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Biogeosciences Discussions

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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General Comments

This paper focuses on both the variations and implications of ([Ba]/[Ca])shell ratios assayed in scallop shells with uniquely high resolution. Our extensive study (3 shells/year, over a 7-year period (1998-2004) and for different sites) in the shells confirms the previous pattern observed in other bivalves (mussels, clams...). The shells also punctually record ubiquitous transient events among scallop communities as transient summer events. This comprehensive dataset underscores a reproducible process occurring in summer providing extensive Ba inputs in the surrounding habitat of the bivalve scallops. It thus demonstrates the extent of such summer events that cannot be resolved with

discret dataset obtained until now. It brings a new perspective on processes related to Ba enrichment in bivalve shells. Using an extensive database that includes hydrological, chemical, biological parameters, we can restrict the alternative potential processes proposed in the past literature. This paper demonstrates further that the exact mechanism for Ba enrichment in bi-valves still remain elusive, until specific in situ intensive experiments can be performed. We show that the complexity of this estuarine system is uniquely traced to the pelagic/benthic processes in the Ba cycle, resulting in significant Ba inputs at the sediment water interface (SWI). Thus our conclusions are based on: (1) Using our published methodical approach, maximum ([Ba]/[Ca])shell ratio measured in the shell are reproducible among scallop populations. These event reoccur among years, ubiquitously among sites, comparable among other bivalve species and thus can be integrated in future bi-valve biogeochemical time series for further validation; (2) The absolute dating allowed by the scallop shell daily growth and the specific quantification of Ba concentrations in each stria. As such records of maximum ([Ba]/[Ca])shell ratio are confirmed to be initiated by a pelagic biogenic process transferred to the benthos. This cannot be explained by a simple biogeochemical monitoring dataset and argues against a simple use of ([Ba]/[Ca])shell ratio as a routine paleo productive tracer.

Specific Comments The final author comments contain both the previous the author comments published online and now the answer to other referee comments.

- p3667, line 2 In the revised manuscript, the precision "(2-year old; 3 shells/year)"; was removed and replaced in the second sentence such as: "A methodical evaluation of the ([Ba]/[Ca])shell ratio was performed for the first time and demonstrates that ([Ba]/[Ca])shell profiles are 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)."

- p3667, line 15 The abbreviation SWI is redefined as "sediment water interface".

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- p3667, line 25 The first and second sentences are rewritten: "Since 1965, trace elements in mollusc shells were investigated because bivalves form in their shells successive calcium carbonate layers, potential archives of conditions experienced by the organism during its life time (Dodd, 1965; Lorens, 1980; Klein, 1996a; Klein, 1996b; Stecher, 1996). The main aim of these studies was to use trace element records in shells as a bio indicator of environmental conditions."

- P3668, line 5-10 In agreement with the comment, the sentence was changed: "Coastal waters are enriched in Ba in the low to mid salinity ranges during estuarine mixing by either freshwater inputs of dissolved Ba or Ba release from river-born particulate phases (Coffey et al., 1997;Shaw et al., 1998;McCulloch et al., 2003). Alternatively Ba input can occur from the exchange of Ba-rich ground waters and pore waters within the tidal prism (Shaw et al., 1998)." The bibliographic reference is 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 ephippium; 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, Comptopallium radula, Argopecten purpuratus; Lorrain, 2002;Thébault, 2005;Gillikin et al., 2008)."

- P3670, line 3 Bivalves don't ingest especially barite; they can also ingest all forms of barium that can be input to the SWI. "As barite" was removed in the sentence.

- p3671, line 5 "Different ecological characteristics" This is elaborated 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) influenced by 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 exposed to low anthropogenic inputs such as the Ria de Vigo (Spain, Atlantic

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Ocean, 42°10N, 8°50W) or the Bay of Brest (France, Iroise Sea, Roscanvel bank, 48°20N, 4°30W)."

- p3671, line 14 The hydrodynamics of 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 by tides, and may represent an oscillating volume of 40% during spring tides (see Chauvaud et al. 1998).This contribution is thus not negligible. Tidal exchange may influence the hydrodynamic / hydrology of the bay but not the ecosystem. Otherwise, the role of sunlight is very important for the primary productivity in most estuaries, although this is not specific to the Bay of Brest.

- p3672, line 14 Pre-ablation of the shell surface was done also by Vander Putten et al. (1999). It is right. This reference was 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.

- p3672, line 14-line 25 The CaCO3 pellets used for our external calibration do not originate from a mixed shell powder. Thus, our "lab made"; standards did not contain any organic matter. The referee #1 suggested that our standards were not "real" matrix matched. However, these standards were prepared with pure CaCO3 (Merck, Suprapur) calcite powders. Xray diffraction analyses (unpublished results) were performed on our "lab made" CaCO3 standards demonstrating a pure diffraction spectrum of calcite. The crystal structure is thus the same as the scallop shells Pecten maximus. The percentage of organic matter in calcite bivalve shells is usually less than 5% (see below). That's why it seems appropriate to use the term "matrix-matched". This methodological approach was validated by analyses of Ca-rich CRM and already published in Analytical Bioanalytical Chemistry in 2007 by our group (Barats et al., 2006). Although the organic content of the scallop shell was not measured, analyses were performed only in the outer layer of the scallop shell. The organic matrix represents usually less than 5%. A recent study of Takesue et al. (2008) revealed higher organic content in clams (19%). But they demonstrate also that "... Ba contents were

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unchanged by the removal of organic matter". This conclusion supports that Ba occurs exclusively in shell aragonite of clams and are a good candidate for external proxy relationships. This result agrees with the use of Ca weight content about 40% to calculate our ([Ba]/[Ca])shell ratios. This explanation is added in the revised manuscript: "Mollusc shells were recognized to contain less than 5 % of organic matrix in calcite or aragonite shells (Carroll et al., 2006;Levi-Kalisman et al., 2001). The shell is thus composed by minimum 95% of CaCO3, i.e. a minimum shell Ca content of 38%. In comparison with the Ca concentration of 40%, the error is only of 5%. This study thus used a shell Ca content of 40% because scallop shells have a calcite structure. While the exact percentage of organic matter remains unknown, yet likely less than 5 %, the analytical error will be negligible. A recent study of Takesue et al. (2008) revealed higher organic content in clams (19%), but they demonstrated also that Ba assay in shell content was unchanged by the removal of organic matter. This conclusion underscores that while Ba occurs exclusively in shell aragonite of clams, the analytical result agrees with the use of Ca concentration about 40% to calculate our ([Ba]/[Ca])shell ratios."

- 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 naturally not alive, as they were sampled at the end of the year (e.g. in November), and only at this date were killed. Knowing the sampling 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 SEM (Scanning Electron Microscopy) photographies. In the same time, a calendar date is also attributed to each analysed stria (one analyse each third stria). The shell growth period depends on the seawater temperature (must be higher than 10°C) and generally extends from April to November.

- p3673, line 20 Both Ba and Mn were analysed in dissolved seawater ($<0.6\mu$m) 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

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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."

- p3673, line 26 The fact that Ba analyses in suspended matter was done at RMCA (Royal Museum for Central Africa, Belgium) was added in the text. David Cardinal from the RMCA was also acknowledged in the paper.

- p3674, line 8 "NO2+" was replaced by "NO2-".

- p3674, line 27 "Most of ([Ba]/[Ca])shell maxima occurred during a 20-day period." As this sentence is confusing, it was 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. As it has been already referenced on p3676 line 15, it is not reported again here.

- p3676, line 5 "A mean ([Ba]/[Ca])shell profiles exhibited a background ratio of 0.535 ś 0.134 μmol/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 the average plus 3 times the standard deviation on the average. The sentence is changed as: "Background ([Ba]/[Ca])shell ratio was obtained after the exclusion of peculiar data (i.e. Ba/Ca peaks) exhibiting higher ratio than the average values plus 3 times the standard deviation. A mean ([Ba]/[Ca])shell profiles exhibits a background ratio of 0.535 ś 0.134 μmol/mol..."

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

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previously reported by Gillikin et al. (Gillikin et al., 2008)." The data presented in the Figure are not those of Gillikin et al. They are those from our work and they are similar to those previously obtained by Gillikin et al. In this study, the effect of scallop age was only investigated for 2- and 3-year old scallops because the older scallops are, the shorter growth period is, and the more difficult the striae backdating is.

- p3676, line 27 The data presented in Table 1 compare the results obtained between 2 individuals using r2 values. These coefficients are usually higher than 0.7 and the probability below 0.05. There are some exceptions: with shell 1 in 2000, with shell 2 in 2004, and all shells in 2000. That's why some r2 values are not exceptional. If the entire database is considered, we can demonstrate a high reproducibility of the Ba/Ca ratio in shell profiles.

- P3676-3677, line 27 It is true that the general pattern described here is true only for 3 of the 7 year period. It is thus 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 was 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) are indicated in Table 2. Generally, higher Ba contents were measured in aragonite structure and also in calcitic shells such as mussels (ex.: Vander Putten's studies). Gillikin et al., who also performed calibrations with CaCO3 standards, measured similar Ba contents in calcitic scallop shells as in our study. This suggests the validation of our methodological approach.

- p3677, line 26 This is a confirmation of this study that's why there is no reference. The sentence is changed as "Differences in ([Ba]/[Ca])shell content can be related to the bivalve species, its physiology, or differences in analytical methods" to avoid a potential misunderstanding.

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- p3678, line 12 The term "matrix-matched" is replaced by "CaCO3".

- p3678, line 12 As indicated by the referee #1, the shell mineralogy was demonstrated not to influence background or maximum ([Ba]/[Ca])shell ratios. This sentence was added: "Gillikin et al. (2008) demonstrated however that shell mineralogy have no effect on ([Ba]/[Ca])shell ratios (Gillikin et al., 2008)."

- p3678, line 15 The text agrees with this comment because it indicates that some studies used CaCO3 standards such as Belloto and Mikeley, 2000; Thébault, 2005; Gillikin et al., 2006; 2008 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. 2006 and 2008 was also systematically analysed in our group to confirm the accuracy of the calibration performed with our "lab made" CaCO3 standards. As previously reported in Barats et al. 2007, our method was certified against other CRM materials. Our paper does not state that all previous studies based on NIST standards are wrong (as understood by the referee #1), as much many of them revealed similar results. It underlined however that: 1- Ba concentrations in NIST standards are significantly higher than those measured in shells; 2- That for some laser ablation units, it is necessary to use CaCO3 standards.

- p3679, line 1-5 The mistake on the unit for the ratio Ba/Ca (μmol/mol instead of μmol/l) is corrected.

- p3679, line 21 We supposed that there are additional Ba inputs at the SWI to explain ([Ba]/[Ca])shell maximum events because: 1- it was the case in 2000 both in dissolved and particulate phases; 2- the scallop age was demonstrated not to be influenced during this event; 3- it is the most probable pathway for other years; 4- a physiological effect was not demonstrated.

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

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- p3680, line 8-12 The sentence was confused because: - the first part line 8-9 "A proposed 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 ([Ba]/[Ca])shell scallop 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 maxima"

- p3681, line 8 There 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 within the shell. It is our choice not to extend the discussion on the description of these statistical data. Even if these statistical results are significant, statistics alone cannot explain directly the process influencing the occurrence and the amplitude of Ba peak events in shells. This however highlights environmental parameters influencing indirectly Ba input 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 * was removed.

- p3692 Table 2 In the explanation *, the term "matrix matched" was replaced by "CaCO3". This is the case also for Gillikin et al. (2008, 2006). We agree with referee #1 that the time resolution was better than seasonal for most of the studies. The time resolution was noted such as "monthly or better". Two missing references (underlined by the referee #1) were added: Torres et al. (2001) and Takesue et al. (2008). Takesue et al. (2008) presented ([Ba]/[Ca])shell ratio along the shell from the umbo to the ventral margin without any dating. The reference to Fritz et al. (1990) is not added

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because they didn't investigate variations of ([Ba]/[Ca])shell ratio along shells.

- p3693 Table 3 This statistical table indicates: 1- only the significant direct correlations between the amplitude of ([Ba]/[Ca])shell maximum ratio and other environmental parameters that include POC, PON and Chl a. 2- only the significant relationships expressing the amplitude of ([Ba]/[Ca])shell maximum ratio according to other environmental parameters. These statistical results are not conclusive and in themselves cannot demonstrate a direct influence of the biogeochemical events observed and the occurrence of ([Ba]/[Ca])shell maximum events. They strongly indicate however a potential link between the nitrogen cycle and the intensity of these events.

- P3694 Figure 1 The sites Quiberon and Belle Ile, influenced by the Loire River, are indicated in the map. Only the site of Vigo in Spain is 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 is the profile of Ba/Ca shell ratio and in grey variations of chlorophyll a concentration. This precision was added in the legend of the figure.

- P3697 Figure 4 There are two sharp increases 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 subjected to upwelling events and thus not the hypothetic input of deep oceanic seawater. Otherwise, the bay of Brest should be influenced by riverine input. Even if this influence is not direct during much of the year, it still may be an eventual source of Ba. Anne Lorrain thesis (2002) demonstrated however that riverine inputs have no direct influence on ([Ba]/[Ca])shell maxima (for example, flood in April and no ([Ba]/[Ca])shell maxima). These ([Ba]/[Ca]) ratios were measured in seawater from the SWI, i.e. at only 1 m of the bottom. The explanation of these 2 ([Ba]/[Ca]) maximum ratios were thus unclear because of complex pelagic/benthic processes occurring at the SWI. This complexity of Ba cycling was also underlined by the Ba shell record.

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