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Biogeosciences Discussions



# *Interactive comment on* "Ion microprobe assessment of the heterogeneity of Mg/Ca, Sr/Ca and Mn/Ca ratios in *Pecten maximus* and *Mytilus edulis* (bivalvia) shell calcite precipitated at constant temperature" *by* P. S. Freitas et al.

**P. S. Freitas et al.**

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We appreciate the thoughtful comments provided by both referees and hope that we are able to properly address the issues raised. We have revised the manuscript carefully considering the advice and criticism offered by these referees. Below we explain the changes made in accordance to the comments made.

R. Takesue REFEREE (1) COMMENTS

"Specific comments: Sentence structure (...)" The text has been revised to improve clarity.



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Interactive Discussion

Discussion Paper

"Abstract, l. 12-13: (...)" The text has been altered and the reference to Mg control on Sr and Mn removed.

"Abstract, line 14-15: (...)" The text has been altered and a sentence was added.

"p. 1269, l. 6 and 15(...)" The text has been altered.

"p. 1270, l. 25(...)" Citations have been added.

"p. 1273, l. 10: (...)" Definition has been added.

"p. 1273, l. 13(...)" The specimens used in this study were part of a larger experiment that covered a range of temperature from 10 to 20°C. A temperature of 20°C was chosen for this study due to the larger shell growth at this temperature relative to 10°C or 15°C. Although 20°C is close to the high-end temperature range for these species, specimens of both species showed normal growth and no particular sign of stress.

"p. 1273, l. 2(...)" Text has been altered.

"p. 1274, l. 2(...)" Text has been altered, with a sentence added.

"p. 1279 and Table 3(...)" Table 3 has been altered to include the standard error rather than standard deviation.

"p. 1280, last paragraph(...)" A sentence has been added regarding Mg/Ca and Sr/Ca ratios.

"p. 1283-4, Section 5.1(...)" Text has been altered accordingly.

"p. 1284, l. 18-21(...)" For each growth interval, SGR was compared to mean profile TE ratios.

"p. 1284, l. 25(...)" A sentence has been modified within the text to highlight this issue.

"p. 1285, l. 16(...)" The statement is that SGR does not exert a general influence on the incorporation of Sr and Mn in the M. edulis shell. Of the expected positive correlation of Sr and Mn with SGR, along the SIMS profiles and along two growth bands, only in one



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growth band did Sr vary according to a potential control by SGR. This observation thus seems to exclude a generalized influence of SGR on shell Sr and Mn composition.

"p. 1286, l. 3(...)" This text has been removed. The objective of the text was to point out that the two species have outer-pallial spaces with different characteristics. M. edulis has a permanent outer-pallial space, while the one in P. maximus is of a non-permanent nature. Isolation of the EPF from seawater occurs in both species at the moment of shell deposition, and that is how we and Carriker (1992; Prismatic shell formation in continuously isolated (Mytilus edulis) and periodically exposed (Crassostrea virginica) extrapallial spaces - Explicable by the same concept, American Malacological Bulletin, vol. 9, 2, 193-197) have interpreted Clark (1974). We argued that in the latter species periodical exposure of the outer EPS/EPF (at times other than during shell deposition) and shell surface to seawater, due to retraction of the mantle from the shell margin towards the pallial cavity, may have an influence in the elemental composition of the extra-pallial fluid. Fig 3a refers to M. edulis and not P. maximus, the latter species being the one in which outer shell trace element enrichment occurs.

"p. 1287, Section 5. (...)" The section title and text have been altered. We are unsure if the crystal texture, prismatic in M. edulis (low Mg/Ca) versus foliated in P. maximus (high Mg/Ca), plays a significant role with respect Mg/Ca ratios. P. nobilis has a prismatic calcite layer and Mg/Ca ratios are even higher than in the foliated calcite of P. maximus. In addition, Mg/Ca ratios in P. maximus change dramatically from the outermost to the innermost shell, both areas having an irregular foliated structure, and thus suggest that other process(es) than the difference between foliated versus prismatic texture is (are) responsible for such change. A comment on the species differences in mean element/Ca ratios has been added to the beginning of section 5.

"p. 1289, l. 9(...)" The text and reasoning have been corrected.

"p. 1288, l. 21(...)" Text has been added.

"p. 1291, l. 1(...)" The comment from the reviewer refers to a section of the text where



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there is no mentioning of axes, crystallographic or shell growth. It is thus difficult for us to understand context surrounding the need for clarification.

"p. 1292, Section 7(...)" Barats et al. (2008) present Mn data from P. maximus grown in several locations in NW France (Table 1), where mean shell Mn/Ca ratios range from 6.5ś1.7 to 18ś9 ?mol/mol, whilst in the present study mean Mn/Ca ratios of a single stria (upper 50 ?m of profile P2) were 16ś5 ?mol/mol. The observed magnitude and variability of stria Mn/Ca ratios in our shell (16ś5 ?mol/mol) is similar to the ones observed by Barats et al. (2008), particularly to the variability in high Mn/Ca ratios P. maximus shells (from 12ś2 to 18ś9 ?mol/mol). From these comparisons, we consider that Mn/Ca ratios in the stria of our shell were not significantly higher or more variable than reported by Barats et al. (2008). Barats et al. (2008) obtained Mn/Ca ratio profiles in P. maximus shells from one LA-ICP-MS measurement in each stria, while we report several SIMS Mn/Ca measurements (n = 5) in a single stria. In addition, the exact location within the stria of the LA-ICP-MS sampling location by Barats et al. (2008) is not shown. Location of sampling within the single stria or the outermost calcite of our study appears to influence Mn/Ca ratios. For instance, Mn/Ca ratios within the lower 30 ?m of the stria (10ś2 ?mol/mol) or within the 50 ?m just beneath the stria (10ś2 ?mol/mol), are both lower and less variable than taking the whole of the stria into consideration. Clearly, these considerations further support the need to study the extent and causes of small-scale variability of element/Ca ratios in bivalve shells.

As discussed by Barats et al. (2008), the difference in P. maximus shell absolute Mn/Ca ratios obtained by different studies (not considering possible differences in analytical methods) are most likely associated with locality-specific environmental and growth conditions, e.g. river inputs of Mn, the role of phytoplankton blooms and Mn recycling between sediment and the water column.

"p. 1292, last parag(...)" Order of sections has been changed.

"p. 1306, Table 3(...)" Table 3 presents mean element/Ca ratios for each growth interval,



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as sampled by different SIMS profiles. A reference to Figure 3, in which the depths of each growth interval are defined, has been introduced. However, none of the mean element/Ca ratios presented in Table 3 represent exactly element/Ca ratios of the outer or inner shell regions. For instance, during the growth interval T2, profile P2 sampled the outer shell region and part of the mid shell region, while profile P3 sampled the outer shell region but not in its entirety.

"p. 1307, Table 4(...)" Legend text has been altered.

"p. 1310, Figure 2a(...)" White boxes and lines have been changed to black.

"p. 1311, Caption 2a(...)" Caption text has been altered.

"p. 1313, Caption 3(...)" Caption text has been altered.

"p. 1316, Caption 5(...)" Caption text has been altered.

"Technical corrections:"

All text has been corrected, if it has not been deleted or changed.

"p. 1268, l. 8(...)" Stria is singular and striae plural.

"p. 1280, l. 7(...)" SIMS profiles are not interior or exterior, but rather sample across the shell from the outer surface to the inner surface. We discuss the variability of element/Ca ratios in different shell regions, which are clearly identified in the text.

"p. 1280, l. 11(...)" Same response as above.

C. Lazareth REFEREE (2) COMMENTS

"General comments "I am not convinced by the part on EPF (section 5.3) because I think that it is not sufficiently supported by the results. Discussions that rely on works done on non biogenic carbonate (e.g. sector zoning) must clearly state that results obtained on non biogenic carbonate may not (in my point of view even more than 8220;probably not8221;) be appropriate to biogenic carbonates. Same remark for the



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works on foraminifera cited. Text has been altered to include the referee8217;s comments.

"Specific comments p. 1272, section 2(...)" Text has been edited accordingly.

"p. 1272, L. 6(...)" Text has been altered to "every second day". It is stated in the text that salinity was measured every fourth to eighth day. On line 3, page 1273, we state that we used d18Owater, which was sampled at a higher frequency (every 2 days), to obtain a salinity record with higher temporal resolution.

"p. 1272, L. 12-13(...)" The seawater samples collected during this experiment were analysed with seawater samples associated with a separate culturing experiment, which is not reported here. The "independent solution" was a synthetic solution of concentrations similar to seawater and that was made up from high purity single-element standards.

The text has been modified to remove any confusion.

"p. 1272, L. 14(...)" Data were systematically corrected for instrumental drift, to obtain the best possible analytical precision possible, as obtained from the repeat measurements of the CASS-4 seawater certified reference material. The text has been modified to remove any confusion.

"p. 1273, L. 2-7(...)" Text has been altered to remove any confusion.

"p. 1273, end(...)" Text has been altered.

"p. 1274, first sentence(...)" Text has been altered to remove any confusion.

"p. 1274, L. 4(...)" According to Carter (1990b) and Taylor et al. (1969) the region of the shell that was sampled in this study consists only of the outer irregularly orientated foliated layer. Text has been altered to remove any confusion.

"p. 1274, L. 6-7(...)" Text has been altered.



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"p. 1274, L.15(...)" We cannot state unequivocally whether the inner layer was sampled or not. We could not observe the inner nacreous aragonite layer in the SEM images at the magnification used, although the layer could have been present, albeit thin. Some of the SIMS profiles were, however, located between the umbo and the pallial line (see Fig. 3), an area of M. edulis shells described to posess a thin inner aragonite layer.

"p. 1279, L. 2 (...)" Sentence has been altered to clarify meaning, i.e. that the dependence of element/Ca ratio variability on SIMS profile depth, particularly in P. maximus, makes it difficult to compare mean growth interval element/Ca ratios of sampled by different profiles. For instance, comparison of mean element/Ca ratios for growth interval T2 from profiles P2 and P3 is strongly influenced by the fact that T2 within P3 is located in the outer shell, while in P2 it is not.

"p. 1279, L. 15(...)" Text has been altered with a sentence added.

"p. 1280; L. 12(...)" See comment above.

"p. 1280, L. 20 to 28(...)" Text has been altered and most deleted. Part of the text was moved to section 2, on the description of SIMS profiles (Line 229).

"p. 1281, L. 3(...)" Text has been deleted.

"p. 1281, L. 6-10(...)" The text was included to explain how precipitation rates vary along the inner shell surface. Text has been altered.

"p. 1282, last sentence (...)" Section 4.2 has been altered and some text deleted.

"p. 1283, L. 23-25(...)" If the effect of pH on Mg/Ca ratios is similar for bivalves and foraminifera a 0.14 unit decrease in pH could explain an increase of 8.4

"p. 1285, L. 7-10 (...)" Sentence has been removed.

"p. 1286, L. 9(...)" The text in this section has been altered.

"p. 1286, L. 14-16(...)" The objective of this sentence is to state that element/Ca



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ratios of shell deposited contemporaneously, at different locations on the inner shell surface, can differ significantly. Tables 3 and 4 report mean values for growth intervals/growth bands. The large standard errors and standard deviations observed for mean element/Ca ratios of different growth intervals do mean that differences in mean element/Ca ratios are not significant. Large differences in the variation of element/Ca ratios of shell deposited contemporaneously at different locations on the inner shell surface are, however, clear from Figures 2 and 3. For instance, in the case of Mg/Ca ratios of both species for the T3 growth interval, mean Mg/Ca ratios of the three profiles are generally not significantly different, but in P. maximus there is a clear difference in Mg/Ca ratios for growth interval T3, in shell sampled by SIMS profile P3 compared to shell sampled by SIMS profiles P1 and P2. In the former profile Mg/Ca ratios reach almost 20 mmol/mol, whilst in the latter profiles Mg/Ca ratios are fairly stable at ca. 5.5 mmol/mol. In M. edulis, Mg/Ca (and Sr/Ca) ratio profiles for growth intervals T2 and T3 are clearly different (Figure 5), although mean element/Ca ratios are not (Table 4). Going from the outer to the inner shell surfaces, shell was both formed during different growth intervals and also at different locations on the inner shell surface. The observed variation of element/Ca ratios with profile depth, particularly for Mg/Ca ratios in P. maximus, suggests that such variability mainly reflects differences in location of shell formation rather than differences in the time of shell formation.

"p. 1287 end and start of 1288(...)" Text in this section has been altered to focus on crystal orientation/faces.

"p. 1288, L.14-15 (...)" Sentence has been rephrased.

"p. 1291, before section 6(...)" There are only a few studies on the possible influence of the organic matrix on element/Ca ratios in bivalves, mostly in M. edulis, and none in P. maximus. That is why we mainly cite work on M. edulis. Text has been altered for clarity.

"p. 1292, L. 17(...)" Text has been altered.



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"Technical corrections":

All text has been corrected, if it has not been deleted or changed.

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Interactive comment on Biogeosciences Discuss., 6, 1267, 2009.