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Biogeosciences
Discussions

Interactive comment on "δ^{11}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 anonymous reviewer for their critical analysis of our manuscript and their helpful comments. We believe that we can address all of the major comments as indicated in the discussion below.

-The manuscript by Sutton et al reports the boron isotope compositions of various marine calcifyers (coralline red alga, urchins, worm, coral, oyster). All the samples came from culture experiment (T=25_C, pCO2=409 μatm) and so should record the same _11B values if no vital effects are present. The _11B range of all the data is about 20‰ and seems to show the biological control on the calcification pH. I found the data interesting, but I think that there are a lot of repetitions through the text. Even

if it is mentioned in the case of coralline red alga, the influence of B3 is not really taken into account. For example, the presence of B3 was also shown in corals, and it was not described in the text. In the figures, the symbols should be different between the calcium carbonate polymorphs.

Author response: We agree that we could expand the discussion on the influence of B3. We assume that in the case of corals, the reviewer is referring to Rollion-Bard et al. 2011b. We did not include a discussion for B incorporation in corals since, as the second reviewer pointed out "NMR is not useful for quantifying % boric acid incorporation (see and reference Balan et al., "First-principles study of boron speciation in calcite and aragonite" GCA 193, 2016)". Although NMR gives evidence that trigonal boron is present in the calcite lattice, it cannot determine whether boric acid was in fact incorporated or if the trigonal boron originated from borate (see alternative mechanisms of boron incorporation in for example Klotchko, 2006; Noireaux et al., 2015).

However, we agree with the reviewers that we should expand our discussion within section 4.2 to provide more information on the different factors (including seawater pH and calcifying fluid pH) that can influence the speciation of boron and δ11B for inorganic calcite and aragonite. We will expand our discussion on this section to make our arguments more clear and include an extra figure (see attached Figure 5) with the following Figure caption: "The influence of pH on the speciation of boron and δ11B (adapted from Rollion-Bard, 2011b). The solid and dashed curves represent the δ11B composition that would result from the incorporation of different amounts of B(OH)3 into the marine carbonates. The dashed vertical lines represent the calculated pH based on the assumption that 0% B(OH)3 is incorporated into temperature coral and 0%, 30% and 75% B(OH)3 is incorporated into coralline alga."

-L53: B(OH)4- -L85: please mention the study of Noireaux et al (2015) -L142: please mention the study of Noireaux et al (2015) -L151-152: Please mention the studies of Rollion-Bard et al (2003, 2011) -L154: Please mention the study of Jorgensen et al (1985)

Author response: We will mention these studies.

-L108, 127: "2" must be in superscript -L327: "range in range", please correct -L358: please remove the part of the sentence concerning boron isotopes. In this sentence, it is explained that there is an enrichment of 11B in corals and that it is supported by 'boron isotope analyses' (of course!). -L477: Kakihana et al (1977) instead of Kakihana (1977) -section 4.3.3: It was already mentioned, please delete this section Table 3: 'JCp-1' instead of 'JCP-1'. -L420: Klochko et al (2006), instead of Klochko (2009) -Table S1: In the caption, specify the pKa and alpha used.

Author response: These will be changed

-section 4.3.3: It was already mentioned, please delete this section

Author response: We think that this information is important to keep in the manuscript since it allows us to present a hypothesis that might explain the wide range of δ11BCaCO3 (20 ‰ observed for the species evaluated in this study. In addition, we would like to add a reference to table 4 to highlight the importance of this information: "Furthermore, there appears to be a moderate inverse relationship between the species' relative ability to elevate calcification site pH and their empirically determined vulnerability to ocean acidification (Table 4)."

-L221: Interest for what? Why the data are not shown in the manuscript?

Author response: The other elements (Ca, Na, Ba, U) are of interest to analyse since they can indicate whether the sample matrix has been washed out of the column. To be more clear, we will change this sentence to: Small aliquots of each sample were measured by single collector HR-ICPMS prior to analyses by MC-ICPMS to verify the retention of B on the column and removal of other elements (e.g. Ca, Na, Ba, U).

The B data are shown in the manuscript, see lines 275-278.

-L243-244: It was already mentioned, please delete

Author response: I disagree, we did not state "Boron yields are evaluated by tracking B throughout the entire procedure." prior to this sentence.

-L256: I suppose that there are older references than McCulloch et al (2014) for the MC-ICP-MS method.

Author response: Yes, this is true. McCulloch et al. 2014 did a great job of describing the development of the MC-ICP-MS method for the analysis of B isotope analyses and in this case we felt it useful to cite a recent paper that summarizes the state of the art on method development. We will change the citation as follows: (see McCulloch et al, 2014 for up-to-date summary of methods).

- section 3.1.1.: Do you have an idea why the measurements on JCt-1 are more variable?

Author response: The JCt-1 measurements in our study were variable for the different methods of sample injection (NH3 and d-DIHEN) but we did not see this variability for other samples or standards analysed with the same methods. We are not sure why the d-DIHEN method did not provide accurate results for JCt-1, but this has not influenced our conclusions. Further, the errors are still within acceptable limits as can be seen by the variability of the inter-laboratory study (lines 280-281).

-L288, 324: please add the errors on the _11B values

Author response: We didn't think it was necessary here since we are indicating the overall range in δ11B values. We present the error bars related to the δ11B of each species in the sentences that follow.

-L290: Why the error on the _11B value of the coralline alga is so high?

Author response: As the reviewer noted, the intra-specific (same species but different organisms) reproducibility for the red coralline alga is large, however, the intra-organism (sub-sampling the same organism) and analytical reproducibility is not (see Table 3). This suggests that there is significant geochemical variability across the

skeleton of this organism, but the analytical reproducibility is robust. We will make a more specific note of this in the text starting on line 289: ". . .and summarized in the text that follows. Note that the average data presented here (Table 4) represent intra-species reproducibility (i.e. measured differences between individual organisms of the same species), which can be substantial however, the intra-organism (sub-sampling of same organism) and analytical reproducibility (Table 3) are typical of single organism δ11B analyses."

-L334: No, in Noireaux et al (2015) there is a clear effect of the mineralogy (see figure 1)

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 CaCO3 (borate/boric acid ratio higher in aragonite than calcite), B incorporation alone does not appear to influence boron isotope fractionation."

-L370-371: What would be the pH of calcification if there is effectively 30% of B3? The _11B value of coralline alga could result from the combination of a pH increase and the incorporation of a certain proportion of B3.

Author response: The reviewer asks an interesting question that can not be answered simply but does merit an extended discussion in the manuscript. Several related factors might influence the boron isotope composition of a calcifying organism including: the pH at the calcification site, the influence of pH on the speciation of B at the calcification site, boric acid incorporation into the calcite matrix, and the influence of boric acid on the trigonal structure of the lattice. Cusack et al. (2015) suggested that 30% of B in the calcite of a different coralline algae species was present in the trigonal B3 form; however, this does not necessarily suggest that the calcification fluid contained 30% boric acid or that 30% boric acid 70% borate was incorporated into the calcite

lattice. Further empirical work is needed to clarify this relationship. However, if we were to ask the hypothetic scenario; what would be the pH at the calcification site be if 30% boric acid was available at the calcification site prior to biomineralization., we can answer that the calcification site pH would still be as high as 9, which is well above the ambient seawater pH of 8.1 (see table 4). As mentioned above, we will expand our discussion on this section to make our arguments clearer and include an extra figure (see attached Figure 5) with the following Figure caption: "The influence of pH on the speciation of boron and δ11B (adapted from Rollion-Bard, 2011b). The solid and dashed curves represent the δ11B composition that would result from the incorporation of different amounts of B(OH)3 into the marine carbonates. The dashed vertical lines represent the calculated pH based on the assumption that 0% B(OH)3 is incorporated into temperature coral and 0%, 30% and 75% B(OH)3 is incorporated into coralline alga."

-section 4.2.3: What are the calculated pH if the results of Noireaux et al (2015) for inorganic calcite are taken into account?

Author response: We agree with the reviewers that we should expand our discussion within section 4.2 (as described previously in this response to reviewer) to provide more information on the different factors (including pH) that can influence the speciation of boron and δ11B for inorganic calcite and aragonite.

-L402: please remove 'Notably....worm tubes'

Author response: We will change this to: "To our knowledge these are the first reported B isotope measurements for worm tubes"

-L420: please remove 'Notably....oysters'

Author response: We will change this to: "To our knowledge these are the first reported B isotope measurements for oysters"

-L495: It is obvious. I do not see the point here.

Author response: We thought it was important to clarify this point since it may not be obvious to all readers the extent to which alpha varied and our aim is to make the manuscript accessible to readers who may not all be very familiar with the boron isotope proxy so some basic statements like this can be valuable.

Figure 1: Please use the alpha of Klochko et al (2006) and specify in the caption the pKa used and the alpha used.

Author response: We will modify the figure attached above. The calculations are based on pKb = 8.1 (in seawater at 25 °C and a salinity of 35 under atmospheric), alpha=1.0272, d11Bsw=39.61

Figure 2: Please add data of Reynaud et al (2004), Lécuyer et al (2002), Farmer et al (2005). Please use the full name species of the foraminifera. 'Brachiopod' instead of 'Brochiopod'; 'Penman' instead of 'Penmen'.

Author response: We aim to show boron isotopic composition from the most studied marine biogenic carbonate archives including corals, foraminifera and bivalves. We also want to show that the data has been reported to follow different borate fractionation curves. Therefore, we have chosen studies that have more than two boron data points in a wide range of pH conditions, which aim to calibrate/validate the 11B-pH proxy in different species. For the above purpose, we will also replace the reference from Foster et al., 2008 to Holcomb et al., 2014, Sanyal et al., 1996 and Henehan et al., 2013.

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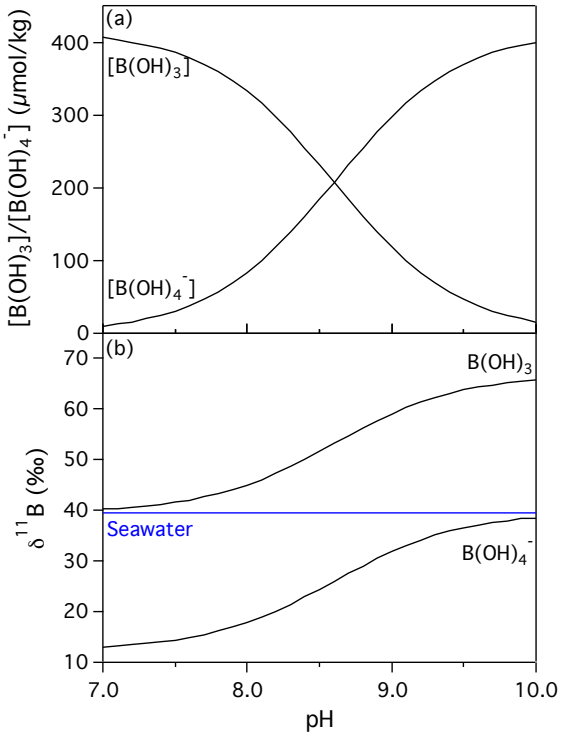

Fig. 1. Modified Figure 1

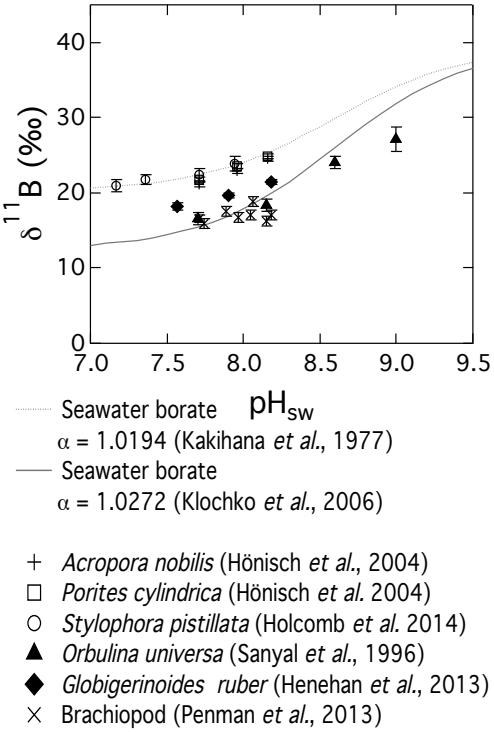

Fig. 2. Modified Figure 2

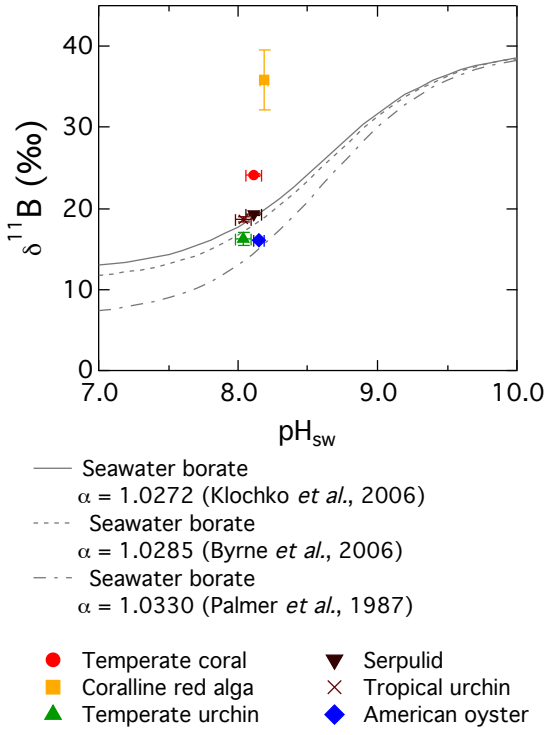

Fig. 3. Modified Figure 4

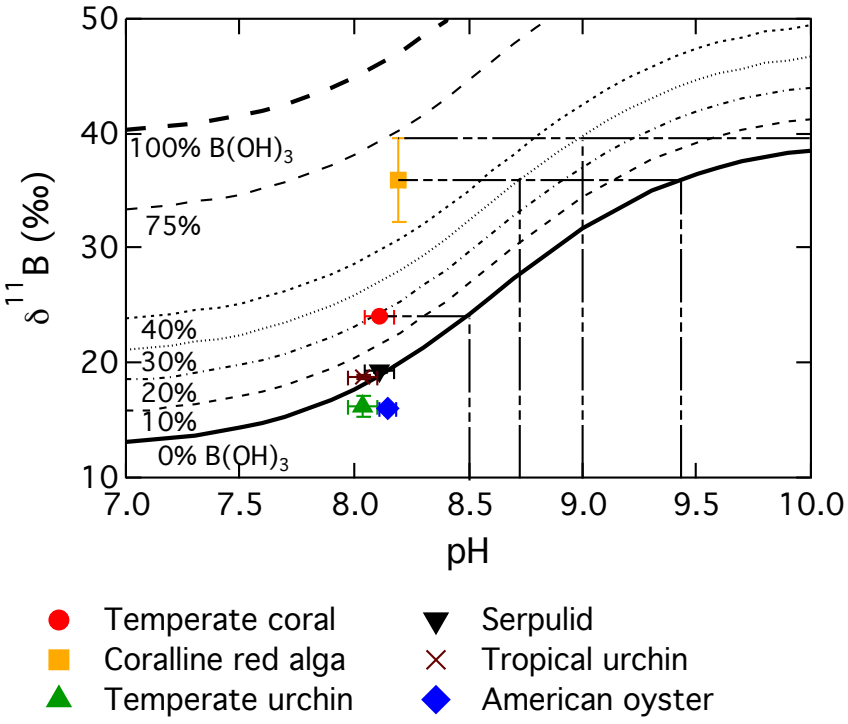

Fig. 4. New Figure 5