

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 is an interesting contribution that adds more data to look at some of the outstanding questions surrounding the boron-based proxies. The finding regarding bicarbonate ion is interesting, and builds on previous work by Allen et al in (2012). The boron isotope measurements are also interesting, although I have some concerns about the spread in the data and the calculation and propagation of uncertainties, and would suggest the authors at some point explicitly mention that the uncertainty poses limitations for how much can be interpreted from these data. As a relatively young technique I would also suggest that including some measurements of widely analysed calcium carbonate standard material (such as JCP or JCT) would be really helpful in clearly demonstrating the efficacy of the technique, and would add to the citation potential of the article.

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As a general point, I would suggest that this paper would be strengthened considerably with the inclusion of measurements of open ocean *O. universa*. This would test the hypothesis put forward for the apparently muted vital effects- if open ocean *O. universa* show a different isotopic ratio compared to the cultured individuals, then it could support their argument and constitute important evidence for hypotheses surrounding microenvironment alteration driving vital effects. It would also address the issue of bicarbonate control- since there are a number of studies that show that just because these patterns can be seen in culture, it doesn't mean they will hold up outside of the lab. It would also go some way to addressing Reviewer #1's point that the study is somewhat incremental in its current form and scope.

In the face of the data from Babila et al., Henehan et al., Salmon et al. (2016, EPSL) and the excellent review by Allen and Hönisch (2012), the authors should remove suggestions of using B/Ca as a proxy for the second carbonate system parameter, unless they can show evidence to support this relationship standing up out of the culture lab. Again, in that sense more data would be helpful. But also, the data are out there- why not plot some published open ocean data against bicarbonate if the argument is being made that this is reliable? In fact, in our 2015 G-cubed paper we actually plot open ocean B/Ca against borate/bicarbonate, just as the authors suggest should work, and there is no relationship.

More generally, there are a few instances in the intro and discussion where preference is given to detailing the findings of older, and since superceded studies, rather than cutting straight to the new data coming out of the community and dealing with the questions they raise. For instance in the case of B/Ca, a lot of time is dedicated to older studies that look at patterns in KD (Foster, 2008; Yu et al. 2007), even though Allen and Hönisch rightly state that the parameter itself has its flaws, and even though there are much more recent papers on B/Ca with more relevant findings that aren't mentioned.

In summary, I would suggest that with substantial revisions to the areas outlined and

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ideally with additional open-ocean data, this paper could be published.

Specific points:

Lines 25-27: the sentence here does not make the necessary link between borate substituting into carbonate and why this would then make it a carbonate ion proxy. Need to point out in a sentence like this that borate is more abundant at higher pHs.

Line 37-40 (and throughout): I have some serious concerns over the point being made here- that B/Ca is a useful second carbonate system parameter. Many experiments have shown (including ours- Henehan et al. 2015, G3) that you can produce a pH dependent shift in B/Ca in culture experiments where you change only the carbonate system. However, in the open ocean these relationships often fall down, because there are other controls on boron incorporation- see for example my paper, or excellent papers by Babila et al, or Allen and Hönisch (2012) or a really great paper just out by Kate Salmon et al. in EPSL. This abstract, and indeed the paper, is strongly advocating the use of B/Ca to derive the whole carbonate system, but this is based only on culture experiments and ignores the evidence in other papers that shows that really B/Ca is not at all reliable in open ocean foraminifera as a tracer of the carbonate system. These open ocean studies must be considered and the claims on behalf of B/Ca as a proxy needs to be removed.

Line 68: Line beginning 'At low'.. This sentence would be better off earlier where you mention pH-dependent speciation in Line 65. As it stands the thread of the paragraph is a little disjointed.

Line 79: Suggest removing pteropods from here since people don't tend to use them for boron work.

Lines 81-85: Pioneering as these studies were, the field has moved on quite a lot since then, and I am not sure I see the logic in dwelling so long on the specific findings of these studies when they have been superseded by better estimates of these pH

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values. Indeed, this whole paragraph isn't really necessary. The authors could make their point very quickly with one statement that 'The boron isotope-pH proxy is a widely used palaeoceanographic tool (a few example references).'

Line 111-113: Which studies use this approach?

Line 113-114: Surely a changing CCD depth wouldn't invalidate the approach strictly speaking, it would just mean you can't use one estimate for a whole long term time series- you have to estimate for each data point?

Line 95: proven, rather than proved.

Line 107: I may be missing something but I'm not sure I see the link with the hydrological cycle?

Lines 93-114: I'm not convinced that the authors are right to present alkalinity as such a paralysingly big problem as the tone of this passage suggests- it surely depends what the goal is. If the goal is to reconstruct CO₂ changes, yes alkalinity introduces some uncertainty and it would be better if we knew it, but alkalinity has a relatively small influence on pCO₂ values reconstructed from pH, and many studies can just factor in the uncertainty on these estimates into their error propagation. I would suggest the authors reword this somewhat to just make the point that knowing the second parameter would be great to reduce uncertainty in CO₂ estimates, rather than present it as such a very acute problem with the proxy. The other question is whether the propagated uncertainty in alkalinity reconstructed from a second proxy (taking into account measurement and calibration uncertainty) would be any lower than the margin of error that can be garnered from things like CCD depth. In reality, given the error bars in figure 2 for example, it would probably be just as large.

Line 130: This is not correct. See for example Fig. 2 of Allen et al. (2012), where pH is kept constant but carbonate ion concentration is varied. Indeed, the authors state that pH was kept constant but carbonate ion increased in Line 128. It's not clear to me what

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the distinction is between the decoupled chemistry of Allen et al and that of Kaczmarek et al? Allen et al. raised [DIC] and tweaked pH via acid and base addition, so did these authors- what's the big difference?

Line 136-138: The authors state here that they believe that this is due to a covariation of nutrients and other carbonate system parameters. I would urge them to read the paper again- since the aim of this paper was to test the carbonate system control on B/Ca, we of course tested carbonate system parameters explicitly and B/Ca ratios show no correlations with carbonate system parameters. We also tested for covariation of phosphate with carbonate system parameters (some of these plots are given in the paper) and they show no relationships (p values greater than 0.05, and R2 values <0.1. On this point, the authors are mistaken, and this must be removed. What's more, the findings of the paper, which are directly contrary to the idea that B/Ca can be used in open ocean settings to derive a second carbonate system parameter, should be properly incorporated into the discussion (as with the findings of Babila et al. and Salmon et al.). I am happy to answer any questions the authors have to address any misconceptions about this study.

Line 193: How were the seawater d11Bs measured? This is presumably a different way from the foraminiferal shells, and so there is the potential for the different analytical approaches to introduce absolute offsets here. These details are critical if we are to evaluate these numbers in an absolute sense, and need to be added. Measurements of natural seawater could also be added to give a feel for the typical reproducibility of the approaches for a standard everyone has.

Line 197: It's not clear to me why Martinez-Boti should be cited here for a salinity of 38.

Line 261: Faraday should be capitalised

Lines 306, 310: 'seawater scale' is a particular definition of pH, and not to do with boron. Better to say 'normalised to natural seawater'.

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Line 342 (and Fig. 3): The choice of uncertainty calculation here seems wrong. The authors show that the repeat measurements of foram d11B within a test vary by far more than the calculated internal error of a single measurement described in Equation 2. It is therefore not reasonable to apply the single measurement uncertainty estimate to the 'whole test' d11B value, as it only accounts for the measurement uncertainty and not the variability between measurements. The best approximation of the uncertainty of the 'true' average bulk-test boron isotope ratio would in this case be 2 standard deviations of the variability within the test- these should be the error bars on Fig. 3 if they are to be truly representative of true variability. On top of this, when presenting the data in 'normal d11Bsw' space, the authors should also propagate the uncertainty stemming from the uncertainty in experimental seawater d11B- since these values are also critical and the uncertainty on these numbers is very large in some cases.

Line 355: Foster identify a relationship between carbonate ion and KD, not strictly B/Ca ratios. This is a really important distinction since Allen and Hönisch (2012) point out that the way KD is calculated can drive a correlation without any coherent pattern in raw B/Ca ratios.

Line 360-365: This is what Allen et al. (2012) did, and the conclusions reached are largely the same as this study. It seems therefore odd to mention two older studies in this paragraph first in Foster (2008) and Allen et al. (2011), but not mention the more relevant study right from the off. It has the effect of almost suggesting this study is the first to do this, but in fact it is largely replicating what Allen et al. (2012) did.

Line 376-379: What is Fig. 5.1C? The discussion is a little odd here. Since the argument with competition is that B/Ca will correlate with the ratio of borate to carbon species, then these observations are to be expected: changing carbonate ion without changing pH changes the denominator, and changing pH without carbonate ion changes the numerator in altering boron speciation. So these are two sides of the same coin.

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Line 391-392: This sentence as it is currently phrased suggests that Yu et al. (2007) would support bicarbonate being critical here rather than DIC or carbonate ion. However, this is not strictly true: Yu et al. (2007) never tried to regress against borate/DIC in that paper. Just because they present borate/bicarbonate in this paper, it doesn't rule out the possibility that the correlation with borate/DIC or borate/carbonate might have been stronger. This passage therefore needs to be rewritten.

Line 412-414: Is there any a priori reason for us to ever expect this? If so, it might be good to give it here.

Line 423: Need to be clearer here – values for what? Borate ion.

Lines 437-441: Note again, this is fine in culture, but is ignoring plenty of open ocean data that suggests that the control of HCO₃⁻ on B/Ca is overwhelmed by competing controls.

Lines 462-464: Again, this is suggesting that these culture observations can be transferred to the open ocean when a number of more recent studies that the authors do not cite here (and should) show that these relationships don't hold up outside of the lab.

Fig 3: In panel A, these data from other studies are all plotted on one d11B-pH plot. But critically, pK*B differs between each study. Therefore some of the variation in behaviour of d11B with pH in each study can derive from a different pK*B in each case. This is why we have moved towards plotting things in d11Bcalcite-vs-d11Bborate space. To represent these data in an informative way, each datapoint needs to be normalised to a single pK*B, which is clumsy to try and do. I would advise that the authors plot these data in a calcite vs borate d11B crossplot instead. How also were the lines constructed between points? Also, as mentioned above, error bars should also account for the uncertainty in d11Bsw that is carried through into these normalised d11B values. Why are there no error bars on pH, also? There should be. Finally, I see no benefit in plotting the Kakihana et al borate ion curve in panel A at all- this value is defunct, and has been shown to be erroneous (Rustad et al. 2010), so why plot it?

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