Biogeosciences

Discussions

Open Access

EGU

BGD

Interactive comment on "Decoupled carbonate chemistry controls on the incorporation of boron into *Orbulina universa*." *by* E. L. Howes et al.

E. L. Howes et al.

ella.l.howes@gmail.com

Received and published: 16 October 2016

"general comments" The submitted discussion paper provides a boron data set (d11B and B/Ca) of foraminifera from a culturing study performed modifying pH and [CO3 2-] in a decoupled way. It relates to an interesting topic: proxy calibration for paleoreconstruction of key parameters of the marine carbonate system. While the efforts involved in culturing are truely acknowledged the extend of data and its discussion unfortunately are not great. As it stands I would consider this manuscript as a data brief and I am not convinced it will make an exciting contribution to BG.

Again, we are a bit disappointed by the little justification provided by the reviewer to conclude that this manuscript will not make "an exciting contribution to BG". As argued above in our reply to the first reviewer, this is the first paper that reports the boron

isotope response in a planktonic species under experimentally decoupled carbonate chemistries (Allen and Hönisch (2012), who also decoupled the carbonate chemistry, only reported its impact on B/Ca). As such, laboratory experiments are the only way to develop a mechanic understanding of what the primary drivers of shell chemistry are. We therefore believe that this is a valuable addition to the scientific literature, especially for the growing "boron community".

"specific comments" Most of the method section's content can be found in the cited literature. Thus, it get's too much space in the manuscript and could be moved into a dedicated part of the supplements. The normalization procedures for d11B read confusing. I assume d11B of the culturing water has been measured, as the data are provided in table 1. I do miss information on how these data have been generated. I would assume using MC-ICPMS, relative to NBS SRM-951?

We think that the method section is important. Where possible we refer to the literature. The first author is a native English speaking person and read through the section on normalization procedures again and made the appropriate changes. We have also added a section on the boron analyses of the culture water:

"Culture water analysis Boron isotopic composition of the culture media were analysed by means of a Thermo$^{®}$ Element XR, a single collector, sector field, high-resolution inductively coupled plasma mass spectrometer, fitted with a high-sensitivity interface pump (Jet pump) as described in Misra et al. (2014). Boron isotopic composition is reported as per mil (‰ deviation from NIST SRM 951a (11B/10B = 4.04362 ± 0.00137) (Catanzaro, 1970) where: $\delta^{11}B\_sample$ (‰=[((_^(11/10))B)_sample/((_^(11/10))B)_(NISTSRM 951a) -1]×1000 Boron isotope analyses were made following a Sample – Standard Bracketing (SSB) technique. NIST 951a was used as the standard and samples were concentration matched, typically at 5 %, with the standard and were analysed in quintuplicate. The accuracy and precision of the analytical method was assessed by comparing 11B measurements of seawater (from the Atlantic Ocean) and secondary boron standards (AE 120, 121, 122) with published (accepted) results. Our

estimate of 11BSW of 39.80.4‰ (2s, n = 30) are independent of sample size and are in agreement with published values of 39.6 ± 0.4‰ (Foster et al., 2010) and 39.7 ± 0.6‰ (Spivack and Edmond, 1987). Moreover, our 11B estimates of SRM AE-120 (-20.2 ± 0.5 ‰ 2s, n = 33), SRM AE-121 (19.8 ± 0.4 ‰ 2s, n =16), SRM AE-122 (39.6 ± 0.5 ‰ 2s, n = 16) are identical, within analytical uncertainty, to accepted values (Vogl and Rosner, 2012). Information about sample preparation for analysis can be found in the supplement provided in Kaczmarek et al.(2015)."

The water composition is massively modified (10xB concentration and about 35 permill lighter than natural seawater). That's fine, the normalization should allow for comparability of the data. So, water data are presumably expressed relative to NBS951 (conventional delta11B notation). LA-MC-ICPMS data relate to NIST SRM-610. Nothing is mentioned about any further normalization, regarding differences between both SRMs. It appears the authors assume both to have identical boron isotopic composition.

That is correct. It has been shown by several studies (Kasemann et al., 2001; le Roux et al., 2004; Fietzke et al., 2010) that both standards are isotopically the same within analytical uncertainty.

When using a standard of an entirely different matrix during the laser analysis of foraminifera (silicate vs. carbonate), and ablating quite different amounts of both, some justification is needed to convince readers that no offsets (analytical artefacts) compromise the data.

Femto second laser ablation is matrix independent, i.e. it does not require a matrix matched standard and therefore allows us to use NIST SRM 610 (a glass) for carbonates. The fs laser ablation process is fundamentally different from ns laser ablation used by most people. When the pulse length is shorter than 10 ps (Hergenröder et al., 2006) the laser energy can be deposited into the material before it can thermally equilibrate. Femtosecond ablation also provide smaller aerosol particle sizes. The matrix independency of fs laser ablation has been demonstrated by many papers (some of

which published in journals that are usually read by geochemists and paleoceanographers) (e.g. Chmeleff et al., 2008; Horn et al., 2006; Oeser et al., 2014; Schuessler and von Blanckenburg, 2014; Kaczmarek et al., 2015; Lazarov et al., 2015; Lazarov and Horn, 2015) and therefore allows us to use NIST SRM 610 for the carbonates.

As the boron concentrations can differ between samples and standard and different matrices require more or less energy for ablation, the repetition rate was chosen such that the signal of sample and standard at the ion counters was comparable. This is important for normalization of the sample to the known ïĄď11B of the standard.

References

Chmeleff, J., Horn, I., Steinhoefel, G. and von Blanckenburg, F. (2008) In situ determination of precise stable Si isotope ratios by UV-femtosecond laser ablation high-resolution multi-collector ICP-MS. Chemical Geology 249, 155-166.

Fietzke, J., Heinemann, A., Taubner, I., Bohm, F., Erez, J., and Eisenhauer, A.: Boron isotope ratio determination in carbonates via LA-MC-ICP-MS using soda-lime glass standards as reference material, J. Anal. Atom. Spectrom., 25, 1953–1957, 2010.

Horn, I., von Blanckenburg, F., Schoenberg, R., Steinhoefel, G. and Markl, G. (2006) In situ iron isotope ratio determination using UV-femtosecond laser ablation with application to hydrothermal ore formation processes. Geochimica et Cosmochimica Acta 70, 3677-3688.

Kasemann, S., Meixner, A., Rocholl, A., Vennemann, T., Rosner, M., Schmitt, A. K., and Wiedenbeck, M.: Boron and Oxygen Isotope Composition of Certified Reference Materials NIST SRM 610/612 and Reference Materials JB-2 and JR-2, Geostandard.Newslett., 25, 405–416, 2001

Kaczmarek, K., Horn, I., Nehrke, G. and Bijma, J. (2015) Simultaneous determination of δ11B and B/Ca ratio in marine biogenic carbonates at nanogram level. Chemical Geology 392, 32-42.

Lazarov, M. and Horn, I. (2015) Matrix and energy effects during in-situ determination of Cu isotope ratios by ultraviolet-femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy 111, 64-73.

Le Roux, P. J., Shirey, S. B., Benton, L., Hauri, E. H., and Mock, T. D.: In situ, multiple-multiplier, laser ablation ICP-MS measurement of boron isotopic composition (δ11B) at the nanogram level, Chem. Geol., 203, 123–138, 2004.

Oeser, M., Weyer, S., Horn, I. and Schuth, S. (2014) High-Precision Fe and Mg Isotope Ratios of Silicate Reference Glasses Determined In Situ by Femtosecond LA-MC-ICP-MS and by Solution Nebulisation MC-ICP-MS. Geostandards and Geoanalytical Research 38, 311-328.

Schuessler, J.A. and von Blanckenburg, F. (2014) Testing the limits of micro-scale analyses of Si stable isotopes by femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry with application to rock weathering. Spectrochimica Acta Part B: Atomic Spectroscopy 98, 1-18.

Steinhoefel, G., Horn, I. and von Blanckenburg, F. (2009) Matrix-independent Fe isotope ratio determination in silicates using UV femtosecond laser ablation. Chemical Geology 268, 67-73.

We have added the following text to the method section: "It should be noted that the fs laser ablation process is fundamentally different from ns laser ablation. When the pulse length is shorter than 10 ps (Hergenröder and Hommes, 2006) the laser energy can be deposited into the material before it can thermally equilibrate. Femtosecond ablation also provides smaller aerosol particle sizes. Due to the short pulse length, fs laser ablation is matrix independent (e.g. Chmeleff et al., 2008; Horn et al., 2006; Oeser et al., 2014; Schuessler and von Blanckenburg, 2014; Kaczmarek et al., 2015; Lazarov et al., 2015; Lazarov and Horn, 2015), i.e. it does not require a matrix matched standard and therefore allows us to use NIST SRM 610 (a glass) as a reference for carbonates.

As the boron concentrations is different between sample and standard and different matrices require more or less energy for ablation, the repetition rate was chosen such that the signal of sample and standard at the ion counters was comparable. This is important for normalization of the sample to the known ïĄđ'11B of the standard.

Most previous publications on boron isotopes have used "wet chemistry" for which NIST SRM 951 is a perfect standard. We have also used this standard for the analysis of the culture waters. The foraminiferal shells, however, were measured using laser ablation, for which we used a different standard (NIST SRM 610). As shown by several studies (Kasemann et al., 2001; le Roux et al., 2004; Fietzke et al., 2010), both standards are, within analytical uncertainty, isotopically equal. Hence, it doesn't make a difference if values are reported versus one or the other standard."

Have the foraminifera shells been treated chemically prior to laser analyses (e.g.oxydative cleaning)?

Text added lines 226-228: Prior to analysis, specimens were harvested, bleached in NaOCl (active chlorine: 4.6 %) for 6 hours, rinsed four times using de-ionized water, and dried for 12 h at 50 âŮęC.

Nothing is mentioned about the quite large variability within the d11B data of foraminifera within each treatment group. How do you explain this observation?

We like to draw the reviewer's attention to studies about single foram analyses such as that carried out by Rollin-Bard & Erez (2009) using a nanoSIMS and demonstrating a ïĄđ'11B variability between 4.7 to 12.2 per mill. For laser ablation Kaczmarek et al. (2015a,b) demonstrated that intra specimen ïĄđ'11B variability was typically around 5 to 6 permil. The spread shown in our data is due to both inter- and intra-shell variability. Branson et al. (2015) have shown that boron is not homogeneously distributed in foraminiferal shells. In fact, the boron concentration (and hence B/CA) shows distinct high and low concentration boron bands which are probably diachronous with the well-known high and low Mg banding. Recently, Sadekov and his Cambridge colleagues

showed a significant ontogenetic variability in boron concentration (B/Ca) and that the ïĄď11B variability across these bands in the shell wall is about 10 permil (poster at ICP12, Utrecht, 2016)! However, they also showed that the mean ïĄď11B value was close to the ïĄď11B value from wet chemical analysis.

Besides the inter-shell variability, there is also significant variability between individual specimens. De Nooijer et al. (2014), showed that, even for genetically identical specimens (clones) grown under identical conditions, their geochemical signatures can be significantly different. Differences in Sr/Ca and Mg/Ca between clone groups were similar to the intra-clone group variability, suggesting that any genetic differences between the clone groups did not affect trace element partitioning. Instead, variability in Mg/Ca appears to be inherent to the process of bio-calcification itself. There is no a priori reason to assume that this would be fundamentally different for B/Ca or ïĄď11B for that matter.

When applying wet chemical boron isotope analyses, as most other groups do, many foraminiferal shells are combined for single, duplicate or triplicate measurements of the same sample. Hence, intra- and inter-specimen variability is then averaged and the remaining variability within the data is related to analytical issues only (and unrelated to biological/physiological and/or population dynamical impacts).

References

Branson, O., Kaczmarek, K., Redfern, S.A.T., Misra, S., Langer, G., Tyliszczak, T., Bijma, J. and Elderfield, H. (2015) The coordination and distribution of B in foraminiferal calcite. Earth and Planetary Science Letters 416, 67-72.

Kaczmarek, K., Langer, G., Nehrke, G., Horn, I., Misra, S., Janse, M. and Bijma, J. (2015) Boron incorporation in the foraminifer Amphistegina lessonii under a decoupled carbonate chemistry. Biogeosciences 12, 1753-1763.

Kaczmarek, K., Horn, I., Nehrke, G. and Bijma, J. (2015) Simultaneous determination

of δ11B and B/Ca ratio in marine biogenic carbonates at nanogram level. Chemical Geology 392, 32-42.

de Nooijer, L.J., Hathorne, E.C., Reichart, G.J., Langer, G. and Bijma, J. (2014) Variability in calcitic Mg/Ca and Sr/Ca ratios in clones of the benthic foraminifer Ammonia tepida. Marine Micropaleontology 107, 32-43.

And considering this variability I am somewhat surprised the data (figure 3A) do match the inorganic borate curve (Klochko-curve) more or less perfectly. Statistically this is almost impossible, considering the mean 2SE to be >1.5permill.

Obviously, we were very surprised ourselves and checked our calculations several times. If we wanted to cheat we would probably not have come up with a more or less perfect match. Wouldn't that be too obvious? However, at the end we are glad that the reviewer raised this issue as we went through the calculations again and again and did discover a silly mistake in the spreadsheet that was overlooked before and affected the ïĄďˇ11B value at pH 8.05. This has now been corrected.