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**Barium uptake into
the shells of the
Great Scallop**

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High frequency Barium profiles in shells of the Great Scallop *Pecten maximus*: a methodical long-term and multi-site survey in Western Europe

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Abstract

Skeletal barium/calcium ($[Ba]/[Ca]_{shell}$) ratios were measured every third daily striae in 39 flat valves of the Great Scallop *Pecten maximus* (2-year old; 3 shells/year) collected in temperate coastal environments of Western Europe. Variations of $[Ba]/[Ca]_{shell}$ ratio were first demonstrated reproducible for several scallop individuals from the same population, over a 7-year period (1998–2004), and from different coastal environments in France (42–49° N). As in previous studies, $[Ba]/[Ca]_{shell}$ profiles exhibited a background ratio punctuated by transient maxima occurring in summer. Background partition coefficient ($D_{Ba}=0.11\pm 0.03$, in 2000) was similar to that previously reported in *P. maximus* shells ($D_{Ba}=0.18$), suggesting a direct shell uptake of dissolved seawater Ba (Gillikin et al., 2008). Special attention was then dedicated to the complete monitoring of high resolution $[Ba]/[Ca]_{shell}$ profiles in bivalve shells (7 years, Bay of Brest) to better constrain environmental processes influencing both the occurrence and the amplitude of summer peaks. In 2000, seawater Ba analyses underlined significant particulate Ba inputs at the seawater interface (SWI) during $[Ba]/[Ca]_{shell}$ peak events. These Ba inputs are suggested to be subsequent to and rather induced by a pelagic biogenic process. The long term survey revealed first that archived Ba within the shell cannot be used as a direct paleo productivity tracer, and second that complex pelagic/benthic processes in the Ba cycle are responsible of particulate Ba inputs to the SWI, subsequently taken up by the bivalve and recorded as higher $[Ba]/[Ca]_{shell}$ ratios. When these processes will be better constrained, high frequency observations of Ba in scallop shells would provide new insights into filter feeding dynamics and into Ba biogeochemistry in coastal environments.

1 Introduction

The elemental composition of mollusc shells is related to environmental parameters (Dodd, 1965; Lorens and Bender, 1980). As a result, the successively deposited cal-

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cium carbonate layers are potential archives of the varying environmental conditions experienced by the organism during its life time (Klein et al., 1996a; Klein et al., 1996b; Stecher et al., 1996). A recent increasing number of studies investigated Ba content in biogenic carbonates, such as corals, foraminifera, and otoliths (Lea et al., 1989; Lea and Martin, 1996; McCulloch et al., 2003; Sinclair and McCulloch, 2004; de Vries et al., 2005; Sinclair, 2005). Coastal waters are enriched in Ba through its release from river-borne particulate phases during estuarine mixing, in the low to mid salinity ranges (Coffey et al., 1997; Shaw et al., 1998; McCulloch et al., 2003), or through the exchange of Ba-rich ground waters and pore waters within the tidal prism (Shaw et al., 1998). Coralline Ba content was reported as a proxy for discharge and/or sediment load in riverine systems (Sinclair and McCulloch, 2004; McCulloch et al., 2003). However, some sharp Ba peaks do not correlate with tracers of river discharge (Sinclair, 2005). Barium incorporation into carbonate parts of larval protoconchs or stoliths was also demonstrated to be promoted at lower temperature (Zacherl et al., 2003). In recent studies, there was much attention to the skeletal Ba content in mussels (*Mytilus edulis*) (Vander Putten et al., 2000; Gillikin et al., 2006), oysters (*Isognomon ehippium*), (Lazareth et al., 2003), clams (*Mercenaria mercenaria*, *Spisula solidissima*, *Arctica islandica*, *Saxidomus giganteus*) (Stecher et al., 1996; Epplé, 2004; Gillikin et al., 2005; Gillikin et al., 2008), and scallops (*Pecten maximus*, *Comptopallium radula*, *Argopecten purpuratus*) (Lorrain, 2002; Thébault, 2005; Gillikin et al., 2008). In all these studies, $[Ba/Ca]_{shell}$ profiles were usually characterized by a relatively stable background ratio interrupted by sharp intense peaks. The interpretation of some studies is however to date limited by an approximate dating that can be achieved with the investigated bivalves (*Mercenaria mercenaria*, *Mytilus edulis*, *Isognomon ehippium*, *Ensis siliqua*). In both lab and field experiments, the background $[Ba/Ca]_{shell}$ in the common mussel shell (*Mytilus edulis*) was demonstrated to track the $[Ba/Ca]_{water}$ content (Gillikin et al., 2006). Considering the inverse relationship between $[Ba/Ca]_{water}$ and salinity, background $[Ba/Ca]_{shell}$ was considered as a specific indicator of salinity in estuarine environment (Gillikin et al., 2006). Barium was also established as a paleo

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productivity tracer in marine waters, suspended particles and sediments (Dymond and Collier, 1996; Paytan and Kastner, 1996). Stecher et al. (1996) postulated first that, in *Mercenaria mercenaria* and *Spisula solidissima* shells, these $[Ba/Ca]_{shell}$ peaks might be induced by the ingestion of high levels of particulate Ba (Stecher et al., 1996). Bivalves, such as scallop shells, are non-selective filter feeders and can assimilate these Ba-rich particles. Once inside the digestive tract of the bivalve, Ba may be metabolised, at least in part, by being shunted to the extrapalleal fluid (EPF) and sequestered into the shell (Stecher et al., 1996; Vander Putten et al., 2000; Lorrain, 2002; Gillikin et al., 2006). Time resolved $[Ba/Ca]_{shell}$ peaks were suggested to be related to phytoplankton blooms (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003). These Ba-rich particles were supposed to be input by diatom blooms as either biogenic matter, or barite precipitates (Stecher et al., 1996). Gillikin et al. (2006, 2008) indicated that these $[Ba/Ca]_{shell}$ peaks could not be used as a direct proxy of $[Ba/Ca]_{water}$ or phytoplankton production (Gillikin et al., 2006, 2008). These peaks were rather induced by ingestion of barite particles input to the SWI during the phytoplankton decay (Gillikin et al., 2006). Barium is recognized to be accumulated at high levels in phytoplankton, both in diatoms and in dinoflagellates (Fisher et al., 1991). A relatively large pool of labile Ba can be rapidly released during plankton decomposition and acts as the main source of Ba for barite formation in supersaturated microenvironments (Bishop, 1988; Ganeshram et al., 2003). Elevated levels of Ba, both as suspended particulate Ba and sedimentary barite appear linked with oceanic regions of high primary productivity (Dehairs et al., 1980, 1991, 1997; Bishop, 1988). The most commonly accepted hypothesis is that barite forms as a result of passive precipitation through enrichment of sulphate and/or barium in decaying organic material (Bishop, 1988; Stecher and Kogut, 1999; Jeandel et al., 2000; Ganeshram et al., 2003; Dehairs et al., 2000). The formation of specific aggregates or Ba-rich micro-environments was responsible for the Ba enrichment in biogenic particles (Bishop, 1988). These aggregates are related to the diatom extracellular polymeric substances (EPS) produced during summer blooms and their settling (Stecher and Kogut, 1999; Thornton, 2002). The subsequent vertical

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mixing and diatom decay provide a rapid flux and large abundance of biogenic particles transported down to the SWI (Sarhou et al., 2005). This was suggested to induce a sudden pulse of Ba to the epibenthic environment, subsequently ingested as barite in shells and recorded by $([Ba]/[Ca])_{shell}$ maxima (Gillikin et al., 2006). Phytoplankton Ba uptake and barite formation are however recently revealed not sufficient to explain the vertical flux of Ba in oceanic waters (Sternberg et al., 2005). Barium can be adsorbed onto mineral oxides (i.e. Fe, Mn) formed within diatom biogenic particles (Sternberg et al., 2005) which contribute to significant Ba inputs to the SWI.

This study will focus on Ba content in the Great Scallop shell *Pecten maximus* (L.) because these bivalves provide precisely time resolved $([Ba]/[Ca])_{shell}$ profiles (daily scale) and are valuable archives of environmental change in temperate environments (Chauvaud et al., 1998, 2005; Lorrain et al., 2000, 2005; Barats, 2006; Barats et al., 2007, 2008; Gillikin et al., 2008). The Laser Ablation-Inductively Coupled Plasma-Mass spectrometry coupling (LA-ICP-MS) analyses using matrix-matched standards were performed to determine Ba content in calcitic shell striae. Although data can be collected for more than 20 elements (Barats et al., 2007), only Ba results are presented here since this element was extensively used in biogeochemical studies as a tracer of productivity. Significance of $([Ba]/[Ca])_{shell}$ profiles in *P. maximus* is first evaluated for both the background concentration and episodic sharp peaks in a single scallop population from the Bay of Brest (northwest France), among different coastal sites in western Europe, and over a 7-year period (1998–2004) in the Bay of Brest. Second, the $([Ba]/[Ca])_{shell}$ pattern was then compared to the shell growth rate and environmental conditions monitored at reference coastal stations. The potential processes related to both background and maxima $([Ba]/[Ca])_{shell}$ ratio will be then discussed. The overall aim of this study is to provide new evidence for recurrent patterns of $([Ba]/[Ca])_{shell}$ profiles, and to clarify the biogeochemical processes influencing both the background and episodic sharp peaks of $([Ba]/[Ca])_{shell}$ content.

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2 Material and methods

2.1 Study sites and scallop sampling

Different sampling areas in Western Europe (Bay of Seine, Bay of Brest, Quiberon peninsula and Belle Ile, Ria de Vigo) were considered because they represent ecosystems with different ecological characteristics (Barats, 2006). Shells originating from the Bay of Seine (France, English Channel, 49° 30 N, 0° 30 W), Belle Ile and Quiberon area (France, Bay of Biscay, respectively, 47° 20 N, 3° 10 W and 47° 30 N, 3° 00 W) were sampled in open coastal ecosystems influenced by large estuarine inputs (respectively, Seine and Loire rivers) (Fig. 1). Shells sampled in coastal environments such as the Ria de Vigo (Spain, Atlantic Ocean, 42° 10 N, 8° 50 W) or the Bay of Brest (France, Iroise Sea, Roscanvel bank, 48° 20 N, 4° 30 W) were subjected to low anthropogenic inputs. In this study, the main sampling site is the Bay of Brest (Fig. 1): a shallow embayment with more than a half of its surface (180 km²) and with depth of less than 5 m. This ecosystem is mainly influenced by tidal exchange with the Iroise Sea, but also by freshwater input mainly by two small riverine watersheds (80%): the Aulne (1842 km²) with monthly flow rate ranging from 2 to 52 m³/s and averaging 22 m³/s, and the Elorn (402 km²) with monthly flow rate ranging from 1 to 12 m³/s and averaging 5.6 m³/s. The sampling area (Roscanvel) is 30 m deep where the bottom consists of mixed sediments (mud, sand) and selected because scallop density is one of the highest in the Bay of Brest (Chauvaud et al., 2000; Chauvaud et al., 2005).

Three replicates of live juvenile *P. maximus* specimens were collected for each year and site (except in 2002 in the Bay of Brest, $n=2$) during the late autumn period by SCUBA diving in the Bay of Brest and by dredging for other sites. Only the juvenile stage of the shells (the second year of growth) was examined because it exhibits the longest annual growth period. An exception was made for a three-year old *P. maximus* specimen collected in the Bay of Brest in 2003 to examine its third year of growth. The shells were isolated and cleaned by submerging in glacial acetic acid (Merck, analytical grade) for 60 s to remove bio-fouling, rinsed with Milli-Q water ($R=18.2$ M Ω cm) and

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dried. For convenience in visualizing the growth striae, only the flat valve was considered for LA-ICP-MS analysis. A $45 \times 10 \text{ mm}^2$ cross section was cut from each shell using a diamond saw to fit into an ablation chamber.

2.2 Determination of Ba concentrations in shells by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Quantitative analyses of 39 shells were performed by 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 methodology and validation were described elsewhere and summarized here (Barats et al., 2007). Samples were analysed during 2 min at a scan speed rate of $5 \mu\text{m/s}$. For shell analyses, a pre cleaning ablation of the calcite surface was conducted to avoid surface contamination (Wyndham et al., 2004). This pre cleaning step consisted in a quick (around 20 s) pre-ablation of shell surface at a rate of $50 \mu\text{m/s}$. Twenty-eight isotopes including $^{135,137,138}\text{Ba}$, ^{55}Mn and ^{43}Ca were analysed. The intensity of each isotope signal was systematically normalized against the ^{43}Ca signal to compensate for instrumental drift and instability. A matrix-matched external calibration was performed with lab prepared CaCO_3 standards containing Ba concentrations ranging from 0.005 to $19.6 \mu\text{g/g}$ (Barats et al., 2007). The Ba calibration curve displayed a good linearity with a regression coefficient r^2 above 0.998 (Barats et al., 2007). The detection limit was about 3.3 ng/g, and the relative standard deviations obtained for both analytical repeatability (5 integration zones during 1 analysis) and reproducibility (5 successive independent analyses) were below 5% (Barats et al., 2007). Analytical performances obtained for Mn were previously presented (Barats et al., 2007, 2008). The $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ or $([\text{Mn}]/[\text{Ca}])_{\text{shell}}$ ratios were calculated by dividing shell Ba or Mn concentrations by the Ca concentration in the shell (40%) and expressed in $\mu\text{mol/mol}$. Mollusc shells were recognized to contain less than 5% of organic matrix (Carroll et al., 2006; Levi-Kalisman et al., 2001). The shell is thus composed by minimum 95% of CaCO_3 , 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

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content of 40% because the error is negligible and the exact percentage of organic matter remains unknown.

Shell analyses were performed each third striae during the shell growth period (from April to November) to limit the analysis time to approximately 5 h per shell. A date of formation was assigned to each ablated sample, by backdating from the harvest date, based on the daily periodicity of the striae formation in *P. maximus*. An evaluation of the shell growth rate (dorso-ventral linear extension of the shell per unit time), expressed in $\mu\text{m}/\text{d}$, was also performed for each shell by measuring distances between successive striae (growth increment width) using an image analysis technique described by L. Chauvaud (Chauvaud, 1998). A mean $([\text{Ba}]/[\text{Ca}]_{\text{shell}})$ profile and a mean shell growth rate profile were then defined for each year and site averaging the results of 3 shells from a same scallop population. Due to the uncertainties from the backdating of analysed striae and those from the intershell comparison, the incertitude on the date for mean shell profiles was estimated to range from 1 to 7 days.

2.3 Environmental monitoring database

$([\text{Ba}]/[\text{Ca}]_{\text{shell}})$ time series were compared with environmental variables that may influence Ba biogeochemical cycle at the SWI. The Bay of Brest (Roscanvel station) was mainly investigated because of the regular environmental monitoring and the long time series obtained by shell analyses (1998 to 2004). Regular measurements (2–3 days resolution) of Ba and Mn concentrations in dissolved ($<0.6 \mu\text{m}$) and particulate seawater from bottom seawater (1m above the SWI) were also performed in the sampling site (Roscanvel) in 2000 (from February to December). Dissolved samples were acidified in 2% HNO_3 (69–70% Suprapur, Merck) and diluted 30 times. Two internal standards were added (Y and Bi) in diluted samples. Elemental concentrations (Ba, Mn, Mo. . .) were then determined by ICP-MS (X7 serie, Thermo Fisher) by an external and internal calibration. Particulate samples (filters) were digested in closed vials (Savilex, PFA) by an acid mixture (1.5 ml HCl, 1 ml HNO_3 , 0.5 ml HF; suprapur quality) at 95°C during one night. The digested samples were evaporated to dryness at 110°C under a lam-

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inar hood to eliminate the matrix. The residues were dissolved in 2.5 ml of nitric acid solution (HNO_3 2%) and the volumes were adjusted to 11 ml. These samples were analyzed by ICP-AES (THERMO Optek Iris Advantage, Thermo Fisher). Samples were spiked with a mixture of internal standards (Au, Y) before its introduction into the spectrometer to compensate instrumental drift and instability. All these experiments were performed under clean conditions (clean vials, laminar flood, blank procedure. . .).

$([\text{Ba}]/[\text{Ca}]_{\text{shell}})$ time series were also compared with an environmental database. Hydrological (S , T , suspended particulate matter), chemical (O_2 , NO_3^- , NO_2^+ , NH_4^+ , PO_4^{3-} , $\text{Si}(\text{OH})_4$, particulate organic carbon POC or nitrogen PON) and biological parameters (total phytoplankton biomass reflected by chlorophyll- a , abundance of phytoplankton species from 2003 to 2004) were measured at the seawater surface (0–1 m) in a reference station, named the SOMLIT station (Service d'Observation en Milieu Littoral: $48^\circ 22$ N, $4^\circ 33$ W), located in the Bay of Brest at "Sainte Anne" site near to Roscanvel sampling zone, as part of monitoring activities lead by the Institut Universitaire Européen de la Mer (http://www.univ-brest.fr/IUEM/observation/observation_iroise.htm) (Fig. 1). All these measurements were performed at a weekly resolution. Nutrient dynamic in SOMLIT station was previously demonstrated to reflect environmental conditions in Roscanvel (Lorrain, 2002). Phytoplankton composition (hundred species) from 1998 to 2002 were monitored at Lanvéoc ($48^\circ 18$ N, $4^\circ 27$ W), located near to Roscanvel, as a part of the littoral environment monitoring program lead by the Institut Français de Recherche pour l'Exploitation de la MER (IFREMER database, <http://www.ifremer.fr/envlit/surveillance/index.htm#>) (Fig. 1). Phytoplankton identifications were performed in surface seawater (0–1 m) and every 15 days, except in 2004 (weekly resolution).

2.4 Statistical analyses

A statistical data treatment was performed to highlight environmental parameters influencing the occurrence and the amplitude of $([\text{Ba}]/[\text{Ca}]_{\text{shell}})$ peaks. Most of $([\text{Ba}]/[\text{Ca}]_{\text{shell}})$ maxima occurred during a 20-day period. Averaged environmental pa-

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rameters were thus examined over different periods: 4 weeks before – 1 week after (–4W+1W), 3 weeks before – 1 week after (–3W+1W), 2 weeks before – 1 week after (–2W+1W), 1 week before – 1 week after (–1W+1W) the maximum ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios. The choice of such integration periods around the maximum of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) 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 delayed response between changes in the water column, subsequently at the SWI, and its further transcription within the shell. This allowed a good overlapping between ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) maxima and environmental datasets. The influence of transient events was tested taking into account 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 ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) maxima and others variables. Multiple regression analyses were considered to express the amplitude of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) maxima according to several independent factors. The relationships were significant if the probability was below $p < 0.05$, and moderate-to-strong if $r^2 > 0.7$ and if all the ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) maxima agreed with the relationship, i.e. if the Cook's distance was below $d_{\text{cook}} < 1$.

3 Results and discussion

3.1 Definition of a general pattern for ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) profiles

3.1.1 Reproducibility of background and episodic maxima of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios among a single scallop population

The reproducibility of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios was previously demonstrated for 2-year old scallops from the Bay of Brest (Barats et al., 2007). Here the variations of

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$([Ba]/[Ca])_{shell}$ ratios were examined in 2003, for 2-year old shells and for 3-year old shells from the Bay of Brest (Fig. 2). Two-year old scallops, analysed for its juvenile stage, revealed a high reproducibility of $([Ba]/[Ca])_{shell}$ profiles ($r^2 > 0.78$, $p < 0.05$, $n > 60$) (Table 1, Fig. 2). A mean $([Ba]/[Ca])_{shell}$ profiles exhibited a background ratio of $0.535 \pm 0.134 \mu\text{mol/mol}$ (calculated removing data during shell Ba/Ca peaks), and two significant enrichments from July to August (respectively, $3.80 \pm 0.74 \mu\text{mol/mol}$ the 20th of July, and $1.72 \pm 0.12 \mu\text{mol/mol}$ the 26th of August) (Fig. 2b, Table 1).

This $([Ba]/[Ca])_{shell}$ profile demonstrates a high inter individual reproducibility among scallops of the same age for both background content and summer peak events with similar occurrence dates and amplitudes (Fig. 2a). Analyses of a 3-year old scallop from a same population (shells collected the same year and site) were also performed for the third year of the shell growth. The $([Ba]/[Ca])_{shell}$ ratios for this 3-year old scallop revealed a similar pattern than those obtained for the 2-year old scallops (Fig. 2b). This result suggests that background or maxima of $([Ba]/[Ca])_{shell}$ ratios are not related to a specific physiological or biological effect related to the scallop age. $([Ba]/[Ca])_{shell}$ profiles were then compared to those previously reported in 2003 for 2- and 3-year old scallops from the Bay of Brest (Fig. 2b) (Gillikin et al., 2008). These results are remarkably in agreement and highlight first the precision of both analytical techniques (LA-ICP-MS versus acid dissolution – High Resolution ICP-MS), and second the significant reproducibility of $([Ba]/[Ca])_{shell}$ profiles among a same scallop population whatever scallop age.

3.1.2 Recurrence of $([Ba]/[Ca])_{shell}$ profiles over a 7-year period (1998–2004, Bay of Brest) and among different coastal sites (Western Europe)

The $([Ba]/[Ca])_{shell}$ profiles were then examined on a specific population (Bay of Brest) over a 7-year survey. Inter-shell comparison of $([Ba]/[Ca])_{shell}$ profiles obtained for 3 scallop replicates confirmed first the significant reproducibility of these profiles among a single population (usually, $r^2 > 0.4$, $p < 0.05$, $n > 60$) (Table 1). Variations of mean $([Ba]/[Ca])_{shell}$ ratios ($n=3$) over the 7-year period revealed a general pattern with a sta-

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ble background ratio interrupted by 2 summer maxima of year-dependant intensities (Fig. 3, Table 1). The background ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratio was about $0.56 \pm 0.12 \mu\text{mol/mol}$ and rather homogenous among the year (%RSD < 20). Concerning the summer ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) peaks, the first one occurred from mid June to July and was usually the most intense ($0.91\text{--}4.7 \mu\text{mol/mol}$). The second one occurred from end July to early September and presented a lower maximum ratio ($0.73\text{--}2.83 \mu\text{mol/mol}$). The year 2000 exhibited the weakest maxima of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios ($1.03\text{--}0.73 \mu\text{mol/mol}$). An opposite pattern was observed in 1999 and in 2002 where the most intense peak was not the first one. The year 2002 remained unusual with 4 ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) peaks ($1.86, 1.31, 1.55, 2.83 \mu\text{mol/mol}$).

The background and maximum (Ba/Ca)_{shell} ratios obtained in different ecosystems (Bay of Seine, Bay of Brest, Belle Ile, Quiberon, Ria de Vigo) were summarized in Table 2. This inter-site study shows a similar ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) pattern with background content ranging from 0.44 to $0.68 \mu\text{mol/mol}$ and ubiquitous maxima in summer. The range of maximum ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios was similar in all locations ($0.73\text{--}5.3 \mu\text{mol/mol}$) corresponding to a 1.3–9 fold enrichment.

These results characterize a recurrent ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) profile typology at all sites and years, with a flat background content interrupted by a first intensive peak in early summer (mid-June to July) and a second weaker one in late summer (August to early September).

3.1.3 Comparability of archived Ba signals in other bivalve shells

These recurrent ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) profiles observed for *P. maximus* shells are demonstrated similar to those recorded in bivalves from other coastal environments (Table 2). The background ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratio and summer peaks (max 9 times the background in *P. maximus* shells and until 34 times the background for other bivalves) was slightly lower in *P. maximus* shells. Differences in ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) content is suggested to be related to the bivalve species, its physiology, or differences in analytical methods. For example, the maximum intensity of ($[\text{Ba}]/[\text{Ca}]_{\text{shell}}$) ratios is particularly high in mus-

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sels and clams (up to $20 \mu\text{mol/mol}$). This may be explained by the preferential precipitation of Ba under the aragonite structure of CaCO_3 (Rimstidt et al., 1998). Higher $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ content is thus suggested to be influenced by the structure of this bivalve (aragonite). Differences in calibration steps can also induce difference in $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratios. Quantitative Ba analyses were performed with LA-ICP-MS using external calibrations with NIST glass standard reference materials (minimum $41 \mu\text{g/g}$ of Ba) (Carré et al., 2006; Lazareth et al., 2003; Pearce and Mann, 2006; Stecher et al., 1996; Vander Putten et al., 1999, 2000). Such external calibration is probably not suitable to accurately measure shell Ba concentrations ranging from 1 to $10 \mu\text{g/g}$, especially considering the different matrix properties and response between glasses and CaCO_3 shells when using some laser ablation units (Belloto and Mikeley, 2000; Barats et al., 2007). External calibrations with matrix matched standards (CaCO_3) was thus preferred in this study and others (Belloto and Mikeley, 2000; Thébault, 2005; Gillikin et al., 2006; Barats et al., 2007). Finally, taking into account the accurate dating of this study, and differences in analytical methods and in bivalve species, all these studies agree with a common profile of $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratio in bivalves, widespread over the world, with a background signal punctuated by sharp summer episodic peaks. This result underlines thus specific ubiquitous processes involved in the increase of $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratio, which are directly related to changing conditions in the scallop environment.

3.2 Biogeochemical processes influencing $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ profiles

3.2.1 $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ background content as an indicator of Ba aqueous concentration

The $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ background ratios in *P. maximus* shells were evaluated in the Bay of Brest over the 7-year period (Table 1) and reveal an average ratio of $0.56 \pm 0.12 \mu\text{mol/mol}$. Ba concentrations in the Bay of Brest were also determined in dissolved and particulate seawater collected at 1 m above the SWI from March to September 2000 (2 or 3 times/week, except from 24 July to 9 September) (Lorrain, 2002). $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ profiles are compared with variations of Ba concentrations

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in seawater (Fig. 4a–b). Variations of dissolved and particulate Ba exhibit concentrations ranging, respectively, from 45 to 100 nmol/l and 0.7 to 9 nmol/l, and averaging 50 and 2 nmol/l. The background Ba/Ca ratio in dissolved seawater in 2000 is about $5.2 \pm 0.5 \mu\text{mol/l}$ (Lorrain, 2002) which is slightly different than the value reported in 2003 ($3.8 \mu\text{mol/l}$) (Gillikin et al., 2008). The ratio calculated in 2003 corresponds to only 3 measurements which is considerably less than in 2000 ($n=43$) and which most probably explain such difference. The major pool of Ba in the seawater at the SWI originates from the dissolved phase. Background $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratios in *Mytilus edulis* mussel shells were previously demonstrated to be directly related to the $([\text{Ba}]/[\text{Ca}])_{\text{sw}}$ ratios of the water in which they grew (Gillikin et al., 2006). For the same scallop species (*Pecten maximus*) and in the same sampling site (Bay of Brest), the partition coefficient D_{Ba} was reported to be 0.18 in 2003 and similar to those obtained for *Mytilus edulis* mussels or *Saxidomus giganteus* clams in other coastal temperate ecosystems (Gillikin et al., 2006, 2008). In our study, the shell Ba partition coefficient (D_{Ba}), evaluated in 2000 using the $([\text{Ba}]/[\text{Ca}])_{\text{sw}}$ ratio in the dissolved seawater phase and the background $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratio measured in shells, was about $D_{\text{Ba}} = 0.11 \pm 0.03$ (Barats, 2006). Taking into account the difference of analytical methods, these results are similar than those already obtained. Background $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratios in *P. maximus* shells may thus be considered as a relevant proxy of Ba aqueous concentrations.

3.2.2 Transient processes related to $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ maximum events

The origin of these $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ maxima Summer $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ maxima underline an important additional source of Ba at the SWI, which in turn will influence both dissolved and particulate Ba concentrations in the *Pecten* habitat. In 2000, dissolved and particulate Ba exhibited increasing seawater concentrations at the end of July concomitantly to the first increasing of $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratio (Fig. 4a–b) (Lorrain, 2002). This maximum of $([\text{Ba}]/[\text{Ca}])_{\text{shell}}$ ratio was 2.6 times higher than the background one, whereas dissolved seawater Ba concentration was only 1.5 times higher than the background one. The increase of dissolved Ba concentration is probably not sufficient to explain the increase

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in skeletal $([Ba]/[Ca])_{shell}$ content. At the end of July, particulate Ba concentration increased until 5 times the background content. This significant increase of particulate Ba may thus provide additional inputs of Ba at the SWI. As bivalves are non specific filter feeder, these additional inputs of Ba-rich particles at the SWI, i.e. in the surrounding *Pecten* environment are supposedly ingested as food, in part digested, transferred to the extrapalleal fluid, and finally archived in the shell (Stecher et al., 1996; Vander Putten et al., 2000; Lorrain, 2002; Gillikin et al., 2006).

A pelagic biogenic process as the initial cause of Ba-rich particles at the SWI and subsequent $([Ba]/[Ca])_{shell}$ maxima The occurrence and the amplitude of summer $([Ba]/[Ca])_{shell}$ peaks were intensively examined in the Bay of Brest over 7 years (1998–2004) because of a regular and complete monitoring of physiological (growth) and environmental parameters (hydrological, biological, chemical).

The influence of the shell growth rate on maximum $([Ba]/[Ca])_{shell}$ ratios is studied to check the external environmental control influencing $([Ba]/[Ca])_{shell}$ peaks. Shell growth rates exhibit some drastic decreases occurring in spring or summer which were previously considered to be mainly induced by lower seawater temperature or the occurrence of specific phytoplankton blooms (Chauvaud et al., 1998; Lorrain et al., 2000). In some cases, such decreases of shell growth rate occurred simultaneous to $([Ba]/[Ca])_{shell}$ maxima, but it is not true for all the year. $([Ba]/[Ca])_{shell}$ maxima cannot thus be directly related to minima of shell growth rate.

The specific survey in 2000 supports rather supplementary dissolved and particulate Ba inputs at the SWI in summer, subsequently taken up by the bivalve to explain $([Ba]/[Ca])_{shell}$ maxima. There are two potential sources providing these Ba inputs: related to benthic or pelagic processes.

First, the examination of hydrological conditions (seawater temperature and salinity) revealed no significant similarity neither with the occurrence, nor with the amplitude of maximum $([Ba]/[Ca])_{shell}$ ratios. Benthic releases due to hydroclimatic events (flood or resuspension) are thus improbable to explain these Ba particulate inputs at the SWI. Benthic release due to more reducing conditions at the SWI can also occur. However,

5 this may provide rather dissolved components. More reductive condition at the SWI promote benthic release of dissolved Mn which was demonstrated to induce increasing shell Mn content in summer (Barats et al., 2008). In 2000, skeletal Mn concentrations were relatively constant, concomitantly to constant seawater particulate Mn content and a low increase of Mn concentration in the dissolved phase (Fig. 4c). The dissolved oxygen concentrations (annual average: 6.1 ± 0.5 ml/l; and summer average from mid-May to mid-September: 6.0 ± 0.3 ml/l) were constant in the Bay of Brest, underlining a well oxygenated seawater. For the other year, even if seawater Mn measurements were not available, archived shell Mn underlined stable content during ($[Ba]/[Ca]_{shell}$)
10 maxima, in disagreement with any benthic Ba remobilisation due to more reductive conditions. The origin of Ba inputs at the SWI is thus rather initiated by a pelagic biogenic process (Lorrain, 2002).

The phytoplankton dynamics were particularly examined because phytoplankton is an important vector for the vertical transport of Ba in oceans (Dehairs et al., 1980, 1991, 2000; Bishop, 1988; Fisher et al., 1991; Jeandel et al., 2000; Sternberg et al., 2005). Chl-*a* concentrations in the seawater, supposed to reflect phytoplankton biomass, exhibited a general pattern with an intense maximum occurring in spring and later ones somewhat smaller in late summer (Fig. 3). Phytoplankton blooms generally occurred in the month preceding ($[Ba]/[Ca]_{shell}$) maxima. In 1998 and 2003, ($[Ba]/[Ca]_{shell}$) profiles revealed a surprising analogy with the variations of Chl-*a* concentrations: 2 maximum events with the first most intense one and inserted by similar time periods. Time lag between the occurrence of maximum Chl-*a* concentration and maxima of ($[Ba]/[Ca]_{shell}$) ratio ranged from 1 week to 3 months (in 2003). In 1999 and 2002, maxima of ($[Ba]/[Ca]_{shell}$) ratio occurred concomitantly to periods of higher Chl-*a* concentration. But, their profile shapes were totally different. In 2001, a year particularly productive, the maxima of ($[Ba]/[Ca]_{shell}$) peak events were surprisingly weak; whereas in 2004, the lowest productive year, the ($[Ba]/[Ca]_{shell}$) peaks occurred with a significant amplitude, higher than in 2001. These results highlight that Chl-*a* concentration in seawater is not directly related to ($[Ba]/[Ca]_{shell}$) maxima. Consequently,
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archived Ba in shells cannot be considered as a prominent proxy of the primary productivity. Statistical data treatment revealed however significant single correlations between the amplitude of maximum $([Ba]/[Ca])_{shell}$ ratios and the maximum of Chl-*a* concentrations during the different integrated periods ($r^2 > 0.64$, $p < 0.05$, $n = 16$; Table 3) suggesting thus the influence of the total biomass on the amplitude of $([Ba]/[Ca])_{shell}$ maxima.

Special attention was then focussed on the phytoplankton composition during the whole summer period. Two genera among the hundreds of other species were revealed recurrent and dominant: diatoms of *Chaetoceros* spp. and dinoflagellates of *Gymnodinium* spp. Other genera were only found to be punctual and often minor during the period of increased $([Ba]/[Ca])_{shell}$ ratios. In 1998, 1999, 2001 and 2002, the first maximum $([Ba]/[Ca])_{shell}$ occurred simultaneously or within a short time lag of dominant *Chaetoceros* spp. blooms, whereas the later ones usually during *Gymnodinium* spp. blooms (Fig. 5). In 2000, *Chaetoceros* spp. exhibited 3 blooms, the most intense over the 7-year period (Fig. 5). But, only the second one could be attributed to a maximum of $([Ba]/[Ca])_{shell}$ ratios, the lowest one over the 7-year period. In 2001, a *Gymnodinium* spp. bloom, the most intense over 7-year period, occurred concomitantly to $([Ba]/[Ca])_{shell}$ ratios close to the background concentration (Fig. 5). These 2 specific blooms cannot thus influence the amplitude or the occurrence of maximum $([Ba]/[Ca])_{shell}$ ratios. Neither of these two species, nor these genera (diatoms or dinoflagellates), and nor the phytoplankton abundance are directly correlated with these $([Ba]/[Ca])_{shell}$ maximum events.

Various chemical parameters (dissolved oxygen, nutrients, POC, PON) are examined. But, none exhibited similar transient events such as maxima in $([Ba]/[Ca])_{shell}$ ratio, except for POC and PON concentrations (Fig. 5). Considering maximum concentrations of POC and PON in the month preceding the maximum $([Ba]/[Ca])_{shell}$ ratios, single correlations were obtained between the amplitude of maximum $([Ba]/[Ca])_{shell}$ ratios and maxima of POC and PON concentrations ($r^2 > 0.58$, $p < 0.05$, $n = 16$) (Table 3). Multiple regression analyses revealed an usual relationship expressing the amplitude

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of maximum $([Ba]/[Ca])_{shell}$ ratio according to particulate organic matter and favoured by increasing content of nitrates and PON and decreasing nitrite content in the seawater ($r^2 > 0.70$, $p < 0.30$, $n = 16$) (Table 3). These statistical relationships agree with an initial pelagic biogenic process involved in supplementary Ba inputs at the SWI to explain the maximum $([Ba]/[Ca])_{shell}$ events. In the month preceding $([Ba]/[Ca])_{shell}$ maxima, diatom blooms were usually dominant. These taxa grow rapidly when nitrate is available and maintain high uptake capacity event at low nitrate concentrations (Carter et al., 2005). Nutrient availability governing the amplitude of phytoplankton blooms and its composition (Chauvaud et al., 2000; Le Pape et al., 1996; Ragueneau et al., 2002), higher dissolved inorganic nitrogen in the seawater during the month preceding $([Ba]/[Ca])_{shell}$ maxima promotes the primary productivity (Carter et al., 2005). Higher phytoplankton content induces then the production of higher inputs of PON in seawater. Periods of higher summer productivity and post-bloom conditions may thus influence the amplitude of maximum $([Ba]/[Ca])_{shell}$ ratio.

3.2.3 Processes involved in Ba-enrichment at the SWI that evidence subsequent $([Ba]/[Ca])_{shell}$ maxima

This study underlines the influence of an initial pelagic biogenic process on the occurrence and the amplitude of maximum $([Ba]/[Ca])_{shell}$. These processes are un-specific to phytoplankton genera and rather related to post-bloom summer conditions. The episodic $([Ba]/[Ca])_{shell}$ maxima in *P. maximus* shells are supposed to be induced by a trophic uptake of supplementary particulate Ba inputs at the SWI. These Ba-enriched particles may originate either from scavenging of phytoplankton-derived particles or from a benthic post-bloom remobilization. A pathway leading to particulate Ba enrichment within the water column and scavenged to the SWI is most plausible (Ganeshram et al., 2003; Sternberg et al., 2005). Different pathways were established to explain Ba enrichment in particles at the SWI: such as Ba adsorption in phytoplankton cells, barite formation during phytoplankton decay, Ba enrichment in exopolymeric substances (EPS), or Ba adsorption onto mineral oxides formed within diatom biogenic

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particles.

Chaetoceros spp. blooms are usually dominant during the month preceding maximum $([Ba]/[Ca])_{shell}$. The agglomeration of EPS is specifically reported during bacterial decomposition of these *Chaetoceros* spp. blooms; and promoted in response to nutritional stress, which is the case in this study (depleted concentrations of nitrates and nitrites in seawater) (Passow and Alldredge, 1995; Stecher and Kogut, 1999; Alldredge et al., 1995; Thornton, 2002). Both colloidal organic material and EPS are particularly enriched in Ba by five orders of magnitude (Quigley et al., 2002). Ba-rich EPS may thus support inputs of Ba-enriched particles at the SWI.

Among the different pathways (Ba adsorption in phytoplankton cells, barite formation during phytoplankton decay, Ba enrichment in EPS, or Ba adsorption onto mineral oxides formed within diatom biogenic particles), the accurate process inducing Ba enrichment in particles at the SWI cannot be clearly identified. This study underlines however that a pelagic biogenic process initiates the bivalve uptake of Ba-enriched particles.

4 Conclusions

Barium profiles obtained in this methodical survey of Great Scallop shells from temperate waters of north western France agree with those of other bivalve species previously investigated. Similar to all bivalves analyzed to date, the $([Ba]/[Ca])_{shell}$ profiles are characterized by a relatively constant background mainly governed by the ambient seawater dissolved Ba, and the occurrence of sharp summer $([Ba]/[Ca])_{shell}$ maxima. In 2000, Ba measurements in seawater allowed identifying that particulate Ba inputs can be the dominant pathway explaining $([Ba]/[Ca])_{shell}$ maxima. Pelagic biogenic processes are supposed to initiate seawater Ba enrichment at the SWI, subsequently taken up by scallops and translated by increased $([Ba]/[Ca])_{shell}$ ratio. Examination of the complete dataset (1998–2004) underlined that $([Ba]/[Ca])_{shell}$ maxima occurred under summer post-bloom conditions, and that their amplitude depended on particulate

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organic matter and particularly on the nitrogen species turnover. This whole dataset confirms that:

1. records of maximum ($[Ba]/[Ca]_{shell}$) ratio cannot be used directly as a relevant paleo productive tracer, and
2. complex processes occur in the pelagic/benthic Ba cycle and are responsible of significant Ba inputs at the SWI. If these processes are better constrained, scallop ($[Ba]/[Ca]_{shell}$) records could provide a high temporal resolution proxy of Ba biogeochemistry in coastal environments.

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Table 1. Intershell comparison of $([Ba]/[Ca])_{shell}$ profiles and interannual comparison (1998–2004) of both mean background and mean peak intensity (named by the time of order of the peak) of $([Ba]/[Ca])_{shell}$ ratios ($n=3$) in scallops from the Bay of Brest.

Year	Intershell reproducibility of Ba profiles Correlation coefficients				Background shell Ba/Ca ratios ($\mu\text{mol/mol}$)		Maxima of shell Ba/Ca ratios ($\mu\text{mol/mol}$)			
	1 vs. 2	1 vs. 3	2 vs. 3	p	Mean \pm SD	%RSD	Date ($\pm 3\text{d}$)	Mean \pm SD	%RSD	
1998 ($n=3$)	0.72	0.78	0.95	<0.05	0.526 \pm 0.074	14	peak 1 12/06/1998	4.67 \pm 1.90	41	
1999 ($n=3$)	0.92	0.95	0.96	<0.05	0.377 \pm 0.031	8	peak 2 04/09/1998	0.898 \pm 0.314	35	
							peak 1 18/06/1998	1.27 \pm 0.48	38	
2000 ($n=3$)	0.48	0.22	0.82	<0.09	0.561 \pm 0.057	10	peak 2 19/07/1999	2.12 \pm 0.84	40	
							peak 1 23/07/2000	1.03 \pm 0.03	3	
2001 ($n=3$)	0.18	0.24	0.46	<0.2	0.657 \pm 0.101	15	peak 2 26/08/2000	0.73 \pm 0.04	5	
							peak 1 22/07/2001	0.971 \pm 0.431	44	
2002* ($n=2$)	0.88	–	–	<0.05	0.533 \pm 0.102	19	peak 2 31/07/2001	1.39 \pm 0.91	65	
							peak 1 14/06/2002	1.86 \pm 0.60	32	
							peak 2 01/07/2002	1.31 \pm 0.42	32	
							peak 3 26/07/2002	1.55 \pm 0.18	12	
2003 ($n=3$)	0.93	0.96	0.87	<0.05	0.535 \pm 0.134	25	peak 4 20/08/2002	2.83 \pm 0.55	19	
							peak 1 20/07/2003	3.80 \pm 0.74	20	
2004 ($n=3$)	0.44	0.78	0.30	<0.05	0.745 \pm 0.175	24	peak 2 26/08/2003	1.72 \pm 0.12	7	
							peak 1 18/06/2004	2.25 \pm 0.99	44	
							peak 2 05/09/2004	1.26 \pm 0.38	30	

* deviation to the mean average concentrations

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Table 2. Barium archives in different bivalve shells according to different ecosystems. Both background and maximum (Ba/Ca)_{shell} ratios are examined. The period of (Ba/Ca)_{shell} maxima are also exhibited.

Bivalves	Species	Structure of precipitation	Location	Ecosystem type	Time resolution	Investigated period	Background Ba/Ca ratios (μmol/mol)	Ba enrichment period	Maximum Ba/Ca ratios (μmol/mol)	[Ba] _{max} / [Ba] _{lbg}	References
Scallop	<i>Pecten maximus</i>	calcite	Bay of Brest, France	Coastal temperate	3 days+ dating	1998–2004	0.56±0.12	late June–early September	0.73–4.7	1.3–9	This study*
			Bay of Brest, France	Coastal temperate	3 days+ dating	2000	Qualitative analysis	July–August	Qualitative analysis	5–9	Lorrain (2002)
			Bay of Brest, France	Coastal temperate	3 days+ dating	2003	0.7	July–August	4	6	Gillikin et al. (2008)
			Quiberon, France	Coastal temperate	3 days+ dating	2000	0.68±0.12	Late May–July	1.3–1.8	2–3	This study*
			Belle Ile, France	Coastal temperate	3 days+ dating	1999–2001	0.68±0.13	June–early August	0.76–5.3	2–7	This study*
			Bay of Seine, France	Coastal temperate	3 days+ dating	2004	0.44±0.04	May	1.36	3	This study*
Scallop	<i>Comptopallium radula</i>	calcite	Ria de Vigo, Spain	Coastal temperate	3 days+ dating	2000	0.52±0.08	July–October	1.3–3.0	2–6	This study*
			Nouméa, New Caledonia	Coastal tropical	4 days+ dating	2002–2003	0.52	January, March, May August, September	0.92–3.7	2–10	Thébault (2005)
Scallop	<i>Argopecten purpuratus</i>	calcite	Rinconada bay, Chile	Coastal	Some days	1999	0.7	June–July	3–12	4–17	Thébault (2005)
Mussel	<i>Mytilus edulis</i>	calcite	Schelde, The Netherlands	Coastal temperate	Seasonal to weekly	1995–2003	3	Spring	20–70	7–23	Vander Putten et al. (1999, 2000); Gillikin et al. (2006)
Oyster	<i>Isognom ephippium</i>	calcite aragonite	Tudor, Kenya; estuary or mangroves	Coastal tropical	Seasonal	1991–1998	1	Monsoon period	5–11	5–11	Lazareth et al. (2003)
Clam	<i>Mesodesma donacium</i>	aragonite	Peru	Coastal	Less than one month	2001–2003 (+fossil)	2 (850)	January, May, September,(?)	10–30 (1500)	5–10 (2)	Carré et al. (2006)
Clam	<i>Chino subrugosa</i>	aragonite	Peru	Coastal	Less than one month	2001–2004	10	January November December	30–40	3–4	Carré et al. (2006)
Clam	<i>Mercenaria mercenaria</i>	aragonite	Delaware Bay, USA	Coastal temperate	Seasonal	1984–1992 (+fossil)	2 (5)	Spring	5–20	3–10 (3–7)	Stecher et al. (1996)
Clam	<i>Spisula solidissima</i>	aragonite	Chesapeake Bay, USA	Coastal temperate	Seasonal	1980–1982	5–40	Spring	5–40	3–20	Stecher et al. (1996)
Clam	<i>Ensis siliqua</i>	aragonite	Great Britain	Coastal temperate	Seasonal	1991–1998	1–5	Usually late summer	2–20	2–4	Pearce and Mann (2006)
Clam	<i>Arctica Islandica</i>	aragonite	German Bight	Coastal temperate	Seasonal	1858–2002	1–3	Spring	10–70	3–20	Epplé (2004)
Clam	<i>Saxidomus giganteus</i>	aragonite	Puget Sound, Washington, USA	Coastal temperate	Seasonal	1992–2001	1	Spring or summer	5–35	5–35	Gillikin et al. (2008)

* represent analyses performed with matrix-matched standards

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Table 3. Single correlations and multiple regression analyses outlining significant relationships between the amplitude of maximum $[Ba/Ca]_{shell}$ ratios ($\mu\text{mol/mol}$) and environmental variables. See text for details using Stabox Pro software for Windows Ver. 6 (Grimmer Software, France).

Significant correlations with maxima of shell Ba/Ca ratio ($p < 0.05$, $n = 16$)					Multiple regressions expressing the amplitude of shell Ba/Ca maxima ($\mu\text{mol/mol}$) according to other variables ($d_{cook} < 1$)						
Integration periods	POC	PON	Chl- <i>a</i>	Adjusted r^2	Relationships	Constant	NO_3^-	NO_2^-	PON	<i>Chaetoceros</i> spp.	
-4w+1w	r^2	0.7	0.76	0.8	0.88	Intensity of shell Ba/Ca maxima p	0.939 0.03	0.365 0.0001	-9.77 0.003	0.0219 0.01	
-3w+1w	r^2	0.58	0.72	0.67	0.84	Intensity of shell Ba/Ca maxima p	0.219 0.3	0.453 0.0002	-8.77 0.003	0.0292 0.001	
-2w+1w	r^2	0.63	0.75	0.65	0.72	Intensity of shell Ba/Ca maxima p	0.8 0.11	0.454 0.03	-13.5 0.01	0.0343 0.005	
-1w+1w	r^2	0.65	0.7	0.64	0.7	Intensity of shell Ba/Ca maxima p	-0.723 0.14		-5.51 0.04	0.0526 0.0001	0.00949 0.05

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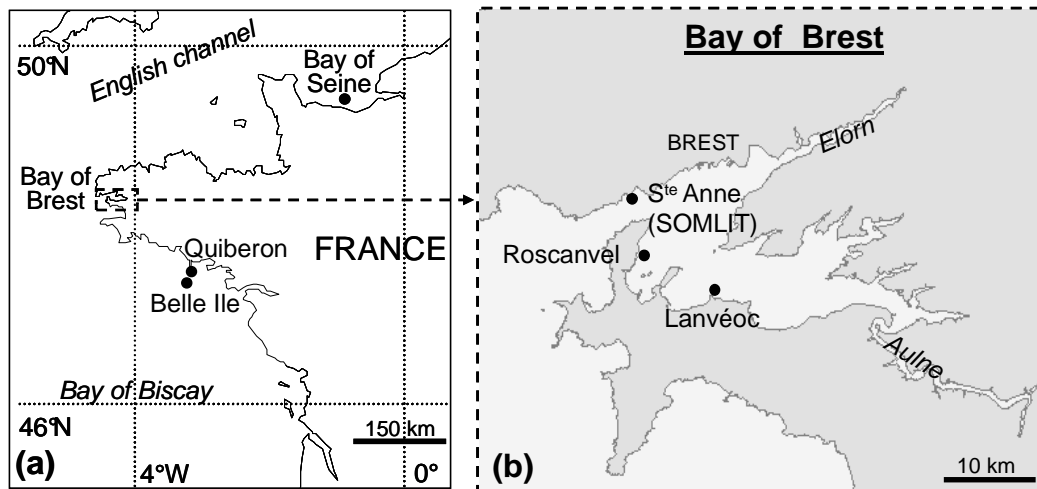


Fig. 1. Maps of the investigated area (Atlantic Coast, France) showing the sampling zones: **(a)** the Bay of Seine ($49^{\circ}30'N$, $0^{\circ}30'W$), the Bay of Brest ($48^{\circ}20'N$, $4^{\circ}30'W$), Belle Ile ($47^{\circ}20'N$, $3^{\circ}10'W$) and Quiberon ($47^{\circ}30'N$, $3^{\circ}00'W$); **(b)** the Bay of Brest in details with all the investigated sites (Roscanvel for the sampling, and the others for regular measurements of environmental parameters).

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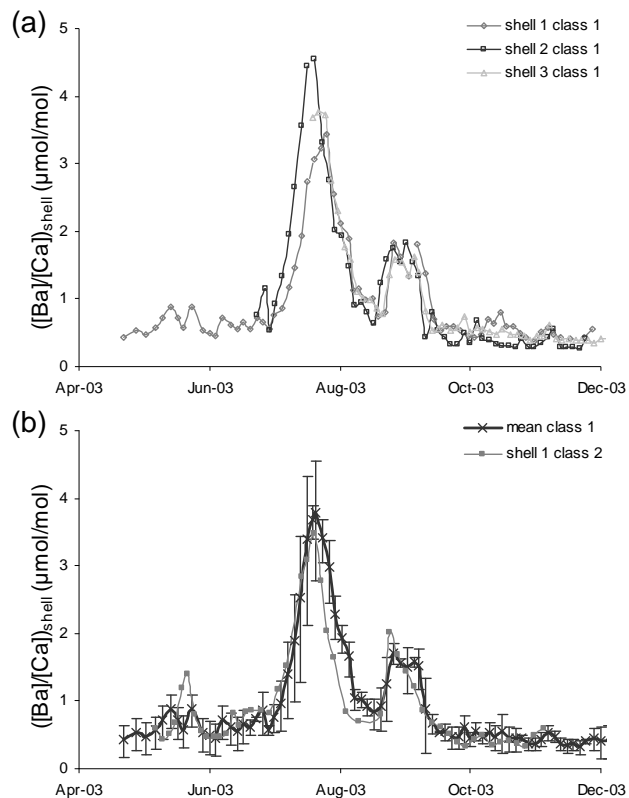


Fig. 2. Comparison of $([Ba]/[Ca])_{shell}$ profiles obtained for **(a)** three 2-year old scallop shells; **(b)** the mean profile of these 3 juvenile shells and one of 3-year old scallop shell. collected in the Bay of Brest (Roscanvel). during the year 2003. to evaluate the inter shell reproducibility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

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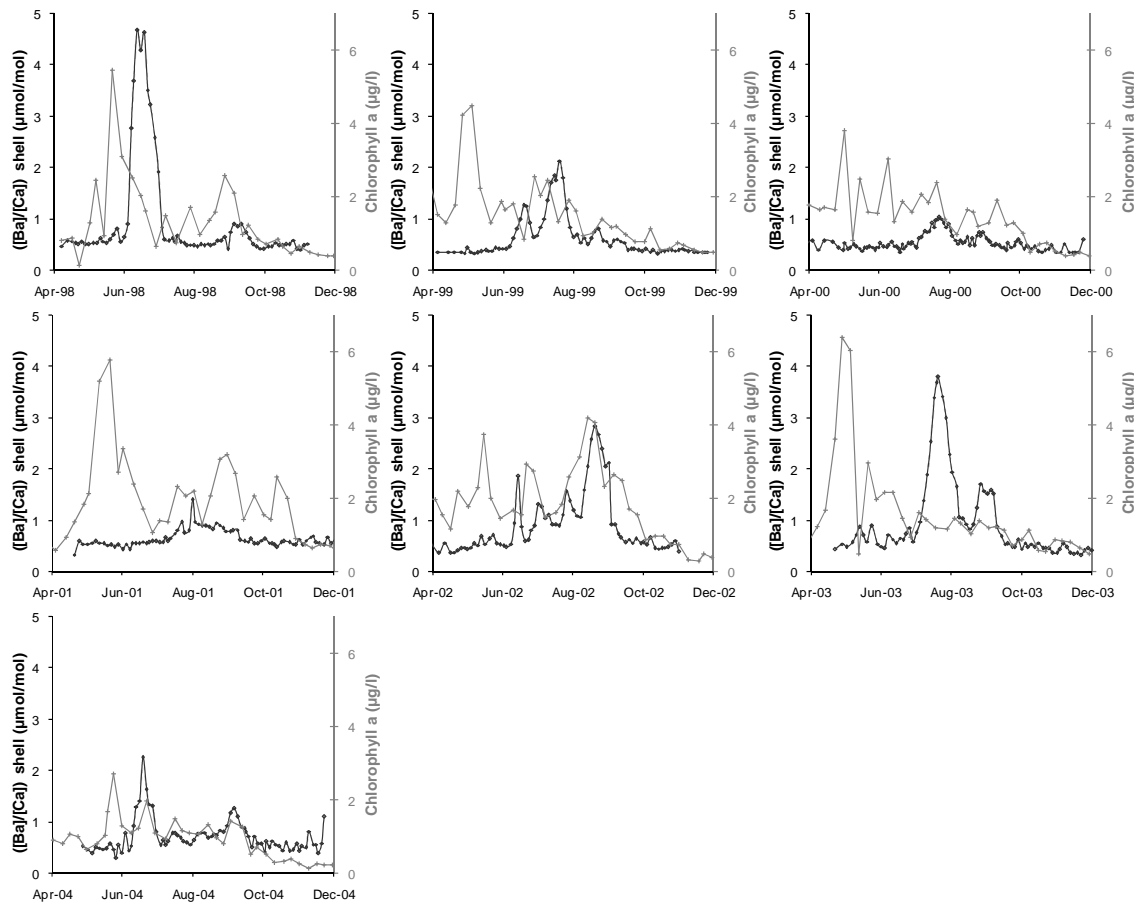


Fig. 3. Variations of mean $([Ba]/[Ca])_{shell}$ ratios (3 shells per year; except in 2002. $n=2$) according to the chlorophyll-*a* concentration ($\mu\text{g/l}$) over 7-year period (1998–2004) in scallops from Roscanvel station (Bay of Brest, France).

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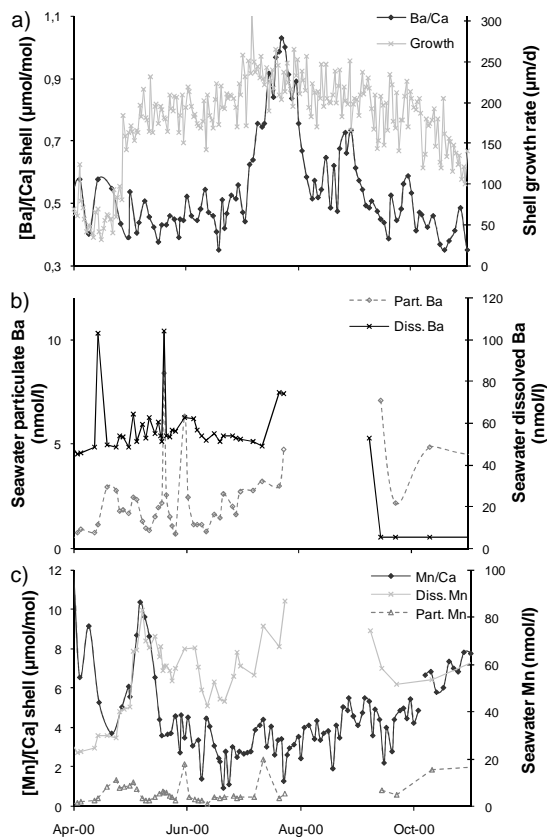


Fig. 4. (a) Mean $([Ba]/[Ca])_{shell}$ profiles ($n=3$) obtained during 2000 in the Bay of Brest, compared with (b) particulate and dissolved Ba concentrations (nmol/l) in dissolved seawater (bottom seawater: 1 m of the SWI). (c) mean shell $([Mn]/[Ca])_{shell}$ profiles, dissolved and particulate Mn concentrations (nmol/l).

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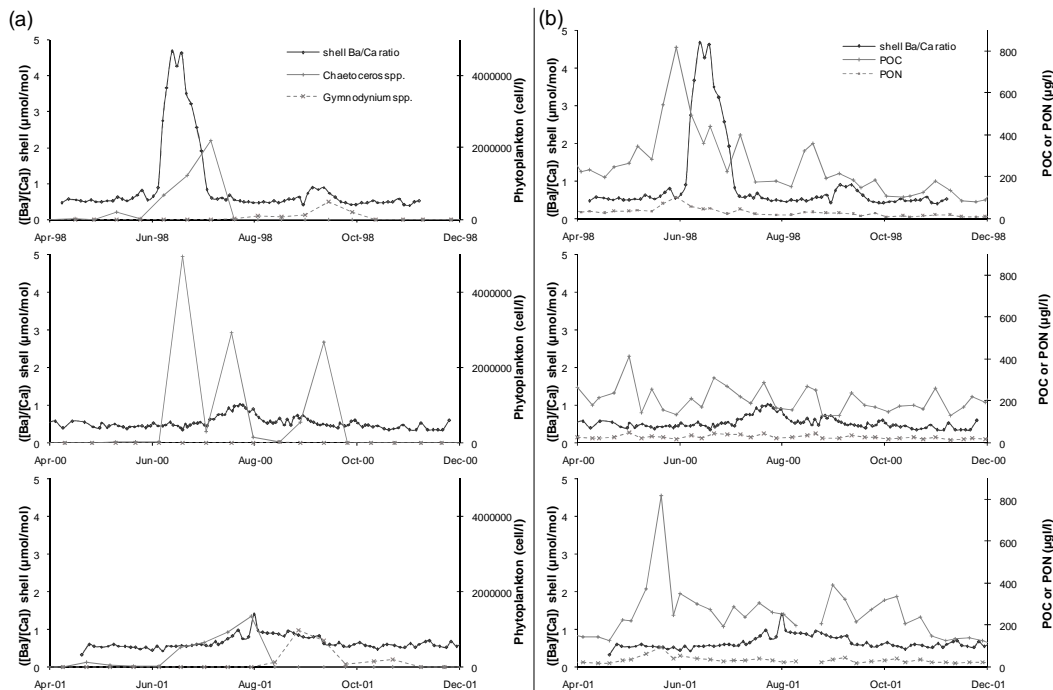


Fig. 5. Example of variations of $([Ba]/[Ca])_{shell}$ ratios for 3 years (1998, 2000, 2001) in shells from the Bay of Brest (France) according to: **(a)** two phytoplankton genera (*Chaetoceros* spp. and *Gymnodinium* spp.). **(b)** particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations ($\mu\text{g/l}$) in seawater.

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