

## ***Interactive comment on “ $\delta^{11}\text{B}$ as monitor of calcification site pH in marine calcifying organisms” by Jill N. Sutton et al.***

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We wish to thank the reviewer for their succinct and thoughtful analysis of our manuscript and criticisms concerning the calculation of pH for calcite d11B.

Our intention with this manuscript was to consider calcification site pH as the primary driver of the observed range in d11B values for the evaluated species as a primary hypothesis, and to discuss whether the values we obtained made sense given what else is known about their bio-calcification strategies including independent measurements of internal pH from other methods (eg. pH sensitive dyes, microelectrodes). Our intention was to set up this hypothesis as a straw man to see whether our data were constant with the idea of primary pH control across these diverse species, and if it was

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not then to discuss other factors that could be at play. At a number of points in the manuscript we also explore possible alternative explanations including mineralogical effects, boric acid incorporation, and we also discuss uncertainties in the calculation of an absolute pH value from carbonate  $\delta^{11}\text{B}$  values.

We agree with the reviewer that it is possible that there are additional complications to the interpretations in calcitic organisms. In particular, the possible incorporation of trigonal boron/boric acid into the skeleton and many of the studies mentioned are already referenced in the text. This was addressed to a degree in the original text. For example, lines 329-331 we state "Boron co-precipitation with inorganic  $\text{CaCO}_3$  (i.e. abiogenic) is known to be dependent on solution pH and inorganic  $\text{CaCO}_3$  precipitation rate, however, the relative abundances of the inorganic B species in solution that are incorporated into inorganic  $\text{CaCO}_3$  (borate ion and boric acid) have been shown to be independent of the parent solution pH (Mavromatis et al. 2015)." and also lines 365-370 where we state "...raising the possibility that coralline red alga incorporate both species of dissolved inorganic boron during calcification. In support of this argument, Cusack et al. (2015) provide NMR data indicating that 30 % of the B incorporated into the coralline red alga *Lithothamnion glaciale* was present as boric acid. However, since the coralline red algae were reared at a pH of 8.1, the  $\delta^{11}\text{B}_{\text{CaCO}_3}$  compositions observed for the coralline alga in the present study would require incorporation of both inorganic species of boron at  $[\text{B}(\text{OH})_3]:[\text{B}(\text{OH})_4^-]$  ratios of ca. 75:25, not the 30:70 ratio observed by Cusack et al. (2015)."

Nevertheless we agree that this information could be more prominently addressed in the main text and propose that a series of changes could be included to address this alternative hypothesis that particularly affects the calcite mineralizing organisms. For example, we can add a clarifying sentence in the abstract and provide more discussion to section 4.2. We believe an interesting aspect of our study is that of the three calcitic organisms analyzed, only one of them has  $\delta^{11}\text{B}$  values (the coralline alga,  $35.89 \pm 3.71 \text{ ‰}$ ,  $n = 3$ ) potentially consistent with boric acid incorporation, as suggested in

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Noireaux et al., 2015, EPSL, Balan et al., 2016, GCA; Branson et al., 2015, EPSL; Mavromatis et al., 2016, GCA. This possibility has also been explored in a NMR based study of coralline algae by Cusack et al. 2015 and we did cite this study on lines 366-370 and provide some discussion, as mentioned above. Nevertheless we agree with the reviewer that aspects of the text could be tightened up in this respect (for example clarifying the findings of Noireaux et al., 2015 as the reviewer highlighted).

The high-Mg calcite urchin species we studied have low  $d_{11B}$  values, with one species even having a value that is actually lower than the seawater borate  $d_{11B}$  value (the temperate urchin *A. punctulata*;  $16.28 \pm 0.86$  ‰,  $n = 3$ ; Tables 3 and 4). Given these values in the two species of urchin-examined incorporation of significant amounts of seawater boric acid with much higher  $d_{11B}$  values, seems unlikely.

In our manuscript we do have a separate section discussing biomineralization strategies of each organism studied (sections 4.2.1 to section 4.2.5), however in response to the reviewer's comment we can certainly expand this.

We also accept that there are of course many previous studies reporting a range of  $d_{11B}$  values in marine organisms. However we believe a striking finding of our study is the extreme range (20 per mil) we observed in species that were cultured in environmentally controlled and equivalent conditions.

-Lines 42-43, some of the references cited here are not related to boron isotopes, e.g. Saenger et al., 2013; Zinke et al., 2014.

Author Response: Originally these references were meant to indicate that corals have disequilibrium "vital" effects in other isotope systems but they can be removed from this sentence since it does not make sense to include them now.

-Lines 46-47 " $^{11}B$  composition of borate in seawater ( $^{11}BSW$ ; Pagani et al., 2005) "  $^{11}B_{sw}$  is commonly used to indicate boron isotope composition of seawater other than that of borate. Please modify.

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Author Response: This should read “d11B composition of borate in seawater (d11B(OH)<sub>4</sub>; Pagani et al., 2005)” and will be changed.

-Line 59, “The 11B of modern seawater is  $39.61 \pm 0.04$  ‰ (Foster et al., 2010)”, 2SD should be used when reporting a replicated and certified value, so the value should be  $39.61 \pm 0.20$  ‰ (Foster et al., 2010).

Author Response: We will fix this.

-Lines 164-168: The setup of culturing experiment should be illustrated in details in the Methods and Materials Section, as well as the method to identify and separate the new growth part of each skeleton or shell for isotope measurement.

Author Response: We can certainly add more information on the culturing setup and information on the method used for new growth identification. To clarify, the cultures presented here were previously reported in another publication, Ries et al., 2009, so we feel it is appropriate to summarize important elements of the culturing setup rather than repeat the very detailed description in that paper.

-Lines 168-171 This is a replicate of Section 2.3, and not an important part for the Introduction, so please remove.

Author Response: We can remove this.

-Line 279 Is the analytical precision shown here 2SD or SD?

Author Response: The analytical precision shown here is 2SD, this will be mentioned in the text.

-Lines 285-286 Please remove this section.

Author Response: We can remove this.

-Lines 333-334 “polymorph mineralogy was not found to influence boron isotope fractionation (Noireaux et al. 2015).” This seems to be in contrary to the conclusion of

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Noireaux et al. 2015 who claim that “Our results indicate that the main controlling factors of  $^{11}\text{B}$  are the solution pH and the mineralogy of the precipitated carbonate mineral”.

Author Response: This is a glaring error on our part. We tried to simplify an argument, and the message was lost in translation. Thank you for picking up on this.

The sentence should read “Although Mavromatis et al. (2015) also found that polymorph mineralogy influences both the B/Ca ratio (higher in aragonite than calcite) and speciation of B in inorganic  $\text{CaCO}_3$  (borate/boric acid ratio higher in aragonite than calcite), B incorporation alone does not appear to influence boron isotope fractionation.

-Lines 336-337 “if shell mineralogy was the primary driver of the observed interspecific variation in  $\text{d}^{11}\text{B}\text{CaCO}_3$  compositions – a trend that is not observed”. As suggested by Noireaux et al. 2015, both solution pH and mineralogy are important factors controlling  $^{11}\text{B}$  in carbonates, differences in calcifying fluid pH may also obscure “this mineralogical trend”, especially the underlying calcification mechanisms of each calcifier remain largely unknown. So, I don’t think mineralogical influences can be easily excluded.

Author Response: We have somewhat touched on this in the points above. We agree that the possibility of boric acid incorporation needs to be discussed. The coralline alga has a  $\text{d}^{11}\text{B}$  value potentially consistent with the mineralogical effect discussed, but not the urchin species.

-Lines 368-370 With such high proportion of trigonal B incorporation, the classic  $^{11}\text{BpH}$  equation cannot be used to calculate the pH, as  $^{11}\text{B}_{\text{carb}} = ^{11}\text{B}_{\text{borate}}$  is the basic assumption for the calculation.

Author Response: As we believe data from only one of our species is potentially (but not necessarily) consistent with significant trigonal B incorporation relative to borate (see responses above) we prefer to discuss this as uncertainty when calculating calcification site pH, adopting the straw man approach we described above.

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-Line 426 but also mineralogy dependent

Author Response: We can add a qualifying addition here.

-Lines 427-432 The premise of using the equation mentioned in the paper to calculate pH by carbonate 11B is that borate ion is the only species that enters into the lattice (for example in aragonite). As suggested by both theoretical calculation and NMR experiment, both boric acid and borate ion exist in the lattice of calcite. Therefore, for those calcite organisms, this 11B-pH equation may not be applicable, and the calculated pH value may not reliably reflect the pH of calcifying fluid.

Author response: This point is largely covered in our response to previous comments.

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