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Biogeosciences Discussions

Interactive comment on "Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO_2 gradients" *by* Maxence Guillermic et al.

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Guillermic et al. present boron isotope measurements of seven species of planktonic foraminifera from seven coretop sediment samples. In addition to providing new and expanded boron isotope calibrations for these taxa, the authors interpret variations in foraminifer δ11B (and to some extent, B/Ca) data in terms of varying calcification depths and microenvironment influences, with particular focus on how light availability at the depth of calcification may impact symbiont photosynthesis.

The introduction, background, materials and methods, and results are well written and clear, and I think the authors' data are a welcome addition to the δ11B community. However, I have significant reservations on aspects of the discussion that will require detailed revisions before this manuscript is suitable for publication.

Three general comments:

1) Foraminifera depth habitats and thermocline depth. To what extent are differences in foraminifera depth habitats between the different studied oceanographic regions simply a function of variations in thermocline depth? This point could be clarified throughout the manuscript. If true, it seems a particularly important outcome of this study is a need to combine planktonic foraminifera δ11B with thermocline depth reconstructions.

2) In section 5.2 (L482-514), the authors posit a primary control of light availability on foraminiferal δ11B deviations from δ11Bborate. While an interesting idea, unfortunately I think the weight of this section is not supported by the authors' data. This whole discussion is essentially predicated on a single T. sacculifer δ11B measurement from the western Equatorial Pacific, which has anomalously low δ11Bforam value (relative to δ11Bborate) compared to previous studies. The authors use this single observation to make a complex argument about how foraminifera calcification depth impacts light availability, which impacts symbiont photosynthesis, which affects microenvironment pH and hence foram δ11B. Not only does this strike me as insufficient evidence to justify a discussion of this length, there are numerous assumptions and issues within the discussion that require referencing and clarification (see detailed comments below).

3) Section 5.4 gives a rather hasty overview of how measuring δ11B in different foraminifera species can reconstruct the upper water column pH and pCO2 gradients. I believe this is one of the big strengths of this paper and would like to see an expanded discussion of the depth profiles. One concern is that there may be some circularity here. If the authors have calibrated δ11Bforam to modern profiles of δ11Bborate, then by default they would correctly reconstruct the pH and pCO2 profile of the water column

with the calibration dataset. There are no free parameters.

Detailed comments

L49. Change “several” to “many” taxa. L50. Specify “we report δ11B data” L62. Either change to carbon pumps, or specify which pump to which you refer (biological?) L54-61: The primary results are a bit vague. I encourage greater specificity in the key results (but see general comments above).

L64-66. Change to “resulting in declining surface ocean pH”. I would caution against calling this decline “steady”.

L73. Change reference to Allen and Hönisch, 2012 for formatting consistency.

L81. also spell out DIC

L89-90. remove Rae et al. 2011 reference here, as this study of benthic forams was not intended to directly constrain atmospheric pCO2.

L90 and 93. These are two separate Martínez-Boti et al. (2015) papers and should be referenced as 2015a (Pliocene) and 2015b (eastern Equatorial Pacific & Subantarctic)

L96-97. Delete first sentence, and change second sentence to “In this study, we make critical additions to the emerging pool of boron isotope data for coretop. . .”

L100. Subscript on 3; e.g., CaCO3

L101 vs. L98. Pick either core-top or coretop throughout the manuscript

L118-120. While interesting, the PETM δ 18O profile work is quite tangential to the current study and should be removed.

L121. Reword to either “Because planktonic foraminifera species..., it is thus. . .” or “Planktonic foraminifera species. . ., therefore it is thus. . .”

L124-125. Either Palmer and Pearson (1998) pioneered this approach and the “perhaps” should be deleted, or someone else did and should be referenced accordingly.

Please revise.

L128-130. This comes across a bit awkward; suggest rewording to something like “Furthermore, δ11B differences between foraminifera species from the same pH makes the acquisition of more modern. . .”

L136. Remove “equal to” (repetitive)

L148-153. The terminology for isotopic fractionation factors and fractionations is incorrect. For Klochko et al. (2006), the fractionation factor, αB, is 1.0272, and the fractionation, εB, is the per mil value of 27.2$\pm$0.6‰Ṡee, e.g., Table 1 in Farmer et al. (2019) GCA. Please change to correct terminology throughout this paragraph.

L166-167. Benthic foraminifera δ 11B are only tangentially relevant to the results of this manuscript, so I recommend deleting this clause and associated references. Unless the benthic δ 11B results directly shed light on your interpretation (as is the case for Amphestegina, below).

L180. Specify that Amphistegina lobifera is a shallow-water, symbiont-bearing benthic foraminifer.

L182. Change “taxon” to “taxa”

L187/Equation 2. To me, this equation is an odd depiction of the cumulative effects of calcification, photosynthesis, respiration and dissolution. Suggest separating into two equations: one for calcification/dissolution, and another for photosynthesis/respiration.

L189-195. Please clarify this paragraph. I think the authors are trying to make the point that, while seawater pH provides a primary control on foraminifer δ11B, microenvironment pH alterations from calcification, respiration, and symbiont photosynthesis also contribute to foraminifer δ11B, and may account for species-specific δ11B offsets. But it is not clear as written.

L212-224. It may be worth noting here (or perhaps earlier) that this manuscript largely

focuses on tropical/subtropical foraminifera.

L255. Were the samples dissolved in 1N HCl or HNO3? And why the two different acid matrices? HCl causes interference issues with ICP-MS measurements. Maybe this does not matter with the microdistillation step, but I'd like to see some explanation (see L260).

L283-286. Recommend splitting this into two sentences, one on the procedural blanks and one on the acid backgrounds/memory effect.

L288. As a field, we need to stop considering NEP as a "standard". It is not sufficiently homogenous to be useful for δ11B analyses in foraminifera, where precisions of «1‰ are absolutely necessary for the vast majority of paleoceanographic purposes.

L296-298. You should cite the Gutjahr et al. Goldschmidt intercalibration abstract that defines multiple laboratory values for JCp-1: "Boron Isotope Intercomparison Project (BIIP): Development of a new carbonate standard for stable isotopic analyses".

L308-310. I'm surprised that the HF matrix prevents a B memory effect on the Neptune+, but not on the Element XR. To my knowledge, both instruments have effectively the same frontend plasma setup. Can you comment more on this? Does this high B background result from other measurements on the XR, e.g., rock digestions with really high B content? Did you swap out cones, etc? (This comment does not necessarily need to be addressed within the manuscript, I'm just curious).

L344. Rephrase to "Two carbonate system parameters are essential to calculate the entire carbonate system".

L349-350 and Figure 4. Please plot the δ11Bborate uncertainties on Figure 4. If they are too small to be observed, please note that in the figure caption.

L360-366. It would be useful to indicate the general ranges of depths for these different foraminifera here. E.g., L363 "shallow mixed layer (0-100 m), with T. sacculifer living or migrating deeper than G. ruber (down to 125 m)."

L380-382. Except your G. ruber results are not consistent at the low δ11Bborate end; they are $\sim$1‰ lighter than Henehan et al. (2013) found in sediment traps. It is very important that you state this observation because this is the principal reason for your elevated δ11Bforam to δ11Bborate slope relative to Henehan and Sanyal.

L397-398. Careful overinterpreting limited data here. If you calculate δ11Bforam-δ11Bborate for all sacc and w/o sacc specimens, I doubt you will find a significant difference in δ11Bforam elevation between the two T. sacculifer forms.

L400-417. This is well put.

L422-424. See above comment on L380-382.

L427-439. It could be worth making an updated version of Henehan et al. EPSL 2016's Figure 7 and including this in the main text.

L433. $p<0.05$

L438-439. One option- you could test the influence of sediment core water depth and foraminifer water depth with a multiple linear regression and see if either influence dominates B/Ca.

L453. Suggest starting a new paragraph with the sentence "We find..." and merging with the below paragraph starting on L456.

L457-459 and again L462-463. This is just another way of saying that the depth of the thermocline differs at each location, correct? If so, really what we need are proxies for thermocline depth.

L474-475. Yes, but this might not matter as much for foraminifera δ11B. At higher latitudes, the seasonality of primary production (& hence foraminifera growing seasons) will be more tightly constrained due to the seasonal progression of winter light limitation and intense vertical mixing and summer nutrient limitation.

L478. Specify seasonal δ11Bborate at a fixed depth

L483. Do not use articles when you can be more specific; it creates unnecessary ambiguity. Here, state "foraminifera δ11B" instead of "the δ11B signature".

Section 5.2 (L482-514) detailed comments:

1) You have not yet discussed symbionts in these different foraminifera species until near the end of the section (L509-512). Be explicit about what is known about symbionts in all studies species with an introductory paragraph at the beginning of this section. How biologically similar are the symbiont assemblages in different foraminifera species? Is their concentration, photosynthetic activity, etc. similar? Do they show the same dependence on light intensity to maintain photosynthetic activity?

2) Following on the above, it is not clear to the reader whether "weaker photosynthetic activity" (L487) corresponds to an absence of symbionts, less active symbionts, lower symbiont density, lower light levels, etc. Please clarify.

3) L490. Is symbiont photosynthetic activity a function of light level alone? What about symbiont composition? This comes across as highly speculative without references; please either include references or phrase as a speculation. (In general, it is fine to speculate a little, as long as the reader is aware that you are speculating).

4) Light intensity in the ocean is not a function of water depth alone; turbidity matters quite a lot. Is it reasonable to compare the light intensity in different oceanographic regions as a function of water depth alone?

4) L492. The negative relationship between Δ11B and water depth in Figure S2 is driven only by the low δ11B measured in western equatorial Pacific T. sacculifer. Have you propagated your uncertainty in depth habitat to δ11Bborate in your calculation of Δ11B as plotted in Figure S2? Looking at the western equatorial Pacific (WP7-01), the 80$\pm$20m depth range from CD2 corresponds to a $\sim$1‰ δ11Bborate range (Fig. 4). (If you include the CD3 estimate of 125$\pm$15 m, the total possible δ11Bborate increases to $\sim$1.5‰. Add on the δ11Bforam measurement uncertainty of $\pm$0.22‰ and I cannot see

how you get a total Δ11B uncertainty of <1‰

5) I do not think linear regression is the appropriate test statistical test for the significance of the Δ11B-water depth relationship, because depending on how you performed the regression, it may not account for the uncertainty on each datapoint. A t-test for mean difference between Arabian Sea, Indian Ocean, and western equatorial Pacific T. sacculifer Δ11B would be more robust. I would bet that such a test will indicate no significant Δ11B difference between the different regions given the small sample sizes. If true, this detailed line of discussion is unnecessary; instead, you can present this as an observation that requires future study to confirm or deny.

L525-527. What do you mean by "higher values " here? Slopes of δ11Bforam to δ11Bborate regressions, or Δ11B, or something else?

Any precipitation rate implications need to be very carefully phrased. The higher "values" for G. ruber and T. sacculifer have large uncertainties, so they are probably not robustly higher than other species (unless a statistical test confirms this to be true). Moreover, it is unclear the extent to which the growth rates of different foraminifera species differ from one another. Nevertheless, your point on higher B/Ca sensitivity to borate/bicarbonate in the shallower species is very interesting.

L540-541. There is no Figure 10?

L541-542. Given the speculative nature of the depth/light effect on symbiont photosynthesis, foraminifer microenvironment pH and thus foraminifera δ11B, change to "which may be explained by the deeper depth habitat for these taxa in the WEP, where lower light levels might reduce symbiont photosynthetic activity". Or remove.

L543-548. See general comment #3

Figure 1. Is this necessary?

Figure 2. Please make the text font larger; the labels and annotations are difficult to read at this size.

Figure 3. It would be interesting to also plot thermocline depth, contoured or otherwise. There are global datasets of mixed layer depth (see https://odv.awi.de/data/ocean/mixed-layer-depths/), which should be a reasonable proxy.

Figure 4. See Figure 2 comment and above comment about including δ11Bborate uncertainty.

Figure 7. I really cannot follow this figure at all. Should there be a pH axis?

Figure 8. See Figure 2 comment.

Figure 9. No caption?

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