

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.

Anonymous Referee #2

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This study aims to interpret pH and temperature effects on the B/Ca composition of a bivalve shell, measured in high resolution by SIMS. Although the authors went through great efforts with this study, the result must have been disappointing. The observed weak correlations do not allow interpretation of a temperature or pH control on the B/Ca ratio in these shells, and certainly exclude the proxy for paleoreconstructions using these bivalves. Such a result is still worth publishing, however, several open questions would need to be addressed to convince the reader that the sample and applied methods are actually suitable to draw these conclusions for bivalves in general:

1. Samples were bleached to remove organic matter but later in the discussion (page

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5600) high B/Ca ratios have been correlated with organic matter rich layers. That implies that organic matter was not entirely removed and much of the small-scale data variability could potentially be explained by organic matter contamination. In comparison to the planktic foraminifer data (Foster, 2008) it has to be pointed out that foraminifers are crushed before chemical cleaning, to expose internal surfaces. Soaking an entire mussel shell in bleach is unlikely comparable in oxidation efficiency. 2. The standards used for this study range in B from 0.3 to 67 ppm, and two standards with 15.6 and 67 ppm B were excluded because of heterogeneity in their B concentration. This result is unfortunate for several reasons. First of all, the vast majority of the samples has B concentrations of 2-12 ppm, i.e. in a range far outside of standard values (<0.7ppm, >29 ppm). How does the calibration curve look like for these standards? Is it linear? Is it expected to be linear? What is the effect on the data uncertainty in such a standardization uncertainty? In addition, uncertainties on carr and oka standards are given as 1 ppm. With B of 0.3 and 0.7 ppm, a 1 ppm uncertainty exceeds the standard value by 100-300%, which seems like a rather poor constraint on the standardization. To gauge the analytical uncertainty, Fig. 3 is not very useful but the ranges or averages of the standard measurements +/- 2 sd should instead be added to Table 1. Also, are there no better/more homogeneous standards available than these? At this point it is hard to gauge whether the heterogeneity comes from the samples or whether this is a general problem of B/Ca analyses by SIMS. 3. The description of the environmental data collection leaves many gaps. How “adjacent” were the physicochemical measurements to the growth habitat of the shell? With such large diurnal and seasonal differences, local differences were likely equally large and thus may bias the correlations. In addition, the pH trend described by Wootton et al. (2008) ranges from ~8.4 to 8.2, and not from 8.4 to 7.8, as suggested on page 5597, line 18. 4. *Mytilus edulis* is known to secrete both calcite and aragonite (e.g. Lorenz & Bender 1980, GCA) and the relative proportion of these minerals depends on temperature. Is it possible that *Mytilus californianus* also secreted both minerals, and that some of the geochemical variability may be explained by that? 5. The correlation coefficients for the environmental corre-

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lations are rather disappointing, and it is not entirely clear to me why the relationships shown in Fig. 6 ($R^2=0.189$ for T and 0.135 for pH) show a poorer correlation than the best fit mentioned in the text (0.256 and 0.192)? With such correlations I would not say that pH and temperature play an “important” role in B incorporation into these shells (Conclusions paragraph). 6. I do not understand what is meant by *G. ruber* and *N. dutertrei* exhibiting a similar patterns to *M. californianus* but *G. sacculifer* should show the opposite trend? In Foster 2008, Fig. 7, all three foraminifer species show negative correlations with temperature and carbonate ion, and there is no opposite trend in either species. It should also be noted that the borate/bicarbonate ratio is temperature dependent, which explains a large part of the “temperature-dependence” of KD. Were the temperature and salinity dependence of borate and bicarbonate considered for the determination of KD? 7. The references are often out of date or otherwise unfitting: Page 5589, line 12: replace Yu et al. (2007) by Hemming & Hanson (1992). The latter study established the incorporation equation. Line 16: Klochko et al. (2009) did not perform any phase transitions. That was done by Sen et al. (1994), who also were the first to show that B occurs in marine carbonates in both trigonal and tetrahedral coordination. Importantly, the coordination could be changed upon phase transitions between aragonite and calcite, but the isotopic composition remained unchanged. It was therefore suggested that B is predominantly adsorbed to the crystal surface as the charged borate species but then may change coordination upon incorporation into the crystal lattice. For this reason I also do not agree with Anders Meiboom’s suggestion that Rollion-Bard’s 2011 NMR study is relevant here or for B incorporation in carbonates in general. The deep-sea coral species studied by Rollion-Bard and co-workers shows extreme vital effects (Blamart et al. 2007), with an isotopic composition much higher than that of any other marine carbonate studied to date. Those results are unlikely applicable to the completely different calcification mechanism of this mussel. Page 5590, Line 3: Replace Hemming & Hanson (1992) by Lee et al. (2010, GCA), who recently determined seawater B concentration of $432.6 \times S/35 \mu\text{mol/kg}$. Line 4: delete Pagani et al. (2005). They never measured any such data. Line 20: Neither

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Foster (2008) nor Hemming & Hanson (1992) measured B concentration over a wide pH range. This was only done by Sanyal et al. 2000 (GCA) and 1996 (Paleoceanography). Page 5592, Line 1: delete Blamart et al. (2007) - they measured deep-sea corals, and Foster (2008) - he measured foraminifers, not bivalves. I can only comment on references here that I am familiar with, but given the poor consistency between text and citations, the authors should thoroughly check all citations.

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