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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.

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I have accepted to review this paper because I am highly interested in the subject. I realized later that I had already reviewed, some time ago now, a previous version of this paper. I note, and appreciate, that the authors took my previous recommendations into consideration.

General comments

In this paper, the authors present new data on element/Ca heterogeneity in bivalve

shells secreted at a constant temperature. To do that they use a high-resolution technique (SIMS) which has not been used previously for such a purpose in bivalve shells. The studied shells were grown under controlled SST while the other parameters were monitored. The material and method section is (almost; only a few points) comprehensive. All along the manuscript, the authors really properly make reference to previous works. Concerning the language, I do agree with the first reviewer (R. Takesue) that a lot of sentences are much too long. This makes the manuscript sometimes hard to follow. I also agree that some discussion could be streamlined somehow. Some paragraphs, giving general information, are not well placed (see specific 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 "probably not") be appropriate to biogenic carbonates. Same remark for the works on foraminifera cited.

Other points are listed below. The most important ones, which need explanation and clarification, are in bold.

This paper gives new insight into trace elements behaviour in bivalve shells and new data that must be taken into consideration to improve the use of trace element proxies for paleoenvironmental reconstructions.

Specific comments

p. 1272, section 2 : An introductory sentence is necessary.
p. 1272, L. 6: I do not understand "every other day". Do you mean that the seawater samples for pH, element/Ca and d18O analyses were collected every day? The frequency of salinity measurements is not specified so that the sentence L. 3, page

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1273 sounds strange.
p. 1272, L. 12-13: I do not understand the following underlined sentence: “Instrumental drift, for the larger batch of solutions that included these seawaters, was monitored by running an independent solution every 10 samples.” And could you specify what was your “independent solution” here.
p. 1272, L. 14: Did you set a threshold above which you corrected the drift or did you systematically do corrections? Should be specified.

p. 1273, L. 2-7: “To obtain a larger temporal coverage of the salinity variation during the experiment the following relationship, with 95% confidence intervals, between salinity and seawater d18O was obtained etc and used to estimate salinity for those dates during the experimental period when only seawater d18O data were available.” How was this equation obtained? Using the paired d18O-salinity data you measured? Two sentences would be better anyway.
p. 1273, end: Add a short sentence to explain why you did SEM analyses.

p. 1274, first sentence: You start talking about P. maximus and then add information on “some pectinid”. Either try to change the sentence or simply delete from “with some”.
p. 1274, L. 4: Why inner layer and myostracum “were not expected”?
p. 1274, L. 6-7: I would change that sentence by “M. edulis shells consist of two primary calcium carbonate”. Why “primary”?
p. 1274, L.15: “if sampled by SIMS analyses”: it is not possible to see if the inner layer was sampled or not?

p. 1279, L. 2 : “However, due to the influence of intra-profile variability on element/Ca ratios, particularly in P. maximus, mean elemental/Ca ratios for each growth interval can not be interpreted solely as representing inter-profile variability.” I do not com-

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pletely agree here because the “intra-profile variability” sometime includes several growth periods. This is specifically the case for all profiles done in P. maximus.
p. 1279, L. 15: Add a sentence for Mg/Ca and Sr/Ca (almost homogeneous).

p. 1280; L. 12: same remark than for p. 1274: can you see if this inner layer has been sampled or not?
p. 1280, L. 20 to 28: This is a general statement that applies for P. maximus also. Try to put it somewhere else in the text.

p. 1281, L. 3: The line “b” is the limit between T1 and T2. Maybe better: “the disturbance mark on the shell surface at the top of profile P5 delineates the break between T1 and T2 when the shell was emerged”. And idem for line c. Nevertheless, I do not see why this information is given here.
p. 1281, L. 6-10: Why do you state that here? This is also a general statement.

p. 1282, last sentence : “i.e. increasing Mg concentrations from the outermost shell to the inner base of the calcite layer.” So here you talk about Mg concentration changing through time. This part of the discussion (from line 10) is a bit confusing to me.

p. 1283, L. 23-25 : The references here concern foraminifera. Should be specified. Moreover, in Lea et al. 99; a 0.1 pH unit increase leads to a 6% Mg/Ca ratio decrease. Here, you have a 0.14 pH unit decrease on the whole period. Could explain (at least partly) the Mg/Ca increase observed on the M. edulis shell profiles?

p. 1285, L. 7-10 : Be careful, from the outer to the inner shell surface (like the SIMS profiles done here), you sampled shell formed at different periods. So, even

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if precipitation rate (and thus potentially element/Ca ratios) differs from the outer to the inner shell surface, element/Ca ratio changes can not be interpreted as solely reflecting kinetic effects. Maybe remove that sentence.

p. 1286, L. 9: "The periodical exposure of the marginal EPS to seawater". In the sentence (quite long) just above, you state that the crystals, not the EPF inside the EPS, are exposed to seawater.
p. 1286, L. 14-16 : I do not see a so clear evidence for that. If you look at Table 3 (e.g. Mg/Ca values in both species for the T3 period) and Table 4 (e.g. compare element/Ca values between P5 and P4 that represent period T2) including the standard deviations, I am not sure that there is a lot of "significant" differences between element/Ca ratios for shell secreted at the same time from the same EPF.
p. 1287 end and start of 1288 : All the references cited here are for non biogenic calcite. I am not sure that those works are directly applicable to biogenic calcite. This must at least be mentioned.
For this part, I do agree with the other referee (R. Takesue) to disuse "sector zoning" but rather talk about "crystal orientation".

p. 1288, L.14-15 : "Calcite crystals produced early during formation of the M. edulis shell, i.e. the outermost 40 μm, are morphologically more varied than the remainder of the calcite layer, with a progressive refinement in the orientation of the planes of adjacent crystals during shell growth (Dalbeck et al., 2006)." I do not understand that. How can you say that the outermost 40 μm of the shell are produced "early"? The shell is secreted all along the mantle at the same time unless you have a reference that says the opposite. Or I misunderstand your sentence which must then be rephrased.

p. 1291, before section 6 : Apart from the L. 15-18, I do not clearly see your interpretation about the possible (or not) influence of organic matrix on element/Ca

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changes in M. edulis although most of the references are about M. edulis.

p. 1292, L. 17: I do not agree including “micro-milling” here as, on the contrary to high-resolution analytical methods like LA-ICP-MS and SIMS, micromilling averages the shell part secreted at a given time, from the outer to the inner part of the shell.

Technical corrections :

p. 1268, L. 5 : Change “P. maximus” in “Pecten maximus”

p. 1272, L. 9: I would add a coma after “ratios”
p. 1272, L. 14: I would add a coma after “analyses”
p. 1272, L. 16: change “relative standard deviation or RSD” by “relative standard deviation (RSD) ”

p. 1273, L. 3: I would add a coma after “experiment”
p. 1273, L. 12-19: Split this sentence which is very long.

p. 1274, L.8-9: I would prefer: “The outer shell layer is finely prismatic calcite **and** the inner layer is a nacreous aragonite, ” rather than “The outer shell layer is finely prismatic calcite with the inner layer being a nacreous aragonite,”
p. 1274, L. 18: I would add a coma after “species”
p. 1274, L. 21: Is it correct to put the accent on “Caméca”?

p. 1275, L. 4: I would put a point after the parenthesis and start then by “For both shells”
p. 1275, L. 5: “For both shells individual profiles traversed the full shell thickness, but **and** in some cases also included other **specific** shell features, i.e. shell surface disturbance marks in both species (Figs. 2 and 3) and a shell surface stria (growth

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ridge present on the surface of the left valve) in P. maximus (Fig. 2)."

p. 1276, L. 5 and L. 7: Change "was" by "is".
p. 1276, L. 23: Use preferentially "peculiar/specific features" here rather than "modified shell structure".

p. 1277, L. 6: change "lowest" by "lower".

p. 1279, L. 21 "change "crystal" by "crystals"

p. 1280, L. 1: change "of lower magnitude" by "lower"

p. 1281, L. 26: "individuals" plural

p. 1283, L. 7: remove "that is also"

p. 1284, L. 22: Add a coma after "In calcite"
p. 1284, L. 23: change the position of the bracket.

p. 1286, L. 4: add a coma after "EPS".
p. 1286, L. 12: a missing "l" at "shell".
p. 1286, L. 8-13: again a long, and thus hard to follow, sentence.

p. 1292, L. 4-5: add a coma before "for both" and after "herein".
p. 1292, L. 21: remove "that"

p. 1293, L. 9-15: Long sentence, almost not understandable.

p. 1294, L. 19: remove coma to "a"
p. 1296, L. 9: Change "contiously" by "continuoulsy"

In Figs. 2; 3 and 5: The name of the profiles (P1; P2; etc) in **bold** would make it easier to follow (and to distinguished from T1; T2; etc).

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