

## ***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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Answer to J. Bijma (referee #3) J. Bijma underlined the fascinating work done in this paper but the paper was too difficult to read as highlighted by other referee. As mentioned before, a serious effort was thus made to re-edit and correct the manuscript within a single part “results and discussion” and to improve the English. All the specific comments have been taken into account and details are given below. The abbreviations are now accurately defined (SWI, PSNZ...) in the revised version. This paper demonstrates however that with an extensive database including hydrological, chem-

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ical, biological parameters, the nature of the involved pathways can be ascertained but not completely resolved. The complexity of such system is directly linked to the pelagic/benthic processes in the Mo cycle, responsible of significant Mo inputs at the SWI. We however confirm in this work that: (1) Based on our methodical approach, maximum ([Mo]/[Ca])shell ratio measured in the shell are reproducible among scallop, population, recurrent among years, ubiquitous among sites, and can be integrated in biogeochemical time series for further validation; (2) Because of the absolute dating allowed by the scallop shell daily growth and the specific quantitative determination of Ba concentration in each stria, records of maximum ([Mo]/[Ca])shell ratio are established to be initiated by a pelagic biogenic process which could not be explained by a simple biogeochemical monitoring dataset; (3) The significant relationship obtained between the maximum Mo/Ca in spring and various biogeochemical variables, but especially the net uptake of silicates and nitrates, suggest a potential connection with diatoms spring time productivity in such temperate ecosystems.

Abstract Page 8043, line 20: It was not clear how the dynamic of spring diatom blooms was related to the extent of ([Mo]/[Ca])shell peaks. The text was thus corrected as follow: “Spring maxima of ([Mo]/[Ca])shell ratio are especially correlated to the extent of the silicic acid and nitrate depletions in seawater between winter and late spring ( $r^2 = 0.878$  and  $0.780$ ,  $p < 0.05$ ,  $n=6$ ) which reflects diatom uptake and productivity in the Bay of Brest. The Mo inputs in bottom waters and subsequent shell enrichment are thus suggested to be directly or indirectly influenced by such biogenic material input to the SWI.”

Introduction Page 8044, line 13-15: *Pecten maximus* shell has been demonstrated to be a powerful tool because each stria can be accurately dated with a daily scale resolution. This specific characteristic is not achievable for all other major bivalves investigated so far, such as mussels, clams... In most cases, only an approximate formation period can be assigned to the analysed striae. This part was rewritten: “An approximate date of formation was usually attributed to the shell deposit to interpret the

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archived information, lacking thus of an accurate time assignment. Different methods such as shell sclerochronology or oxygen stable isotope composition have demonstrated that the Great Scallop *Pecten maximus* (L.) develops the specific feature to precipitate a distinct daily stria of  $\text{CaCO}_3$  on its shell (Chauvaud et al., 1998; Chauvaud et al., 2005). This scallop was then promoted as a good candidate for environmental proxy calibration at a daily scale (Chauvaud et al., 1998; Lorrain et al., 2000; Chauvaud et al., 2005; Lorrain et al., 2005; Barats, 2006; Barats et al., 2008; Barats et al., 2009)."

Page 8044, line 13-15: The authors agree with the referee comments; "Dissolved seawater" is an inaccurate shortcut term to describe the dissolved fraction in seawater. The text was thoroughly examined to avoid this mistake. The sentence was rewritten: "P. maximus is a non-selective filter feeder ingesting both dissolved and particulate material within the bottom waters surrounding the scallop (Chauvaud, 1998; Chauvaud et al., 1998; Chauvaud et al., 2005; Lorrain et al., 2005)."

Page 8045, line 19-20: Mo is usually associated to the manganese oxide phase of the sediment. The reduction of this manganese oxide phase can thus release important amounts of Mo in the overlying waters. The referee suggested showing some equations here, supposedly as equilibrated chemical reaction. The real association of Mo into sedimentary mineral phase can indeed be principally driven by co-adsorption on Mn oxides, but we cannot exclude co-precipitation as well as complexation on organic coating adsorbed onto the minerals. Thus, the complexity to the various sediment bearing Mo phases made almost impossible to constrain it into a simple chemically equilibrated formula, which is thus useless at this stage of the work. "Mo benthic inputs to the SWI can be induced under suboxic conditions via the reduction of sedimentary manganese oxides and leading to Mo release in the overlying water as  $\text{MoO}_4^{2-}$  dissolved species (Crusius et al., 1996; Crusius and Thomson, 2000; Morford et al., 2001; Chaillou et al., 2002; Dalai et al., 2005; Elbaz-Poulichet et al., 2005; Morford et al., 2005). Released Mo at the SWI may then diffuse back in the water column or can be re precipitated (authigenesis) into Mo-Fe-S forms under strict anaerobic conditions

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(Erickson and Heltz, 2000; Sundby et al., 2004; Tribouillard et al., 2004; Zheng et al., 2000)."

Page 8046, line 9-11: The sentence was rewritten: "Recently, a non conservative behaviour of Mo was revealed in the water column of a coastal environment (Wadden Sea, Germany) (Dellwig et al., 2007)."

Materials and methods Page 6, line 142: This part was slightly changed to explained the different step of the sample preparation: "Only the left valve of the shell was considered (Barats et al., 2009; Barats et al., 2007). Shells were cleaned by soaking in 90% acetic acid for 45 60 s to remove bio fouling, rinsed with distilled water, and air dried. A 45x10 mm<sup>2</sup> cross section corresponding to the second year of growth (juvenile stage) was cut along the axis of maximum growth rate (Chauvaud, 1998; Chauvaud et al., 1998). A pre cleaning ablation of the calcite surface was first made before LA-ICPMS analyses to avoid surface contamination. This pre cleaning step consisted in a quick (around 20 s) pre-ablation of the considered shell stria surface at a rate of 50  $\mu\text{m/s}$  (Barats et al., 2007)."

Page 8048, line 5: This part was rewritten: "A date of formation was assigned to each ablated sample by backdating from the harvest date and based on the daily periodicity of stria formation in *P. maximus*. Chronological profiles of trace element contents were then established based on such stria specific date assignment."

Results Page 8049, line 17: The authors stated about 5 significant ( $[\text{Mo}]/[\text{Ca}]$ ) shell peaks. There are indeed 5 maxima in the Figure 1: the first and second were the most intense. The last 3 maxima were less important. In this particular case (other years exhibit only 2 to 3 peaks), the poor resolution between the third and fourth maximum, make it difficult to distinguish between the two. However, the authors decided to maintain the definition of these 5 maxima.

Page 8051, line 18: As recommended by the referee, the Fig. 3 was better described in the main text. "Profiles of ( $[\text{Mo}]/[\text{Ca}]$ ) shell ratio were compared with Chl a concen-

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trations along the growth period (Fig. 3). This figure underlined for some years (1999, 2001) concomitant ([Mo]/[Ca])shell and Chl a maxima. For 3 others years (1998, 2000, 2003), a short delay is observed between the Chl a peak and that of ([Mo]/[Ca])shell. For the remaining years investigated (2002, 2004), a ([Mo]/[Ca])shell maximum is finally preceding the Chl a peak. It is first important to underline that for similar Chl a maxima, ([Mo]/[Ca])shell spring maxima exhibit much more variable extent. This result argue thus against a direct relation with the phytoplankton biomass as measured through the Chl a content. The enrichment in particulate organic carbon (POC) in the water column is also usually associated to maximum of Chl a concentrations and revealed similar variations (Fig. 4). Such as for Chl a, the POC content is not directly related to the occurrence and intensity of spring ([Mo]/[Ca])shell maxima, even if some of these ([Mo]/[Ca])shell maxima matched with a preceding or concomitant POC enrichment.”

Page 8053, line 10: The sentence was also rewritten: “In 2000, Mo dissolved concentrations in seawater...”

Page 8055, line 12: The authors understand the referee’s comments on the Mo partition coefficient. In the text, we are presenting data on the “apparent” or “measured” partition coefficient, if we consider that Mo intake is done through aqueous phase thermodynamic equilibrium. This “apparent” distribution coefficient is drastically changing in May 2000 because two concentrations changes in the calculation: Mo concentrations in shell and in the seawater. Mo shell concentration increased more than Mo concentration in the dissolved phase of the seawater. This drastic change of “apparent” partition coefficient during the ([Mo]/[Ca])shell peak in 2000, cannot be explain by simple thermodynamic equilibrium changes (concentration, temperature, salinity, . . .) thus providing a new argument for the trophic ingestion of Mo by the scallop. Appropriate changes in the text were made to clarify this point. “In order to better constrain the conservative or non conservative behaviour of Mo in the bottom waters of the Bay of Brest (Roscanvel), the evaluation of the “apparent” distribution between the shell and the seawater can be performed, first assuming that the particulate phase Mo is not involved.

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The distribution of Mo between solid carbonate and seawater is expressed by the partition coefficients: with [Mo] the Mo concentration and [Ca] the calcium concentration in shell or in seawater (sw). In 2000, this partition coefficient revealed a background averaging  $DMo = 1.5 \times 10^{-4}$  punctuated by a single drastic spring increase (maximum  $DMo = 0.081$ ) concomitant to the maximum ([Mo]/[Ca])shell event. These results underline also a non conservative behaviour of dissolved Mo in bottom waters, concomitantly to the ([Mo]/[Ca])shell maximum events (i.e. in the carbonate shell matrix). The only known structure of molybdate precipitation with  $Ca^{2+}$  is the powellite form ( $CaMoO_4$ ) with a low solubility of  $521 \mu\text{mol/L}$  (Swinkels et al., 2004). Mo crystallizes neither in a calcite nor in an aragonite structure. This can explain the low background partition coefficient ( $DMo = 1.5 \times 10^{-4}$ ), agreeing with anionic Mo precipitation pathway within the  $CaCO_3$  shell. Second, the drastic spring maximum partition coefficient,  $DMo = 0.081$ , cannot be explained neither by any variations of the physico-chemical conditions in the seawater (i.e. temperature, salinity, Mo dissolved concentration) nor any variations of shell growth physiology (i.e. growth rate measurements). This result suggests that Mo partition coefficient and shell concentrations during the spring enrichment event cannot be described by a direct dissolved Mo uptake. In this particular case, Mo shell uptake from enriched particulate phase must be considered, although no measurements are available in this study.”

Page 8055, line 8 (same comments for the referee 2): Concerning the difference (climatic or hydrologic) between the Wadden Sea and the bay of Brest, this was not clearly detailed in the manuscript because 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

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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 8052, line 29: A special care was dedicated to clarify the statistical result to avoid misunderstanding (ecological state of middle spring...). The text was rewritten: "Statistical data analyses were performed to highlight the parameters potentially related to the amplitude of ([Mo]/[Ca])shell maximum considering a two week period and using the data from the 7-year survey (1998-2004) in the Bay of Brest. Bravais Pearson tests revealed only two significant correlations between the amplitude of ([Mo]/[Ca])shell maximum and the maximum abundance of PSNZ ( $r^2 = 0.53$ ,  $p < 0.05$ ,  $n = 14$ ) or with the maximum abundance of Chl a ( $r^2 < 0.32$ ,  $p < 0.05$ ,  $n = 14$ ). Multiple regression analyses underlined also a relevant relationship expressing the amplitude of maximum ([Mo]/[Ca])shell ratios ( $\mu\text{mol/mol}$ ) according to the maximum relative abundance of PSNZ (%) and the maximum concentration of silicic acid ( $\mu\text{mol/L}$ ) in the seawater ( $r^2 = 0.40$ ,  $p < 0.05$ ,  $n = 14$ ), these two parameters not being significantly correlated. The significance of the regression was improved removing unusual and late ([Mo]/[Ca])shell maximum events in 2003 (peak 3, 4 and 5) ( $r^2 = 0.88$ ,  $p < 0.05$ ,  $n = 11$  and  $d \text{ cook} < 1$ ) :  $([\text{Mo}]/[\text{Ca}])_{\text{shell}} = 0,877 + 0,0261 (\% \text{PSNZ}) - 0,358 [\text{Si}]$ . This relationship exhibited a negative coefficient with silicic acids and a positive one with PSNZ. This can be explained by the fact that silicic acids are actively uptaken by diatoms (Ragueneau et al., 2002) and that PSNZ blooms usually occur during low or depleted silicic acid concentrations in seawater (Gomez et al., 2007; Pan et al., 1998; Parsons and Dortch, 2002; Prego et al., 2007). Such as silicic acids, nitrates are actively up-

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taken by diatoms (Ragueneau et al., 2002). To further establish the underlying association between diatom productivity and Mo enrichment in the scallop shell, the apparent amount of silicic acid or nitrate uptake by diatoms (i.e. "apparent" diatom spring productivity) have been evaluated subtracting the average minimum concentration measured in late spring ( $n=9$ , May and June) to the average maximum one observed in winter ( $n=11$ , December to February). As expected from our previous observations, these "apparent" spring nutrient depletions were significantly correlated to the amplitude of maximum ([Mo]/[Ca])shell ratio both for silicic acid ( $r^2 = 0.878$ ,  $p < 0.05$ ,  $n = 6$ , Fig. 6) and for nitrates ( $r^2 = 0.780$ ,  $p < 0.05$ ,  $n = 6$ ). These results indicate also that the amplitude of maximum ([Mo]/[Ca])shell ratio were not directly related to the total biomass, but rather to diatom productivity resulting in a post-bloom period characterised by silicic acid or nitrate depletion and PSNZ dominance."

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