

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.

A. Barats et al.

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Answer to comments of anonymous referees #1 and #2 Concerning the general comment "on the poor style of the writing", our "native English author" will do a thorough and complete edit of the revised document to resolve all the editorial comments, and more.

- p3667, line 2 In the future draft, the precision "(2-year old; 3 shells/year)" will be removed and replaced in the second sentence such as: "Variations of ([Ba]/[Ca])shell ratio were first demonstrated reproducible for several scallop individuals from the same population (2-year old; 3 shells/year), over a 7-year period (1998-2004), and from different coastal environments in France (42-49°N)".

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- p3667, line 15 The abbreviation SWI will be redefined as "sediment water interface".
- P3668, line 5-10 In agreement with the comment, the sentence will be changed into: "Coastal waters are enriched in Ba during estuarine mixing through freshwater inputs of dissolved Ba or Ba release from river-born particulate phases, in the low to mid salinity ranges (Coffey et al., 1997; Shaw et al., 1998; McCulloch et al., 2003), or through the exchange of Ba-rich ground waters and pore waters within the tidal prism (Shaw et al., 1998)." The bibliographic reference will be also added such as: "In recent studies, there was much attention to the skeletal Ba content in mussels (*Mytilus edulis*) (Vander Putten et al., 2000; Gillikin et al., 2006), oysters (*Isognomon ehippium*), (Lazareth et al., 2003), clams (*Mercenaria mercenaria*, *Spisula solidissima*, *Arctica islandica*, *Saxidomus giganteus*, Asiatic *Corbicula fluminea*) (Stecher et al., 1996; Epplé, 2004; Gillikin et al., 2005; Gillikin et al., 2008, Fritz et al., 1990), and scallops (*Pecten maximus*, *Compotopallium radula*, *Argopecten purpuratus*) (Lorrain, 2002; Thébault, 2005; Gillikin et al., 2008)."
- P3670, line 3 Bivalves don't ingest especially barite. They ingested all the barium that can be input to the SWI. "As barite" will be removed in the sentence.
- p3671, line 5 "Different ecological characteristics" This is explained in the following sentences. Some shells were sampled in open coastal ecosystems influenced by large estuarine inputs: such as those sampled in the Bay of Seine (France, English Channel, 49°30N, 0°30W) submitted to the Seine river inputs, and those sampled near Belle Ile and Quiberon influenced by the Loire river (France, Bay of Biscay, respectively, 47°20N, 3°10W and 47°30N, 3°00W). Others shells were sampled in coastal environments subjected to low anthropogenic inputs such as the Ria de Vigo (Spain, Atlantic Ocean, 42°10N, 8°50W) or the Bay of Brest (France, Iroise Sea, Roscanvel bank, 48°20N, 4°30W).
- p3671, line 14 The Bay of Brest is mainly influenced by freshwater inputs and tidal exchange with Iroise sea (part of Atlantic Ocean). For example, waters are well mixed

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by tides, and may represent an oscillating volume of 40% during spring tides (see Chauvaud et al. 1998). This contribution is thus not negligible. Otherwise, the influence of sun is not significant: first it is not a sunny place and the water column is never stratified.

- p3672, line 14 Pre-ablation of the shell surface was done also by Vander Putten et al. (1999). It is right. This reference will be added. But, there is no other study to my knowledge using LA-ICPMS method with a pre-ablation step previous to shell analyses before this date.

- p3673, line 3 Explanation of the following sentences: "Shell analyses were performed each third striae during the shell growth period (from April to November)..." Scallops were not alive. They were sampled at the end of the year (for example in November), and at this date they were killed. Knowing the sampling date (fishing date) and the fact that *Pecten maximus* scallops form a daily stria on its shell, a calendar date can be attributed to each stria by backdating thanks to MEB photographs. In the same time, a calendar date is also attributed to each analysed stria (one analyse each third stria). The shell growth period depends of the seawater temperature (must be higher than 10°C) and generally extends from April to November.

- p3673, line 26 The fact that Ba analyses in suspended matter was done at RMCA will be added in the text.

- p3673, line 20 Both Ba and Mn were analysed in dissolved seawater (<0.6µm) and in suspended matter. Details concerning Ba analyses in dissolved samples were described in the text just bellow with the following sentences: "Dissolved samples were acidified in 2% HNO₃ (69-70% Suprapur, Merck) and diluted 30 times. Two internal standards were added (Y and Bi) in diluted samples. Elemental concentrations (Ba, Mn,...) were then determined by ICP-MS (X7 serie, Thermo Fisher) by an external and internal calibration."

- p3674, line 8 "NO₂⁺" will be removed and corrected by "NO₂⁻".

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- p3674, line 27 “Most of ([Ba]/[Ca])shell maxima occurred during a 20-day period.” As this sentence is confused, it will be rewritten as: “([Ba]/[Ca])shell maxima events from its beginning to the end usually last 20 days whatever the studied year.”

- p3675, line 24 It is true that Gillikin et al. (2008) reported also Ba/Ca shell ratios in scallop from the Bay of Brest. It is further highlighted p3676 line 15 that’s why it is not reported here.

- p3676, line 5 “A mean ([Ba]/[Ca])shell profiles exhibited a background ratio of $0.535 \pm 0.134 \mu\text{mol/mol}$ (calculated removing data during shell Ba/Ca peaks, i.e. higher than the average plus 3 times the standard deviation on the average)...” A mathematical criterion was used to calculate the background ratio removing all data up to than the average plus 3 times the standard deviation on the average. The sentence will be changed as: “A mean ([Ba]/[Ca])shell profiles exhibited a background ratio of $0.535 \pm 0.134 \mu\text{mol/mol}$ (calculated removing data during shell Ba/Ca peaks, i.e. higher than the average plus 3 times the standard deviation on the average)”

- p3676, line 15 Ba/Ca profiles obtained in our study were compared to those obtained by Gillikin et al. The sentence will be clarified: “([Ba]/[Ca])shell profiles were then compared to those previously reported by Gillikin et al. in 2003 for 2- and 3-year old scallops from the Bay of Brest (Fig. 2b) (Gillikin et al., in press).”

- p3676, line 15 The data presented in the Figure are not those of Gillikin et al. (in press). They are those from our work and ok they are similar to those previously obtained by Gillikin et al. (in press).

- p3676, line 27 The data presented in the table 1 compare the results obtained between 2 individuals with r^2 . These coefficients are usually higher than 0.7. There are some exceptions: with shell 1 in 2000, with shell 2 in 2004, and all shells in 2000. That’s why some r^2 are not really good. But if the entire database is considered, we can remark a high reproducibility of Ba/Ca shell profiles.

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- P3676-3677, line 27 It is true that the general pattern described here is true only for 3 of the 7 year. It will be better to highlight the occurrence of two Ba shell maximum event such as “Concerning the summer ([Ba]/[Ca])shell peaks, the first one occurred from mid June to July and the second one from end July to early September.”. This will be true for all the year except in 2002.

- p3677-3678, line 28 continued next page Higher Ba contents in shells versus calcification structure: The calcification structures (aragonite or calcite) were indicated in the table 2. Generally, higher Ba contents were measured in aragonite structure and also in calcitic shell such as mussels (ex.: Vander Putten’s studies). Gillikin et al., who performed calibrations with matrix matched standards, measured similar Ba contents in calcitic scallop shells than in our study. This suggests the validation of our methodological approach.

- p3678, line1-15 The text agrees with this comment because it indicated that some studies used CaCO₃ standards such as Belloto and Mikeley, 2000; Thébault, 2005; Gillikin et al., 2006; Barats et al., 2007. The use of the CaCO₃ standard MACS from the USGS was not underlined in this paper because this material is not yet certified. Only indicatives values for elemental content are available. This material used by Gillikin et al. was also systematically analysed in our group to confirm the accuracy of the calibration performed with our “lab made” CaCO₃ standards.

- p3679, line 1-5 The mistake of the unit ($\mu\text{mol/l}$ instead of $\mu\text{mol/mol}$) will be corrected.

- p3680, line 1 The sentence describes the variations for particulate Ba (and not total Ba as suggested by referee #2).

- p3680, line 8-12 The sentence was confused because: - the first part line 8-9 “A pelagic biogenic process as the initial cause of Ba-rich particles at the SWI and subsequent ([Ba]/[Ca])shell maxima” was a title 3.2.2.2. - such as p3679, line 21 “3.2.2.1. The origin of these ([Ba]/[Ca])shell maxima” - and such as p3683, line 15 “3.2.2.3. Processes involved in Ba-enrichment at the SWI that evidence subsequent ([Ba]/[Ca])shell

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maxima”

- p3681, line 8 I think it is a grammatical mistake: the other years”, i.e. 1998, 1999, 2001, 2002, 2003, 2004.

- p3682 + P3693 Table 3 A variable time window to integrate environmental parameters was chosen to take in account the potential time lag between a biogeochemical event in the water column and its transcription with the shell. It was our choice not to extend the discussion on the description of these statistical data. Even if these statistical results are significant, this remains statistics and cannot explain directly the process influencing the occurrence and the amplitude of Ba peak events in shells. This permits however highlighting environmental parameters influencing indirectly Ba events.

- p3683 and table 3 These particular phytoplankton species (*Chaetoceros* spp.) were chosen because it is the only one recurrent and abundant during all Ba/Ca shell maximum events. These phytoplankton species are not recognized to contain higher Ba content.

- p3691 Table 1 The explanation * will be removed.

- P3694 Figure 1 The sites Quiberon and Belle Ile, influenced by the Loire river, were indicated in the map. Only the site of Vigo in Spain was not present on these maps.

- P3695 Figure 2 There is a mistake in the legend. Mo is mentioned instead of Ba.

- P3696 Figure 3 In black, it is the profile of Ba/Ca shell ratio and in grey variations of chlorophyll a concentration.

- P3697 Figure 4 There are two sharp increase of dissolved Ba in spring (up to 10nM). Such concentrations were unusual except, as suggested by the reviewer, in deep ocean or river water. The bay of Brest is not submitted to upwelling events which refute the hypothetic input of deep oceanic seawater. Otherwise, the bay of Brest may be influenced by riverine input. Even if this influence may be negligible, the main part of the year, this may be an eventual source of Ba. The comparison of these 2 Ba peaks in

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dissolved content with seawater salinity reveals that these events occur during a period of lower seawater salinity. However, this period is long and cannot explain the sharp increase in dissolved Ba content.

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