

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

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1] General Comment (Overall quality of the discussion paper).

In this cutting-edge work, the authors explored the potential of boron isotopes ( $\delta^{11}\text{B}$ ) in diatoms to be employed as an indicator for seawater pH. The  $\delta^{11}\text{B}$  paleo-pH technique has been extensively tested for foraminifers over the years. Yet, their tests are often scarce/absent in sediments from high latitude regions, where air-sea  $\text{CO}_2$  exchange is particularly dynamic. Given the abundance of diatoms in those areas, robust  $\delta^{11}\text{B}$  calibrations against pH could eventually provide new insights into global carbon cycling, especially on glacial-interglacial timescales.

It is unfortunate that carbonate chemistry of the culture media underwent substantial drifts (by more than 0.5 pH units in some cases), which, as the authors admit, led to some uncertainties in relating diatom B contents and  $\delta^{11}\text{B}$  to seawater pH. Thus, at this stage, the results from this study seem to leave more questions than the clear understanding on how B systematics works in diatoms. However, there is no question that this paper represents an important first step and it is highly worthy of publication.

The manuscript is generally well written. I raise some questions in this review (given below), but I must admit that they most likely stem from my limited familiarity with the process and mechanism of frustule formation in diatoms. Nonetheless, I think the readability of this paper will improve if they are further explained/clarified.

2] Specific comments (Individual scientific questions/issues).

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

- Figure 5: It might be worthwhile to add horizontal error bars (uncertainties for the projected  $\delta^{11}\text{B}$  values for borate due to the drifts in pH). 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?

- 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?

- I feel the manuscript will significantly benefit from having a short paragraph describing

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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 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).

- I have several questions and unclear points in the Section 3.2.2. (also Fig. 7), where possible scenarios for B incorporation in diatoms are discussed. The authors consider contributions of both  $B(OH)_3$  (via passive diffusion) and  $B(OH)_4^-$  (via active uptake) from seawater (Line 353-354). Also considered is a potential (arbitrary)  $\delta^{11}B$  fractionation of  $-10\text{‰}$  between B in SDV and B in frustules. But it was not clear to me how this fractionation was implemented in the calculations presented in Figure 7 (Line 467-468), which is showing nearly  $40\text{‰}$  offset between B in SDV and frustules (as opposed to  $10\text{‰}$  shown by blue vs grey circles). In Line 354-355, the authors provide two assumptions for the calculations presented in Figure 7, which are; (#1) no additional fractionation during active uptake and passive diffusion of B from seawater into the diatom cell and (#2) only  $B(OH)_4^-$  is incorporated into the frustules. 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?

3] Technical corrections.

Line 71: Comma after “(Ishikawa & Nakamura, 1993)”.

Line 74: Could you be more specific on “seawater precipitates”?

Line 94: Could you provide the definition for “K/1 enriched” seawater?

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Line 99: Could you provide the definition for “BOC”?

Line 109: exponential “growth” phase?

Line 251: Comma after “Si”.

Line 287: “(Figure 5)”. I think this should be Figure 4D, which shows B content in the in-house TC460 standard.

Line 353: “actively incorporated”. I feel “transported” or something might be a better word choice over incorporated. Throughout the manuscript, the word “incorporated/incorporation” is used to refer to B in the frustules. But here, what is discussed is the very first step of B acquisition from seawater into the cell, for which I think a different wording is preferred to avoid confusion.

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