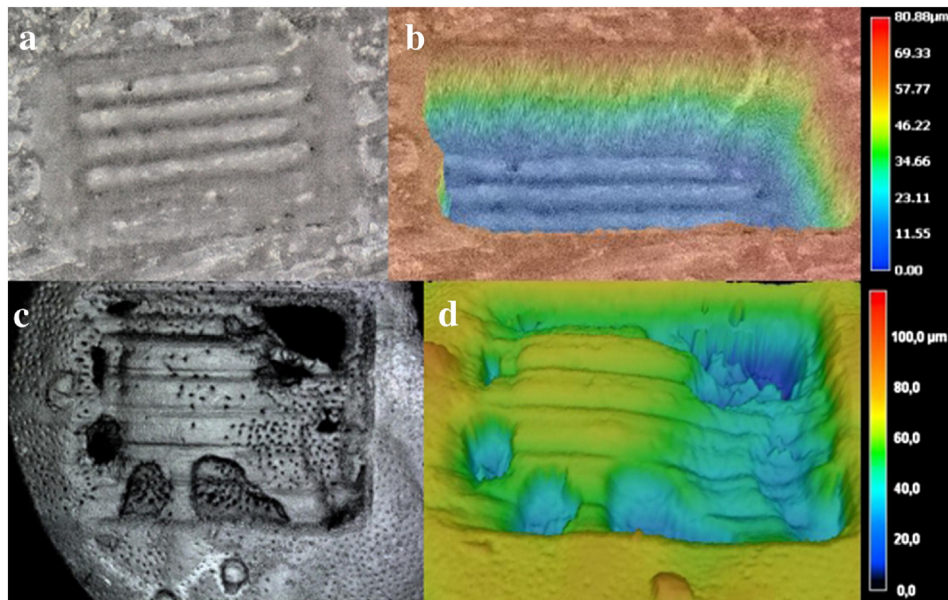
Tables 4 and 5 report i.a. the mean values of the B isotopic signature, B concentration, and B/Ca of both carbonates measured in this study as well as single values. On average the B isotopic composition of the samples is  $18 \pm 0.8\%$  (SD) for the foraminifers and  $21.1 \pm 0.66\%$  (SD) for the coral. The B isotopic composition of benthic foraminifers reported in the literature varies between 15 and 20‰ (Vengosh et al., 1991; Foster, 2008; Rae et al., 2011). For corals it is known that within specimens  $\delta^{11}\text{B}$  can exhibit a range of several ‰ caused by seasonal variation (Hemming et al., 1998) and biological, species specific control on the internal pH close to the site of calcification (Allison and Finch, 2010; McCulloch et al., 2012). For *P. lutea* a variability of 12‰ ( $18.6 \pm 1.5\%$  to  $30.6 \pm 1.6\%$ ) in  $\delta^{11}\text{B}$  is reported (Rollion-Bard et al. (2011)). The mean B concentration of *A. lessonii* investigated here is  $53 \pm 7 \mu\text{g/g}$  (SD). Values reported in the literature for a variety of benthic

foraminifers vary from 10 to 28  $\mu\text{g/g}$  B at an average seawater pH of 8.1 (Foster, 2008). The boron concentration of the same genus as investigated in this study is reported to be 54  $\mu\text{g/g}$  (*Amphistegina* from the Gulf of Aqaba) (Vengosh et al., 1991). The mean B concentration of *P. lutea* is  $61 \pm 3 \mu\text{g/g}$  (SD). Boron concentration values of corals reported in the literature range from 49 to 80  $\mu\text{g/g}$  at an average seawater pH of 8.1 and temperatures between 25 and 29 °C (Vengosh et al., 1991; Hemming and Hanson, 1992; Gaillardet and Allègre, 1995; Trotter et al., 2011). The B isotopic composition and B concentration of the *P. lutea* had already been determined previously using an Axiom MC-ICP-MS and an AttoM HR ICP-MS both in combination with a NewWave UP193 laser ablation unit at IFM Geomar in Kiel, Germany ( $\delta^{11}\text{B} = 22.1 \pm 1.21\%$  (SD); [B] = 26 to 67  $\mu\text{g/g}$ ). Within the limits of uncertainty (SD) the average B isotopic composition and B concentration obtained in this study are identical to the values measured at IFM Geomar.

The main contributors to the precision of the samples are counting statistics and the homogeneity of the isotope ratio  $^{11/10}\text{B}$ . In the following we are going to discuss and evaluate these criteria with respect to our samples.

#### 3.3.1. Foraminiferal samples

The homogeneity with respect to the isotope ratio  $^{11/10}\text{B}$  corresponds to the internal RSE of  $^{11/10}\text{B}$  and is on average 0.52%. In comparison to the RSE of NISTSRM 610 (0.33% and 0.24%) this result represents a worse B isotope homogeneity but lies still within the range of the required precision needed for paleo-reconstructions. The relative counting statistic error of the sum of detected B isotopes is 0.44% (on average based on 30 million detected counts of  $^{11}\text{B}$  and 6.4 million counts of  $^{10}\text{B}$ ). The RSE agrees with the counting statistical evolution. The mean external 2 RSE is 1.44%. However, this result represents the natural B isotope variability rather than the analytical uncertainty. The analytical uncertainty is assessed more adequately by the external reproducibility of the reference material which is on average 0.74%. Since a sufficiently high intensity of B is important for reliable B isotope analysis foraminifers were ablated at a laser repetition rate which guaranties an acceptable B signal. However, this conditions sometimes caused holes in the relatively thin tests (thin tests are



**Fig. 6.** Pictures showing the depth profiles of both samples taken by a digital microscope (coral: a (overview) + b (corresponding depth profile)) and a laser microscope (foraminifer: c (overview) + d (corresponding depth profile)). The coral ablation crater corresponds to four ablation events yielding an ablated volume of  $\sim 680,000 \mu\text{m}^3$  ( $250 \times 190 \times 15 \mu\text{m}$ ) per event. The foraminifer crater corresponds to one ablation event. Laser ablation always included the “knob” visible as a massive calcite. For the calculation of the volume ( $\sim 450,000 \mu\text{m}^3$ ;  $160 \times 140 \times 20 \mu\text{m}$ ) pores and holes were not taken into account.



often observed for cultured foraminifera) of several foraminifera when the laser ablated through negatively affecting the counting statistics. Ablating through the test can theoretically be avoided by setting the raster over a larger area. However, this is limited by the size of the area in the plane of focus. Since foraminifera do not have a flat surface their round shape limits the focus area and therefore the ablation area. Fig. 5a + b shows a comparison between a “rather” homogenous  $^{11/10}\text{B}$  spectrum and a  $^{11/10}\text{B}$  spectrum showing holes in the test where the laser ablated through. The simultaneous detection of B and Ca allows to reject parts in the spectra which represent holes typically visible as negative spikes. However, the counting statistic suffers from this correction. The test diameter of the foraminifera varied between 380 and 520  $\mu\text{m}$  (Table 6) and the thickness of chamber walls was on average 10  $\mu\text{m}$ . About 80% of the individuals from this size fraction showed holes associated with laser ablation. Foraminifera whose spectra showed an internal RSE worse than 0.6‰ have been rejected. These observations do not necessarily mean that single tests of foraminifera are unsuitable for laser ablation. It is important to realize that the specimens investigated in this study grew from their juvenile stage for two months not reaching their final size. Natural growing *A. lessonii* reaches a test diameter of at least 1 mm (Walker et al., 2011) within a life span of at least one year. We preferred to measure cultured specimens of *A. lessonii* because 1) we wanted to reconstruct the pH of the seawater in which *A. lessonii* grew 2) all important parameters of the culture media necessary for pH reconstruction e.g. salinity, temperature and the B isotopic composition could have been measured and did not change during the growth.

### 3.3.2. Coral sample

In contrast to the foraminifera a better homogeneity of the  $^{11/10}\text{B}$  was detected in the coral sample. On average, the internal RSE of  $^{11/10}\text{B}$  of a single measurement was 0.29‰. The relative counting statistic error of the sum of detected B isotopes is 0.27‰ (based on average on 70 million detected counts of  $^{11}\text{B}$  and 16 million counts of  $^{10}\text{B}$ ). The mean external 2 RSE is 0.5‰. In contrast to the foraminifera the coral provides enough material for laser ablation resulting in a much better counting statistics. Furthermore, we did not observe any holes caused by laser ablation although the surface was ablated up to four times. The homogenous distribution of the B isotopes in the coral is occasionally as good as for SRMIST 610. One example of the homogenous  $^{11/10}\text{B}$  is given in Fig. 5c.

### 3.3.3. Sample consumption

The amount of ablated material was calculated for both samples. For the coral the length, width and depth of the ablation craters were determined and the ablated volume calculated using a digital microscope (VHX 5000, Keyence). Fig. 6 (a + b) shows an ablation crater of the coral sample corresponding to four ablation events. The volume of one ablation event is  $\sim 680,000 \mu\text{m}^3$  and the depth is  $\sim 15 \mu\text{m}$ . The ablation craters of foraminifera were measured using a laser microscope (VK-X200, Keyence) (Fig. 6c + d). In Fig. 6 the depth is defined as the distance between the surface of the test (orange to yellow area) and the ablated “knob” a massive calcium carbonate part of the test with less pores (yellow to green area). Blue areas represent cavities between the chamber walls. Chamber walls are labeled in green. Giving a mean ablated depth of 20  $\mu\text{m}$  the amount of ablated material per foraminifer would be on average 1200 ng containing a total amount of B of 0.06 ng. For the calculation of the ablated mass, pores and holes in the tests were not taken into account. Therefore, our calculations represent a low overestimation. An overview of ablated material for each specimen is given in Table 6. To date, Fietzke et al. (2010) presented to our knowledge the only published study about in situ B isotope analysis of natural biogenic carbonates (corals) using LA MC-ICP-MS. The major difference between our studies is the use of faraday cups versus ion counters. The precision using faraday cups on small samples like foraminifera is limited by the noise level of these detectors. Ion counting detectors (as used in this study) show much lower noise levels, thereby

increasing the signal to noise ratio significantly making these detectors more suitable for analysis of single foraminifera. Due to the high number of B cps required when using faraday cups, Fietzke et al. (2010) were forced to use a larger diameter of the laser beam (150  $\mu\text{m}$ ). They ablated a coral sample containing 35  $\mu\text{g/g}$  B at 30 Hz for 30 s and to a depth of 100  $\mu\text{m}$ , corresponding to 5  $\mu\text{g}$  of sample, equivalent to 0.2 ng B. For a better comparison we chose a foraminiferal specimen containing a similar B concentration (32  $\mu\text{g/g}$ , Table 4). The material ablated is 0.73  $\mu\text{g}$  calcite equivalent to 0.024 ng B. Hence, we used eight times less material.

In comparison to bulk analytical techniques the new method represented in this study consumes much less material. However, whereas bulk techniques provide a reliable mean value (mostly based on triplicate analysis of many dissolved tests) one  $\delta^{11}\text{B}$  value from laser ablation is not necessarily representative due to inter- and intra-test variability. Therefore, a representative number of samples has to be analyzed for paleo-applications.

### 3.4. Implications for paleo-applications

Unfortunately, we do not know the  $\delta^{11}\text{B}_{\text{seawater}}$  in which the coral grew. Hence, a pH reconstruction could only be performed for the foraminifera. We reconstructed the pH of the seawater in which the foraminifera grew using (Zeebe and Wolf-Gladrow, 2001):

$$\text{pH} = \text{p}K_{\text{B}} - \log \left( - \frac{\delta^{11}\text{B}_{\text{seawater}} - \delta^{11}\text{B}_{\text{sample}}}{\delta^{11}\text{B}_{\text{seawater}} - \alpha \times \delta^{11}\text{B}_{\text{sample}} - \varepsilon} \right) \quad (5)$$

where  $\text{p}K_{\text{B}}$  is the dissociation constant of boric acid which is dependent on temperature (T) and salinity (S). This value was corrected for T and S after Dickson (1990). The corrected value is 8.59. The B isotopic composition of seawater in which the foraminifera grew was measured using HR-ICP-MS at the university of Cambridge and is  $39.77 \pm 0.44\%$  (2 SD). The B isotopic fractionation factor ( $\alpha$ ) between boric acid and borate is 1.0272 (Klochko et al., 2006), and  $\varepsilon = (\alpha - 1) \times 1000$ . Reconstructed pH values are presented in Table 4. On average, the reconstructed pH ( $8.02 \pm 0.08$ ) matches within errors the measured pH ( $8.08 \pm 0.05$ ) of the culture seawater. Previous studies on B isotopes in foraminiferal tests show that due to the so called “vital effects” foraminifera do not exactly record the pH of the seawater in which they grow (Sanyal et al., 1996; Hönisch and Hemming, 2004; Henehan et al., 2013). For example, symbiont activity strongly influences the pH near the surface of the foraminifera (Köhler-Rink and Köhl, 2000; Zeebe et al., 2003) shifting the B equilibria and consequently, impacts the  $\delta^{11}\text{B}$  signature of the tests (Hönisch et al., 2003). Observations made by Foster (2008) and Rae et al. (2011) suggest that vital effects are more pronounced in planktonic than in benthic species, explaining why reconstructed pH values based on benthic species are in closer agreement with measured pH values. This notion is supported by this study. The good agreement between the measured and reconstructed pH values might be also due to 1) the exact knowledge of the parameters necessary for pH reconstruction 2) the constant conditions (T, S,  $\delta^{11}\text{B}_{\text{seawater}}$ ) during growth. We conclude that a change in the B isotopic composition by  $\pm 0.5\%$  (which equals the mean internal precision) affects the reconstructed pH by  $\pm 0.05$  unit. For paleo-applications this resolution is acceptable. Changes during glacial to interglacial transitions are on the order of 0.3 pH units (Sanyal et al., 1995). However, the variability of  $\delta^{11}\text{B}$  within 13 specimens is 2.48‰ which is equivalent to a reconstructed pH change of 0.23 unit.

Another application of the B proxy is based on its concentration itself. Unfortunately, the reported relationships between the [B] and its controlling factor ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) are species specific (e.g. Yu and Elderfield, 2007; Brown et al., 2011; Rae et al., 2011). Since no calibration for *A. lessonii* exists yet we cannot verify the accuracy and precision of our target variable.

#### 4. Conclusion

In this study we successfully applied a new in situ technique allowing the simultaneous determination of  $\delta^{11}\text{B}$  and B/Ca ratios at the nanogram level (i.e. on single tests of foraminifers) providing two independent proxies for the reconstruction of the full carbonate system. Using the dual detection of B and Ca it is now possible to evaluate the data sets correctly by integrating signals intervals only where Ca was detected. The new technique considerably minimizes the sample size required for the simultaneous determination of B concentration and  $\delta^{11}\text{B}$  as well as the time needed for sample preparation. It was tested on cultured benthic foraminifers and on a piece of coral. Our results show that a sufficient confidence in B analysis can only be achieved if a sufficient amount of material per one analysis is ablated (giving confidence in the precision) and enough individual tests are measured covering the range of the B variability. In the case of the foraminifers small test diameter and thin chamber walls may limit the precision and application of laser ablation on single tests. Within a size range of 380 to 520  $\mu\text{m}$  and a mean B concentration of 53  $\mu\text{g/g}$  the mean internal precision is 0.52‰. For future applications we recommend a careful selection of samples having at least the same size as investigated in this study. For the coral sample an internal precision of 0.29‰ was achieved which is mostly due to the fact that more material of higher B isotope homogeneity was ablated. This result is very promising for paleo-pH reconstructions as well as investigations on seasonal variability in corals. Giving a homogenous  $^{11}\text{B}/^{10}\text{B}$  distribution, this new technique is able to provide sufficient precision of the B isotopic composition for paleo-pH reconstructions. From the pH reconstruction based on the cultured foraminifers we conclude that the mean reconstructed pH value calculated from 13 specimens is in good agreement with the measured one.

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#### References

- Aggarwal, J.K., Mezger, K., Pernicka, E., Meixner, A., 2004. The effect of instrumental mass bias on  $\delta^{11}\text{B}$  measurements: a comparison between thermal ionization mass spectrometry and multiple-collector ICP-MS. *Int. J. Mass Spectrom.* 232 (3), 259–263.
- Allison, N., Finch, A.A., 2010.  $\delta^{11}\text{B}$ , Sr, Mg and B in a modern *Porites* coral: the relationship between calcification site pH and skeletal chemistry. *Geochim. Cosmochim. Acta* 74 (6), 1790–1800.
- Brown, R.E., Anderson, L.D., Thomas, E., Zachos, J.C., 2011. A core-top calibration of B/Ca in the benthic foraminifers *Nuttallides umbonifera* and *Oridorsalis umbonatus*: a proxy for Cenozoic bottom water carbonate saturation. *Earth Planet. Sci. Lett.* 310 (3–4), 360–368.
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., Hattori, K., 2010. In situ characterization of serpentinites from forearc wedges: timing of serpentinization and behavior of fluid-mobile elements in subduction zones. *Chem. Geol.* 269 (3–4), 262–277.
- Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Res. Part A* 37 (5), 755–766.
- Ernst, S., et al., 2011. Benthic foraminifera in a large Indo-Pacific coral reef aquarium. *J. Foramin. Res.* 41 (2), 101–113.
- Fietzke, J., et al., 2010. Boron isotope ratio determination in carbonates via LA–MC–ICP–MS using soda–lime glass standards as reference material. *J. Anal. At. Spectrom.* 25 (12), 1953–1957.
- Foster, G.L., 2008. Seawater pH,  $p\text{CO}_2$  and  $[\text{CO}_2\text{-}_3]$  variations in the Caribbean Sea over the last 130 kyr: a boron isotope and B/Ca study of planktic foraminifera. *Earth Planet. Sci. Lett.* 271 (1–4), 254–266.
- Foster, G.L., Ni, Y., Haley, B., Elliott, T., 2006. Accurate and precise isotopic measurement of sub-nanogram sized samples of foraminiferal hosted boron by total evaporation NTIMS. *Chem. Geol.* 230 (1–2), 161–174.
- Gaillardet, J.M., Allègre, C.J., 1995. Boron isotopic compositions of corals: seawater or diagenesis record? *Earth Planet. Sci. Lett.* 136 (3–4), 665–676.
- Hemming, N.G., Hanson, G.N., 1992. Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmochim. Acta* 56 (1), 537–543.
- Hemming, N.G., Hanson, G.N., 1994. A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chem. Geol.* 114 (1–2), 147–156.
- Hemming, N.G., Guilderson, T.P., Fairbanks, R.G., 1998. Seasonal variations in the boron isotopic composition of coral: a productivity signal? *Glob. Biogeochem. Cycles* 12 (4), 581–586.
- Henehan, M.J., et al., 2013. Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo- $\text{CO}_2$  reconstruction. *Earth Planet. Sci. Lett.* 364, 111–122.
- Hönisch, B., Hemming, N.G., 2004. Ground-truthing the boron isotope–paleo-pH proxy in planktonic foraminifera shells: partial dissolution and shell size effects. *Paleoceanography* 19 (4), PA4010.
- Hönisch, B., Hemming, N.G., 2005. Surface ocean pH response to variations in  $p\text{CO}_2$  through two full glacial cycles. *Earth Planet. Sci. Lett.* 236 (1–2), 305–314.
- Hönisch, B., et al., 2003. The influence of symbiotic photosynthesis on the boron isotopic composition of foraminifera shells. *Mar. Micropaleontol.* 49 (1–2), 87–96.
- Horn, I., von Blanckenburg, F., Schoenberg, R., Steinhofel, G., Gregor, M., 2006. In situ iron isotope ratio determination using UV–femtosecond laser ablation with application to hydrothermal ore formation processes. *Geochim. Cosmochim. Acta* 70, 3677–3688.
- Hou, K., Li, Y., Xiao, Y., Liu, F., Tian, Y., 2010. In situ boron isotope measurements of natural geological materials by LA–MC–ICP–MS. *Chin. Sci. Bull.* 55 (29), 3305–3311.
- Hu, Z., Liu, Y., Li, M., Gao, S., Zhao, L., 2009. Results for rarely determined elements in MPI-DING, USGS and NIST SRM glasses using laser ablation ICP–MS. *Geostand. Geoanal. Res.* 33 (3), 319–335.
- Jacob, D.E., 2006. High sensitivity analysis of trace element poor geological reference glasses by laser ablation–inductively coupled plasma–mass spectrometry. *Geostand. Geoanal. Res.* 30 (3), 221–235.
- Kasemann, S., Meixner, A., Rocholl, A., Vennemann, T., Rosner, M., Schmitt, A.K., Wiedenbeck, M., 2001. Boron and Oxygen Isotope Compilation of Certified Reference Materials NIST SRM 610/612 and Reference Materials JB-2 and JR-2. *Geostandards Newsletter* 25 (2–3), 405–416.
- Kasemann, S.A., Schmidt, D.N., Bijma, J., Foster, G.L., 2009. In situ analysis in marine carbonates and its application for foraminifera and paleo-pH. *Chem. Geol.* 260 (1–2), 138–147.
- Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H., Tossell, J.A., 2006. Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* 248 (1–2), 276–285.
- Köhler-Rink, S., Kühl, M., 2000. Microsensor studies of photosynthesis and respiration in larger symbiotic foraminifera. I. The physico-chemical microenvironment of *Marginopora vertebralis*, *Amphistegina lobifera* and *Amphisorus hemprichii*. *Mar. Biol.* 137 (3), 473–486.
- Lazarov, M., Brey, G.P., Weyer, S., 2012. Evolution of the South African mantle – a case study of garnet peridotites from the Finsch diamond mine (Kaapvaal Craton); part 1: inter-mineral trace element and isotopic equilibrium. *Lithos* 154, 193–209.
- le Roux, P.J., Shirey, S.B., Benton, L., Hauri, E.H., Mock, T.D., 2004. In situ, multiple-multiplier, laser ablation ICP–MS measurement of boron isotopic composition ( $\delta^{11}\text{B}$ ) at the nanogram level. *Chem. Geol.* 203 (1–2), 123–138.
- Lécuyer, C., Grandjean, P., Reynard, B., Albarède, F., Telouk, P., 2002.  $^{11}\text{B}/^{10}\text{B}$  analysis of geological materials by ICP–MS Plasma 54: application to the boron fractionation between brachiopod calcite and seawater. *Chem. Geol.* 186 (1–2), 45–55.
- Liu, Y., Hu, Z., Gao, S., Günther, D., Gao, C., Chen, H., 2008. In situ analysis of major and trace elements of anhydrous minerals by LA–ICP–MS without applying an internal standard. *Chem. Geol.* 257 (1–2), 34–43.
- Longerich, H.P., Jackson, S.E., Günther, D., 1996. Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. *J. Anal. At. Spectrom.* 11 (9), 899–904.
- Louvat, P., Bouchez, J., Paris, G., 2010. MC–ICP–MS isotope measurements with direct injection nebulisation (d-DIHEN): optimisation and application to boron in seawater and carbonate samples. *Geostand. Geoanal. Res.* 35 (1), 75–88.
- McCulloch, M., Trotter, J., Montagna, P., Falter, J., Dunbar, R., Freiwald, A., Försterra, G., López Correa, M., Maier, C., Rüggeberg, A., Taviani, M., 2012. Resilience of cold-water scleractinian corals to ocean acidification: boron isotopic systematics of pH and saturation state up-regulation. *Geochim. Cosmochim. Acta* 87, 21–34.
- Mikova, J., Košler, J., Wiedenbeck, M., 2014. Matrix effects during laser ablation MC ICP–MS analysis of boron isotopes in tourmaline. *J. Anal. At. Spectrom.* 29 (5), 903–914.
- Ni, Y., et al., 2007. A core top assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers. *Paleoceanography* 22 (3), PA3212.
- Rae, J.W.B., Foster, G.L., Schmidt, D.N., Elliott, T., 2011. Boron isotopes and B/Ca in benthic foraminifera: proxies for the deep ocean carbonate system. *Earth Planet. Sci. Lett.* 302 (3–4), 403–413.
- Rollion-Bard, C., Erez, J., 2010. Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminifera *Amphistegina lobifera*: implications for  $\delta^{11}\text{B}$  vital effects and paleo-pH reconstructions. *Geochim. Cosmochim. Acta* 74 (5), 1530–1536.
- Rollion-Bard, C., Chausson, M., France-Lanord, C., 2011. Biological control of internal pH in scleractinian corals: implications on paleo-pH and paleo-temperature reconstructions. *Compt. Rendus Geosci.* 343, 397–405.
- Sanyal, A., Hemming, N.G., Hanson, G.N., Broecker, W.S., 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* 373, 234–236.
- Sanyal, A., et al., 1996. Oceanic pH control on the boron isotopic composition of foraminifera: evidence from culture experiments. *Paleoceanography* 11 (5), 513–517.
- Tiepolo, M., Zannetti, A., Vannucci, R., 2005. Determination of lithium, beryllium, and boron at trace levels by laser ablation–inductively coupled plasma–sector field mass spectrometry. *Geostand. Geoanal. Res.* 29 (2), 211–224.
- Tiepolo, M., Bouman, C., Vannucci, R., Schwieters, J., 2006. Laser ablation multicollector ICPMS determination of  $\delta^{11}\text{B}$  in geological samples. *Appl. Geochem.* 21 (5), 788–801.
- Trotter, J., et al., 2011. Quantifying the pH “vital effect” in the temperate zooxanthellate coral *Cladocora caespitosa*: validation of the boron seawater pH proxy. *Earth Planet. Sci. Lett.* 303, 163–173.

- Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A.R., McCulloch, M.T., 1991. Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochim. Cosmochim. Acta* 55 (10), 2901–2910.
- Walker, R.A., Hallock, P., Torres, J.J., Vargo, G.A., 2011. Photosynthesis and respiration in five species of benthic foraminifera that host algal endosymbionts. *J. Foramin. Res.* 41 (4), 314–325.
- Wara, M.W., Delaney, M.L., Bullen, T.D., Ravelo, A.C., 2003. Possible roles of pH, temperature, and partial dissolution in determining boron concentration and isotopic composition in planktonic foraminifera. *Paleoceanography* 18 (4), 1100.
- Yu, J., Elderfield, H., 2007. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. *Earth Planet. Sci. Lett.* 258 (1–2), 73–86.
- Yu, J., Foster, G.L., Elderfield, H., Broecker, W.S., Clark, E., 2010. An evaluation of benthic foraminiferal B/Ca and  $\delta^{11}\text{B}$  for deep ocean carbonate ion and pH reconstructions. *Earth Planet. Sci. Lett.* 293 (1–2), 114–120.
- Zeebe, R.E., Wolf-Gladrow, D.A., 2001. *CO<sub>2</sub> in Seawater: Equilibrium, Kinetics, Isotopes*. Elsevier Science B.V., Amsterdam.
- Zeebe, R.E., Wolf-Gladrow, D.A., Bijma, J., Hönisch, B., 2003. Vital effects in foraminifera do not compromise the use of  $\delta^{11}\text{B}$  as a paleo-pH indicator: evidence from modeling. *Paleoceanography* 18 (2), 1043.