

Interactive comment on “Reviews and syntheses: Revisiting the boron systematics of aragonite and their application to coral calcification” by Thomas M. DeCarlo et al.

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DeCarlo et al. synthesize the (very recently developed) joint B/Ca- $\delta^{11}\text{B}$ system in aragonite corals as a proxy for coral calcifying fluid chemistry. Coral aragonite $\delta^{11}\text{B}$ has previously been applied as a calcifying fluid pH proxy, while recent studies of synthetic aragonite B/Ca suggest control by $[\text{CO}_3^{2-}]$. If these results apply to corals, then coral aragonite B/Ca may reflect $[\text{CO}_3^{2-}]$ in the calcifying fluid. The ability to reconstruct $[\text{CO}_3^{2-}]$ (from B/Ca) and pH (from $\delta^{11}\text{B}$) allows for solving the carbonate chemistry of coral calcifying fluid, which permits reconstructions of calcifying fluid DIC (among other parameters). This new approach hinges on the veracity of coral B/Ca to $[\text{CO}_3^{2-}]$ re-

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constructions, which these authors test in detail. They also present a calcifying fluid calculation routine that propagates all uncertainties associated with the above calculations.

This is a nicely written and useful contribution, and I do support its publication, but I think it is missing one key component:

Primary concern/recommendation: Coral B/Ca as a $[\text{CO}_3^{2-}]_{cf}$ proxy exploded in the last two years, in large part due to the works of these authors. While this contribution cites requisite previous reasoning (Holcomb et al. Chem Geol. 2016 for synthetic aragonite, and McCulloch et al. Nat. Comm. 2017), I do not find that the rationale for this approach has been sufficiently explored in previous publications. As the authors use this manuscript to comprehensively and quantitatively analyze KD formulations, I strongly encourage them to also take a step back and comprehensively evaluate the B/Ca- $[\text{CO}_3^{2-}]$ proxy system in corals and its inherent assumptions. Adding this to the quantitative treatment already provided would greatly enhance this contribution's readability and utility.

Guiding questions for this background: 1) What is known about patterns in coral B/Ca? How do features of these patterns (seasonal cycles, etc.) imply a relationship to $[\text{CO}_3^{2-}]_{cf}$ and/or $[\text{DIC}]_{cf}$? It seems previously published B/Ca data are already compiled in Figure 8, so this won't require much work.

We will add some discussion on patterns of B/Ca in coral skeletons. However, it is difficult to interpret B/Ca alone because it is not directly related to $[\text{CO}_3^{2-}]$, but rather depends also on borate concentration (i.e. B/Ca depends on both pH and $[\text{CO}_3^{2-}]$). Nevertheless, we will add more acknowledgement of previous studies of coral B/Ca ratios.

2) What is known about coral $[\text{DIC}]_{cf}$, both naturally and in controlled experiments (e.g., Cai et al., 2016; Comeau et al., 2017)? What are the limitations to direct measurements? (Schoepf et al. 2017 gave a nice overview of this, but I would appreciate

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seeing that reasoning here)

We will add a discussion on calcifying fluid DIC. There is a substantial, and currently unresolved, difference between DIC derived from boron systematics ($\text{DIC}_{cf} > \text{seawater}$) and from microsensors ($\text{DIC}_{cf} < \text{seawater}$). We will discuss potential reasons for this difference, and the implications for understanding coral calcification.

3) Two previous studies of paired foraminifera B/Ca and $\delta^{11}\text{B}$ concluded that joint reconstructions of $[\text{CO}_3^{2-}]$ and pH could not be used to reconstruct full ocean carbonate chemistry because the relative uncertainties in reconstructing Alk and DIC were larger than the entire range of these parameters in the modern ocean (Yu et al., EPSL 2010; Rae et al., EPSL 2011). What is different in corals that make this application feasible? I think it probably relates to the much bigger ranges of $[\text{CO}_3^{2-}]$ and/or [DIC] in coral calcifying fluids vs. seawater, but I'd like to hear that from the authors. In general, the coral joint B/Ca and $\delta^{11}\text{B}$ approach needs to be presented within the context of previous (unsuccessful) open ocean efforts.

We will add a discussion of applying boron systematics to reconstruct seawater chemistry. Like the foraminifera studies mentioned, efforts to reconstruct ocean carbonate chemistry with corals are not very successful because the changes within the calcifying fluid often far exceed natural variability of seawater. Thus, while boron systematics is a useful tool for understanding coral calcification and its sensitivity to changes in reef environments, it may not be generally applicable for deriving ocean chemistry. We will make this point clear in the revised manuscript.

Specific comments:

Page 3, L1 (relevant for Section 2): For most boron proxy applications, inorganic carbonate precipitation experiments do not reflect biogenic carbonates as well as our community would like (see, e.g., Allen and Hönisch, 2011; 2012; Uchikawa et al. 2015,

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2017, review in Rae and Foster, 2016; Rae 2018 book chapters). Please defend why applying a KD derived from synthetic aragonite B/Ca is appropriate for coral aragonite in light of issues observed in other boron applications. This discussion could fit well in Section 7 (p. 13).

We will add discussion of this topic. In general, it is difficult to validate the application of Kd derived in abiogenic experiments to coral skeletons because independent data of coral calcifying fluid chemistry are scarce. Microsensor and fluorescent dye measurements of calcifying fluid pH are broadly similar to boron isotope-derived pH, but the one study of calcifying fluid DIC derived from microsensors differs from boron systematics results. However, boron systematics are broadly similar with constraints from U/Ca and Raman spectroscopy, which we will add to the revised manuscript.

Page 5, L31: What might compositional effects on B/Ca partitioning look like? This is a critical point for two reasons: 1) If compositional effects do exist, then B/Ca partitioning is not effectively described by KD, and instead requires additional parameters related to varying solution chemistry than only $[\text{CO}_3^{2-}]$ and $[\text{Ca}^{2+}]$. 2) If compositional effects do exist, then application of B/Ca- $[\text{CO}_3^{2-}]$ approach to coral calcifying fluid would carry additional uncertainty because the calcifying fluid composition is not unaltered seawater (because of ion pumps such as Ca-ATPase) Note: I feel that the authors nicely dealt with comparing the B/Ca data from Mavromatis and Holcomb nicely throughout the manuscript, and their approach of using both datasets to define KD in terms of CO₂ (Equation 12) implies that compositional effects do not matter. But I think it is important for them to note that compositional effects could undermine the application of the B/Ca- $[\text{CO}_3^{2-}]$ approach to non-seawater media (which includes the calcifying fluid).

The reviewer makes a good point here. It is important to note that the Holcomb et al. (2016) experiments include a range of seawater chemical manipulations, including [Mg], [Ca], and [Sr] exceeding changes typically thought to occur within the calcifying fluid, without clear effects on Kd. Thus, we do not think there are

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strong sensitivities of K_d to trace element variations. Yet it is possible that there are subtle effects, which are not apparent in Holcomb et al. (2016) because the fluids are all broadly similar to seawater, but do become apparent in Mavromatis et al. (2015) since the fluid chemistry departs substantially from seawater for many elements. We will discuss this issue further in the revised manuscript.

Page 12, L14-19 and Figure 8: Suggest you change the order of figures, starting from the measured parameters ($\delta^{11}\text{B}$ and B/Ca , in a), then each converted to their independent parameters (pH and CO_3^{2-}), and finally plots vs. DIC, which requires both parameters. It is tough to say whether the correlation between DIC and CO_3^{2-} is "interesting" or even surprising, because the calculation of DIC depends on pH and CO_3^{2-} . Because pH and DIC do not correlate well, changes in DIC are probably principally driven by changes in $[\text{CO}_3^{2-}]$ (and hence coral B/Ca). This could be worth exploring with a sensitivity test.

We agree with this suggestion, and we will revise the order of panels in Figure 8. In terms of deriving DIC, yes it appears to depend most strongly on $[\text{CO}_3^{2-}]$. However, in terms of modification within the calcifying fluid, it may be that CO_2 diffusion drives DIC changes, which in turn affect $[\text{CO}_3^{2-}]$.

Page 14, L16-17: In section 2, the authors state that Holcomb et al. (2016) only performed two experiments at each offset temperature, and that this was insufficient to quantify temperature effects on precipitation rate. Are the data also too limited to find a temperature dependence on B/Ca partitioning?

We will revise the statement regarding the quantification of temperature effects on precipitation rate. The Holcomb et al. (2016) data are generally consistent with Burton and Walter (1987) in that precipitation rate increases with temperature, and the data are sufficient to demonstrate this. However, Burton and Walter (1987) show that the order of the reaction changes with temperature, which requires a full calibration dataset (i.e. more than 2 experiments) for each tem-

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perature. Thus, in the revised manuscript we will describe that we do see a temperature dependence of reaction rate, but that we cannot go as far as Burton and Walter (1987) in quantifying changes in the reaction order. Holcomb et al. (2016) already reported that there was no apparent temperature effect on B/Ca partitioning between 20 and 40 °C.

Figure comments.

Please label panels a) through d) (or however many panels) in each figure (some are missing). I would recommend increasing the font size of these labels; they are difficult to see.

We will add panel labels to all figures.

Figure 6. I only see three line types on here (solid-McCulloch, gray dash-Allison, and then a dot dash that may be both the Holcomb and Equation 12 lines?) If the Holcomb and Equation 12 lines fall on top of each other, please say so in the text and figure caption. Additionally, while the authors MATLAB routine calculates a propagated uncertainty on derived $[\text{CO}_3^{2-}]_{cf}$ and $[\text{DIC}]_{cf}$, no uncertainties are plotted. Please illustrate this uncertainty on Figure 6. How does the propagated uncertainty affect the conclusion about applicability of McCulloch, Holcomb, and Equation 12 lines? Are they truly any different from each other (tested statistically)?

We will revise Figure 6 to more clearly show the separate lines, and we will include error bars.

Figure 7. Panel labeling. Also, do not use $\Delta[\text{CO}_3^{2-}]_{cf}$ in titles, as this is a well-used carbonate chemistry term. Suggest changing titles to " $[\text{CO}_3^{2-}]_{cf}$ difference" or " $[\text{CO}_3^{2-}]_{cf}$ M17 - $[\text{CO}_3^{2-}]_{cf}$ H16". Please specify that $[\text{CO}_3^{2-}]$ is $[\text{CO}_3^{2-}]_{cf}$ on figures and in caption. Finally, the color schemes are a bit tough to follow. In b) through d), white is good, right?

We will change the panel titles as suggested. We prefer to keep the color scheme

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as it is a common (and we believe effective) way to visualize anomalies because it is easy to see where the two formulas are consistent (white) or one higher than the other (red or blue).

Figure 8. Tough figure to read, recommend brighter symbol colors and making the $\bar{E}\bar{G}$ gray shading for the Holcomb et al. data lighter.

We will make the symbol colors clearer and the gray shading lighter.

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