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Interactive comment on “High frequency Barium profiles in shells of the Great Scallop *Pecten maximus*: a methodical long-term and multi-site survey in Western Europe” by A. Barats et al.

Anonymous Referee #1

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Review of High frequency Barium profiles in shells of the Great Scallop *Pecten maximus*: a methodical long-term and multi-site survey in Western Europe. By A. Barats, D. Amouroux, L. Chauvaud, C. Pécheyran, A. Lorrain, J. Thébault, T. Church, and O. X. Donard

General comments -; This manuscript presents barium data from several *Pecten maximus* shells. The aim is to "clarify the biogeochemical processes influencing ... the ... Ba/Ca shell content." Overall, this paper suffers from being very poorly written. Moreover, it also does not bring us any closer in understanding the barium signal in bivalve shells. There are many sentences I could not understand and I do not list all of my

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comments in this review as there are just too many. However, the sheer amount of data is impressive and should eventually be published; albeit with major revisions probably warranting a complete resubmission.

Specific comments

SWI - I think this should be Sediment Water Interface and not Sea Water Interface (also, this should be defined in the main text as well as in the abstract)

The first sentence of the introduction has largely been shown to not be true. Elemental composition of mollusk shells is not generally related to environmental parameters. Nearly all papers from the past years show there is no or only a small link between the two.

The references of the second sentence are rather random. Why do you cite these papers here?

In the Materials and Methods (P3672L15) the authors state that they used matrix matched standards. The use of matrix matched standards is desirable here because the way the laser couples with the sample may effect the measured concentrations. However, the pressed carbonate pellets they used in their study do not contain organic matter, nor is the crystal morphology the same as the bivalve shell. Therefore they are NOT matrix matched standards. They are more similar than the glass NIST standards, but they are by no means matched. The authors themselves state that bivalve shells can contain up to 5% organic matter on line 25 of this page. This 5% is even low. A recent study has demonstrated up to 19% organic matter (Takesue et al GCA in press doi:10.1016/j.gca.2008.09.003). Thereby making the statement on line 25 outdated as well.

P3675L3 - The authors write "Shell analyses were performed each third striae during the shell growth period..." But how is it possible to analyze the shells as they are growing? They were analyzed during the shell growth period?

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Shells from different years were analyzed, so the following statement in P36754L29 is very confusing: "Most of ([Ba]/[Ca])shell maxima occurred during a 20-day period." Also - occurred is misspelled

Technical corrections P3670L3 Shells don not ingest barite! The scallop ingests.

P3671L14: "This ecosystem is mainly influenced by tidal exchange with the Iroise Sea, but also by freshwater input mainly by two small riverine watersheds..." The ecosystem is probably influenced by the sun more than by tidal exchange. This sentence is problematic.

P3672L11: Pre-ablation cleaning was done well before 2004 (the reference here is from 2004). I know Vander Putten et al 1999 (Analytica Chimica Acta 378: 261-272) already used this technique and others before that probably did as well. The citation should be from first time this was done.

Section 3.1.1 The reproducibility of ([Ba]/[Ca])shell ratios was previously demonstrated for 2-year 25 old scallops from the Bay of Brest (Barats et al., 2007). This was also shown by Gillikin et al., 2008 - which is referenced in this manuscript

Section 3.1.1 I would say that peak height is not very reproducible. Shell 1 and 3 are below 4 umol/mol while shell 2 is well above 4 umol/mol.

P3676L5 the authors say they removed the data during the shell Ba/Ca peaks, but do not mention how they did this. Was a mathematical algorithm used or did they just do it by eye?

P3676L15 The authors make the claim that Ba/Ca ratios are not affected by age of the scallop, but they only tested 2 and 3 year old scallops. What about 5 or 6 year old scallops? The one year difference they tested might not be enough to have an effect.

P3676L17 Are these data from Gillikin et al. 2008? It does not say so in the figure

P3676L27 The authors claim that there is a good reproducibility between the three

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replicate shells from each same date, but then say that the R2 is >0.4 . I would say that 0.4 is not very good!

Top of page 3677 The pattern they discuss is present in only 3 of the 7 profiles...

P3677L26 the authors write "is suggested to be" by then never cite anyone.

P3678L3 Gillikin et al 2008 show that there is not an effect of shell mineralogy on Ba/Ca ratios

P3678 There is no basis to say that all the studies that used the NIST glasses are wrong or inaccurate. There have been many and they have similar results. Including Gillikin et al 2008 – where they used both the NIST glass and a pressed calcium carbonate standard and found similar results.

P3678L12 - again - this is not a matrix matched standard

Section 3.2.2 The authors write that the peaks are related to an additional source of Ba at the SWI, but they do not prove this. I do not think we can say this yet. How can they be sure it is not a physiological response to something? Physiological responses can also be well times among populations.

P 3683 - why did the authors choose these particular species of phytoplankton? Are they known to be high in Ba?

Table 1 - the two non-significant data should be listed as such

Table 2 *This table is not complete - there are missing references. A new one by Takesue et al in GCA (in press), plus : Torres, M.E., Barry, J.P., Hubbard, D.A, Suess, E., 2001. Reconstructing the history of fluid flow at cold seep sites from Ba/Ca ratios in vesicomid clam shells. *Limnol. Oceanogr.* 46, 1701-1708. Fritz L. W., Ragone L. M., and Lutz R. A. (1990) Biomineralization of barite in the shell of the freshwater Asiatic clam *Corbicula fluminea* (Mollusca: Bivalvia). *Limnol. Oceanogr.* 35, 756-762.

*Do not list your standards as matrix matched - they are not - plus Gillikin et al 2008

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and 2006 used similar standards, but are not noted this way.

*I do not at all agree with your "Time Resolution" All of the studies that say seasonal are monthly or better. Gillikin et al 2006 approaches what was done in this study on scallops.

Table 3 - I really do not understand this table

Fig 3 I can't see the difference between the two variables very easily

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