Biogeosciences Discuss., 6, C2761–C2768, 2009
www.biogeosciences-discuss.net/6/C2761/2009/

Biogeosciences Discussions

Interactive comment on "Spring molybdenum enrichment in scallop shells: a potential tracer of diatom productivity in coastal temperate environments (Brittany, NW France)?" *by* A. Barats et al.

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Received and published: 29 October 2009

Answer to Referee #2 This referee underlines that this manuscript is a valuable contribution to the domain of paleo proxy validation. The main drawback from this referee is the writing quality of the manuscript. A serious effort was made (1) to re-edit a more straightforward "results and discussion" section divided in 3 independent parts which avoid further confusion , and (2) to thoroughly edit and improve the English style and grammar (lastly corrected by a native English lecturer). The new "results and discussion" section organization present a single part "results and discussion" where 3

axes were developed: (1) the validity of using Mo as a new tracer (reproducibility), (2) the influence of environmental conditions on the occurrence and the amplitude of the ([Mo]/[Ca])shell enrichment, (3) and finally transient biogeochemical processes potentially associated to spring Mo uptake in the scallop shell. All the specific comments have been taken into account for the manuscript revision and a detailed list is given below.

Specific comments: Materials and methods - The figure 1 was completed to present how the shell section was cut to perform the laser ablation - ICPMS ([Mo]/[Ca])shell profile. (see fig 1 in attach file) A schematic visual description of our protocol has also been electronically published in Photonics Spectra (February 2008, p.30, http://www.photonics.com/Content/ReadArticle.aspx?ArticleID=32241) and is shown below. (see fig 2 in attach file)

- Page 8048, line 23: The statistical data treatment was not explained in details as a previous article is already describing such standard method (Barats et al. 2009 BG). This is done in the new text: "A statistical data treatment was performed to highlight environmental parameters that co vary with the amplitude of ([Mo]/[Ca])shell maximum events. Most ([Mo]/[Ca])shell maxima could be defined by about 10 sampling points along the shell (1 point every 3 days), corresponding to a duration of one month (30 days). The most intense section of ([Mo]/[Ca])shell maxima was generally characterised by a period of 15 to 21 days (i.e., 5 to 7 sampling points) whatever the year. We thus decided to choose integration periods of 2 weeks around the maximum of ([Mo]/[Ca])shell , which was consistent with the lower resolution obtained for most of environmental parameters and the uncertainty due to the backdating of shell striae. These integration periods took into account an eventual lag between changes in the water column, at the SWI, and its further transcription within the shell. The data integration approach is thus similar to the one used to investigate ([Ba]/[Ca])shell maxima (Barats et al., 2009), and allowed a good overlapping between ([Mo]/[Ca])shell maxima and environmental datasets. The influence of transient events was tested taking the

maximum value during the considered period. Bravais Pearson tests and multiple regression analyses were performed with Stabox Pro software for Windows Ver. 6 (Grimmer Software, France). Bravais Pearson tests were used to highlight univariate correlations between the amplitude of ([Mo]/[Ca])shell maxima and others variables. Multiple regression analyses were considered to express the amplitude of ([Mo]/[Ca])shell maxima according to several independent factors. " - Page 8048, line 19: More details were given concerning the analyses dissolved Mo and the collection of bottom waters. The term "bottom water" is also preferentially used to better reflect the operational sampling protocol: "Bottom waters were regularly sampled (every 2-3 days) by a diver-operated Niskin sampler positioned and closed horizontally at 1 m above the SWI to avoid any disturbance the SWI and thus to preserve the characteristic of the bottom water column. After collection the samples were filtered (< 0.6 μm, Nucleopore) and acidified in 2% HNO3 (69-70% Suprapur, Merck). Before analysis, they were diluted 50 times with Milli-Q water (Millipore). Two internal standards were also added (Y and Bi) in the diluted samples. Mo dissolved concentrations were then determined by ICP-MS (X7 series, Thermo Fisher) by external and internal standard calibration. " We agree that dissolved Mo concentrations in bottom waters are not reflecting what is exactly happening at the SWI. However, we observe that such variation of the Mo content in bottom waters is directly coincident to the variations of Mo in the shell (in 2000). We can thus easily assume that the increase of Mo dissolved concentrations measured in May 2000 in the bottom waters is reflecting a global pelagic process (bloom to post-bloom conditions) which will also influence Mo content at the SWI (intense sedimentation). - Page 8045, line 5: The acronym SWI was defined here: sediment water interface (and also in the abstract). - Page 8047, line 25: The text was rewritten: "The ([Mo]/[Ca])shell ratios were calculated dividing shell Mo concentrations by the calcium concentration in the shell (400 mg/g), and expressed in μmol/mol (Barats et al., 2009;Barats et al., 2008;Barats et al., 2007). Shell Ca concentration was supposed to be constant all along the shell surface. Recently, the variability of the Ca concentration in the same collection of scallop shells was investigated (Richard, 2009). This concentration was

found to be constant within a same stria and all over the surface of the shell, at about 390 $\pm$ 10 mg/g, confirming a homogeneous Ca shell distribution." - Page 8047, line 6: The different sites were precisely defined with geographical coordinates in the new tex. A map of these different sites was previously published in our paper focused on Ba (Barats et al. 2009 BG). This point was added in the text: "Description of this complete database and a map of the different sites was previously reported (Barats et al., 2009)."

Results and discussion The results and discussion sections were merged in a single part to avoid misunderstanding in the revised version of the paper. The core of the manuscript shows 3 independent results and discussion section that can be easily outlined to improve clarity. - As mentioned by the referee #2, the uncertainty of about 3 days on the backdating of ([Mo]/[Ca])shell profile can affect the inter-individual correlation (Table 1). For example, in 2001, an excellent correlation (r2=0.99) was obtained between the shell 2 and 3 whereas there were weak correlations (r2=0.37 or 0.57) between the shell 1 and 3 or the shell 1 and 2. This difference can be thus related to an approximate backdating of the shell 1. - Page 8049, line 11: The 5 successive peaks of ([Mo]/[Ca])shell ratios were clearly shown in Figure 1a. In the text, the sentence described the averaged profile which is presented in Figure 1b. The text was slightly changed to clearly describe the Figure 1a and 1b. "([Mo]/[Ca])shell concentrations showed a similar profile with average background concentrations below the detection limit (<2.7 nmol/mol), and 5 significant enrichments from May to October (Fig. 1a). A comparison of these Mo profiles among the 3 individual scallop shells reveals significant correlations (r2 >0.73, p <0.05, n >60; Table 1). This result underlines a statistically high reproducibility of ([Mo]/[Ca])shell profiles among a same scallop population. As a consequence, an averaged ([Mo]/[Ca])shell profile, defined as a mean of 3 shell profiles, can be established and shows also significant spring and summer enrichments (Fig. 1b; Table 1)." - Page 8049, line 20: There was a mistake in the text. The sentence must call fig. 1b instead of 2b. This is corrected in the revised version. - Page 8050, line 19: The referee found that the explanation concerning the inter-annual reproducibility was not clear. The Table 1 showed however 2 clear conclu-

sions: (1) a high intershell reproducibility whatever the year and (2) a similar pattern for ([Mo]/[Ca])shell profile exhibiting an intense spring peaks. The comparison is based on the analysis of 19 shells (so n=19). The previous value n>60 was taking in account the fact that more than 60 individual striae analyses were made for each shell. More information was thus added in the text to clarify this point. "([Mo]/[Ca])shell concentrations showed a similar profile with average background concentrations below the detection limit (<2.7 nmol/mol), and 5 significant enrichments from May to October (Fig. 1a). A comparison of these Mo profiles among the 3 individual scallop shells reveals significant correlations ($r^2 > 0.73$, $p < 0.05$, $n > 60$; Table 1). This result underlines a statistically high reproducibility of ([Mo]/[Ca])shell profiles among a same scallop population. As a consequence, an averaged ([Mo]/[Ca])shell profile, defined as a mean of 3 shell profiles, can be established and shows also significant spring and summer enrichments (Fig. 1b; Table 1)." - Page 8051, line 9: Comptopallium radula was correctly written in the new version. - Page 8052, line 11: The acronym PSNZ was first defined such as Pseudonitzschia spp.. - Page 8053, line 10: As explained just before, Mo dissolved concentrations were measured in bottom waters and the authors assumed that increased Mo concentration 1 m above the SWI can directly reflect Mo content variations at the SWI, and thus probably the variations of the Mo content available for scallop. Details on the sampling method were given in the new text (see before). - Page 8055, line 4: The difference between the Wadden Sea and the bay of Brest was not clearly detailed in the manuscript. For our purpose, the interest of the measurements and the findings from the Wadden Sea is mainly the fact that Mo cannot be conservative in the water column of a coastal sites depending mostly on seasonal and biological pelagic features. The comparability of the two investigations is rather limited as both the objectives and the experimental approaches are distinct. In the Wadden Sea, Mo seawater content was measured in the water column and exhibited increased concentrations in the particulate phase and depleted ones in dissolved phase whereas in the Bay of Brest, only dissolved Mo concentrations could be measured and in bottom waters. In addition, the main biogeochemical features and turnover of both sites are

also dissimilar, thus Mo cycling in both sites might be controlled by different processes, although they show both non conservative pathways at different extent and period. The text was shorten: "This assumption is also supported by a seasonal non conservative behaviour of Mo previously observed in coastal North Sea waters off Germany (Dellwig et al., 2007) which exhibits transient enrichment and depletion of Mo concentration in the particulate and dissolved phases, respectively. However, the comparison between this study and our work remains difficult to address considering the distinct experimental approaches and characteristics of the two ecosystems." -Page 8058, line 13: This part was slightly modified: "Mo inputs at the SWI can thus be induced by a diatom biogenic material downward flux. Diatoms are the more efficient Si scavengers among the marine phytoplankton due to the large cell size and density (Sarthou et al., 2005). Mo enrichment in bottom waters may therefore be driven by such biogenic material flux to the SWI. Spring ([Mo]/[Ca])shell enrichments are thus supposed to follow scallop uptake of Mo at the SWI. The scallop ingestion of phytoplankton cells grown on NO_3^- (such as diatoms) and containing high levels of Mo for the activity of nitrate reductase, or the ingestion of important amounts of resuspended microphytobenthos cells grown on NO_3^- was previously proposed to explain ([Mo]/[Ca])shell maxima (Thébault et al., 2009). Our data may support these assumptions, but none of these pathways can be completely demonstrated. The processes governing either Mo scavenging by biogenic particles and its further uptake by the scallop remain to be elucidated." - Table 1: The authors agree with the referee. The Table 1 presented ([Mo]/[Ca])shell ratios rather than concentrations. It was corrected in the new text. - Figure 5: The unit of the salinity was removed.

Interactive comment on Biogeosciences Discuss., 6, 8041, 2009.

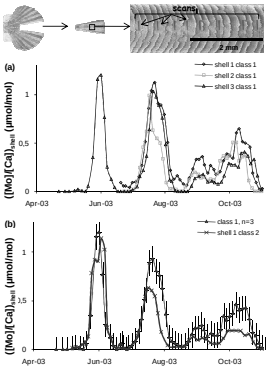

Fig. 1. new figure 1

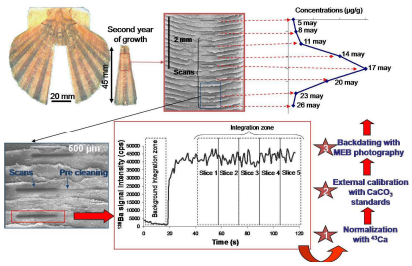

Fig. 2. explanation of the method