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## ***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.***

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### General comments:

The authors address the complex, poorly-understood topic of trace element incorporation in calcite biominerals and use extensive evidence from the scientific literature to explain their data. This work advances understanding about the processes that influence trace element incorporation in calcite bivalve shells by showing that order-of-magnitude concentration changes can occur in shells in the relative absence of environmental change. The authors then use concentration differences in coeval parts

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of the shell as evidence against certain processes thought to influence trace element incorporation in calcite. Thus although the nature of the experimental work does not allow the authors to demonstrate mechanisms influencing trace element incorporation, the authors are able to narrow down the possibilities that may lead to future avenues of research.

The authors use a relatively novel application of SIMS to show trace element compositional heterogeneity on spatial scales of <100 microns. While their results come from only 1 specimen of each species, they state upfront that this is an initial preliminary assessment, so the lack of reproducibility should not be counted against the value of this study.

The manuscript is well-written with only a handful typographical and grammatical errors. However, I recommend using fewer complex run-on sentences for clarity. The manuscript is well-referenced. The title and figures are appropriate and I have made a comment on the abstract. Some of the background and discussion could be streamlined in instances when they are not directly related to this study or lead to a hypothesis that will be eliminated, but that can be left to the authors' discretion.

#### Specific comments:

**Sentence structure:** The authors use overly-long, complex sentences to convey multiple lines of evidence and relationships. An example of one such sentence is p. 1289, lines 9-18. Since the information itself is complicated, I recommend using short, concise sentences with linking phrases.

**Abstract, l. 12-13:** Your strongest evidence was for the mechanisms a) crystal orientation and size, b) role of the organic matrix. Evidence for Mg control on Sr and Mn was mixed (in which case I think it was not a probable mechanism since lattice distortions should have the same effect in all calcite shells).

**Abstract, line 14-15:** Recommend re-stating the final sentence to emphasize the lack of small-scale variation in Mg/Ca ratios in the interior of shell, which is consistent with the constant temperature control. Based on the plus-or-minus 1-sigma error bars

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(Table 3), Sr/Ca and Mn/Ca are also relatively homogeneous in the interior of the shell. The important thing to remind readers is that paleo-environmental investigations will likely analyze cross-growth band profiles in the interior of the shell, which makes these tracers more promising tools.

p. 1269, l. 6 and 15: The use of "appreciating"; and "appreciation"; would more accurately be stated as "quantifying" or "understanding".

p. 1270, l. 25: Three studies examining spatial patterns, please cite Lorens and Bender (1980), Klein et al. (1996b) and Carre et al. (2006).

p. 1273, l. 10: Not all readers will be familiar with the term shell height, please define.

p. 1273, l. 13: Please comment on why a temperature of 20 degrees C was chosen for the culturing experiments. This is at the high-end of the natural range for these bivalves, is it stressful or ideal?

p. 1273, l. 20: Define shell growth rate here (SGR, p. 1284) since you mention shell growth.

p. 1274, l. 2: Describe ornamentation (striae) here.

p. 1279 and Table 3: When the standard deviations are taken into account, the outer layers have similar mean TE compositions. The standard error is probably more appropriate since the numbers of data points differ, and may show the patterns you describe.

p. 1280, last paragraph: Please mention why Sr/Ca and Mg/Ca results are not discussed.

p. 1283-4, Section 5.1: It is sufficient to say that Sr/Ca and Mg/Ca did not vary and that salinity and pH changes were small and had no effect on Sr/Ca and Mg/Ca. Omit sentences 3, 5, 6.

p. 1284, l. 18-21: Are you comparing SGR to the outer layer chemistry, inner, or both?

p. 1284, l. 25: These growth rate relationships from the literature are all for inorganic calcite. The authors should inform readers that inorganic mineral precipitation is not necessarily a corollary for organic matrix-mediated biomineral precipitation. The authors \*assume\* that the inorganic Mn/Ca rate relationship holds for bivalve shell

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calcite.

p. 1285, l. 16: One set of results does not support the working hypothesis, the other set does. Please explain how you arrived at the conclusion, without resolving this discrepancy, that SGR did not influence Sr or Mn.

p. 1286, l. 3: Clark (1974) was cited as evidence that the outer-pallial space is periodically exposed to ambient seawater. However, this is not the correct reference, as Clark (1974) states that "it does not seem likely that even orderly shell growth requires anything beyond stability (and, of course, isolation from seawater) from its substrate" in the next-to-last paragraph. Whether or not there are other studies showing that seawater fills the outer-pallial space of Pecten, I am not sure that this is an appropriate explanation. As shown in Fig. 3a, the pallial line is several millimeters from the ventral margin and this entire shell surface is exposed to the outer pallial fluid. Clearly this length scale does not coincide with the outer 170 microns of the shell where trace elements are enriched.

p. 1287, Section 5.5: Since sector zoning is inherent to calcite, the causal factor affecting metal/Ca ratios is the orientation of crystals, as the authors describe in the text. I recommend the disuse of "sector zoning" in the section title. The phrase "SIMS sampling of sector zoning" is more accurately stated as SIMS sampling of different crystal faces. Do the author want to mention in this section the consistently higher mean element/Ca ratios in *P. maximus* compared to *M. edulis*? Could this be due to the prismatic versus foliated textures? Crystal size?

p. 1289, l. 9: Your mean values in Table 3 show relatively uniform element/Ca values in the interior of the shell, which suggests that folia with different orientations does not have a strong influence.

p. 1288, l. 21: Clark (1974) presents further evidence of unstructured crystallography in the striae and at the outer shell surface. Below the disordered zone, his SEM images clearly show well-ordered foliated crystals.

p. 1291, l. 1: please clarify "axes", crystallographic or shell growth?

p. 1292, Section 7: Do the authors have any comments on Barats et al. (2008) which

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show lower Mn concentrations and reproducible Mn/Ca profiles measured in the striae of *P. maximus* shells from the Bay of Seine?

p. 1292, last parag.: The important thing to focus on is not the disturbance lines but the reproducible Mg/Ca ratios mid-shell. Elevated element/Ca ratios seem to be limited to the outer surface layer, so recommend to readers that this region be avoided during analyses. In fact, I recommend switching the order of Section 6 and Section 7 to leave readers with the most promising results from your study.

p. 1306, Table 3: indicate which are outer or inner values, perhaps draw a box?

p. 1307, Table 4: I suggest using the terminology "Outer surface" and "Inner surface" rather than "Margin" and "Umbo"

p. 1310, Figure 2a: Please use a black box to outline SIMS transects. This is the most important notation on the figure, yet it is the most difficult to discern with a white box.

p. 1311, Caption 2a: State that SIMS profiles run vertically across the shell, from outer to inner surfaces. Describe how SIMS profiles are marked. The description of the shaded region should be moved to 2b. Use a larger font for the scale bar (illegible). In 2b, move (or omit) the description of the margin/umbo orientation to 2a and cite the direction of growth arrow drawn on the reflected-light photo. Recommend using the terminology "error bars are smaller than the symbols"

p. 1313, Caption 3: Same comments about a black box for SIMS transects, larger font for the scale bar, and the description of error bars.

p. 1316, Caption 5: Similar comment about the description of error bars.

Technical corrections:

p. 1268, l. 8: "striae" and all other instances in the manuscript

p. 1270, l. 17: "focused"

p. 1273, l. 19: "week's"

p. 1276, l. 16: "differences" plural; omit "between each profile" redundant.

p. 1280, l. 7: "interior" profiles or similar terminology to distinguish from outer region.

p. 1280, l. 11: same comment.

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p. 1282, l. 2: insert "a" general increase  
p. 1282, l. 3: insert "have" lower mean ratios  
p. 1282, l. 23: delete "more"  
p. 1283, l. 8: change "absent" to "rarely preserved"  
p. 1284, l. 23: move left parenthesis to read "(e.g."  
p. 1296, l. 3 and 8: Clark (1974) see correct format below.  
p. 1296, l. 12: "shell"  
p. 1296, l. 20: The sentence beginning with Furthermore needs to be constructed as:  
"X and Y are in close proximity, separated by ..."  
p. 1296, l. 25: change "inner" to "growing" for clarity  
p. 1297, l. 3: should read substitution "for" Ca by Mg  
p. 1293, l. 11: omit "may" for clarity  
p. 1293, l. 12-11: omit "higher and variable" and "from observed", redundant  
p. 1293, l. 15-16: omit "in a field-based culturing experiment", redundant  
p. 1295, l. 7: omit the period after "UK."  
p. 1304, caption: add parentheses  $(1\text{-}\sigma/\text{mean})^*100$   
p. 1305, caption: symbol error  $p?0.05$

## References:

Barats, A., Amouroux, D., Pecheyran, C., Chauvaud, L., and Donard, O.F., 2008, High-frequency archives of manganese inputs to coastal waters (Bay of Seine, France) resolved by LA-ICP-MS analysis of calcitic growth layers along scallop shells (*Pecten maximus*), *Environ. Sci. Technol.*, 42: 86-92.

Carre, M., Bentaleb, I., Bruguier, O., Ordinola, E., Barrett, N.T., and Fontugne, M., 2006, Calcification rate influence on trace element concentrations in aragonitic bivalve shells: evidences and mechanisms, *Geochim. Cosmochim. Acta*, 70: 4906-4920.

Clark, G.R., II, 1974, Calcification on an unstable substrate: marginal growth in the mollusk *Pecten diegensis*, *Science*, 183: 968-970.

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