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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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This paper presents B/Ca data at a high spatial resolution across a mussel shell and discusses its potential as a pH indicator. The study is interesting but I have some concerns about the treatment of the data. In particular the authors produce a growth model for the shell by matching shell B/Ca data to environmental data (P5594). They then compare the shell B/Ca and environmental data to explore the relationship between shell chemistry and environment. This is somewhat circular and is not an appropriate strategy. The growth model for the shell should be produced independent of the B/Ca data to allow the relationship between shell B/Ca and environment to be

rigorously tested. The authors conclude that both pH and temperature play important roles in controlling the incorporation of B in the shell. I cannot see that this statement is supported by the data. Figure 6 demonstrates very weak correlations between shell B/Ca and pH/temperature. It is not clear that these relationships would be significant if the error in the assigned age of the shell was included in the pH/temperature data.

Sampling resolution - The shell is 156 mm long and grew over a period of $\sim$10 years. So the mean growth rate is $\sim$40 microns/day. The SIMS sample spot size is 50 microns so the authors have not sampled B/Ca at monthly resolution (stated in results), they have sampled $\sim$ 1 day in every months growth. Shell growth is more rapid in the outer annual layers (Fig 1) and is not linear throughout the year, so some SIMS analyses in the outer layers will have sampled < 1 days growth. It seems likely that adjacent SIMS analyses may have sampled shell deposited at different stages of the diurnal cycle when seawater pH follows a large variation (of 0.24 pH units). Could this account for some of the large shell B/Ca variations?

Growth model - It would be better to plot B/Ca against shell length (mm) in figures 3 and 4 rather than using the growth model as this gives a better reflection of the data. Please include the positions of the growth bands. Also, note that a few mussels were present at the study site before 1999 (Paine and Trimble, 2004) and that mussels were recruited into the population after 1999. So the authors cannot be certain that the shell studied settled in 1999. The known date of collection and the examination of annual bands in the shell provides a much better argument for the dating of the analysed shell material.

SIMS standardization - Please include full details of the analyses. What was the primary beam current? What primary, contrast and field apertures were used? What were the approximate count rates for B and Ca? Standardization is a problem, as noted. I think the authors must accept that the accuracy of their data is probably poor. I do not see that this is a problem. So long as individual analyses are precise, the authors can discuss variations across the chronology and between shell layers. However it is

important that they demonstrate that instrument drift does not affect their data and that they define the precision of their analyses. Please state how this was done e.g. they could analyse within a small area of the coral standard each day to ensure that relative ion yields remain stable. How did they calculate the precision of each analysis? How were the error bars in figures 3 and 4 calculated? Environmental data - pH probes are notorious for drifting when calibrated and it seems that the probe was deployed for several months. Was it recalibrated over this period? How much did it drift? How were the pH data checked? What is the estimated precision of the pH measurements?

The authors use GLODAP data to estimate DIC, TA and CO2. I do not think that this is appropriate. The authors have collected pH data from close to the mussel collection site. These show a large pH diurnal variation, reflecting kelp photosynthesis and respiration. This biological activity will significantly affect seawater DIC and CO2. It is unlikely that the GLODAP values, from a site a considerable distance away (almost 1 degree latitude) and of an unknown bottom water depth, will be comparable. I think the authors should cut this and the subsequent calculation of Kd (which is already very tenuous due to the inaccuracy of the SIMS standardization) from the manuscript. Concentrate on discussing variations in B/Ca across the shell.

Section 4. - Use statistics to compare the B/Ca concentrations of the different layers (4.1.1.). Indicate the position of the winter bands on the graphs (p5600, line 24). There is huge variation in B/Ca between some points made at the same location in a single layer in the chronology (figure 4). There is almost no discussion of this observation in the manuscript. The authors consider that this may be environmentally driven but could it instead reflect the distribution of organic materials in the shell? If the authors make a second analysis almost immediately adjacent to the first, do they still observe the same high B/Ca? It is not possible to discern seasonal variations in pH and temperature in Figure 5. Perhaps remove the symbols and plot just a line to make this clearer. Figure 6 plots shell B/Ca against pH and temperature. Put error bars on this figure and ensure that the error bars indicate the error in the pH/temperature variation associated with the

error in the assigned shell age. Are these relationships still significant? It is more usual to plot the dependent variable i.e. B/Ca, on the y axis.

There are many inaccuracies in the referencing. I have noted several but the authors should recheck the others. E.g. p5589, line 7. Neither Hemming and Hanson or Yu and Elderfield demonstrate that pH affects B/Ca in biogenic carbonate, although both discuss the relationship. It would be better to refer to studies culturing biogenic carbonate or precipitating inorganic carbonate over a range of pH to support this point. P5589, Line 12. Yu et al 2007 did not demonstrate that borate is the primary B species in carbonate. P5590, line 15. Honisch et al., GCA, 2004 and Allison et al., 2010, GCA, measure both B/Ca and d11B in corals.

Abstract - rewrite the abstract in line with the Biogeosciences guidelines. In particular the abstract should be intelligible to the general reader without reference to the text. At present the abstract summarises the methodology but not the results of the study.

P5589, line 9. Dissolved B in seawater is predominantly borate and boric acid. Other species exist but are ignored due to their low concentrations.

P5599, line 10. Suggests that SIMS analyses averaged 1-2 weeks growth. This does not fit with the growth rate of the shell and requires further discussion.

P5605, line 23. Foster L.C. not Foster G.L.

Legend to figure 3.Include a full legend for this figure to replace 'Standard heterogeneity index'.

Legend to figure 4. I do not think this is raw data.

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