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

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This study presents boron data (B/Ca and d11B) for planktonic foraminifera O. universa cultured in a decoupled carbonate system. The authors concluded that the B/Ca ratios correlate with [B(OH)4-/HCO3-], while the d11B values depend solely on pH. Although the data are fundamentally valuable, the culturing system is a concept recycled from a report by Kaczmarek et al. (2015b, BG), who used benthic foraminifera A. lessonii. Moreover, the discussion is repetitive. In addition, the quality of the data and the discussion are inferior compared to that earlier report. If this work cannot venture beyond a case study, I think that it is difficult to justify its publication in BG.

We are a bit disappointed by the little justification provided by the reviewer to conclude that he or she thinks "that it is difficult to justify its publication in BG". We do agree

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Discussion paper

that the concept used by Kaczmarek et al., 2015 (BG) is the same as the one used here. This was on purpose and makes perfect sense as the research comes from the same group and the aim was to have comparable experimental conditions for a benthic (Kaczmarek et al., 2015) and a planktonic species (this paper). Although, one could argue that there is maybe no a priori reason to expect that planktonic and benthic foraminifera behave differently, it remains to be investigated and documented. In addition, this is the first paper that investigates 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: Methods: d11B data should be normalized to NIST SRM 951, not NIST SRM 610, as most of the cited reports of the literature do.

The reviewer is absolutely right that most of the cited reports in the literature normalize ïĄď11B to NIST SRM 951. This is due to the fact that almost all previously published papers on B/Ca and ïĄď11B use "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 femto second laser ablation, for which we had to use a different (solid) 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. It should be noted that fs laser ablation is matrix independent, i.e. it does not require a matrix matched standard and therefore allows us to use NIST SRM 610 for carbonates (also see the reply to reviewer 2).

We have changed the text as follows (line 320): "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, for comparison between ïĄď11B O. universa and ïĄď11B of B(OH)4- the isotopic difference between the two standards can be neglected and it does not make a difference if values are reported versus one or the other standard.”

L345: Is d11B = 18.8‰ at pH 8.05 a mean value of the three experiments with different [CO3 2-] concentrations? Justify that calculation. This is also inconsistent with Fig. 3A.

We thank the reviewer for pointing this out. We have forgotten to change the numbers in the table. As the number of ablations per experimental condition is limited we have given preference to using median values. In a perfect Gausian distribution, the median has the same value as the mean. However, if the number of data points is low, the distribution may not be Gausian and then the median is less sensitive to “outliers”. The justification for plotting the mean of all [CO32-] experiments is that in the real ocean pH and [CO32-] co-vary. By combining ïĄď11B for a range of [CO32-] we provide a number that can be used in modern surface waters having different [CO32-] (239 to 534μmol kg-1). It should be noted that the median ïĄď11B of the combined experiments at different [CO32-] is 18.8‰ but the same as for the intermediate [CO32-] at 285 μmol/kg. This [CO32-] at pH 8.05 is comparable to a [CO32-] of 296 μmol kg-1 at pH 7.9 and a [CO32-] of 258 μmol kg-1 at pH 7.7.

We have corrected the inconsistency with Fig. 3A.

L347-349: In spite of the large analytical error, it is difficult to conclude that no significant effect of [CO3 2-] on d11B was found.

We agree with the reviewer, that there is an effect of [CO32-] on ïĄď11B and this is now discussed in the text. However, in reality this effect will be minor as in the real ocean pH and [CO32-] co-vary and the range of [CO32-] is much more limited than in our experimental treatments).

We have added a paragraph to the result section: "δ11B increases with increasing [CO32-] at constant pHT from 17.2‰ at 238 μmol/kg CO32- to 19.9‰ at 534 μmol/kg CO32- (Table 3; Fig 3B). Applying ANOVA with a Bonferroni test, which is best suited for a limited number of pairs, the p-value of the overall ANOVA is 0.00203, demonstrating a significant difference between two or more population means. The difference between the mean δ11B values of the [CO32-] treatments 239 and 286 μmol/kg were close to significance but only between 239 and 534 μmol/kg the difference was significant (Supplement Table 3). Because, this range in [CO32-] is beyond that of the real ocean and because pH and [CO32-] co-vary, we believe that this observation is only important for a better understanding of the δ11B controls and does not significantly impact existing calibrations."

Is there any correlation between B/Ca and d11B?

As expected, based on first principles, there is a correlation between B/Ca and ïĄď11B. We have added 2 plots in the supplement file and a short paragraph in the results section:" Based on first principles, we predict a positive correlation between B/Ca and ïĄď11B because at higher pH not only the isotopic composition of borate gets heavier but its concentration also increases. Figures 2A (supplement) shows the individual B/Ca, ïĄď11B pairs per treatment. As expected for individual LA shell analyses is the inter specimen variability quite large. Individual B/Ca ratios vary by almost 50% in each treatment and individual ïĄď11B values vary by ca. 4-6‰ per treatment (cf. Kaczmarek et al., 2015b). Although one could argue for a positive trend between B/Ca and ïĄď11B in some of the treatments, we believe that the individual B/Ca, ïĄď11B pairs within a treatment demonstrate are However, the average values for the four treatments with [CO3-2] between 238 – 297 μmol kg-1 do show a positive correlation between B/Ca and ïĄď11B. The "outlier" (treatment at pH 8.05; [CO3-2] = 534) can be explained by the, relative to the other pH = 8.05 treatments, high [HCO3-].".

L447-448: The meaning of “The proxy should therefore be ground-truthed using core top samples” is unclear.

Even if experimental data provide insight into fractionation mechanisms, field verification (both water column and sediment) is needed to investigate how seasonality, population dynamics and other environmental factors, not tested under controlled laboratory conditions, affect their geochemistry and to which extend. It also allows verification of which species are suited best for paleo reconstructions (O. universa is just our lab rat). This issue is extensively discussed in the reply to Michael Henehan.

References: The cited Hanehan et al. (2015) is missing from the list of references.

We thank the reviewer for point this out. The reference has been added.

Tables 1 & 3: Order the data at pH 8.05 in ascending order according to [CO3 2-].

Very good point. Done!

Fig. 3: Put alphabet characters on each graph. The median values are shown as red circles, not black.

We have added the alphabet characters and changed black to red.

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