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Biogeosciences Discussions

Interactive comment on "Exploring B/Ca as a pH proxy in bivalves: relationships between Mytilus californianus B/Ca and environmental data from the northeast Pacific" *by* S. J. McCoy et al.

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Response to Reviewer 1:

We would like to thank Dr. Meibom for his feedback. Indeed it would have been a useful for reconstructions of ocean pH to find a strong correlation between B/Ca and pH, but we believe that this lack of correlation is still an important result. In addition our paper makes three other important contributions (a) method development for reproducible boron concentration measurements by ion microprobe (b) a new strategy for dealing with non-linear growth rates in bivalves (and potentially other organisms) and (c) discussion of biological controls on B concentrations during calcification. In fact

understanding biomineralization across species is an important topic as we consider how carbonate forming organisms may be affected by future changes in ocean chemistry. Documenting how mussels behave (at least geochemically) in response to large changes in local pH is a vital part of this understanding. Although we agree to some extent with Referee #2 that the Rollion-Bard (2011) paper may not be directly relevant to our data as it deals with B incorporation in corals, which have a different calcifying mechanisms from that of bivalves, we do agree that a more detailed discussion regarding possible mechanisms for boron incorporation into marine biogenic carbonates would enhance the discussion of our results.

Response to Reviewer 2:

We would like to thank Referee #2 for such detailed feedback to our manuscript. The issues raised are addressed in detail below, and will be amended in the text. The details of B incorporation into biogenic carbonates remain unclear, even in foraminifera which have been examined the most closely, and studies such as ours emphasize the need to test B incorporation in different species and in different environments to explore those mechanisms. While our results could be viewed as 'disappointing' in light of the low correlations found between shell B/Ca and both pH and temperature, these results are undoubtedly valuable as another piece of the B system puzzle. This study used ion microprobe so that we could look in high resolution at weekly variability in B concentration, and compare the different parts of the shell to examine calcification mechanisms. We chose not incorporate B isotopic measurements into our dataset because it could not be analysed at such high resolution using this method. Undoubtedly it will be of great interest to look at boron isotopes in the future (as mentioned in our conclusions), as this second part of the boron system is likely to provide new insight into the mechanisms calcification in M. californianus.

Here we step through the specific points raised by the reviewer:

(1) Samples were cleaned according to other methods commonly used in bivalve geo-

chemical analysis, and the procedure will only remove organics from surface layers, not from internal layers. Because ion probe measurements are ablated directly from the sample surface, we did not have a powdered sample and thus were not able to remove organic matter by solution. We recognize that organic material is likely to remain in the sample, and indeed we discuss this buildup of organic residue, particularly in winter layers as a mechanism for changing the B concentration.

(2) We agree that the standards for B/Ca are problematic and we stress this in our paper. Indeed we consider it one of the major contributions of our work that we were able to document which of these standards are suitable for ion probe analyses, and to find a method that gives reproducibility on repeat analyses of the bivalve at the 5% level. The ion probe standard concentrations were determined by solution ICP-MS, which homogenizes a portion of the crystal that is larger than that sampled by ablation and thus provides an average value. In order to get an accurate B concentration by ion microprobe, we deliberately measured standards over the entirety of the crystal. This approach led to low precision, but improved accuracy. Although we excluded the two highly heterogeneous standards, their average values each time they were measured still fell on the standard curve (see attached Figure). As is typical for ion probe calibration curves, our B counts to B concentration gave a linear fit. We will include the figure in the final version of the paper to make the data available. Whilst the uncertainties on the standards were high because of the heterogeneous B distribution, we were able to use our method to get reproducible results. We assessed the true reproducibility by analyzing the same spot on the mussel, itself using the daily working calibration curve, and were able to reproduce the data at the 3% level on a single day and 5% between days (as described in the text). This result is clear evidence that the heterogeneity in the standards is real, but that with careful calibration the ion microprobe can give accuracy and relatively precise data for this type of sample As mentioned above we will show our standard curves as an additional figure to improve the clarity of our discussion of the calibration curves. We included Figure 3 because we think it helps to show the spatial scale and total heterogeneity of the standards relative

to one another.

(3) Environmental data was collected approximately 10 m from the collection site of the shell. Thus, distance is unlikely to account for the low correlation observed between environmental parameters and shell chemistry. The pH measurements described in Wootton et al. 2008 match our description of the pH data (8.4-7.8 pH units, Fig. 5, in the text p. 5597, Section 2.5, lines 15-19), and are furthermore the exact dataset that we used for our analysis. The data shown in our manuscript have been resampled at a lower temporal frequency using a rolling mean to match the frequency of B/Ca sampling (instead of every 30 min as originally measured). Regardless, the instrumental coastal dataset shows a definitive statistical trend in pH with no large fluctuations in either salinity or temperature. One of the unique advantages of our study was a detailed, directly measured instrumental coastal record with a distinct trend in pH in the same locale as the sampled shell with excellent age control that provided an optimal opportunity to investigate whether bivalve B/Ca is controlled by pH. Given this close spatial proximity, and the low correlation, we do not recommend the use of B/Ca as a pH proxy in marine bivalves.

(4) Mytilus edulis does indeed secrete both calcite and aragonite, however the mineralogy of M. californianus differs from that of its relative Mytilus edulis. Unlike other mussel species, M. californianus secretes all calcite except for a very thin nacreous layer between the inner and outer prismatic layers (see Figure 1). This layer is very thin and was analyzed in our study.

(5) We thank the reviewer for pointing out the inconsistency between the R2 values listed in the text and in the caption for Fig. 6. The values listed in the caption for Fig. 6 are Adj. R2, while the text lists R2. We will amend the figure caption to include both. The statistically significant correlation between growth temperature and shell B/Ca implies that temperature does appear to play a role in the incorporation of B into bivalve shells. Temperature appears to have a stronger correlation to B/Ca than pH. We feel that this result is important, because it would seem more likely that B/Ca

would be controlled primarily by pH. We do agree with Referee #2 that the use of the phrase 'important role' may be overstating the correlation. Instead we will change the conclusion to stress that may be a relaveant parameter as the biogeochemical community continues to explore the B/Ca and its controls.

(6) To determine KD, we first ran our parameters through the CO2sys excel macro, which corrects for both temperature and salinity (stated in Section 2.5 Environmental and hydrographic data and also Section 3.3 Calculation of KD). The major point we hoped to make in comparing our M. californianus data with Foster's (2008) foraminifera data was to show that we see a smaller response in shell chemistry in the mussel compared to foraminifera, which exhibit larger changes in shell chemistry for a relatively small change in seawater chemistry. We argue that this implies very strong physiological control (vital effects) in M. californianus compared to foraminifera. Our language in lines 1-5 on p. 5604 (end of Section 4.2.2) was not sufficiently clear to convey our meaning, and will be adjusted. We did not mean to imply that the three species of foraminifera exhibit different trends in B/Ca vs. B(OH)4-/HCO3-, as all show a positive trend (and so does M. californianus). Rather, we mean that two of them show the same general pattern as M. californianus –a positive trend, but with a large spread over the x-axis (B(OH)4-/HCO3-) and a smaller range in y (B/Ca), while G. sacculifer shows a larger relative change in B/Ca range in both. Our revised manuscript contains a clearer discussion of Fig. 7.

(7) We have checked the citations brought to our attention, and amended inconsistent or outdated citations. We have checked all remaining citations in anticipation of submitting a revised manuscript.

Interactive comment on Biogeosciences Discuss., 8, 5587, 2011.

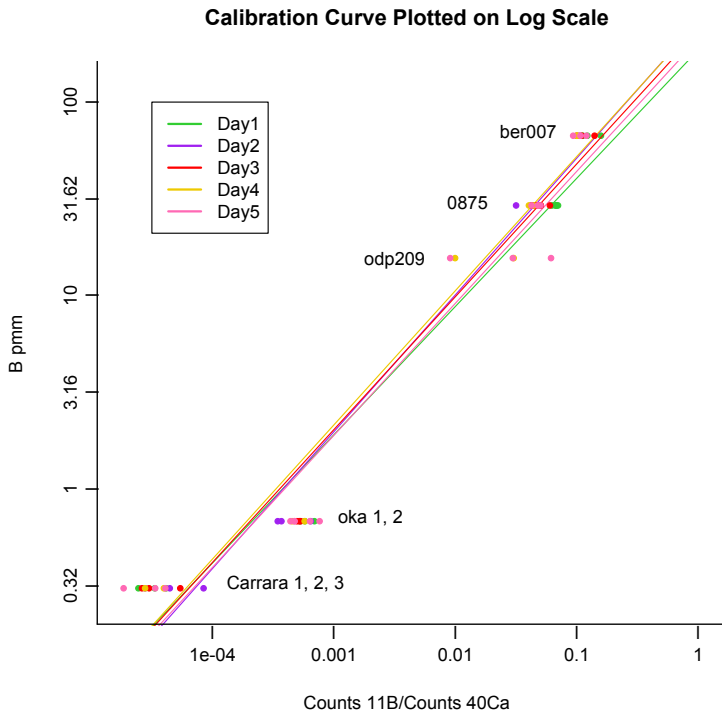

Fig. 1. AC Fig 1. Calibration curves for each day plotted on a log scale. Standards are labelled on the graph.