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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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Thanks again to all reviewers. Their collective advice and comments have greatly improved our manuscript.

We would like to thank Dr. Allison for her thorough review of our manuscript. Her main concerns focus on the growth model we have proposed for *M. californianus*. We have reworded parts of the manuscript to improve our description, and briefly outline our approach here. There were three parts to assignment of the age model (A) known recruitment and collection dates (B) visible banding (C) consideration of variable growth rate during the year. Prior publications (e.g., Lutz and Rhoads, 1977) have shown that

Mytilus bivalves exhibit variable growth rates during the season, usually dominated by temperature and feeding rates, so we would be extremely surprised if the growth rates of mussels growing in this dynamic environment were linear. Given this knowledge, we decided that we should try and assess possible growth rate models by comparing our shell B/Ca data to pH and temperature. Ideally we would construct a completely independent seasonal growth rate model, perhaps using some sort of decay-based method – but we do not know of a method that can be used at such high resolution. The reviewer is correct that if our final conclusions depended on this correlation then our approach would indeed be circular, however even in this 'best case scenario' of using B/Ca to look at the seasonal growth rate we do not see a particularly strong relationship between pH or temperature and shell B/Ca. Even in this study where we have environmental data immediately adjacent to sample collection, a strong linear trend in pH, and using the optimal growth model to assess a pH-B relationship - we still find weak evidence for a pH-B or temperature-B relationship in *M. californianus*. We acknowledge that we overstated the importance of such a relationship in our final conclusion, and have rewritten that section to be more in line with the prior discussion.

Here we address the specific points raised by the reviewer. Please note that figure numbers refer to figures in the Discussion Paper, not the revised manuscript.

1) Sampling resolution. Reviewer three makes a calculation of the sampling resolution based on the overall dimensions of the bivalve. Whilst this may give a sense of the overall growth rate, it does not represent the details of the mussel's growth. The total length of the entire bivalve shell is 156 mm, but this is not the length or thickness of the sampled regions. We sampled the growth bands from several different regions of the *M. californianus* shell in cross-section, including the inner prismatic layer, outer prismatic layer, and beak, which grow rather differently (refer to Fig. 1). As discussed in the text (and above), many bivalves do not grow continuously or linearly, so it is not appropriate to assume continuous growth over the year. For these reasons we believe that each spot actually represents a longer time period than a day, as described in the

text.

2) Growth model. During our early consideration of the data we did of course plot the data against distance, but it was quickly apparent that it was not an appropriate way to look at the data because of the strong seasonal changes in growth rate. As we discuss in our introduction (last paragraph on p5590), one of the goals of this study was to try and assess seasonal growth rate changes, and whilst our approach may not be perfect, we consider it a step in the right direction. We agree that two strong points in our growth rate model are known recruitment date and visible annual bands, and are thus able to date the material through two independent chains of evidence. We are also in the fortunate position of knowing the recruitment date because we have been working at the collection site for 26 years and have intimate knowledge of its ecological dynamics. For this reason we are confident in our assignment of the individual age or the ages of shell layers with respect to years as assigned through known collection date, and therefore we do not include uncertainty of year in our calculations.

3) SIMS Standardization. The other reviewers also raised some questions about the standardisations used during this study. We completely agree that standardising is not only very important, it is also very difficult. We did not expect standardising to become such an important focus of the study as we expected these previously used standards to be more homogeneous. The primary ion beam used was ^{133}Cs^{+}, typically 5-6 nÅ, rastered over 30 by 30 μm. We measured the secondary ions ^{11}B^{-} and ^{40}Ca^{-} with a mass resolving power (MRP) of 3100 to separate ^{40}Ca from ^{24}Mg^{16}O. A field aperture of 15 by 15 μm was placed at the centre of the rastered area so that an effective central 15 by 15 μm area was analyzed. Our count rates were on average approximately 250 cps and 50,000 cps for $^{11}B^{-}$ and ^{40}Ca^{-}, respectively. 11/40 mass ratios measured for 10 cycles had a 1-sigma standard error of 0.6To account for instrument drift, we measured repeat analyses on the *M. californianus* sample (p5596 line 27). Using these analyses, which measured within 3% on a given day and within 5% across days, we chose to assign 5% error on our measurements in Figure 4.

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4) Environmental data. The aim of this study was to report novel data and analysis on *M. californianus* B/Ca and compare to already published environmental data (Wootton et al. 2008). Although methodology is discussed therein, we add some details again. Specifically, the pH probes were cleaned and calibrated with NBS standards generally every 2 weeks throughout the time deployed. Drift was accounted for in the measurements by developing a non-linear statistical relationship between pH and time since service, assuming that the relationship represented drift, and subtracting it from the pH data.

5) GLODAP hydrographic data. We agree that GLODAP data and other oceanographic datasets obtained from the open ocean are not ideal for comparison to coastal settings. The data utilized in our calculations were measured from the surface ocean (0m – p5597 line 20). These data were used to allow direct comparison with other B studies and also because there are no other data are available for this region. The GLODAP data used was to supplement some parameters not measured directly (i.e. regional seawater ion concentrations). Anthropogenic CO_2, DIC, and Alk were not taken directly from the GLODAP dataset, but were calculated using primarily directly measured seawater variables and some seawater ion concentrations from GLODAP. In fact, those variables are not even available for any sampling site in that region. Indeed, there is globally a lack of carbon cycle data collected in good proximity to bivalve populations.

6) Section 4. Reviewer 3 addresses variation in B/Ca between points made at the same location in the chronology (seen in Fig 4). We believe that Reviewer 3 is referring to measurements from winter bands, and that she refers to their locations along our sample transect within the shell. These winter excursion points do not represent replicate samples of different concentration but rather sampling on a winter growth line, during which time the internal shell experiences dissolution and little growth. We agree that this change could reflect distribution or accumulation of organic materials in the shell as well as environmental events (i.e. storms), and we discuss both possibilities

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in the text (Section 3.1 and Section 4.1.2). We did perform repeat analyses both on 'growth season' shell material and also on winter banding, both to explore repeatability of those high measurements and also to ask whether shell banding morphology was affecting the ion beam in some way. We concluded that these winter excursions are a true feature of shell chemistry. As requested, we have amended figures and quantified differences between shell layers.

Specific corrections –

Abstract – We have extended the abstract to include a summary of our results.

Citations – In response to both Reviewer 2 and 3's comments, we have corrected all citations brought to our attention and checked all remaining citations in anticipation of submitting a revised manuscript.

P5589 – Thank you for the correction, we have amended this line to read " Dissolved B is found predominantly as boric acid . . ."

P5599 – We are confident in our assessment of sampling resolution, discussed above.

Figure 5 – Plotting characters on Figure 5 have been changed to show the seasonal patterns more clearly.

Figure 6 – Reviewer 3 asks us to include error associated with assigned shell age in this figure. Assigning error in this situation is difficult, as we have used a growth chronology model to assign specific dates within each year. Furthermore, each B/Ca data point represents a time-averaged sample that is in turn compared to temperature and pH data that is also time-averaged, in this case. We would argue that our estimated age error is small enough, as our data points in this figure are all time-averaged (on both axes), that the size of the plotting characters precludes a clear presentation of error estimates on the plot. The aim of Figure 6 is to show general patterns of correlation (or poor correlation, in this case) and not specifically to provide a temperature or pH equation for the B/Ca proxy. B/Ca ratios are expected to be a function of pH (and of

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temperature). However, as we are exploring the potential of using B/Ca as a predictor of pH, we chose to orient the axes in such a way as to show pH as the response variable.

Legend to Figure 3 – We have added a full visual legend to Fig. 3.

Caption to Figure 4 – The figure legend has been changed to read “Plots of complete ion probe B/Ca data from each shell layer, including measurements from winter bands. The locations of winter bands are indicated by vertical dashed shaded lines.”

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