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**Spring Mo shell
enrichment: a tracer
of diatom
productivity?**

A. Barats et al.

Spring molybdenum enrichment in scallop shells: a potential tracer of diatom productivity in coastal temperate environments (Brittany, NW France)?

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Skeletal molybdenum/calcium ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) ratios were recently examined in bivalves. These ratios were determined by quantitative LA-ICP-MS analyses every third daily striae (i.e. a temporal resolution of 3 days) in 36 flat valves of the Great Scallop shells *Pecten maximus* (2-year old; 3 shells/year) collected in temperate coastal environments of Western Europe (42 to 49° N). Variations of ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) ratio were significant and reproducible for scallops from a same population, from different years (1998–2004) and from different coastal temperate locations. ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) exhibits typical profiles characterized by a background content, below the method detection limit ($<0.003 \mu\text{mol/mol}$) for most of the shell growth period, which is punctuated by a significant transient enrichment ($0.031\text{--}2.1 \mu\text{mol/mol}$) mainly occurring from May to June. The Bay of Brest (France) was especially investigated because of long term observations on scallop communities, environmental variables, and high resolution analyses of dissolved Mo in bottom seawater in 2000. In 2000, dissolved Mo exhibited significant increasing concentration just preceding a maximum of ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) ratio. The environmental conditions preceding ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) maximum events, both in 2000 and over the 7-year survey indicates a direct influence of the scallop environmental conditions at the sediment water interface subsequent to the intense and periodic spring bloom event. Spring maxima of ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) ratio were found to be specifically related to the dynamic of spring diatom blooms and to the extent of the subsequent silicate depletion. ($[\text{Mo}]/[\text{Ca}]_{\text{shell}}$) records reveal thus unexpected biogeochemical routes of Mo, potentially related to coastal spring productivity.

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1 Introduction

Mollusc bivalves grow through an incremental deposit of calcium carbonate layers with the specificity for most species to exhibit a temporal marking (Stecher et al., 1996; Chauvaud et al., 2005, 1998). Bivalves can preserve within their own exoskeleton a chronological record of environmental variations that they experienced during their life. Following this growth particularity, several investigations demonstrated that variations of the elemental composition archived along the shell growth axis can be used as proxies for coastal biogeochemical processes (Dodd, 1965; Lorens and Bender, 1980; Klein et al., 1996a, b). For most of the species (*Mercenaria mercenaria*, *Mytilus edulis*, *Isognomon ehippium*, *Ensis siliqua*), trace element profiles within the shell provide chronological records of environmental conditions experienced by the bivalves (Puente et al., 1996; Stecher et al., 1996; Giusti et al., 1999; Vander Putten et al., 2000; Richardson et al., 2001; Lazareth et al., 2003; Gillikin et al., 2005). The interpretation of the archived information is however to date lacking of accurate time assignment of the measurements. The Great Scallop *Pecten maximus* (L.) behave the feature to deposit a daily distinct stria of CaCO_3 on its shell, previously demonstrated by different methods (sclerochronology, stable isotope) (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 (Barats et al., 2009, 2008; Chauvaud et al., 1998, 2005; Barats, 2006; Lorrain et al., 2000, 2005). This bivalve grows in coastal environments over a wide range of latitudes (30° to 60° N) and bathymetry (1 to 500 m). At temperate latitudes such as in France (Brittany), the scallop shell exhibits (I) a fast daily growth rate (max $350 \mu\text{m}$ per day) and (II) an extended growth period (from mid-April to end-November) during the second year of growth (Chauvaud, 1998; Chauvaud et al., 2005). The shell growth rate is influenced by seawater temperature (scallop grows only if $T_{sw} > 9-10^\circ\text{C}$), and limited by massive or toxic phytoplankton blooms (Lorrain et al., 2000; Owen et al., 2002a, b). *P. maximus* is a non-selective filter feeder ingesting both dissolved seawater and all compartments of particulate matters (Chauvaud, 1998;

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Chauvaud et al., 1998, 2005; Lorrain et al., 2005). The variations of trace element shell concentrations provide significant high frequency archived information (Freitas et al., 2005, 2006; Lorrain et al., 2005; Barats, 2006; Barats et al., 2007, 2008). For example, manganese (Mn) concentrations along the shell were recently demonstrated mainly governed by concentrations in dissolved Mn at the SWI being themselves controlled by freshwater inputs and benthic remobilizations (Freitas et al., 2006; Barats et al., 2008). More recently, $([Mo]/[Ca])_{shell}$ ratios were examined because their variations highlighted intriguing profiles with an annual sharp increase (Barats et al., 2007; Thébault et al., 2009).

Molybdenum (Mo) is one of the most abundant transition group metals in seawater, mainly present as the oxy anion MoO_4^{2-} in oxygenated environment (Collier, 1985). Mo is generally considered as conservative in pelagic waters with a concentration averaging 110 nmol/L in marine environment suggesting a little influence of biogeochemical processes on its abundance (Collier, 1985). Coastal Mo distribution is governed by freshwater-seawater mixing (Dalai et al., 2005). Some studies highlighted however that Mo can also present a non conservative behaviour in coastal waters: both at the sediment-water interface (SWI) (Adelson et al., 2001; Chaillou et al., 2002; Crusius et al., 1996; Elbaz-Poulichet et al., 2005) and in the water column (Tuit and Ravizza, 2003; Dellwig et al., 2007). Mo benthic inputs to the SWI can be induced under suboxic diagenetic conditions via the reduction of sedimentary manganese oxides and leading to Mo release in the overlying water as 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 (Erickson and Heltz, 2000; Sundby et al., 2004; Tribovillard et al., 2004; Zheng et al., 2000). In the water column, molybdenum assimilation by diazotrophic cyanobacteria and phytoplankton is an essential catalytic factor for the majority of N_2 -fixing organisms and many nitrate reductase systems (Collier, 1985; Hille, 2002). Mo availability may act to limit N fixation in marine ecosystems,

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and consequently, may limit primary productivity (Marino et al., 1990; Cole et al., 1993). Various marine phytoplankton species were investigated for their cellular Mo contents which were reported to be rather low and homogeneous (3.3 mmol Mo/mol of P, or 3.1 $\mu\text{mol/L}$ of cellular volume) among the 15 phytoplankton species investigated (diatoms, green algae, coccolithophores) (Ho et al., 2003). This concentration obtained under identical culture conditions was apparently independent of the phytoplankton species and did not exhibit any specific assimilation related to the phylogenetic origin of the investigated species, as it can be observed for other micronutrients (Ho et al., 2003; Quigg et al., 2003). Recently, Dellwig et al. (2007) revealed a non conservative behaviour of Mo in the water column of a coastal environment (Wadden Sea, Germany) (Dellwig et al., 2007). In summer, Mo was demonstrated to be enriched in suspended particulate matter and depleted in dissolved phase of the seawater. The bacterial decomposition of phytoplankton was reported to promote the release of organic compounds and the formation of Mo-enriched aggregates which may thus settle to the SWI to be rapidly decomposed by microbial activity contributing to a substantial release of Mo in bottom waters (Dellwig et al., 2007).

Through the observation of $([\text{Mo}]/[\text{Ca}])_{\text{shell}}$ ratio along the daily striae of *P. maximus*, the objectives of this study are first to evaluate $([\text{Mo}]/[\text{Ca}])_{\text{shell}}$ profile as a potential archive of specific biogeochemical processes occurring at the sediment-water interface and second to provide a new confirmation of the Mo non-conservative behaviour in coastal waters. The quantitative micro-analysis of shell Mo content was previously developed using Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) and matrix-matched standards (Barats et al., 2007). Quantitative chronological profiles were defined with an accurate date and concentration assignment for each measured stria. A first evaluation of $([\text{Mo}]/[\text{Ca}])_{\text{shell}}$ profiles is first performed in different scallop populations and years to highlight the reproducibility, ubiquity and periodicity of the $([\text{Mo}]/[\text{Ca}])_{\text{shell}}$ maxima. These maxima are then examined over a 7-year period and particularly in 2000, according to the bivalve physiology and ecological constraints. The main biogeochemical processes influencing the occurrence and the

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extent of $([Mo]/[Ca])_{shell}$ maxima are finally discussed.

2 Materials and methods

2.1 Studied site and scallop sampling

Three live juvenile specimens of *P. maximus* were collected for each year and studied site (except in 2002 in the Bay of Brest, $n=2$). Shells were collected in the Bay of Brest at Roscanvel station ($n=3$ shells per year, 1998–2004, except in 2002: $n=2$), off Belle Ile in 1999 ($n=3$), 2000 ($n=4$) and 2001 ($n=3$), off Quiberon in 2000 ($n=3$) and in the Bay of Seine in 2004 ($n=3$). Scallops were collected during the late autumn period by SCUBA diving in Roscanvel and by dredging for other ecosystems. Details concerning sampling sites were previously reported (Barats et al., 2009). Only the left valve of the shell was considered (Barats et al., 2009, 2007). A $45 \times 10 \text{ mm}^2$ 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) and cleaned before LA-ICP-MS analyses (Barats et al., 2007).

2.2 Determination of trace element concentrations in shells

Quantitative analyses of trace elements within shells were performed by a LA-ICP-MS method consisting of coupling a UV laser ablation unit (LSX 100 UV 266 nm, Cetac Tech.) to an ICP-MS (X7 serie, Thermo Fisher). The methodological approach and analytical performances were described in details elsewhere (Barats et al., 2009, 2008, 2007). Briefly, a matrix-matched external calibration was performed with lab prepared CaCO_3 pellets. The Mo calibration curve displayed a good linearity with a determination coefficient above 0.99. The detection limit was about 27 nmol/g, and the relative standard deviations obtained for both analytical repeatability and reproducibility were below 7%. The $([Mo]/[Ca])_{shell}$ ratios were calculated dividing shell Mo concentrations

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by the calcium concentration in the shell (40%), and expressed in $\mu\text{mol/mol}$ (Barats et al., 2009, 2008, 2007). Shell analyses were performed each third striae to obtain a temporal resolution of 3 days. A date of formation was assigned to each ablated sample by backdating from the harvest date and based on the daily periodicity of striae formation in *P. maximus*, conducing to the definition of trace element shell profiles. The incertitude on the chronological time-scale of mean shell profiles was estimated to be ± 3 days. An evaluation of the shell growth rate was also made using an image analysis technique previously described (Chauvaud, 1998).

2.3 Environmental monitoring

In order to relate $([\text{Mo}]/[\text{Ca}]_{\text{shell}})$ time-series and environmental parameters able to influence Mo biogeochemical cycle at the SWI, an intensive environmental survey was conducted in the Bay of Brest, at Roscanvel, where scallop shells were sampled from 1998 to 2004. Weekly Chlorophyll *a* data originated from measurements at the SOMLIT station (also in the Bay of Brest), as part of monitoring activities of the Intitut Universitaire Européen de la Mer (http://www.univ-brest.fr/IUEM/observation/observation_iroise.htm). Weekly database of seawater nutrient and phytoplankton species also originated from the SOMLIT station. Description of this complete database was previously reported (Barats et al., 2009). A specific survey was also performed at Roscanvel in 2000 (from February to December). Such as Ba and Mn in Barats et al. (2009), Mo dissolved concentrations ($< 0.6 \mu\text{m}$) were regularly measured (2–3 days resolution) in bottom seawater (1 m above the SWI).

2.4 Statistical analyses

A statistical data treatment was performed to highlight environmental parameters that exhibit any co variations with the amplitude of $([\text{Mo}]/[\text{Ca}]_{\text{shell}})$ maximum events. Most of $([\text{Mo}]/[\text{Ca}]_{\text{shell}})$ maxima could be defined by about 10 sampling points along the shell (1 point every 3 days), which corresponded to a duration of one month (30 days). The

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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. This result was similar to those previously obtained for $([Ba]/[Ca])_{shell}$ maxima (Barats et al., 2009). The same statistical data treatment was thus performed (Barats et al., 2009).

3 Results

3.1 Reproducibility, ubiquity, periodicity and variability of the spring $([Mo]/[Ca])_{shell}$ enrichment

3.1.1 Reproducibility of $([Mo]/[Ca])_{shell}$ profiles in a same scallop population from Bay of Brest (Brittany)

Three scallops from the Bay of Brest (Roscanvel) were analysed for their juvenile stage (second year of growth) in 2003 (Fig. 1a). $([Mo]/[Ca])_{shell}$ concentrations showed a similar profile with average background concentrations below the detection limit (<2.7 nmol/mol), and significant spring or summer enrichments (Fig. 1a). A comparison of these 3 scallop Mo profiles revealed 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. A mean $([Mo]/[Ca])_{shell}$ profile, defined as the average of 3 shell profiles, revealed 5 significant enrichments from May to October (Fig. 1b; Table 1).

Analyses of a three-year-old scallop from the same population were performed for its third year of shell growth corresponding also to the year 2003 (Fig. 2b). Comparison of average juvenile $([Mo]/[Ca])_{shell}$ profile with one of a three-year-old scallop revealed similar variations. Background $([Mo]/[Ca])_{shell}$ concentrations remained always below the detection limit and maximum of $([Mo]/[Ca])_{shell}$ ratios occurred simultaneously in all shell samples during spring or summer. These results state that: (1) $([Mo]/[Ca])_{shell}$ ratios present an important enrichment in spring or summer, significantly reproducible

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among a single scallop population; (2) these $([Mo]/[Ca])_{shell}$ maxima do not show any relation with specific physiological or biological effect related to the scallop age.

3.1.2 Ubiquitous occurrence of $([Mo]/[Ca])_{shell}$ maxima in several scallop populations from coastal temperate environments

5 The comparison of $([Mo]/[Ca])_{shell}$ profiles from 1998 to 2001 in 3 different sites is displayed in Fig. 2a. This representation highlights a good reproducibility of these shell profiles both for the intra- and inter-annual variations. Examination of $([Mo]/[Ca])_{shell}$ profiles in the different ecosystems studied on the Atlantic coast (North western, France) reveals a general pattern with similar background concentration below the
10 detection limit and significant maxima of $([Mo]/[Ca])_{shell}$ ratio occurring in spring or summer (Table 2). The amplitude of these maximum $([Mo]/[Ca])_{shell}$ ratios was site- and year-dependent (Table 2). The recurrence and ubiquity of this $([Mo]/[Ca])_{shell}$ pattern along the north-west French coast provide a reasonable assessment of strong inter-population similarities of Mo uptake by scallops within these environments and
15 strengthen the extent of this event.

3.1.3 Recurrence of $([Mo]/[Ca])_{shell}$ maxima in scallop shells sampled from the Bay of Brest (Brittany) among a 7-year period

An inter-annual study was carried out over a 7-year period (1998 to 2004) in the Bay of Brest (Roscanvel). An intershell comparison of $([Mo]/[Ca])_{shell}$ profiles of 3 juvenile scallops was performed over this period and still confirmed the significant reproducibility of
20 $([Mo]/[Ca])_{shell}$ profiles ($r^2 > 0.37$, $p < 0.05$, $n > 60$; Table 1). $([Mo]/[Ca])_{shell}$ profiles exhibited also the general recurrent pattern, except in 2003: a background content under the detection limit and a single episodic transient peak of $([Mo]/[Ca])_{shell}$ ratio occurring in spring (May–June) (Table 1, Fig. 3). This spring time $([Mo]/[Ca])_{shell}$ maximum
25 presented highly variable maximum ratio depending on the year (Table 1). Additional $([Mo]/[Ca])_{shell}$ maxima were also measured in summer, but exhibited lower intensities

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than the first spring time event.

This 7-year survey demonstrates first the inter-annual recurrence of $([Mo]/[Ca])_{shell}$ profiles with their significant spring time peaks. Second, this intense peak of $([Mo]/[Ca])_{shell}$ ratio was characterised by its significant reproducibility among a single population (3 juvenile scallop shells per year) and its occurrence in spring. Third, the high reproducibility of spring $([Mo]/[Ca])_{shell}$ enrichment (intra-individual, inter-annual, inter-site) would indicate rather an environmental control on Mo incorporation within shells. It is interesting to note that Thébault et al. (2009) highlighted also a similar pattern of $([Mo]/[Ca])_{shell}$ ratio in tropical scallops (*Comptopallium Radula*, New Caledonia) showing the global extent of such environmental process.

3.2 Influence of environmental conditions on the occurrence and amplitude of the $([Mo]/[Ca])_{shell}$ enrichment

3.2.1 Influence of water column biogeochemistry on $([Mo]/[Ca])_{shell}$ enrichment in the Bay of Brest (1998 to 2004)

The complete environmental database was examined along the 7-year survey (1998–2004) in the Bay of Brest and compared to spring $([Mo]/[Ca])_{shell}$ maxima events. Profiles of $([Mo]/[Ca])_{shell}$ ratio and Chl *a* concentrations along the growth period covaried similarly (Fig. 3). Maxima of $([Mo]/[Ca])_{shell}$ ratio matched with a preceding or concomitant maximum of Chl *a* concentrations which was usually associated to POC enrichment in the water column whatever the year (Figs. 3 and 4). The general trend observed exhibits high concentrations of Chl *a* in spring (April to May) related to a subsequent higher $([Mo]/[Ca])_{shell}$ maximum ratio from May to June (in 1998, 2001, 2003).

The phytoplankton composition in the preceding weeks of the $([Mo]/[Ca])_{shell}$ maximum was always dominated by diatoms (up to 87%), even in summer 2003. The recurrent and dominant phytoplankton genera (among the hundred considered species) were three diatom genera: *Chaetoceros spp.*, *Pseudonitzschia spp.* and

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Rhizosolenia spp. Maxima of $([Mo]/[Ca])_{shell}$ ratio generally occurred before *Chaetoceros spp.* blooms, and concomitantly with *Pseudonitzschia spp.* and *Rhizosolenia spp.* blooms. In summer 2003, $([Mo]/[Ca])_{shell}$ maxima were mainly concomitant to dominant *Chaetoceros spp.* blooms (except in October). Late $([Mo]/[Ca])_{shell}$ maxima events might be induced by subsequent atypical phytoplankton blooms, eventually caused by exceptionally warmer conditions during summer 2003.

$([Mo]/[Ca])_{shell}$ maximum events usually occurred during a characteristic period of nutrient decrease or depletion during late spring conditions. The highest concentrations of silicic acids measured in winter and further phytoplankton uptake in spring were always related to important maxima of $([Mo]/[Ca])_{shell}$ ratio (Fig. 4d). The comparison of $([Mo]/[Ca])_{shell}$ profiles with PSNZ and silicic acid concentrations underlined also the occurrence of a PSNZ bloom and decreasing or minimum silicic acid concentration preceding or concomitant to $([Mo]/[Ca])_{shell}$ maxima (Fig. 4d). Statistical data analyses were performed to highlight the parameters potentially related to the amplitude of $([Mo]/[Ca])_{shell}$ maximum. Whatever the studied period, Bravais Pearson tests revealed only moderate significant simple correlations ($r^2 < 0.46$, $p < 0.05$, $n = 14$). The amplitude of maximum $([Mo]/[Ca])_{shell}$ ratios was correlated to the relative maximum abundance of *Pseudonitzschia spp.* (PSNZ) ($r^2 > 0.34$, $p < 0.05$, $n = 14$) for the 3 different integrated periods. Multiple regression analyses underlined also, whatever the studied period, relevant relationships expressing the amplitude of maximum $([Mo]/[Ca])_{shell}$ ratios according to the relative abundance of PSNZ and the silicic acid concentrations in the seawater ($r^2 > 0.40$, $p < 0.05$, $n = 14$), these two parameters being not significantly correlated. These relationships were all the more improved removing unusual and late $([Mo]/[Ca])_{shell}$ maximum events in 2003 (peak 3, 4 and 5) ($r^2 > 0.79$, $p < 0.05$, $n = 11$ and $d_{cook} < 1$) (Table 3). The best relationship was observed for the -1W+1W period ($r^2 = 0.88$, $p < 0.05$, $n = 11$ and $d_{cook} < 1$) (Table 3). Statistical results, expressing the amplitude of $([Mo]/[Ca])_{shell}$ enrichment according to silicic acids and the relative abundance of PSNZ in the seawater ($r^2 > 0.40$, $p < 0.05$, $n = 14$), exhibited a negative coefficient with silicic acids and a positive one with PSNZ. These statistical results underline

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an ecological state of the spring middle period for the occurrence of $([Mo]/[Ca])_{shell}$ maxima events, i.e. the occurrence of a spring diatom bloom and the subsequent decrease of nutrient concentrations in seawater.

3.2.2 Time series evolution of $([Mo]/[Ca])_{shell}$ ratio versus dissolved Mo concentration in 2000 (Bay of Brest)

Data from the annual collection of scallop shells were especially examined in 2000, together with a large array of environmental variables continuously monitored in the Bay of Brest and regular measurements of dissolved Mo in bottom seawater to depict major biogeochemical features influencing spring $([Mo]/[Ca])_{shell}$ maximum events.

In 2000, Mo concentrations in dissolved seawater exhibited a stable background concentration of 132 ± 11 nmol/L punctuated by only one significant 3-fold maximum the 12th of May (428 ± 31 nmol/L) (Fig. 5a). The distribution of Mo between solid carbonate and seawater is evaluated by the partition coefficients expressed as: $D_{Mo} = ([Mo]/[Ca])_{shell} / ([Mo]/[Ca])_{sw}$ with [Mo] the Mo concentration and [Ca] the calcium concentration in shell or in seawater. In 2000, this partition coefficient revealed a background averaging $D_{Mo} = 1.5 \times 10^{-4}$ punctuated by a single drastic spring increase (maximum value: 0.081) concomitant to the maximum $([Mo]/[Ca])_{shell}$ event. These results underline thus a non conservative behaviour of dissolved Mo at the SWI, concomitantly to the $([Mo]/[Ca])_{shell}$ maximum events (i.e. in the carbonate shell matrix). Mo inputs, archived as maximum $([Mo]/[Ca])_{shell}$, probably occurred in the close environment of the scallop at the SWI.

Benthic origin of Mo inputs was first examined because of the extended knowledge on benthic processes that may provide such Mo inputs (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). Variations of $([Mn]/[Ca])_{shell}$ ratio in 2000 were also examined concomitantly to $([Mo]/[Ca])_{shell}$ ratio, because $([Mn]/[Ca])_{shell}$ ratio were found to be correlated to both riverine and benthic inputs under reductive summer conditions in the Bay of Seine (Barats et al., 2008). In the Bay of Brest,

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variations of $([Mn]/[Ca])_{shell}$ ratio in 2000 were: slightly decreasing in spring, steady in summer and slightly increasing in fall (Fig. 5b). Dissolved Mn in seawater in May was not significantly enriched than the rest of the year, and the water column was well mixed and oxygenated by the tidal dynamic which argues against reductive conditions (Fig. 5a–c). The Bay of Brest was also submitted to lower freshwater inputs than in the Bay of Seine which explain lower variations of dissolved seawater Mn and $([Mn]/[Ca])_{shell}$ ratio (Fig. 5b). $([Mo]/[Ca])_{shell}$ pattern was different than those of $([Mn]/[Ca])_{shell}$, demonstrating a different biogeochemical behavior at the SWI. Examination of the intra annual variations of $([Mo]/[Mn])_{shell}$ ratio reveals a steady ratio averaging $700 \mu\text{mol/mol}$ punctuated by a maximum of $0,250 \text{ mol/mol}$ during the $([Mo]/[Ca])_{shell}$ maximum event (Fig. 5a).

Mo inputs at the SWI are then rather supposed to be induced by pelagic biogenic processes. In May 2000, the phytoplankton abundance was increasing. Chl *a* and POC concentrations displayed two maximum concentrations (respectively, the 2nd and the 15th of May) with the maximum one the 2nd of May (respectively, $[Chl\ a]=3.8 \mu\text{g/L}$ and $[POC]=412 \mu\text{g/L}$) (Fig. 5d). The variations of $([Mo]/[Ca])_{shell}$ ratio revealed only a peak 15 days after the first maximum Chl *a* and POC concentrations, the most intense spring phytoplankton bloom. The second maxima of Chl *a* and POC occurred after the spring maxima of $([Mo]/[Ca])_{shell}$ ratio, and showing no consequence on $([Mo]/[Ca])_{shell}$ ratio. The pelagic biogenic process influencing $([Mo]/[Ca])_{shell}$ maxima is thus specific to the spring post-bloom period. In 2000, nutrient dynamic over this productive period was previously described at the SOMLIT site (Ragueneau et al., 2002). Due to large nutrient loads in spring, this first phytoplankton bloom was dominated by diatoms (up to 94%). The dominant phytoplankton genera were *Skeletonema costatum* spp., *Chaetoceros* spp., *Pseudonitzschia* spp. and *Rhizosolenia* spp. It is interesting to note that a maximum of NH_4^+ concentration (the 9th of May) was first subsequent to the first Chl *a* and POC maxima and second, concomitant with the increasing of Mo concentrations in dissolved seawater (Fig. 5).

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4 Discussion

4.1 Origins of the spring Mo enrichments in the scallop shell

This study confirms first the non conservative behaviour of Mo in coastal temperate environment. This was previously observed in coastal North Sea waters off Germany revealing a Mo enrichment in the particulate phase (7 times higher) and a Mo depletion in the dissolved phase in July 2005 (0.6 times lower) (Dellwig et al., 2007). The difference observed between these two studies is supposed to be induced by: (1) the different hydrologic and climatic conditions of the ecosystem (Bay of Brest, 49°30 N; Wadden Sea, 53°44 N), and (2) the different sampling methods (dissolved Mo concentrations were measured at the SWI in our study and in the water column by Dellwig et al., 2007). In our study, the spring non conservative behaviour of Mo underlined significant inputs of Mo at the SWI preceding about 5 days the $([Mo]/[Ca])_{shell}$ maximum event (17th of May). This lag may be induced by both the epibenthic transfer and the scallop uptake of Mo, before Mo shell precipitation. Scallop uptake of this Mo input is suggested to induce increasing of $([Mo]/[Ca])_{shell}$ ratio.

Molybdenum occurs in an anionic form in seawater as molybdate MoO_4^{2-} (Collier, 1985). The only known structure of molybdate precipitation with Ca^{2+} is the powellite form ($CaMoO_4$) with a low solubility of $521 \mu mol/L$ (Swinkels et al., 2004). Mo crystallizes neither in a calcite nor in an aragonite structure. This can explain the low background partition coefficient ($D_{Mo}=1.5 \times 10^{-4}$), agreeing with anionic Mo precipitation pathway within the $CaCO_3$ shell. Second, the low spring maximum partition coefficient (maximum value: $D_{Mo}=0.081$) suggests that Mo shell uptake is not only associated to direct dissolved uptake of molybdate. Metal bioaccumulation in marine organisms such as bivalve species, was previously suggested to be induced by a dietary uptake of metal bound to particles (Luoma and Rainbow, 2005). A study on Mo bioaccumulation in scallop tissues and organs revealed the greatest concentration of Mo in the digestive gland (Bustamante and Miramand, 2005). Punctual measurements on

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Pecten maximus species from Roscanvel (January 2003) lead also to the highest Mo concentration in digestive gland (167 ± 63 nmol/g) which represents 69% of the total Mo in the bivalve (soft tissues plus shell) (Barats, 2006). In addition, the Mo in digestive gland appears to be mostly bound to a soluble fraction (Bustamante and Miramand, 2005). These Mo soluble compounds would be related to their binding to cytosolic proteins in the digestive gland (Bustamante and Miramand, 2005). Scallop digestion of biogenic particles would thus provide available dissolved Mo compounds, which can then precipitate in the calcite shell. Both shell uptake of dissolved and particulate Mo can be thus considered to induce maximum $([Mo]/[Ca])_{shell}$ events. Until now, the kind of Mo inputs (dissolved or particulate) responsible of $([Mo]/[Ca])_{shell}$ enrichment cannot be objectively established.

4.2 Transient biogeochemical processes potentially associated to spring Mo uptake in the scallop shell

Several investigations focussed on the Mo exchange at the SWI, via its precipitation with sulphide or its remobilization via manganese reductive dissolution (Chaillou et al., 2002; Crusius et al., 1996; Elbaz-Poulichet et al., 2005; Morford et al., 2005). Examination of $([Mn]/[Ca])_{shell}$ ratio concomitantly to $([Mo]/[Ca])_{shell}$ confirm that benthic inputs from reductive dissolution of Mn oxides is probably not a major source of Mo for the shell. Such as Thébault et al. (2009), the benthic origin for this $([Mo]/[Ca])_{shell}$ enrichment is thus refuted.

Thébault et al. (2009) suggested the ingestion of N_2 -fixing cyanobacteria to explain $([Mo]/[Ca])_{shell}$ peaks. The dominant marine N_2 -fixing cyanobacteria are *Trichodesmium spp.* and *Richelia intracellularis* (Sellner, 1997). *Trichodesmium spp.* blooms may not occur because of too low seawater temperature in spring ($<21^\circ C$). *Richelia intracellularis* is a small cyanobacterium living in endosymbiotic association within the diatom genera *Rhizosolenia*, *Hemiaulus* and *Chaetoceros*. This association of *R. intracellularis* as an endosymbiont in *Rhizosolenia* or *Chaetoceros* diatoms usually occurs in warm tropical seawater (Gomez et al., 2005), and is specific to nitrate depleted

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ecosystems such as the Baltic Sea or the North Atlantic Ocean and rarely observed in coastal temperate environment (Sellner, 1997; Villareal, 1992). This first hypothetic process cannot be thus conclusive for such temperate coastal ecosystem exhibiting important nitrate inputs from human activities (Ragueneau et al., 2002).

5 ([Mo]/[Ca])_{shell} peak events were usually recorded from May to July and correspond to the first major phytoplankton bloom period occurring in the water column of temperate coastal environments. This first major phytoplankton bloom is dominated by diatom species. Scallop Mo uptake and its spring enrichment may thus be related to diatom productivity. Until now, none of these diatom species has been recognized to have an
10 effect on Mo biogeochemistry in the marine environment. Mo concentrations in phytoplankton species were rather reported homogeneous among different phylogenetic origin (diatoms, dinoflagellates) (Ho et al., 2003; Quigg et al., 2003). ([Ba]/[Ca])_{shell} ratio were commonly investigated because of a potential linkage between these Ba shell records and primary productivity (Vander Putten et al., 2000; Lazareth et al., 2003;
15 Barats et al., 2009; Gillikin et al., 2006, 2008; Stecher et al., 1996; Fritz et al., 1990, Stecher, 1996). In a tropical environment, Thébault et al. (2009) recently revealed a certain synchronism of ([Mo]/[Ca])_{shell} and ([Ba]/[Ca])_{shell} peaks in the shell of the tropical scallop *Comptopallium Radula*. In our temperate ecosystem, ([Mo]/[Ca])_{shell} and ([Ba]/[Ca])_{shell} profiles exhibited however different patterns. The usual pattern
20 of ([Mo]/[Ca])_{shell} ratio exhibited only one spring peak whereas the usual pattern of ([Ba]/[Ca])_{shell} ratio exhibited some peaks in summer (Barats et al., 2009). These differences highlight thus a Ba-specific biogeochemical process influencing ([Ba]/[Ca])_{shell} maxima as demonstrated by Barats et al. (2009), and an independant route for Mo.

25 Statistical results, expressing the amplitude of ([Mo]/[Ca])_{shell} enrichment according to silicic acids and the relative abundance of PSNZ in the seawater ($r^2 > 0.40$, $p < 0.05$, $n = 14$), 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 pumped 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

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and Dortch, 2002; Prego et al., 2007). The amplitude of maximum $([Mo]/[Ca])_{shell}$ ratio was also directly related to the difference of average silicic acid concentrations between winter (January and February) and spring (May and June ($r^2=0.878$, $p<0.05$, $n=7$, Fig. 6). In spring, silicic acid was totally pumped by diatoms (Ragueneau et al., 2002). These results reveal 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 depletion and PSNZ species dominance. Releases of substantial amounts of Mo from organic matter degradation during an algal decay at the SWI were previously suggested to be the best explanation for Mo enrichment in bottom waters (Kunzendorf et al., 2001; Dellwig et al., 2007). The observation in 2000 of increasing NH_4^+ concentrations in seawater concomitantly to higher Mo concentrations in dissolved seawater agree also with a rapid mineralization of settling biogenic material during the post bloom period (Bally et al., 2004). Mo inputs at the SWI are thus supposed to be induced by diatom settling and its subsequent microbial decomposition under specific biogeochemical conditions. The diatom scavenging was demonstrated to be the most effective among the marine phytoplankton species due to the large cell size and density (Sarhou et al., 2005). Mo epibenthic enrichment in bottom waters may therefore derive from the specific downward transport to the SWI of biogenic particles derived from diatoms. Spring $([Mo]/[Ca])_{shell}$ enrichments are thus supposed to be subsequent to scallop uptake of these Mo inputs at 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 also previously proposed to explain $([Mo]/[Ca])_{shell}$ maxima (Thébault et al., 2009). However, the processes governing either Mo scavenging by biogenic particles or its uptake by the scallop have still to be elucidated.

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This study is the first one investigating $([Mo]/[Ca])_{shell}$ ratio in bivalves from temperate environments. General $([Mo]/[Ca])_{shell}$ profiles were highlighted for scallops from a same population, different years (1998–2004) and coastal temperate ecosystems in north western France (42 to 49° N) showing a background concentration (<2.7 nmol/mol) punctuated by a transient maximum in spring (May to June). This study reveals a new evidence of the non conservative behaviour of the molybdenum in coastal waters suggesting an ecological process influencing Mo transport in coastal environment, and specific Mo enrichments in the surrounding shell habitat (SWI) during spring time. The periodicity of the spring $([Mo]/[Ca])_{shell}$ enrichments and their extents were explained by (1) the silicate loading in winter, (2) its uptake for spring diatom productivity, (3) and the diatom settling and its subsequent microbial decomposition. The shell archives are thus able to depict a non conservative behaviour of Mo in coastal waters, which was not investigated to date during spring time and supported by a pelagic biogenic process related to diatom productivity. The use of Mo records in *Pecten maximus* shells may further serve as a new proxy for biomonitoring study in coastal temperate environments which can be extended for other marine biogenic carbonates.

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Table 1. Intershell comparison of $([Mo]/[Ca])_{shell}$ concentration profiles archived in *Pecten maximus* shells from a same population (Bay of Brest, Roscanvel station) over a 7-year period (1998–2004) and presentation of $([Mo]/[Ca])_{shell}$ peaks (named by the time order) observed for each year. The maximum of $([Mo]/[Ca])_{shell}$ concentrations and the date of this maximum were averaging from 3 shells (except 2002 and 2004).

n=19 Shells	Intershell reproducibility of Mo profiles				Molybdenum shell enrichments				
	Correlation coefficients			ρ	Date (± 3 d)	$([Mo]/[Ca])_{shell}$ concentrations ($\mu\text{mol/mol}$)			
	1 vs 2	1 vs 3	2 vs 3			Mean	SD	%RSD	
1998 (n=3)	0,89	0,89	0,98	$<10^{-28}$	peak 1	9-Jun	0,735	\pm 0,288	39
					peak 2	10-Jul	0,130	\pm 0,071	55
1999 (n=3)	0,95	0,72	0,52	$<7 \cdot 10^{-6}$	peak 1	7-May	0,194	\pm 0,126	65
2000 (n=3)	0,85	0,97	0,91	$<3 \cdot 10^{-19}$	peak 1	17-May	1,10	\pm 0,52	47
2001 (n=3)	0,53	0,37	0,99	$<0,004$	peak 1	15-May	1,53	\pm 0,63	41
					peak 2	21-Jun	0,037	\pm 0,031	84
2002* (n=2)	0,88	–	–	$<2 \cdot 10^{-25}$	peak 1	7-May	0,126	\pm 0,031	25
					peak 2	4-Jun	0,072	\pm 0,019	26
2003 (n=3)	0,87	0,90	0,73	$<6 \cdot 10^{-25}$	peak 1	1-Jun	1,20	\pm 0,05	4
					peak 2	20-Jul	0,930	\pm 0,261	28
					peak 3	4-Sep	0,251	\pm 0,157	63
					peak 4	25-Sep	0,341	\pm 0,031	9
					peak 5	6-Oct	0,460	\pm 0,167	36
2004* (n=2)	0,46	–	–	$<0,004$	peak 1	9-May	0,062	\pm 0,051	83

*For these specific years, only two shells were analysed.

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Table 2. $([Mo]/[Ca])_{shell}$ ratios archived in bivalve shells from different coastal temperate ecosystems. Both background, maximum of $([Mo]/[Ca])_{shell}$ ratios and $([Mo]/[Ca])_{shell}$ enrichment factors are examined according to the occurring period of $([Mo]/[Ca])_{shell}$ shell enrichments.

Coastal temperate ecosystems	Investigated period	Background $([Mo]/[Ca])_{shell}$ ratio ($\mu\text{mol/mol}$)	$([Mo]/[Ca])_{shell}$ enrichment periods	Maximum of $([Mo]/[Ca])_{shell}$ ratio ($\mu\text{mol/mol}$)	$(([Mo]/[Ca])_{shell})_{max}/(([Mo]/[Ca])_{shell})_{bkg}$
Bay of Brest, France (48°20 N, 4°30 W)	1998–2004	<0.003	May–July*	0.037–1.53	13–562
Quiberon, France (47°30 N, 3°00 W)	2000	<0.003	May	1.78	654
Belle Ile, France (47°20 N, 3°10 W)	1999–2001	<0.003	May to July	0.094–2.00	34–735
Bay of Seine, France (49°30 N, 0°30 W)	2004	<0.003	May	0.355	131

* supplementary Mo peaks in September–October 2003

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Table 3. Multiple regression analyses highlighting intensity of $([Mo]/[Ca])_{shell}$ peaks according to different integration periods ($-nW+1 W$ representing the period from n week before to 1 week after the Mo shell enrichment), transient environmental conditions reflected by maximum values during the considered period and the most significant parameters (silicic acid concentrations and *Pseudonitzschia spp.* abundance).

Integration periods	Adjusted r^2	p	Cook distance	Multiples regressions considering only transient conditions (maxima)				
				Relations				
-3W+1W	0,80	<0,05	<1	Intensity of $([Mo]/[Ca])_{shell}$ peak ($\mu\text{mol/mol}$)	=0,860–0,358	Silicic acid concentrations ($\mu\text{mol/L}$)	+0,0314	<i>Pseudonitzschia spp.</i> abundance (%)
-2W+1W	0,79	<0,05	<1	Intensity of $([Mo]/[Ca])_{shell}$ peak ($\mu\text{mol/mol}$)	=0,822–0,356	Silicic acid concentrations ($\mu\text{mol/L}$)	+0,0272	<i>Pseudonitzschia spp.</i> abundance (%)
-1W+1W	0,88	<0,005	<1	Intensity of $([Mo]/[Ca])_{shell}$ peak ($\mu\text{mol/mol}$)	=0,877–0,358	Silicic acid concentrations ($\mu\text{mol/L}$)	+0,0261	<i>Pseudonitzschia spp.</i> abundance (%)

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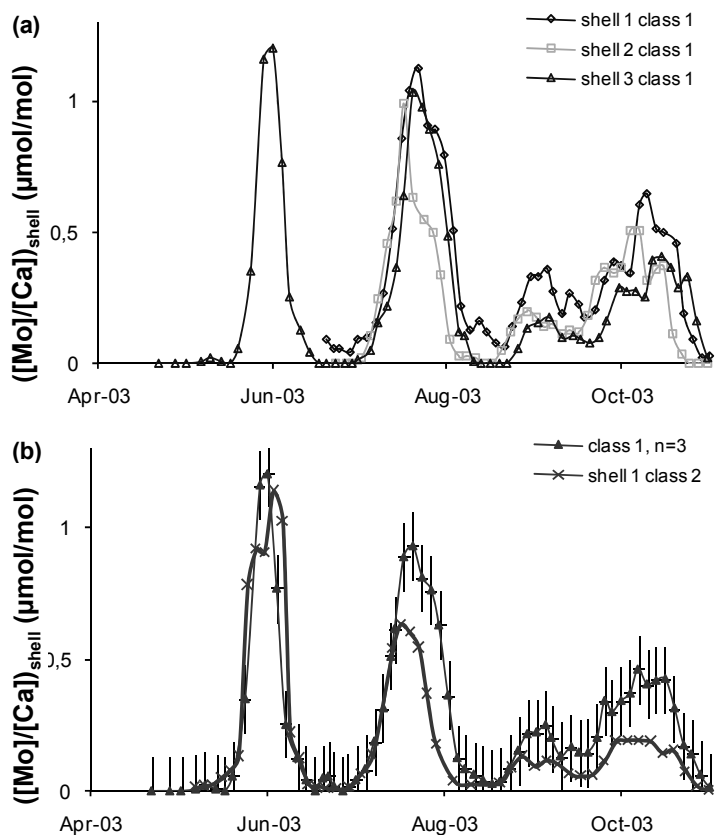


Fig. 1. Comparison of $([Mo]/[Ca])_{shell}$ concentration profiles obtained for **(a)** three juvenile scallop shells (class 1); **(b)** the mean $([Mo]/[Ca])_{shell}$ concentrations of 3 juvenile shells and one 3-years old scallop shell (class 2), collected in the Bay of Brest (Roscanvel), during the year 2003, to evaluate the inter shell reproducibility of $([Mo]/[Ca])_{shell}$ variations.

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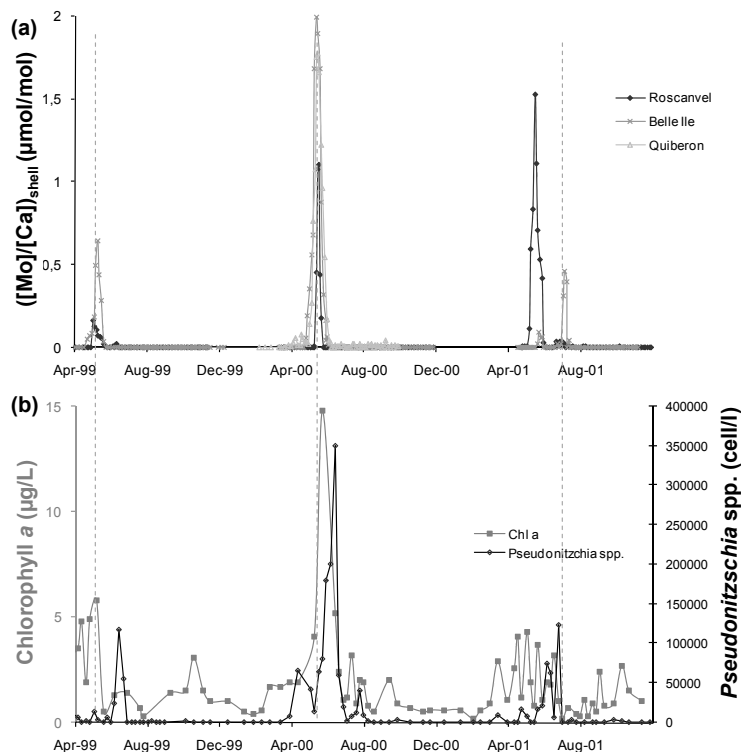


Fig. 2. Comparison of mean $([Mo]/[Ca])_{shell}$ profiles from 1999 to 2001 **(a)** from 3 investigated sites in French Brittany to examine $([Mo]/[Ca])_{shell}$ peak ubiquity: Roscanvel (black lines), Belle Ile (dark grey lines), Quiberon (light grey lines); and **(b)** with the phytoplankton dynamic (total biomass with chlorophyll *a*, and specific diatom dynamic with *Pseudonitzschia* spp.) monitored at Quiberon station, close to the sampling zone named Quiberon, and the closest monitoring station from Belle Ile sampling zone. Mean $([Mo]/[Ca])_{shell}$ profiles is the average of 3 shell profiles per year (except in 1999 and 2000 for Belle Ile, $n=4$).

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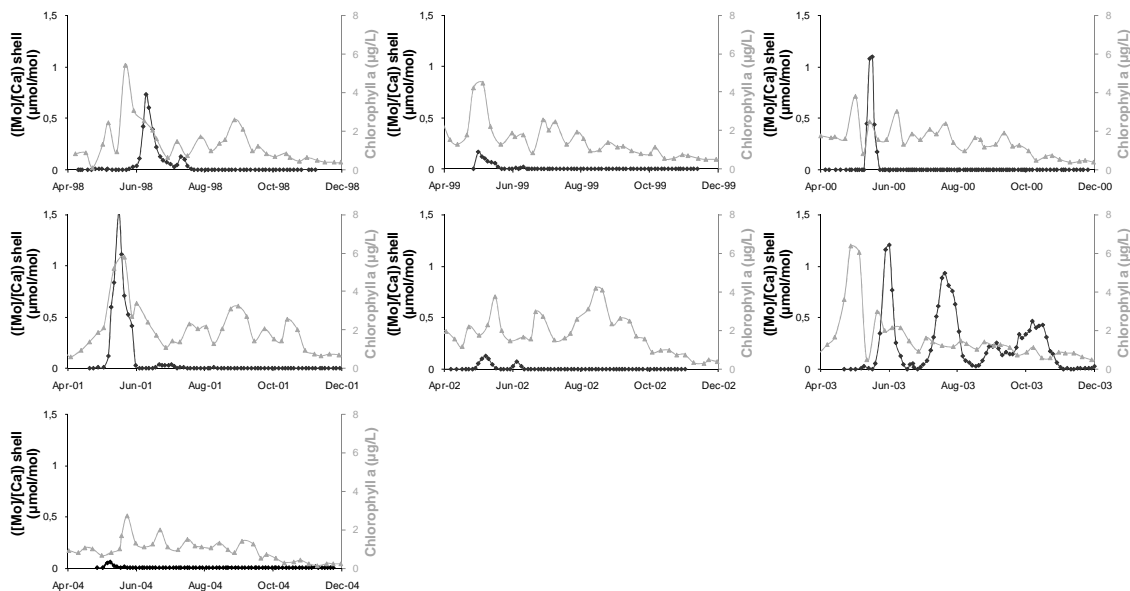


Fig. 3. Mean $([Mo]/[Ca])_{shell}$ profiles in shells ($n=3$) from Roscanvel over a 7-year period (1998–2004) compared to chlorophyll *a* ($\mu\text{g/L}$) concentrations measured at SOMLIT station in the Bay of Brest ($48^{\circ}21\text{ N}$, $4^{\circ}33\text{ W}$), nearby the sampling zone (Roscanvel).

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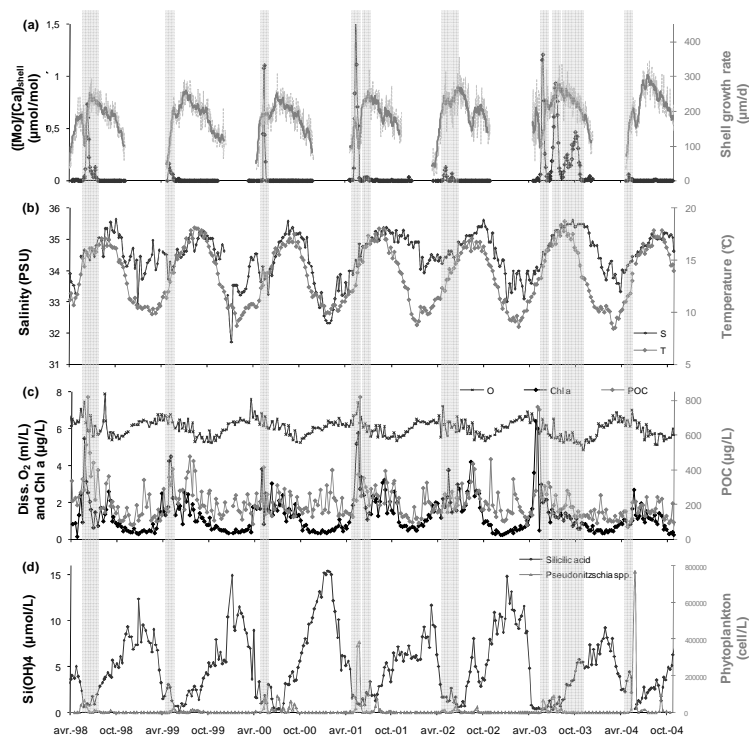


Fig. 4. (a) Mean $([Mo]/[Ca])_{shell}$ concentration profiles ($n=3$) from Roscanvel over a 7-year period (1998–2004) compared to shell growth rate ($\mu\text{m/d}$); (b) salinity (PSU) and temperature ($^{\circ}\text{C}$); (c) dissolved oxygen (mL/L), chlorophyll *a* ($\mu\text{g/L}$) and particulate organic carbon (POC in $\mu\text{g/L}$); (d) silicic acid concentrations ($\mu\text{mol/L}$) and *Pseudonitzschia* spp. abundances (cell/L) in seawater. Environmental monitoring data (weekly resolution) are originating from SOMLIT station ($48^{\circ}21\text{ N}$, $4^{\circ}33\text{ W}$), except in 2003 and 2004 for diatom abundance (Lanvéoc station ($48^{\circ}18\text{ N}$, $4^{\circ}27\text{ W}$); 15-days resolution), both stations being in the Bay of Brest nearby the sampling zone named Roscanvel.

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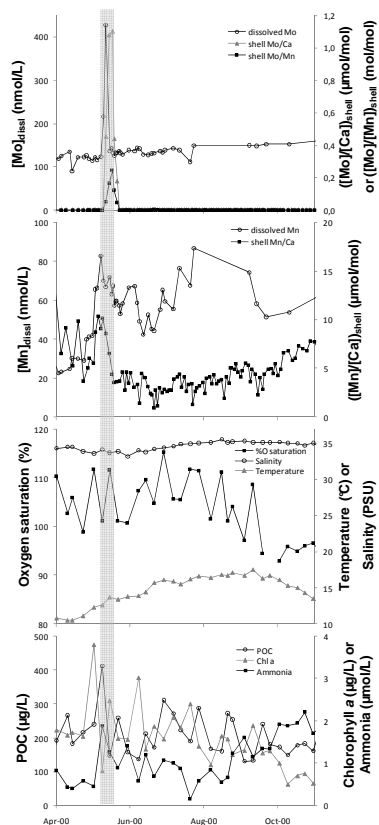


Fig. 5. (a) Mean $([\text{Mo}]/[\text{Ca}])_{\text{shell}}$ and $([\text{Mo}]/[\text{Mn}])_{\text{shell}}$ profiles ($n=3$) obtained in 2000 in the Bay of Brest and Mo concentrations (nmol/L) in dissolved seawater (sampled at 1 m of the SWI) compared with (b) mean $([\text{Mn}]/[\text{Ca}])_{\text{shell}}$ profiles and dissolved Mn concentrations (nmol/L); (c) seawater temperature ($^{\circ}\text{C}$), salinity (PSU) and oxygen saturation (%); and (d) particulate organic carbon (POC), chlorophyll *a* ($\mu\text{g/L}$) and ammonia ($\mu\text{mol/L}$) concentrations.

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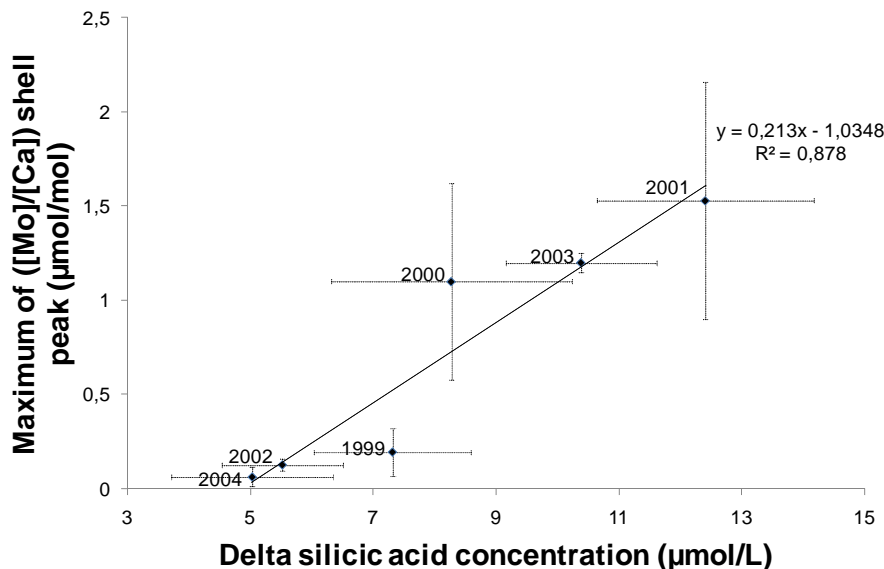


Fig. 6. Relationship between maximum intensity of spring $([Mo]/[Ca])_{shell}$ peak ($\mu\text{mol/mol}$) and the difference of average silicic acid concentration ($\mu\text{mol/L}$) between winter (January and February) and spring (May and June), i.e. a delta silicic concentration.

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