

Review of Sutton et al.
Jesse Farmer

Overview: Excellent job revising by the authors. This is now very close to publication quality. I have one major and several minor (mostly copyediting) comments. I recommend this for publication once the major comment on the introduction is addressed.

Big stuff:

Check table #s; they do not correspond to their order in the text.

L44-48: I think the presentation would be clearer if this section is moved down to the paragraph starting on line 76. At that point you have introduced the relevant factors (α , pK_B^*) in lines 49-75.

L71-85 (and including L44-48): As in the previous version, there is still a misrepresentation of how the community gets between carbonate $\delta^{11}B$ measured on a mass spectrometer and pH. You actually get this right at the end of the discussion (L504-509), but this needs to be in the introduction and not the discussion. I will revoke any copyright claim to this and recommend the authors include the following:

First, there is the theoretical model for $\delta^{11}B_{\text{borate}}$ varying with pH_{sw} , given by the following equation (please include and cite Zeebe and Wolf-Gladrow, 2001):

$$pH = pK_B^* - \log\left(\frac{\delta^{11}B_{CaCO_3} - \delta^{11}B_{sw}}{\delta^{11}B_{sw} - \alpha_B * \delta^{11}B_{CaCO_3} - \epsilon_B}\right)$$

Uncertainties in this model stem from uncertainties in the variables pK_B^* , $\delta^{11}B_{\text{sw}}$, and primarily α (as you discussed on L59-71 and evaluate in the discussion). Pagani et al. (2005), Foster and Rae (2016) have nice discussions of these uncertainties that you can cite here.

2) Using $\delta^{11}B_{CaCO_3}$ to derive pH_{sw} requires knowledge of the relationship between $\delta^{11}B_{CaCO_3}$ and $\delta^{11}B_{\text{borate}}$. One option is to assume that $\delta^{11}B_{CaCO_3} = \delta^{11}B_{\text{borate}}$, as was done by early studies (e.g., Hemming and Hanson, 1992). However, Sanyal et al. (2000-GCA and 2001-Paleoceanography) pointed out that different carbonates (inorganic calcite, *O. universa*, and *G. sacculifer*) exhibited offset relationships to $\delta^{11}B_{\text{borate}}$. To quote from the 2001 Paleoceanography paper (emphasis added):

“It is noteworthy that empirical $\delta^{11}B$ versus pH curves for both biogenic and inorganic calcite plot close to the calculated $B(OH)_4^-$ curve, indicating that the charged species is preferentially incorporated into the carbonates. A parallel offset, however, was identified between the theoretical $B(OH)_4^-$ curve and the empirical $\delta^{11}B$ vs. pH curve of both *O. universa* and inorganic carbonates. This

suggests that the calculated $B(OH)_4^-$ curve cannot be directly applied to estimate paleo-pH from the $\delta^{11}B$ of all carbonates.”

Thus, it was known that $\delta^{11}B_{CaCO_3} \neq \delta^{11}B_{borate}$ even before Pagani et al. (2005). As a result, empirical calibrations between $\delta^{11}B_{CaCO_3}$ and $\delta^{11}B_{borate}$ are needed to calculate pH, as discussed by Hönisch et al. (2007-comment on Pagani et al. 2005), Foster (2008), Henehan et al. (2013), Farmer et al. (2015), Henehan et al. (2016), and Foster and Rae (2016). The current practice of the field is to use these empirical calibrations to calculate $\delta^{11}B_{borate}$ from $\delta^{11}B_{CaCO_3}$, and then use the above theoretical model (with its uncertainties) to calculate pH_{sw} . In other words, $\delta^{11}B$ -based paleo-pH reconstructions do not assume that $\delta^{11}B_{CaCO_3} = \delta^{11}B_{borate}$.

This leads in nicely to your Section 1.3 (L138) because your study interrogates one reason why $\delta^{11}B_{CaCO_3}$ may not equal $\delta^{11}B_{borate}$ (namely, $pH_{cf} \neq pH_{sw}$).

In addition, this has one small and one big implication for the manuscript. First, on L71-75 you state “empirical species-specific calibrations between $\delta^{11}B_{CaCO_3}$ and pH_{sw} are likely more appropriate than theoretical α values”. This is not correct! The empirical species-specific calibrations are presented as between $\delta^{11}B_{CaCO_3}$ and $\delta^{11}B_{borate}$. To get from $\delta^{11}B_{borate}$ to pH requires the theoretical model (equation above), which depends on α . See/cite equation 1 in Hönisch et al. (2007) and equations 24 and 26 in Foster and Rae (2016). To summarize, empirical calibrations are not more appropriate than theoretical α values; in fact they require α , but they are more appropriate than assuming that $\delta^{11}B_{CaCO_3} = \delta^{11}B_{borate}$.

Second, because this manuscript presents $\delta^{11}B_{CaCO_3}$ values at only a single pH, you do not know the true relationship between $\delta^{11}B_{CaCO_3}$ and $\delta^{11}B_{borate}$ for your calcifiers. Therefore your calculated pH values must assume that $\delta^{11}B_{CaCO_3} = \delta^{11}B_{borate}$. If this study attempted to reconstruct paleo-pH, this assumption would invalidate the reconstruction and the pH values should be treated with suspicion. However, because you do not have a range of pH values for each specimen, you are essentially forced to assume that $\delta^{11}B_{CaCO_3} = \delta^{11}B_{borate}$. That is OK for the purpose of exploratory studies like this one, just be sure to state this assumption explicitly in the text (see my comment on L327). In general, you have done well to highlight this assumption throughout the discussion.

Specific changes:

L108: remove “forecasted,” atmospheric pCO_2 has definitely risen!

L114: change “that they need” to “needed”

L170-171: Specify what efforts were made to minimize sample exposure to laboratory air. Did you take the caps off just before analysis?

L187: As this is the first mention of a table in the text, this should be Table 1.

Sections 2.3 and 2.4: You use MQ and UHQ interchangeably throughout; please change all to UHQ (or MQ).

L210-211: You mention this later on L228 how the UHQ water was pH buffered; please specify that detail here as this is the first mention of pH buffered water.

L265: Briefly summarize why d-DIHEN reduces memory effects, as you do for the ammonia injection.

L282: Typo- NH₃ subscript should be on $\delta^{11}\text{B}$

L280-285: For comparison of the standard values, you should do a formal statistical test (t-test) for differences of averages. The d-DIHEN $\delta^{11}\text{B}$ values for Jct are just barely within overlapping 2sd of the Gutjahr values and are probably significantly different with an alpha of 0.05.

L312: Again, a formal statistical test is needed here to support this assertion.

L327: Here you should say something like “Because our specimens come from only a single pH, we cannot constrain whether the relationship between $\delta^{11}\text{B}_{\text{CaCO}_3}$ and $\delta^{11}\text{B}_{\text{borate}}$ significantly differs from unity, as is observed in other marine calcifiers (refs or cite intro section). Therefore, we assume that $\delta^{11}\text{B}_{\text{CaCO}_3}$ reflects only $\delta^{11}\text{B}_{\text{borate}}$, and thus that only borate ion is being incorporated into CaCO_3 . Given this assumption, the wide variation in $\delta^{11}\text{B}_{\text{CaCO}_3}$...”

L331-343: Two items of note here:

- 1) It is worth mentioning that Mavromatis and Noireaux experiments are from solutions with quite different chemistry than seawater, and thus the appropriateness of their conclusions for marine carbonates are still uncertain.
- 2) The B speciation from these experiments was derived via NMR. However, NMR only tells coordination state (tetrahedral/trigonal). Because there are multiple possible B incorporation pathways and B coordination (see/cite Balan et al., 2016), NMR cannot distinguish between boric acid and borate. On L 335, I would rephrase this to say “and coordination of B in inorganic CaCO_3 (tetrahedral/trigonal ratio higher in aragonite than in calcite)”. Then say that if coordination reflected the borate/boric acid ratio, aragonite-producing species should have a universally lower $\delta^{11}\text{B}$ than calcite-producing species because $\delta^{11}\text{B}_{\text{borate}}$ is always lower than $\delta^{11}\text{B}_{\text{boric acid}}$.

L367: Same point on NMR being coordination; at best this *may* represent boric acid incorporation.

L373-376: There it is! Excellent, move this discussion up to L331-343 area when you first discuss Mavromatis/Noireaux data, and then reference it again here.

Section 4.2.2 There are multiple instances where spaces are needed between words and at ends of sentences—check this.

Section 4.2.3 Interesting. Without tooting my own horn here, I'd recommend mentioning that the relative $\delta^{11}\text{B}$ deviations are quite similar to that observed in the high-Mg calcite of bamboo corals by Farmer et al. 2015. Perhaps there is something systematic about $\delta^{11}\text{B}$ in HMC?

L404: space between “initially” and “produce”

L425: “which has been attributed to”

L504-509: Here you say what you should in the introduction. Remove this from here and incorporate this into the intro.

Fig. 1 caption: note typo on pK_B

Fig. 2: please mention why you chose these particular datasets to show; there are a lot more B isotope data available than just this figure. Also, please narrow the y-axis to between 10 and 40 per mil.

Fig. 5: Nice figure! Could you also draw a line for the oyster and temperate urchin back to $\delta^{11}\text{B}_{\text{borate}}$, and then down to pH?