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Simultaneous determination of $\delta^{11}B$ 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 $\delta^{11}B = 18.0 \pm 0.83‰$ (SD) with an average internal precision of 0.52‰ (RSE). The boron concentration was 53 ± 7 μg/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 ($CaCO_3$) are powerful tools to reconstruct the physico-chemical conditions of the environment. The incorporation of boron (B) into biogenic $CaCO_3$ 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 CO_2 concentration.

In seawater B mainly exists as boric acid (BOH_3) and borate (BOH_4^-) whose species distribution and isotopic composition is strongly pH dependent (Dickson, 1990). The B isotopic composition of coral and foraminiferal $CaCO_3$ provided strong evidence that only borate is incorporated into $CaCO_3$ (Hemming and Hanson, 1992). Hence, the B isotopic composition of $CaCO_3$ 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 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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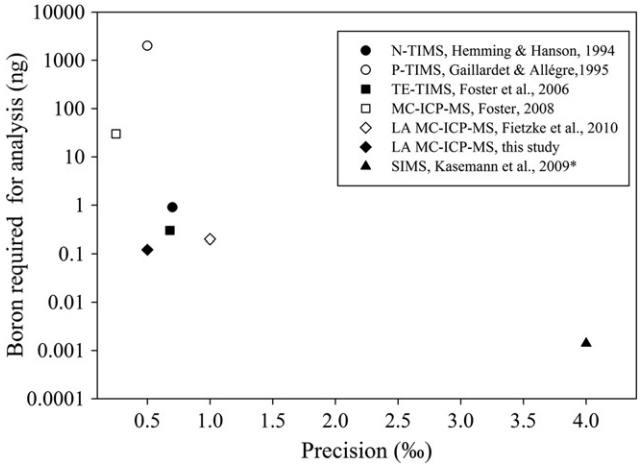

Fig. 1. Precision and amount of required boron for various analytical techniques for boron isotope analysis in carbonate matrices (corals and foraminifers (TE-NTIMS)). *Required B amount was calculated assuming a sputter rate of 0.0066 μm^3/nAs.

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 μm scale. This can help to develop a process based understanding of B incorporation into foraminiferal $CaCO_3$, 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 ~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 ~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.

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 $\delta^{11}B$ 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 $\delta^{11}B$ 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 μm 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 $\delta^{11}B$ and B/Ca ratios of cultured, benthic foraminifers (*Amphistegina lessonii*) and a natural grown coral sample (*Porites lutea*).

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 $CaCO_3$ 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

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