

Interactive comment on “Marine bivalve geochemistry and shell ultrastructure from modern low pH environments” by S. Hahn et al.

S. Hahn et al.

sabine.hahn@rub.de

Received and published: 12 January 2012

Dear editor, dear anonymous reviewers,

Thank you for giving us the possibility to respond to the thought provoking discussion of our paper. We greatly appreciate the time invested and the dedication of the reviewers. Many of the suggestions made are feasible and will lead to an improved paper.

Rationale:

In the revised version we will clarify our long-term research aims to avoid confusion. Similar to the reviewers, we believe that the response of the bivalves to transplantation into an area with naturally high CO₂ is highly interesting and the main point of the paper. Nevertheless, in our view, this paper is clearly more than the documentation

C5272

of effects of the transplantation as it also reveals how mollusc shells record stress events that can be preserved in the geological record. We see similar features (non-equilibrium isotope values; disordered shell structure) in our controlled low-pH tank experiments under way. In the tank experiments, the mussels were not transplanted and control specimens do not show these features. The data shown in our paper are thus a first step towards an improved understanding of bivalve archive response to high CO₂ stress. We will ensure this aspect is clearer in the revised version of the paper.

Anonymous Referee #1 Received and published: 6 December 2011

1. Overall quality of paper The paper is both novel and significant, but unfortunately its conclusions are somewhat disappointing as stated in the manuscript. It is a valiant attempt to characterize the influence of increasing dissolved CO₂ levels in seawater on a carbonate secreting marine invertebrate, but with mixed results. Some scientific problems with their isotopic compositions also compromise the outcome of the results and should be rectified in a revised version of this manuscript.

Our Reply: We are pleased to see that you find the paper both novel and significant. We below reply to your specific comments.

2. Specific comments (1) Reviewer: The paper claims on lines 116-117 “no differences in seawater isotope ratios were noted between test sites” In actuality, the isotope data are from Pierre (1999, table 3) and that publication only lists delta¹³C values for a site far from Ischia and Naples, nothing near Ischia. Did the authors collect and analyse their own?

Our Reply: We originally did not sample the water, this was done by friends from Naples and we analyzed these samples at Bochum. We re-sampled the seawater in the meantime in order to better capture potential seasonal variability. The results are very similar to those reported in Pierre (1999). We will need to make it clear that these measurements were so similar and that we have data from the harbour.

C5273

(2) Reviewer: They used *M. edulis* from Sylt as reference material, why not *M. galloprovincialis* from the harbor of Ischia, the same location of source for transplanted material? Especially a concern, since *M. edulis* was collected dead from a shell bed (abraded and worn).

Our Reply: *Mytilus edulis* was - in our view - a good addition to *M. galloprovincialis* because it shows *Mytilus* data from an undisturbed control site. We, however, follow the comments of both referees and will delete the *M. edulis* data from the revised manuscript.

(3) Reviewer: Table S1 is critical to the text of the manuscript and should be incorporated into the main body and not the supplement.

Our Reply: We agree and will incorporate this table in the main body of the text.

(4) Reviewer: The biggest concern is with the stable isotope results. They sampled the periostracum plus calcite, calcite, calcite plus aragonite and aragonite portions of the shell. The first and third are mixtures of unknown proportion and thus offer up meaningless results and should be dropped from the data tables, results, discussion, etc. Fig. 8: delete all results for MIXED samples, expand and concentrate on investigated interval not whole shell (compresses trends). Furthermore, the third mixture also suffers from differences between carbon and oxygen isotopes in calcite and aragonite (cf. Rubinson, M., Clayton, R.N., 1969. Carbon-13 fractionation between aragonite and calcite. *Geochimica Cosmochimica Acta*, 33: 997-1002; and Tarutani, T., Clayton, R.N., Mayeda, T.K., 1969). The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. (*Geochimica Cosmochimica Acta*, 33: 987-996). So, to compare and plot on the same graph we need to normalize one set of values. All the discussion about isotope values from the nacreous layer and the calcitic one are mute because NO adjustment for mineralogical fractionation was made or mentioned in the text. Instead, the authors observe remarkable differences (lines 499-501) and it questions the bulk data from bivalve shells. Indeed,

C5274

what it does is question their results!

Our Reply: We agree that the values must be normalized and will do so in the revised version. We politely disagree with the statement that data comprising sampling powder with unspecified proportions of both calcite and aragonite should be deleted from the ms. This is because we performed this study to explore the potential of fossil shell material as an archive of stressed environments. If present, aragonitic shell material in many fossil carbonate archives will be altered, partly or entirely. A carbonate geochemist or oceanographer might conclude that you cannot use this material. However, paleoceanographers and geologists use such material as archives and study diagenesis to separate signal from noise. In addition, some of these shells are so thin, that extracting enough sample powder (micro drill) for analytical work from either the aragonite or the calcite portions of the shells is not feasible except perhaps with a laser. We intend to show to the reader what the aragonite data show, what the calcite data show and what the bulk sample shows. We will emphasize the potential and pitfalls of this approach more clearly in our revised ms. The papers mentioned by the reviewer (Rubinson et al., 1969 and Tarutani et al., 1969) both deal with inorganic (lab precipitation experiments) calcite-aragonite isotope signature. In contrast, previous work dealing with the complex issue of organic mollusc calcite versus aragonite (e.g., Lécuyer et al., 2004; Martinique Island) showed that the aragonitic inner layer and the bulk shell (including calcitic outer layer representing about half of the total weight) secreted by the gastropod *N. tessellata* have similar mean $\delta^{18}\text{O}$ values. Furthermore, Lécuyer et al. (2004) pointed out that calcite precipitated by the bivalve *C. virginica* has a mean $\delta^{18}\text{O}$ value indistinguishable from several species of aragonitic bivalves co-existing at the same location (see text in Lécuyer et al., 2004; page 301, second paragraph on left side). There are more papers dealing with the topic of biological controls on aragonite versus calcite isotope geochemistry in molluscs. This is a debated and important topic and our data are novel and significant. We normalized aragonite values for calcite in Fig. 8. Normalized aragonite values are now more negative but the general trends are similar to those of the non-normalized data plots. Figure 9 is calcite only, there is

C5275

no change.

(5) Reviewer: The discussion in Section 3.3.3. is a real concern. Line 311 talks about ' . . calcite layer. . . ', whereas line 324 talks about ' . . .bulk. . . '. Which is it???

Our reply: This is a misunderstanding? Section 3.3.3 is still part of the Results chapter and describes differences in shell chemistry.

(6) Reviewer: Thus far, the only valid conclusion is that transplantation caused a shock in both chemistry and microstructure, because the post transplant time at the acidified sites was too short. Agree, which in itself is very IMPORTANT!

Our reply: Thank you for your comment. Yes, the transplantation shock is a key result. For the overall goal of this study, however, the recognition of how bivalve archives respond to environmental stress (shell thinning, disordered ultrastructure, non-equilibrium oxygen isotope fractionation etc.) is perhaps even more significant from our perspective.

(7) Reviewer: Other conclusions are not supported especially since water isotope compositions are not available, although claimed in table 1.

Our reply: Please see point 1.

(8) Reviewer: What is meant by 'outer' and 'inner' layers, calcite, aragonite or mixed layers????

Our reply: The inner layer of the shell refers to the aragonite layer, while the outer layer is the calcite layer. We will make sure that this is clear in the revised ms.

(9) Reviewer: Minor language and terminology comments.

Our reply: Consider it done.

Answers to Anonymous Referee #2 Received and published: 17 December 2011

General comments: The MS by Hahn et al. uses a multi-technique approach to investi-

C5276

gate the relationships between pH and bivalve geochemistry (with possible application of bivalves as palaeo-pH proxies). While impressive attempts were made by the authors to account for mussel transplantation to a new site as part of the experimental procedure, as discussed by the authors themselves, that process appears to prevent the MS from conclusively determining relationships between pH and geochemistry. At present, the MS is therefore a good description of shock responses by mussels in the natural environment rather than the basis for using mussels as pH-palaeoproxies.

Please see our comments in the introduction to this revision note.

Specific comments:

(1) Reviewer: 2.1. Field study. The sudden movement of the mussels to a new, low-pH, environment without an acclimation period to a gradually reduced pH suggests that this study is investigating shock responses to environmental change. This is acknowledged by the authors themselves and they suggest it as a problem in the experimental design to explain the absence of conclusive results. I suggest the authors re-focus the MS, and their hypotheses, to investigate mussel shock responses rather than providing baseline data for the use of mussels as proxies. Similarly, the 68 day experiment lends itself well to determining shock responses rather than adaptation to longer-term changes in pH. That said, by including more data on the transplanted control mussels (see below) the authors may still be able to glean some geochemical proxy type information assuming the transplantation control mussels show little, or no, response to the transplantation itself.

Our reply: Thank you for this comment. In hindsight, we would have redesigned the experiment including longer experimental time and so on. Whilst this paper was in review, we performed – in collaboration with our colleagues from marine biology in Kiel (Dr. F. Melzner) – tank culturing experiments with *Mytilus* using different pH values etc. We implement many of these comments in these experiments and will publish the data in future manuscripts. We, however, lack the financial support to refocus our study and

C5277

to analyze many additional shells from Ischia. We feel that the data shown here have their merits as such but will of course try to implement this comment as good as we can.

(2) Reviewer: 2.2 Materials: this section would be better suited to the introduction.

Our reply: OK

(3) Reviewer: 2.5 Sea water carbonate chemistry: a new section 2.5 should be added which describes how the sea water carbonate chemistry was determined in detail. Questions include: was CO₂sys used, were nitrate and phosphate measured, were alkalinity and pH the only variables used to calculate DIC etc.

Our reply: Background information is given in: Hall-Spencer et al., 2008; Martin et al., 2008; Rodolfo-Metalpa et al., 2010 and Cigliano et al. 2010. We cite this work.

(4) Reviewer: 3.1 Macroscopic observations: Include the image of a mussel from the control transplantation to make all the comparisons easier to visualise. Including the *Mytilus edulis* as a reference double control is a nice addition, but it would be preferential for the authors to use *M. galloprovincialis* from the collection site. If such a mussel is available this should be used instead of the *M. edulis*. If not, I suggest removing all the *M. edulis* data as they are confusing to the reader (I had to think for quite a while as to why it was included). This will make the MS much easier to follow.

Our reply: We agree, please see our comment to reviewer 1.2.

(5) Reviewer: 3.1 lines 20-25: this is an interesting bit! This should be presented as a graph with error bars and a schematic of the mussel for navigation. Our reply: We agree, please see our comment to reviewer 1.3. We will try to add a graph with error bars etc.

(6) and (7) Reviewer: 3.1 EBSD: Both in the text and the Figures 4 and 5 the authors should also include the same data collected for the control transplanted mussel as comparison. This will allow the reader to determine the relative impacts of trans-

C5278

plantation and pH on the changes in structure. 3.1 EBSD line 18: Again pole figure of the control mussel should be included. I suggest point rather than contoured pole figures are used; contoured pole figures use interpolated data. The authors could include maps and pole figures before transplantation, directly after transplantation and at the end of the experiment to provide orientation data on shock vs adaptation by the mussels.

Our reply: We will try to generate these data and implement them.

(8) Reviewer: 3.3.1 Elemental abundances: The authors should show similar maps for the control transplanted mussel.

Our reply: It is the privilege of the reviewer to request unlimited additional data and the burden of the authors to work within the usual constraints regarding analytical time and funding. Please note, BG limits the number of figures for a paper.

(9) Reviewer: Regarding figure 6, I appreciate that the maps probably need to be of different dimensions as the shell gets thinner, however, it leaves open the possibility that patterns observed in map 2 could represent a section of the patterns observed in map 4 as the size and magnification of the maps differs. To be certain that the patterns differ in reality, the maps should be presented at the same magnification and if possible the same dimensions.

Our reply: Thank you for this comment. We do not have the resources to reanalyze several maps and we will not have access to sufficient machine time in near future.

(10) Reviewer: I don't think figure 7 is necessary; the space would be better taken up with a figure showing the control transplanted mussel data equivalent to figure 6 as described above.

Our reply: We politely disagree. We realize that the reviewer suggests re-focusing the paper. This is a valid suggestion but not our aim. We would like to document the shell ultrastructure at the hinge and the mid shell. Please note the very interesting pattern

C5279

in Na and Mg in the different shell layers.

(11) Reviewer: 3.3.2 Isotopes. This is interesting, but confusing to follow. I suggest that only data on the calcite layer are presented in this section.

Our reply: Please see our reply to reviewer 1.4. We agree, this is a complicated story.

(12) Reviewer: Figure 8: I think this plot could go in the supplementary material as it does not directly give information pre / post translocation. Also, the dashed vertical lines should be in all or none of the plots and the font size needs to be increased.

Our reply: We consider this an important data set and prefer to keep it this way.

(13) Reviewer: 3.3.3. Isotope time series: A large portion of these results could be placed in a table making them easier to interpret. There is a lot of information here so a table will help the reader digest the data.

Our reply: We do show these data in supplement table 3 and assert that the explanatory text is required.

(14) Reviewer: 4.1 Mytilus: this section would be better suited to the introduction as well as the first part of section 4.2

Our reply: OK but the Introduction should not become too longwinded (see also comment 2.2.).

(15) Reviewer: Minor language comments.

Our reply: Consider it done.

Thank you for your professional work!

Sabine Hahn and Adrian Immenhauser

Interactive comment on Biogeosciences Discuss., 8, 10351, 2011.