

## ***Interactive comment on “The pH dependency of the boron isotopic composition of diatom opal (*Thalassiosira weissflogii*)” by Hannah K. Donald et al.***

**Hannah K. Donald et al.**

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We thank this reviewer for his comments and we are pleased that he favours publication and recognises the importance of this contribution. In order to harvest sufficient biomass from our dilute batch cultures we had to let them continue longer than we would have if we were going to avoid significant pH drift. We agree with the reviewer that this is a weakness of this current study but we do acknowledge this in the manuscript and recommend a different approach for subsequent studies. We respond to the rest of RC2's in turn below.

RC2:“I would love to see figure-S1 in the main body of the paper (with proper data

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legend), which nicely compares the [B] vs pH relationship revealed here and previously in Mejía et al. (2013). Or alternatively, I recommend to include the data by Mejía et al. (2013) in Figure 5B”

As mentioned in our response to RC1, we will now include these data as a figure in the main body of our revised manuscript.

RC2: “Figure 5: It might be worthwhile to add horizontal error bars (uncertainties for the projected 11B values for borate due to the drifts in pH).”

This is a good idea and something we will do in the revised manuscript.

RC2: “In addition, I am curious if the authors considered more of a threshold-type response (e.g., step-wise increase) for the relationship between diatom B contents and seawater pH (Panel B), rather than linear regression?”

This is an interesting point but given the uncertainties in both pH and [B] we would prefer not to overly fit curves to the observed dataset. The statistics suggest a linear fit describes the data adequately (albeit with some scatter) and such a two stepped relationship is not consistent with the data from Mejia et al.

RC2:” Regarding the in-house TC460 standard used for validating the analytical methods. It was clear to me that the variations in B contents in the TC460 shown in Figure 4C were due to supplemental additions of different amounts of the NIST SRM951 reference material. But this appears not the case for the variations in B contents shown in Figure 4A. Then, do they simply reflect the differences in the amounts of TC460 dissolved?

The variations in B content shown in Figure 4A reflect variations in the amount of boron loaded onto the columns. We will make this clear in the revised manuscript.

RC2:”I feel the manuscript will significantly benefit from having a short paragraph describing the process of how diatoms produce their frustules, including how silicic acid is gained from seawater into the cell and what happens afterwards (especially in the

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Silicate Deposition Vesicles: “SDV”) to deposit silica frustules. Perhaps, the paragraph should also have brief description of carbon acquisition for photosynthesis (Line 364-371), to which an active intake of seawater borate is linked (Line 364-372).”

These are good points and something we can add to the revised manuscript relatively easily.

RC2:”I have several questions and unclear points in the Section 3.2.2. . . . I think it is safe for authors to acknowledge that assumption #1 is an entirely open question at this stage. Furthermore, I wonder how assumption #2 is possible. I presume SDV plays central roles for frustule formation (silica polymerization?). But it is mentioned that the internal pH of SDV should be around 5.5 (Line 334, Line 347). At such pH, essentially all of dissolved B should exist as  $B(OH)_3$ , not  $B(OH)_4^-$  (Fig. 6). How can you incorporate something that does not exist?”

We readily acknowledge that our model is preliminary and contains assumptions that will be difficult to test. The reviewer however has identified an interesting point here that although we were aware of, for the sake of simplicity we did not expand on in our original model description. At pH 5.5 although the concentration of  $B(OH)_4^-$  is low it is still present, i.e. at  $S = 35$  and  $T = 20$ ,  $B(OH)_4^- = 0.3 \text{ umol/kg}$  (around 200x lower concentration than at pH 8). While this perhaps does present a challenge to our model, we should point out that when purifying boron for MC-ICPMS analysis we load our samples at pH 5.5 onto anion exchange columns. Since these use an anion exchange resin with a high partition coefficient for borate, they rapidly remove the small amounts of borate in solution. The remaining dissolved boron respeciates at a fast rate to maintain equilibrium, and this produces more borate that in turn removed by the resin. This cycle repeats until all the boron is removed from the solution, and this occurs at such speed that we have quantitative boron removal in the 10-minute transit time through the resin bed. While we acknowledge the partition coefficients involved in silica deposition in diatoms are unlikely to be as high as for our boron-specific resin, this does at least offer a mechanism for how significant amounts of boron could be

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incorporated as borate even though the pH is low in the SDV. We will add more detail in this regard to the revised manuscript with the new schematic discussed in response to RC1.

In response to the other part of this comment – the SDV does play a very important role in the formation of the opal frustule. This will be made clear in the revised manuscript.

The remainder of RC2's comments are minor and will be corrected in the revised manuscript.

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**BGD**

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