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Li/Ca enrichments in great scallop shells (*Pecten maximus*) and their relationship with phytoplankton blooms

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Abstract

Phytoplankton dynamics in coastal oceans is a major component of the global biogeochemical carbon cycle, and is currently affected by global change through modifications in levels of primary productivity and composition of phytoplankton communities. Despite many attempts, no straightforward geochemical proxy has been found yet in marine biogenic carbonates for reconstruction of past phytoplankton dynamics with high temporal resolution. Here, we report on sub-weekly variations of lithium-to-calcium ratios ($\text{Li}/\text{Ca}_{\text{shell}}$) along the axis of maximum growth of great scallop shells (*Pecten maximus*) collected alive between 1999 and 2007 in the bay of Brest, northwest France. Inter-individual variability of $\text{Li}/\text{Ca}_{\text{shell}}$ time series was very low, suggesting an environmental control on the incorporation of Li within shells. Conversely, inter-annual variability of $\text{Li}/\text{Ca}_{\text{shell}}$ was high, with limited seasonal $\text{Li}/\text{Ca}_{\text{shell}}$ variations in 2001 and 2007, and the presence of Li enrichments from May to July in 1999 and 2004. Comparison of these results with shell growth measurements (increment width) and environmental parameters suggests (i) that shell calcification rate is likely the main factor controlling incorporation of Li in *Pecten maximus* shell calcite, (ii) that seawater temperature has only a weak positive influence on $\text{Li}/\text{Ca}_{\text{shell}}$ of this species over the range 8–18°C, and (iii) that during diatom blooms, additional amounts of Li may be trapped in the shell following dissolution of Li-rich frustules of edible species in the digestive tract of scallops, being responsible for $\text{Li}/\text{Ca}_{\text{shell}}$ peaks. Therefore, we suggest that $\text{Li}/\text{Ca}_{\text{shell}}$ ratio may be a novel proxy for timing and magnitude of diatom blooms in coastal ecosystems. Analysis of ancient shells may thus provide useful information on past phytoplankton dynamics and on the importance of recent shifts observed from diatoms to non-siliceous phytoplankton in coastal areas affected by anthropogenic activities.

Keywords: bivalve, calcite, lithium, shell growth, phytoplankton, diatom

1. Introduction

In the past decades, a consensus emerged in the international scientific community: human activities have, or will shortly have, consequences on the structure and functioning of all the Earth's ecosystems, especially on coastal areas of the world ocean (Jackson, 2001). Coastal zones are one of the most dynamic interfaces of the biosphere, both from a geochemical and a biological point of view (Twilley et al., 1992); therefore, they hold an important place along the land-sea continuum. The most significant anthropogenic impacts affecting coastal ecosystems are related to changes in inputs of sediments, organic and inorganic pollutants, and above all, nutrients (nitrogen, phosphorus). The latter can induce changes of trophic conditions (up to eutrophication) and disturbances in phytoplankton dynamics (changes in primary production levels, in bloom frequency, in the composition of microalgal communities such as shifts from diatoms to dinoflagellates; Cloern, 2001). Phytoplankton are the keystone organism of the oceans. Indeed, although they account for only 0.1% of the total photosynthetic biomass on Earth, phytoplankton are responsible for nearly half of the biospheric net primary

production, annually fixing ca. 50 PgC by photosynthesis (Field et al., 1998). About 14% of this global ocean production, along with 80–90% of new production, takes place in coastal oceans that yet occupy less than 0.5% of the ocean volume (Chen et al., 2003). As a consequence, phytoplankton dynamics in the coastal zone is undoubtedly a major component of the global geochemical carbon cycle. Beyond this impact, these tiny ocean primary producers also serve as the base of the ocean food chain, supplying food for higher trophic levels; therefore their abundance determines the overall health of ocean ecosystems and fisheries.

In order to assess the respective roles of natural variability and anthropogenic activities in the current changes in structure and functioning of coastal ecosystems, it is crucial to quantify past phytoplankton dynamics, especially on levels of primary productivity and composition of phytoplankton communities which both seem to be affected by global change (Sarmiento et al., 2004; Miller et al., 2006). A problem is that conventional monitoring time series (electronic instruments, periodic water sampling) are relatively sparse, scattered, often very short (especially for phytoplankton) and therefore, do not encompass low frequency cycles of natural variations of coastal environments (Jack-

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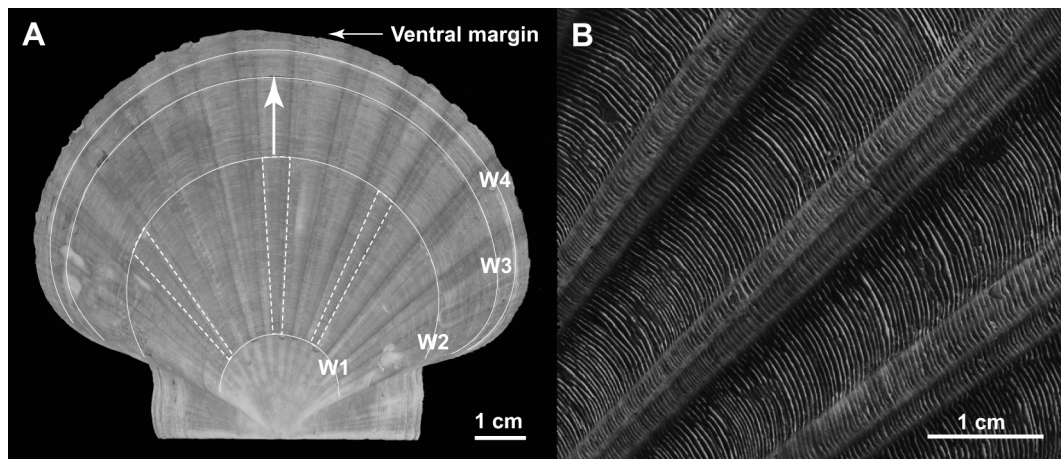


Figure 1: (A) Upper surface of the left valve of *Pecten maximus*. W1–W4 correspond to winter marks deposited during spring growth restart. Dashed areas indicate the different sections analysed for elemental concentrations in shell #6. White arrow is the axis of maximum shell growth. (B) Daily growth increments can be observed without any treatment aside from surface cleaning.

son, 2001). In this context, biological records of environmental variability appear as the best way of extending conventional records related to phytoplankton dynamics over long time periods. These biological records are obtained by deciphering environmental proxies incorporated within biogenic archives during their growth (e.g., corals, sclerosponges, mollusc shells). These organisms form their external calcium carbonate (CaCO_3) skeleton periodically, which leads to the formation of growth lines that can be used as chronological landmarks.

Many of the processes occurring in these highly dynamic coastal oceans take place on short time scales, ranging from days to weeks: this is especially true for phytoplankton dynamics. Corals and sclerosponges provide useful data on past ecological variability at a seasonal time scale, at most, but they are not suited to reconstruction of past phytoplankton dynamics. On another hand, bivalve mollusc shells have an outstanding potential for high-resolution palaeoecological studies because (i) most of them form distinct daily growth structures and, therefore, provide information on high-frequency variations of palaeoenvironmental conditions, (ii) many species grow very fast (tens to hundreds of $\mu\text{m d}^{-1}$), and (iii) some bivalves have a lifespan of many centuries. For instance, bivalve mollusc shell analysis recently led to palaeoenvironmental reconstructions of seawater temperature (Schöne et al., 2011), oceanic circulation (Wanamaker Jr. et al., 2008), climatic oscillations such as North Atlantic Oscillation or El Niño Southern Oscillation (Schöne et al., 2003; Carré et al., 2005), or pollution (Gillikin et al., 2005).

Surprisingly, and despite many efforts to assess the potential of these shells as high-resolution palaeoproductivity archives, no straightforward relationship has ever been found between isotopic or elemental composition of shells and phytoplankton dynamics in seawater. Attempts to use the carbon isotope composition ($\delta^{13}\text{C}_{\text{shell}}$) as a palaeoproductivity proxy have not been successful, partly because a large part of the carbon required for mollusc shell calcification originates from the bivalve metabolism (Lorrain et al., 2004; McConnaughey and Gillikin, 2008). However, a recent

study suggested that variations of this geochemical variable in shells of the great scallop *Pecten maximus* reflected food availability (including phytoplankton cells), which may be useful for ecophysiological studies (Chauvaud et al., 2011). In the past decade, sharp peaks have been observed in ontogenetic profiles of Ba/Ca ratio in some bivalve shells (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003; Gillikin et al., 2006, 2008; Barats et al., 2009; Thébault et al., 2009a). Several of these studies suggested a linkage between phytoplankton biomass (especially diatoms) and barium incorporation into the shell structure. However, many bivalve species do not display such relationships, suggesting that factors controlling variations of Ba/Ca in shells are numerous and complex, so that it cannot be considered as a universal proxy for phytoplankton dynamics (Gillikin et al., 2008). Finally, two recent studies suggested that Mo/Ca may be used as a proxy for spring productivity in coastal ecosystems (Thébault et al., 2009a; Barats et al., 2010), but this barely studied element must be investigated in other bivalve species to confirm this hypothesis. Aside from Ba and Mo, an important set of elements was analysed by our research group in shells of *Pecten maximus* from the bay of Brest, France. Amongst them, lithium presented very intriguing time series that evoked patterns of phytoplankton dynamics in the bay.

Lithium has barely been investigated in marine biocarbonates. Most studies dealt with foraminifera where Li/Ca ratio was suggested to be a proxy either for temperature, for Li/Ca ratio in seawater, or for oceanic carbonate ion concentration (Delaney et al., 1985; Hall and Chan, 2004; Marriott et al., 2004b; Hathorne and James, 2006). The only known study dealing with Li/Ca in bivalves was performed on aragonitic shells of the ocean quahog *Arctica islandica* (Thébault et al., 2009b). It was suggested that calcification rate and/or river inputs of Li-rich silicate particles were likely the main factors controlling incorporation of Li in shell aragonite. However, the relatively low shell growth rates of *Arctica islandica* prevented thorough investigations of high-frequency variations of Li/Ca.

Conversely, *Pecten maximus* is a very interesting species

because of its very high shell growth rate (up to 350–400 $\mu\text{m d}^{-1}$), its lifespan (up to 12 years), and the production of clearly visible annual and daily growth lines, called striae (Chauvaud et al., 1998; Figure 1). Moreover, this species has a wide biogeographical distribution, extending from southern Morocco to the Lofoten Islands (Norway), including the Mediterranean Sea (Malaga). It is especially abundant all along the French, Irish, British and Scottish coasts, and can be found between 0 and 500 m water depth (Chauvaud et al., 2005). Finally, its shell is composed of foliated calcite (Larvor et al., 1996) and is relatively immune to dissolution and recrystallization (Hickson et al., 1999), thus offering good opportunities for assessing palaeoenvironmental conditions.

The aims of this paper are (i) to analyse time series of Li/Ca variations in shells of *Pecten maximus* over several years between 1999 and 2007 in the bay of Brest, (ii) to compare these variations to environmental data obtained from a high-frequency monitoring station located close to our study site, (iii) to review the different processes that may explain incorporation of Li in shell calcite, and (iv) to assess the potential of Li/Ca_{shell} enrichments as proxies for phytoplankton dynamics.

2. Material and methods

2.1. Study area

Our study site, the Roscanvel bank, is located in the bay of Brest (Brittany, northwest France; Figure 2), a semi-enclosed marine ecosystem of 180 km² connected to shelf waters (Iroise Sea) by a narrow and deep strait (2 km width, 40 m depth). This bay is a shallow basin with an average depth of 8 m. Two rivers, the Aulne (catchment area = 1792 km²) and the Elorn (catchment area = 379 km²), are responsible for up to 80% of the total freshwater input in the bay. Both catchments are composed of proterozoic and palaeozoic sedimentary rocks (shales and sandstones), punctuated with some more recent granite intrusions. Tidal amplitudes reach 8 m during spring tides, resulting in an oscillating volume that is 40% of the high tide volume; this induces short-term variability in hydrographic parameters and mixing of water masses (Chauvaud et al., 2005).

The Roscanvel bank (30 m water depth), is located in the western part of the bay of Brest (Figure 2). It is characterized by mixed sandy and silty sediments, and is known to host a large population of great scallop *Pecten maximus*. The Roscanvel bank has marine characteristics as bottom-water salinity only decreases down to 32.5 during winter flood tides, whereas it is quite stable (34–35) from spring to fall, ie. when scallops accrete calcite (Chauvaud et al., 1998).

2.2. Environmental parameters

Environmental parameters were monitored weekly from 1999 to 2007 at the SOMLIT-Brest station located at the outlet of the bay (Figure 2). Water sampling and measurements were performed at 1 m depth at slack high tide in mean tidal conditions, in order to favour the oceanic signal more than the influence of riverine inputs. Temperature and salinity were measured with a Sea-Bird SBE 19 CTD profiler (Sea-Bird Electronics, Inc.). For the determination of chlorophyll *a* concentration, 1 L of seawater collected using a Niskin bottle was filtered onto Whatmann GF/F filters. The analysis was done according to Yentsch and Menzel (1963) using a calibrated Turner 111 fluorometer. Water samples for phytoplankton species determination were preserved in Lugol's solution. Species were identified and counted by examination on an inverted microscope. Unfortunately, no information is available on phytoplankton community composition over the period 2005–2007, thus preventing comparison of Li/Ca_{shell} with in situ biological data.

Temperature and salinity measured at SOMLIT-Brest are known to reflect very precisely environmental conditions at Roscanvel bank (Lorrain, 2002). On another hand, there are some differences in the composition of phytoplankton communities and timing of blooms between both stations; if blooms of dominant diatom and dinoflagellate species occur approximately at the same time at SOMLIT-Brest and Roscanvel, their intensities could differ significantly. Moreover, many minor species observed at SOMLIT-Brest are typically oceanic and are not found at Roscanvel. Consequently, we only considered cell counts for diatom species (i) that are known to be dominant species at Roscanvel (Chauvaud et al., 1998; Lorrain et al., 2000), and (ii) that represented more than 10% of total diatom counts at SOMLIT-Brest over the period 1999–2004. The same strategy was applied to dinoflagellates. Therefore, we used counts of *Chaetoceros* spp. (30% of total diatoms), *Dactyliosolen fragilissimus* (formerly *Rhizosolenia fragilissima*; 10%), *Guinardia delicatula* (formerly *Rhizosolenia delicatula*; 17%), and *Pseudo-nitzschia* spp. (10%). All together, these species represented two thirds of diatoms counted at SOMLIT-Brest between 1999 and 2004. As for dinoflagellates, *Gymnodinium* spp. represented 60% of total dinoflagellates between 1999 and 2004.

2.3. Shell sampling and growth measurements

Live scallops were collected from Roscanvel bank using SCUBA diving. Individuals of age class I (ie. specimens that have lived only one 1st of January) were sampled on 21 November 2001 ($n = 3$ shells born in 2000), on 3 September 2004 ($n = 3$ shells born in 2003) and on 5 November 2007 (n

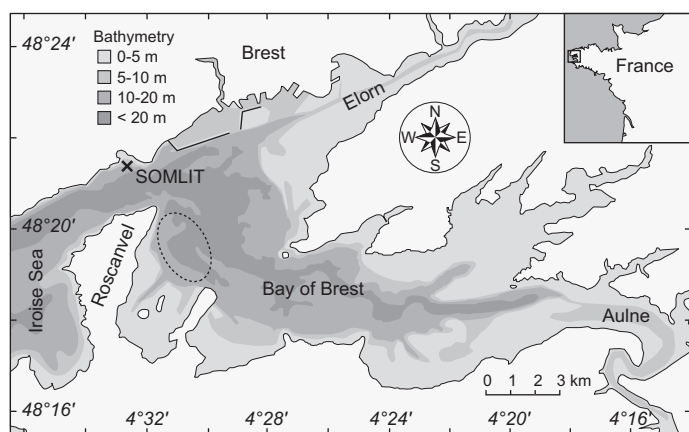


Figure 2: Shell sampling location in the Bay of Brest, northwest France (Roscanvel bank: dashed ellipse) and SOMLIT-Brest water monitoring station (black cross).

= 4 shells born in 2006). For all these specimens, we analysed the part of the shell between the first winter growth mark and the ventral margin. This portion corresponded to shell material formed in 2001, 2004, and 2007, respectively (ie. during the second year of growth). In addition, age class III specimens were collected on 23 March 2001 ($n = 3$ shells born in 1998). For these three individuals, we analysed shell material located between the first and the second winter growth mark, ie. calcite formed in 1999. Analysis of shell material formed between the first and the second winter growth mark was chosen because this second year of growth corresponds to the longest annual growth season, and thus provides the longest annual calcitic record (Figure 1). In the bay of Brest, scallops in their second year grow from late March-early April to November (Chauvaud et al., 1998).

Before shell growth and elemental analyses, the upper surface of the left valves was cleaned by soaking for 3 minutes in 90% acetic acid. They were then rinsed by deionized water and air-dried. Daily shell growth rates (DSGR) were determined by measuring distances between successive daily growth striae along the axis of maximum growth using the image analysis method described by Chauvaud et al. (1998). On the basis of the daily rhythm of striae formation, absolute dates of precipitation were assigned to each stria by backdating from the last deposited stria at the day of collection (see Chauvaud et al. (2005) for elaboration).

2.4. Elemental analyses

Using a micromilling device (New Wave Research) equipped with a 300- μm tungsten carbide drill bit, calcite powder was milled directly from the upper surface of the left valve of the shells, along the axis of maximum growth. One stria was milled every three striae, a sampling strategy corresponding to ca. two calcite samples per week of shell growth (sub-weekly resolution). Sample preparation and analyses were performed at the Pôle Spectrométrie Océan (Plouzané, France). All samples were prepared in a class 10000 clean laboratory. Ultra-pure deionized water (resistivity = 18.2 $\text{M}\Omega\cdot\text{cm}$) was used for material cleaning and acid dilutions. Nitric acid solutions (commercial grade, Merck) were purified by distillation in sub-boiling silica glass stills (Quartex). All material (polypropylene centrifuge tubes, disposable pipette tips, etc.) was pre-cleaned using 5% HNO_3 and rinsed with ultra-pure deionized water.

A known weight of each shell sample (average weight = 127 μg) was transferred into a pre-cleaned polypropylene centrifuge tube, dissolved in 2% HNO_3 , and spiked with a known amount (about 7 μL) of a mono-elemental thulium solution (Tm concentration = 77.9 ng g^{-1}). Thulium was used as an internal standard to correct short- and long-term instrumental drift (see Barrat et al. (1996) and Bayon et al. (2009) for detailed information on this method). External calibration was performed using an in-house multi-element solution prepared from certified stock solutions. This calibration solution was prepared so that it closely matched the calcium carbonate matrix and elemental composition of mollusc shells.

Elemental concentrations were measured on a Thermo Electron Element2 high-resolution inductively coupled

plasma mass spectrometer equipped with an ASX 260 auto-sampler (CETAC Technologies). Solutions were introduced via a Teflon nebulizer and a Peltier cooled cyclonic spray chamber. The Element2 was equipped with a glass injector and a set of nickel sampler and skimmer cones. Along the course of this study, plasma power ranged between 1270 and 1310 W and argon flow rates were 16.06 L min^{-1} (cooling gas), 0.54–0.65 L min^{-1} (auxiliary gas), and 0.95–1.35 L min^{-1} (nebulizer gas). The Element2 was operated in medium resolution ($m/\Delta m = 4000$) and measured isotopes were ^7Li and ^{43}Ca (among other elements not presented in this article). Concentrations were calculated using the Tm addition method. Details on the calculations can be found in Bayon et al. (2009). Briefly, for each sample, elemental concentrations were calculated using the sample mass, the amount of Tm added, and by calibrating the raw data acquired during the measurement session against the unspiked (no added Tm) in-house multi-element solution, run after every five samples.

Precision (degree of reproducibility) and accuracy (degree of veracity) of our procedure were controlled through analyses of (i) a certified reference material purchased from the National Research Council of Canada (FEBS-1: red snapper *Lutjanus campechanus* saggital otolith; certified values in Sturgeon et al., 2005), and (ii) a *Pecten maximus* in-house reference material (left valve of a specimen from the bay of Brest, crushed and carefully homogenized). Repeated measurements of these reference materials yielded a precision (relative standard deviation) of 2.05% (average $\text{Li}/\text{Ca}_{\text{FEBS-1}} = 4.32 \mu\text{mol mol}^{-1}$; $1\sigma = 0.09 \mu\text{mol mol}^{-1}$; $n = 12$) and 7.76% (average $\text{Li}/\text{Ca}_{\text{Pecten}} = 22.50 \mu\text{mol mol}^{-1}$; $1\sigma = 1.75 \mu\text{mol mol}^{-1}$; $n = 109$). Accuracy was extremely good with a Li concentration value in FEBS-1 of $0.304 \pm 0.007 \text{ mg kg}^{-1}$ (mean \pm standard deviation) compared with the recommended value of $0.305 \pm 0.044 \text{ mg kg}^{-1}$. Our method slightly overestimated Ca concentration (+ 6%) with a measured value in FEBS-1 of $407\,000 \pm 9\,000 \text{ mg kg}^{-1}$ (mean \pm standard deviation) compared with the recommended value of $383\,000 \pm 14\,000 \text{ mg kg}^{-1}$.

In order to check the reproducibility of $\text{Li}/\text{Ca}_{\text{shell}}$ ratios along a given shell, one specimen collected on 5 November 2007 (shell #6) was also analysed for elemental content along three different axes of shell growth: the central axis (ie. axis of maximum shell growth), an axis on the left side of the shell, and another one on the right side.

2.5. Statistical analyses

Differences in $\text{Li}/\text{Ca}_{\text{shell}}$ ratios between left, central and right axes of shell #6 were tested with an analysis of variance after verification of homoscedasticity with Bartlett's test ($\alpha = 0.01$). Tukey HSD (Honestly Significant Difference) post-hoc test was used to identify which axis differed from the other ones. Simple and multiple linear regressions were performed between $\text{Li}/\text{Ca}_{\text{shell}}$ and possible explanatory variables (seawater temperature, salinity, chlorophyll a concentration, and daily shell growth rate) for each single year (1999, 2001, 2004, and 2007) and for the whole dataset (1999–2007). Before performing multivariate regressions, we used the Schwartz's Bayesian Information Criterion (BIC) to select the best subset of explanatory variables. Finally, a model II regression was used to fit $\text{Li}/\text{Ca}_{\text{shell}}$

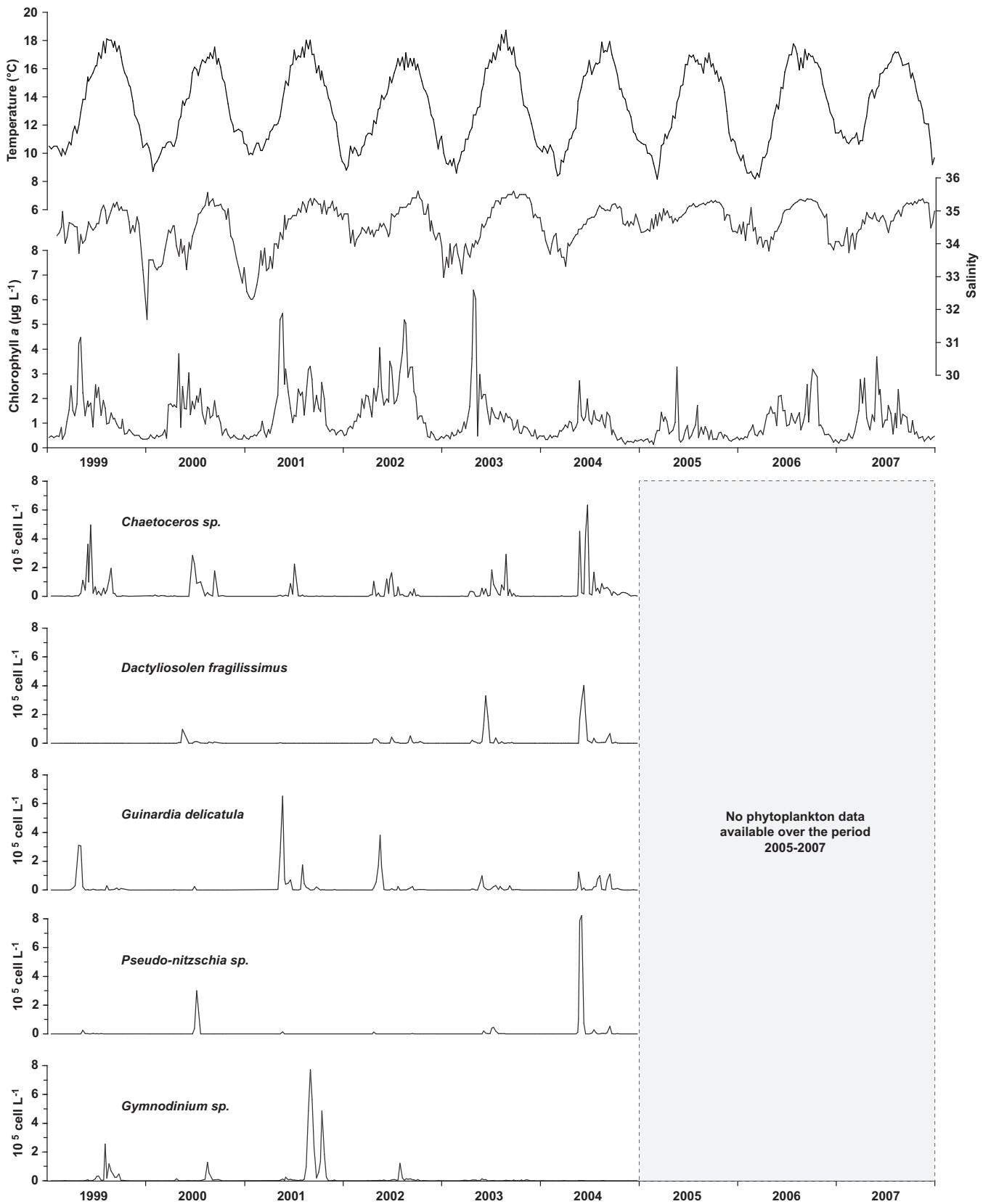


Figure 3: Variations of physical (temperature, salinity) and biological (chlorophyll *a* concentration, phytoplankton counts) parameters recorded at the SOMLIT-Brest monitoring station from 1999 to 2007. Note that phytoplankton counts are not available between 2005 and 2007.

and DSGR (Standard Major Axis). All statistical analyses were performed with R, using “leaps” (for BIC model selection criteria) and “lmodel2” (for model II regressions) packages.

3. Results

3.1. Variability of environmental parameters between 1999 and 2007

Temperature variations at SOMLIT-Brest displayed a clear seasonal signal over the study period, with an annual temperature range from 8.0°C in 2007 to 10.1°C in 2003 (Figure 3). Water temperature was lowest between mid-January and mid-March (mean 1999–2007 = 8.8°C; $\sigma = 0.6^\circ\text{C}$) and reached a maximum in August–September (mean 1999–2007 = 17.7°C; $\sigma = 0.5^\circ\text{C}$). Over the same period, there were minor fluctuations in surface salinity, usually ranging between 33 and 35.6. Salinity drops during winter and early spring corresponded with increases in Aulne and Elorn flows. Exceptional surface salinity decreases were recorded in January 2000 (31.7) and January 2001 (32.3). These quite low salinities were likely restricted to surface waters and did not influence scallops in Roscanvel bottom water. Intra-annual salinity ranges varied from 0.97 in 2005 to 3.84 in 2000. These temperature and salinity values were very similar to bottom-water values measured at Roscanvel by Chauvaud et al. (1998).

Chlorophyll *a* concentration ranged from 0.12 $\mu\text{g L}^{-1}$ in February 2005 to 6.39 $\mu\text{g L}^{-1}$ in April 2003 (Figure 3). Largest annual phytoplankton blooms were recorded in May, except in 2002 (maximum concentration in August) and in 2006 (maximum concentration in October), with varying intensities depending on the year (from 2.70 $\mu\text{g L}^{-1}$ in 2004 to 6.39 $\mu\text{g L}^{-1}$ in 2003). The mean chlorophyll *a* value was 1.2 $\mu\text{g L}^{-1}$ over the study period. This value masked some inter-annual variations, especially in 2002 (highest mean annual concentration of 1.8 $\mu\text{g L}^{-1}$) and in 2005 (lowest mean annual concentration of 0.6 $\mu\text{g L}^{-1}$).

Most of this chlorophyll *a* was contained within cells of the diatom genus *Chaetoceros* (Figure 3). This genus was present in the water column every year, with concentrations reaching 634 670 cell L^{-1} on 22 June 2004. Highest abundances were recorded in 1999 and 2004, whereas 2001 was characterized with only two small blooms (< 250 000 cell L^{-1}). Another abundant diatom, *Dactyliosolen fragilissimus*, displayed important blooms at SOMLIT-Brest in 2003 and 2004 (up to 402 730 cell L^{-1} on 8 June 2004). This species presented very low levels from 1999 to 2002 (< 100 000 cell L^{-1}). The diatom *Guinardia delicatula* formed large blooms in 1999, 2001, and 2002, up to 653 877 cell L^{-1} (in May 2001), but displayed low levels in 2000, 2003, and 2004 (< 150 000 cell L^{-1}). The fourth genus of diatoms abundant at SOMLIT-Brest was *Pseudo-nitzschia*. These species were usually not present in the water column, except in July 2000 and in May 2004 when they formed a very large bloom up to 822 931 cell L^{-1} . One dinoflagellate genus, *Gymnodinium*, presented quite high levels between 1999 and 2002, with two large blooms in late August (773 478 cell L^{-1}) and mid-October 2001 (486 388 cell L^{-1}). It should be mentioned that another dinoflagellate species, *Karenia mikimotoi* (formerly *Gymnodinium nagasakiense*), represented 23% of total dinoflagellates at SOMLIT-Brest, because of a unique

large bloom in August 2002 (678 321 cell L^{-1}). Finally, maximum chlorophyll *a* concentrations recorded in 2000 and 2003 were related to diatom blooms of *Thalassiosira* spp. (196 997 cell L^{-1} on 2 May 2000; 5% of total diatoms at SOMLIT-Brest) and *Cerataulina pelagica* (444 357 cell L^{-1} on 28 April 2003; 4% of total diatoms).

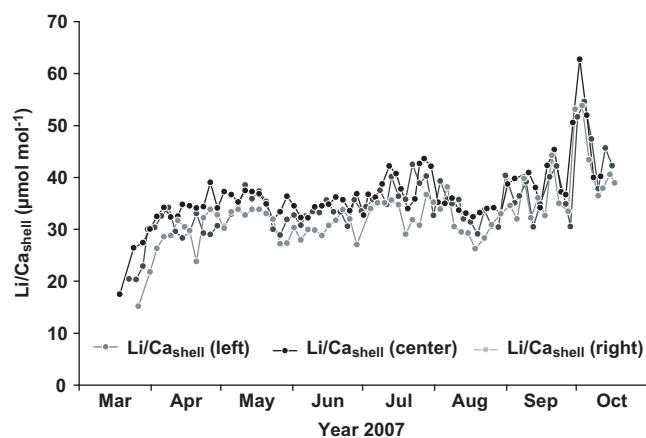


Figure 4: Temporal variations of Li/Ca ratios along left, central, and right axes of growth of shell #6 collected on 5 November 2007.

3.2. $\text{Li}/\text{Ca}_{\text{shell}}$ time series and daily shell growth rate

$\text{Li}/\text{Ca}_{\text{shell}}$ ratio time series along the three axes of growth were remarkably similar, with highest ratios recorded at the same time between 2 October 2007 and 4 October 2007 (Figure 4). Average $\text{Li}/\text{Ca}_{\text{shell}}$ ratio on left, central, and right axis were 34.54 $\mu\text{mol mol}^{-1}$ ($\sigma = 5.81 \mu\text{mol mol}^{-1}$), 36.40 $\mu\text{mol mol}^{-1}$ ($\sigma = 5.83 \mu\text{mol mol}^{-1}$), and 32.79 $\mu\text{mol mol}^{-1}$ ($\sigma = 5.86 \mu\text{mol mol}^{-1}$), respectively. These small differences were statistically significant (Bartlett’s test: $\chi^2_{\text{Bartlett}} = 0.006$, $df = 2$, $p = 0.997$; ANOVA: $F = 6.56$, $df = 2$ and 206, $p = 0.002$); post-hoc test indicated that average $\text{Li}/\text{Ca}_{\text{shell}}$ ratio on the right axis was significantly lower than on the central axis.

Temporal variations of $\text{Li}/\text{Ca}_{\text{shell}}$ displayed a high degree of synchronism (inter-individual reproducibility), whatever the year (Figure 5). On another hand, $\text{Li}/\text{Ca}_{\text{shell}}$ showed very different trajectories in 1999, 2004, and in 2001 and 2007. In 1999, all three specimens presented a kind of exponential increase in $\text{Li}/\text{Ca}_{\text{shell}}$ from ca. 20 $\mu\text{mol mol}^{-1}$ in March to 190–250 $\mu\text{mol mol}^{-1}$ (depending on the specimen) between 2 July 1999 and 4 July 1999. $\text{Li}/\text{Ca}_{\text{shell}}$ then decreased down to values around 30–40 $\mu\text{mol mol}^{-1}$ at the end of July and stayed at this level until December. In 2004, $\text{Li}/\text{Ca}_{\text{shell}}$ presented values around 30–40 $\mu\text{mol mol}^{-1}$, except from the end of May to the end of July. During that period, all three specimens displayed a high degree of synchronism, presenting the same profiles punctuated with three main $\text{Li}/\text{Ca}_{\text{shell}}$ peaks at the beginning of June (90–95 $\mu\text{mol mol}^{-1}$), at the end of June (90–100 $\mu\text{mol mol}^{-1}$), and in mid-July (65–75 $\mu\text{mol mol}^{-1}$). In 2001 and 2007, $\text{Li}/\text{Ca}_{\text{shell}}$ values fluctuated between 15 and 50 $\mu\text{mol mol}^{-1}$ all year long, except a little sharp peak around 65–70 $\mu\text{mol mol}^{-1}$ at the beginning of October 2007 on the four studied specimens. Given the very low inter-individual variability in $\text{Li}/\text{Ca}_{\text{shell}}$ and the sharpness of $\text{Li}/\text{Ca}_{\text{shell}}$ peaks, it is likely that the latter resulted from transient phenomena in the water column (environmental forcing).

Table 1: Annual minimum, maximum, and mean values of $\text{Li}/\text{Ca}_{\text{shell}}$ and daily shell growth rate of each *Pecten maximus* specimen analyzed over the period 1999–2007.

Year	Shell	$\text{Li}/\text{Ca}_{\text{shell}}$ ($\mu\text{mol mol}^{-1}$)			DSGR ($\mu\text{m d}^{-1}$)		
		Min.	Mean	Max.	Min.	Mean	Max.
1999	#103	19.05	50.03	243.83	40.66	202.32	329.29
	#105	17.02	50.79	191.22	86.17	229.91	377.09
	#106	16.48	48.53	202.28	45.08	176.69	307.64
2001	#5	14.87	28.86	43.09	42.17	176.34	298.25
	#10	19.90	32.01	48.53	57.52	176.29	262.42
	#12	20.24	34.87	47.22	53.44	177.37	274.62
2004	#1	15.19	47.89	93.41	37.11	227.82	340.16
	#2	18.39	47.94	90.43	36.88	244.44	385.60
	#3	21.14	50.83	100.96	61.47	228.24	409.84
2007	#5	15.64	35.97	63.53	68.17	213.06	377.27
	#7	18.32	34.51	70.01	30.98	167.84	290.74
	#666	18.49	35.18	70.09	47.11	177.98	285.14
	#6	17.49	36.40	62.74	42.43	166.19	306.47

Daily shell growth rate varied by an order of magnitude over a given growing season from minima around $35\text{--}50 \mu\text{m d}^{-1}$ to maxima reaching $250\text{--}350 \mu\text{m d}^{-1}$, with very little inter-individual variability (Figure 5). Whatever the year, shell growth restarted at the end of March after a winter growth cessation, and reached maximum values in June–July. Significant differences were observed in shell growth trajectories between years. In 1999, scallops exhibited a sharp increase in DSGR from March to July, and then a slow decrease until the following winter growth cessation. Shell growth, however, was abruptly reduced in May 1999 ($-75 \mu\text{m d}^{-1}$). In 2001, shell growth slightly increased from March to mid-May, suddenly dropped down to ca. $90 \mu\text{m}$

d^{-1} at the end of May, abruptly increased to reach maxima in July, and then slowly decreased until November. The latter decrease was punctuated with a growth retardation in September 2001. Shell growth trajectory was quite similar in 2001 and 2004, at least until the end of August. No data were available after August 2004 as shells were collected before the end of the growing season. Finally, in 2007, DSGR sharply increased from $35 \mu\text{m d}^{-1}$ in March to ca. $220 \mu\text{m d}^{-1}$ in April, and stayed around $150\text{--}250 \mu\text{m d}^{-1}$ until October (except at the end of May 2007 when a sudden decrease down to $100 \mu\text{m d}^{-1}$ was observed). Note that all geochemical and shell growth data obtained on each of the 13 specimens analysed in this study can be retrieved in Table 1.

Table 2: Summary of simple and multiple linear regressions performed with $\text{Li}/\text{Ca}_{\text{shell}}$ as response variable, and seawater temperature, salinity, chlorophyll *a* concentration and daily shell growth rate as explanatory variables.

	Estimate	Std. error	<i>T</i>	<i>p</i> -value	<i>F</i> -statistic	Adjusted r^2	<i>p</i> -value
<i>Year 1999</i>							
Temperature	3.57	2.83	1.261	0.216	1.59 on 1 and 32 <i>df</i>	0.018	0.216
Intercept	-3.57	43.58	-0.082	0.935			
Salinity	-6.44	17.21	-0.374	0.711	0.14 on 1 and 32 <i>df</i>	-0.027	0.711
Intercept	274.36	597.17	0.459	0.649			
Chlorophyll <i>a</i>	9.52	6.45	1.475	0.150	2.18 on 1 and 32 <i>df</i>	0.034	0.150
Intercept	37.23	11.01	3.382	0.002			
DSGR	0.40	0.10	4.113	< 0.001	16.92 on 1 and 32 <i>df</i>	0.325	< 0.001
Intercept	-24.92	19.09	-1.305	0.201			
DSGR	0.55	0.13	4.286	< 0.001	10.41 on 2 and 31 <i>df</i>	0.363	< 0.001
Temperature	-5.22	3.06	-1.703	0.099			
Intercept	27.25	35.81	0.761	0.452			
<i>Year 2001</i>							
Temperature	2.05	0.33	6.255	< 0.001	39.12 on 1 and 30 <i>df</i>	0.552	< 0.001
Intercept	0.53	4.99	0.107	0.916			
Salinity	6.64	1.24	5.380	< 0.001	28.94 on 1 and 30 <i>df</i>	0.474	< 0.001
Intercept	-199.19	42.89	-4.644	< 0.001			
Chlorophyll <i>a</i>	-0.25	0.91	-0.279	0.782	0.078 on 1 and 30 <i>df</i>	-0.031	0.782
Intercept	32.00	2.09	15.289	< 0.001			

Continued on next page

Table 2 – Continued from previous page

	Estimate	Std. error	T	p-value	F-statistic	Adjusted r^2	p-value																																																																																																																																																																																																																																																									
DSGR	0.10	0.01	9.021	< 0.001	81.38 on 1 and 30 <i>df</i>	0.722	< 0.001																																																																																																																																																																																																																																																									
Intercept	14.64	1.94	7.533	< 0.001				DSGR	0.08	0.01	5.533	< 0.001	44.06 on 2 and 29 <i>df</i>	0.735	< 0.001	Salinity	1.95	1.22	1.595	0.122	Intercept	-50.11	40.64	-1.233	0.228	<i>Year 2004</i>								Temperature	3.94	1.39	2.826	0.010	7.99 on 1 and 20 <i>df</i>	0.250	0.010	Intercept	-8.12	20.13	-0.403	0.691	Salinity	16.70	8.06	2.072	0.051	4.30 on 1 and 20 <i>df</i>	0.136	0.051	Intercept	-528.31	278.03	-1.900	0.072	Chlorophyll <i>a</i>	12.94	9.04	1.432	0.167	2.05 on 1 and 21 <i>df</i>	0.046	0.167	Intercept	32.46	11.31	2.871	0.009	DSGR	0.18	0.05	3.638	0.002	13.23 on 1 and 21 <i>df</i>	0.357	0.002	Intercept	6.94	11.65	0.596	0.558	DSGR	0.45	0.12	3.862	0.001	11.10 on 2 and 19 <i>df</i>	0.490	< 0.001	Salinity	-40.19	15.98	-2.516	0.021	Intercept	1332.06	526.90	2.528	0.020	<i>Year 2007</i>								Temperature	1.50	0.68	2.199	0.037	4.83 on 1 and 25 <i>df</i>	0.129	0.037	Intercept	13.44	10.28	1.307	0.203	Salinity	19.07	4.69	4.064	< 0.001	16.52 on 1 and 25 <i>df</i>	0.374	< 0.001	Intercept	-628.31	163.42	-3.845	< 0.001	Chlorophyll <i>a</i>	-3.96	1.76	-2.254	0.033	5.08 on 1 and 25 <i>df</i>	0.136	0.033	Intercept	41.62	2.89	14.427	< 0.001	DSGR	0.07	0.03	2.146	0.042	4.60 on 1 and 25 <i>df</i>	0.122	0.042	Intercept	23.92	5.72	4.181	< 0.001	DSGR	0.05	0.03	2.087	0.048	11.55 on 2 and 24 <i>df</i>	0.448	< 0.001	Salinity	17.69	4.46	3.971	< 0.001	Intercept	-589.57	154.56	-3.815	< 0.001	<i>Years 1999–2007</i>								Temperature	2.73	0.94	2.911	0.004	8.48 on 1 and 113 <i>df</i>	0.062	0.004	Intercept	0.62	14.15	0.044	0.965	Salinity	4.45	4.71	0.944	0.347	0.89 on 1 and 113 <i>df</i>	-0.001	0.347	Intercept	-112.90	163.50	-0.691	0.491	Chlorophyll <i>a</i>	0.40	2.29	0.173	0.863	0.03 on 1 and 114 <i>df</i>	-0.009	0.863	Intercept	40.77	4.13	9.882	< 0.001	DSGR	0.21	0.03	6.539	< 0.001	42.76 on 1 and 114 <i>df</i>	0.266	< 0.001	Intercept	1.42	6.38	0.223	0.824	DSGR	0.24	0.04	6.678	< 0.001	22.92 on 2 and 112 <i>df</i>	0.278	< 0.001	Salinity	-7.29	4.37	-1.668	0.098	Intercept	249.99
DSGR	0.08	0.01	5.533	< 0.001	44.06 on 2 and 29 <i>df</i>	0.735	< 0.001																																																																																																																																																																																																																																																									
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DSGR	0.45	0.12	3.862	0.001	11.10 on 2 and 19 <i>df</i>	0.490	< 0.001																																																																																																																																																																																																																																																									
Salinity	-40.19	15.98	-2.516	0.021																																																																																																																																																																																																																																																												
Intercept	1332.06	526.90	2.528	0.020				<i>Year 2007</i>								Temperature	1.50	0.68	2.199	0.037	4.83 on 1 and 25 <i>df</i>	0.129	0.037	Intercept	13.44	10.28	1.307	0.203	Salinity	19.07	4.69	4.064	< 0.001	16.52 on 1 and 25 <i>df</i>	0.374	< 0.001	Intercept	-628.31	163.42	-3.845	< 0.001	Chlorophyll <i>a</i>	-3.96	1.76	-2.254	0.033	5.08 on 1 and 25 <i>df</i>	0.136	0.033	Intercept	41.62	2.89	14.427	< 0.001	DSGR	0.07	0.03	2.146	0.042	4.60 on 1 and 25 <i>df</i>	0.122	0.042	Intercept	23.92	5.72	4.181	< 0.001	DSGR	0.05	0.03	2.087	0.048	11.55 on 2 and 24 <i>df</i>	0.448	< 0.001	Salinity	17.69	4.46	3.971	< 0.001	Intercept	-589.57	154.56	-3.815	< 0.001	<i>Years 1999–2007</i>								Temperature	2.73	0.94	2.911	0.004	8.48 on 1 and 113 <i>df</i>	0.062	0.004	Intercept	0.62	14.15	0.044	0.965	Salinity	4.45	4.71	0.944	0.347	0.89 on 1 and 113 <i>df</i>	-0.001	0.347	Intercept	-112.90	163.50	-0.691	0.491	Chlorophyll <i>a</i>	0.40	2.29	0.173	0.863	0.03 on 1 and 114 <i>df</i>	-0.009	0.863	Intercept	40.77	4.13	9.882	< 0.001	DSGR	0.21	0.03	6.539	< 0.001	42.76 on 1 and 114 <i>df</i>	0.266	< 0.001	Intercept	1.42	6.38	0.223	0.824	DSGR	0.24	0.04	6.678	< 0.001	22.92 on 2 and 112 <i>df</i>	0.278	< 0.001	Salinity	-7.29	4.37	-1.668	0.098	Intercept	249.99	149.14	1.676	0.097																																																																																													
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3.3. Multivariate statistical analyses of $\text{Li}/\text{Ca}_{\text{shell}}$ variations

Simple and multiple linear regressions provided interesting information on variables that may explain $\text{Li}/\text{Ca}_{\text{shell}}$ variations (Table 2). As inter-individual variability in $\text{Li}/\text{Ca}_{\text{shell}}$ time series was very low for a given growing season (Figure 5), we calculated average $\text{Li}/\text{Ca}_{\text{shell}}$ profiles for each year. Simple regressions performed on each year indicated that the variable with the strongest statistically significant ($p < 0.05$) relationship with average $\text{Li}/\text{Ca}_{\text{shell}}$ was DSGR in 1999 ($r^2 = 0.325$), in 2001 ($r^2 = 0.722$), and in 2004 ($r^2 = 0.357$), and salinity in 2007 ($r^2 = 0.374$). Except in 2007 ($r^2 = 0.136$; $p = 0.033$), chlorophyll *a* concentration did not present a significant relationship with $\text{Li}/\text{Ca}_{\text{shell}}$. Seawater temperature relationship with $\text{Li}/\text{Ca}_{\text{shell}}$ was strong in 2001 ($r^2 = 0.552$; $p < 0.001$), weak albeit significant in

2004 ($r^2 = 0.250$; $p = 0.01$) and 2007 ($r^2 = 0.129$; $p = 0.037$), and non-significant in 1999 ($r^2 = 0.018$; $p = 0.216$). Multiple linear regressions performed for each year with the two best explanatory variables (selected using the Schwartz's Bayesian Information Criterion: DSGR and temperature in 1999; DSGR and salinity in 2001, 2004, and 2007) were all statistically significant ($p < 0.001$). However, the only variable that was always statistically significant in these models was DSGR (together with salinity in 2004 and 2007). These models explained between 36.3 and 49.0% of average $\text{Li}/\text{Ca}_{\text{shell}}$ variability in 1999, 2004 and 2007, suggesting that most of this variability resulted from another parameter (see discussion below on phytoplankton species). On another hand, our multivariate model explained 73.5% of $\text{Li}/\text{Ca}_{\text{shell}}$ variability in 2001, ie. when no $\text{Li}/\text{Ca}_{\text{shell}}$ peaks

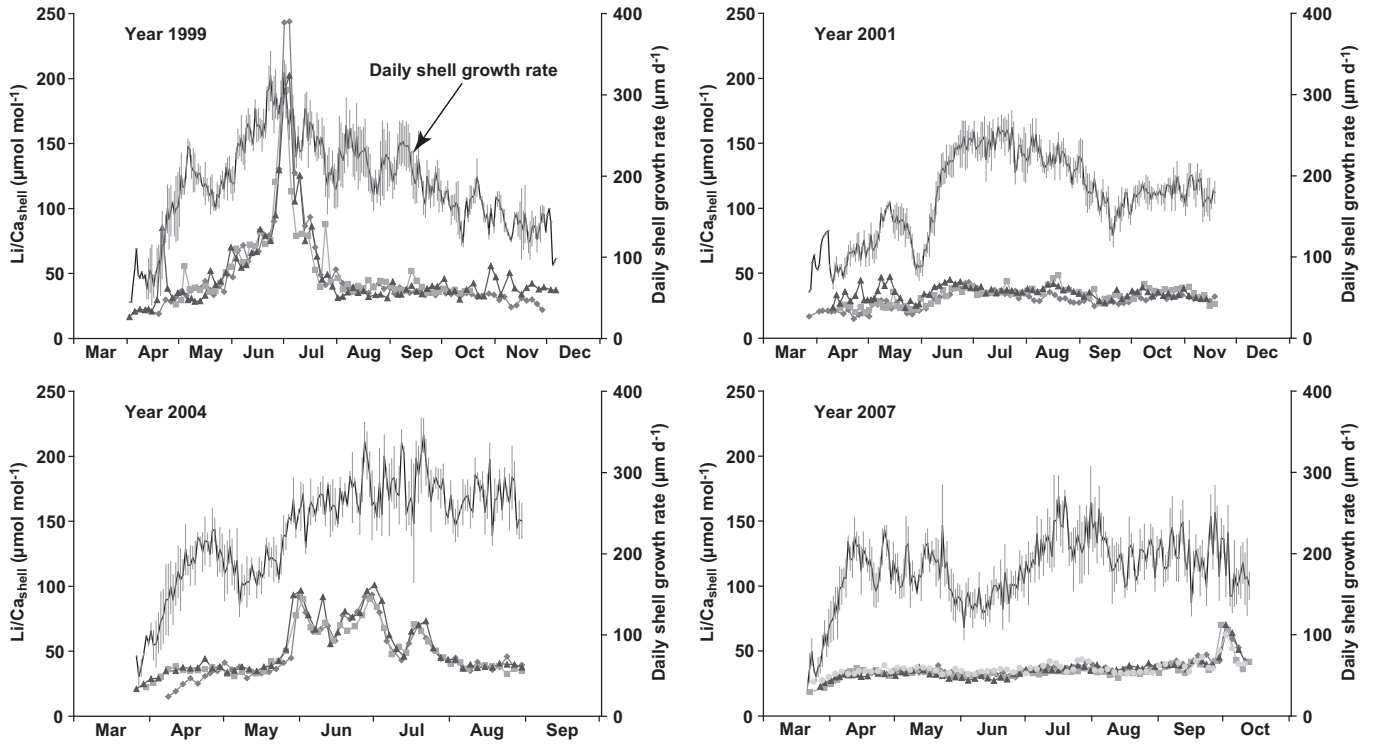


Figure 5: Time series of $\text{Li}/\text{Ca}_{\text{shell}}$ (greyscale symbols) and average daily shell growth rate (black line; ± 1 standard error) in 1999 ($n = 3$ shells), 2001 ($n = 3$), 2004 ($n = 3$), and 2007 ($n = 4$).

were recorded in the shells. Most of this variability was explained by DSGR as salinity was not a significant predictor in this model ($p = 0.122$). When all years were considered as a single dataset covering the period 1999–2007, the only variables that significantly explained some part of the $\text{Li}/\text{Ca}_{\text{shell}}$ variability were DSGR ($r^2 = 0.266$; $p < 0.001$) and, to a lesser extent, seawater temperature ($r^2 = 0.062$; $p = 0.004$).

Graphical outputs confirmed results of these statistical analyses. Average $\text{Li}/\text{Ca}_{\text{shell}}$ profiles are displayed on Figure 6, together with average DSGR and seasonal variations of seawater temperature and salinity, i.e. the three variables that could most likely explain variations of $\text{Li}/\text{Ca}_{\text{shell}}$ (see Table 2). We increased the vertical resolution of the y -axis in comparison with Figure 5 in order to get a better insight of baseline variations of $\text{Li}/\text{Ca}_{\text{shell}}$ time series. It appeared clearly that $\text{Li}/\text{Ca}_{\text{shell}}$ peaks were not induced by variations of DSGR, temperature or salinity. None of these parameters presented sharp increases or decreases synchronous with $\text{Li}/\text{Ca}_{\text{shell}}$ peaks (Figure 6). Therefore, the statistically significant relationships described between average $\text{Li}/\text{Ca}_{\text{shell}}$ variations on one hand, and DSGR, temperature or salinity on the other hand, very likely pertained to variations of baseline $\text{Li}/\text{Ca}_{\text{shell}}$. Outside peak periods, variations of baseline $\text{Li}/\text{Ca}_{\text{shell}}$ tended to follow the same pattern as seasonal variations of DSGR. This was particularly striking for shells collected in November 2001 and, to a lesser extent, in November 2007 (part of the time series between March and September 2007, i.e. before the early October $\text{Li}/\text{Ca}_{\text{shell}}$ peak). This growth– $\text{Li}/\text{Ca}_{\text{shell}}$ relationship was also visible on 1999 and 2004 shells, between March and May 1999, between August and December 1999, and from March to May 2004 (i.e. outside the peak periods). Cross-plots of $\text{Li}/\text{Ca}_{\text{shell}}$

versus DSGR, established for each year, confirmed these observations (Figure 7). In 2001, i.e. the year when shells did not present $\text{Li}/\text{Ca}_{\text{shell}}$ peaks, $\text{Li}/\text{Ca}_{\text{shell}}$ and DSGR presented a strong and highly significant relationship (Standard Major Axis regression, $n = 237$, $r = 0.86$, $p < 0.001$; Figure 7). In 1999, 2004, and to a lesser extent 2007, growth– $\text{Li}/\text{Ca}_{\text{shell}}$ relationships, although statistically significant ($p < 0.001$), were weaker ($r \leq 0.64$) and deviated from the relationship established in 2001. Slopes of these relationships ($0.160 \leq \text{slope} \leq 0.550$) were higher than in 2001 (slope = 0.107), reflecting the presence of $\text{Li}/\text{Ca}_{\text{shell}}$ peaks in 1999, 2004, and 2007 (Figure 7).

On another hand, no obvious relationship was observed between variations of baseline $\text{Li}/\text{Ca}_{\text{shell}}$ and variations of temperature and salinity (Figure 7). This was especially noticeable in May 2001 when $\text{Li}/\text{Ca}_{\text{shell}}$ decreased abruptly whereas temperature and salinity did not present any significant decrease nor abrupt increase. This confirmed equivocal results of simple and multiple linear regressions between $\text{Li}/\text{Ca}_{\text{shell}}$ and these two environmental variables (Table 2).

3.4. Variations of excess $\text{Li}/\text{Ca}_{\text{shell}}$

In order to investigate determinism of $\text{Li}/\text{Ca}_{\text{shell}}$ peaks, we made the assumption that $\text{Li}/\text{Ca}_{\text{shell}}$ variations were mostly controlled by DSGR outside peak periods (which was confirmed by statistical analyses and graphical outputs; Table 2 and Figures 6–7). We selected data obtained on shells collected in November 2001, that did not present $\text{Li}/\text{Ca}_{\text{shell}}$ peaks, to derive the growth–baseline $\text{Li}/\text{Ca}_{\text{shell}}$ relationship:

$$\text{Li}/\text{Ca}_{\text{shell}} = 0.107 \times \text{DSGR} + 12.824 \quad (1)$$

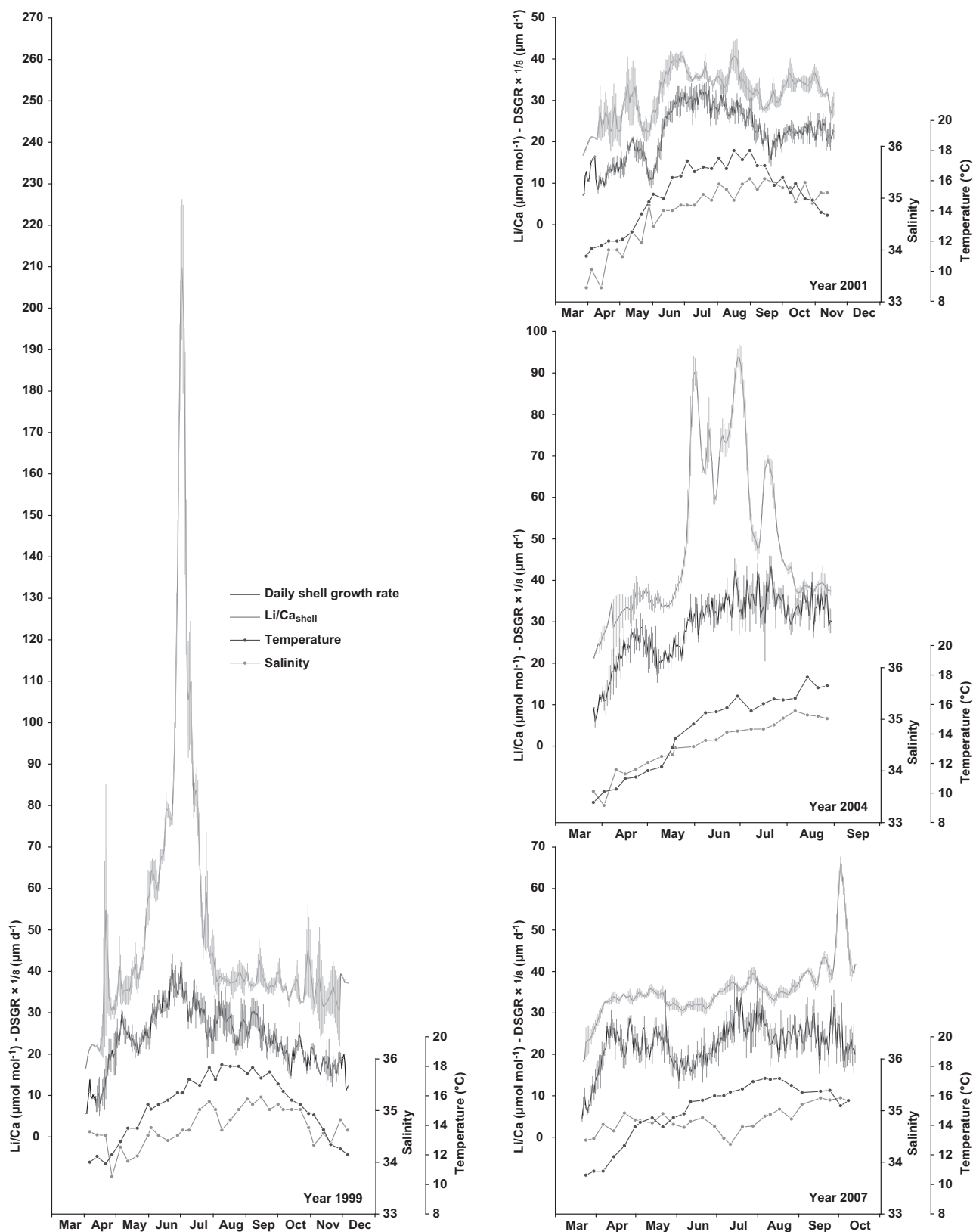


Figure 6: Time series of average $\text{Li/Ca}_{\text{shell}}$ (grey line; ± 1 standard error), average daily shell growth rate (DSGR; black line; ± 1 standard error), seawater temperature (black dotted line) and salinity (grey dotted line) in 1999 ($n = 3$ shells), 2001 ($n = 3$), 2004 ($n = 3$), and 2007 ($n = 4$), revealing co-variations of shell growth and baseline $\text{Li/Ca}_{\text{shell}}$.

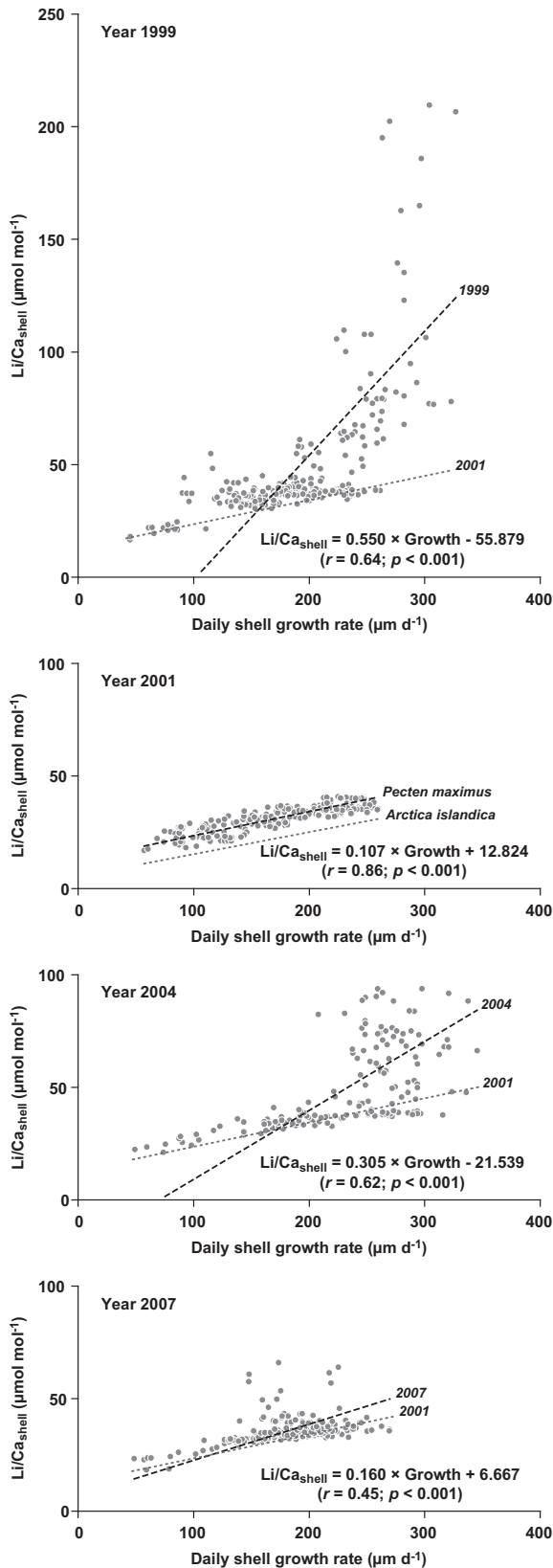


Figure 7: Cross-plots of average Li/Ca versus daily shell growth rate for years 1999, 2001, 2004, and 2007. Model II regression lines (SMA; black dashed line) are presented together with regression statistics. For comparative purposes, (i) 2001 SMA regression line is displayed on cross-plots for years 1999, 2004, and 2007 (grey dotted lines), and (ii) Li/Ca versus daily shell growth rate regression line calculated for *Arctica islandica* (Thébault et al., 2009b) is presented on the 2001 cross-plot (grey dotted line).

Then, we predicted Li/Ca_{shell} variations for each year using average daily shell growth data and Equation 1, assuming that baseline Li/Ca_{shell} variations were only caused by variations in DSGR. Time series of the difference between predicted and observed Li/Ca_{shell}, so-called excess Li/Ca_{shell} (Li/Ca_{excess}), are displayed on Figure 8, together with DSGR and phytoplankton abundances (except for year 2007 when no phytoplankton data were available). Phytoplankton species were split into two groups: (i) edible diatoms (*Chaetoceros* spp. and *Dactyliosolen fragilissimus*), ie. diatoms that have no negative influence on scallop growth in the bay of Brest, and (ii) toxic (*Gymnodinium* spp., harmful dinoflagellates responsible for red tides; Landsberg, 2002) and aggregate-forming or chain-forming species (*Guinardia delicatula* and *Pseudo-nitzschia* spp.) that can hamper scallop growth (Chauvaud et al., 1998; Lorrain et al., 2000; Nézan et al., 2010).

Temporal variations of edible diatom abundance tended to mimic those of Li/Ca_{excess}, with a time lag of ca. 3 weeks (Figure 8, upper panels). This was particularly striking in 2004 (proportionality between Li/Ca_{excess} and edible diatom peaks). In 1999, intensity of the edible diatom bloom recorded at SOMLIT-Brest was close to 500 000 cell L⁻¹ on 10 June 1999; this did not seem sufficient to induce the large Li/Ca_{excess} peak recorded in early July 1999. However, this bloom was much larger on Roscanvel Bank than at SOMLIT-Brest, as indicated by the environmental survey performed by Lorrain et al. (2000) in 1999 exactly where our scallops were collected (9 June 1999: 1 458 000 cell *Chaetoceros* spp. L⁻¹). On the other hand, neither large edible diatom bloom nor Li/Ca_{excess} peak were observed in 2001.

3.5. Relationship between shell growth retardation and phytoplankton blooms

Several growth retardation episodes were recorded on 1999, 2001, and 2004 shells (Figure 8, lower panels). In 1999 and 2001, main accidents always occurred a few days after blooms of *Guinardia delicatula* (May 1999 and May 2001) and *Gymnodinium* spp. (September 2001). Some toxic blooms, however, did not seem to hamper shell growth (August 1999 and October 2001). In 2004, a severe growth retardation was observed but was not preceded by a bloom. Finally, a very large bloom of *Pseudo-nitzschia* spp. occurred on 24 May 2004 (> 800 000 cell L⁻¹), ie. 2 weeks after the growth accident. It should be kept in mind, however, that the timing of blooms may be slightly different at SOMLIT-Brest and Roscanvel.

4. Discussion

Lithium content has rarely been investigated in marine biogenic carbonates in comparison with other elements such as Mg, Sr, or Ba. Most studies on Li/Ca ratio in biocarbonates dealt with foraminifera (Delaney et al., 1985; Delaney and Boyle, 1986; Hall and Chan, 2004; Marriott et al., 2004b; Hathorne and James, 2006; Lear and Rosenthal, 2006; Hendry et al., 2009; Lear et al., 2010), and to a lesser extent with corals (Marriott et al., 2004a; Montagna et al., 2006) and brachiopods (Delaney et al., 1989). The

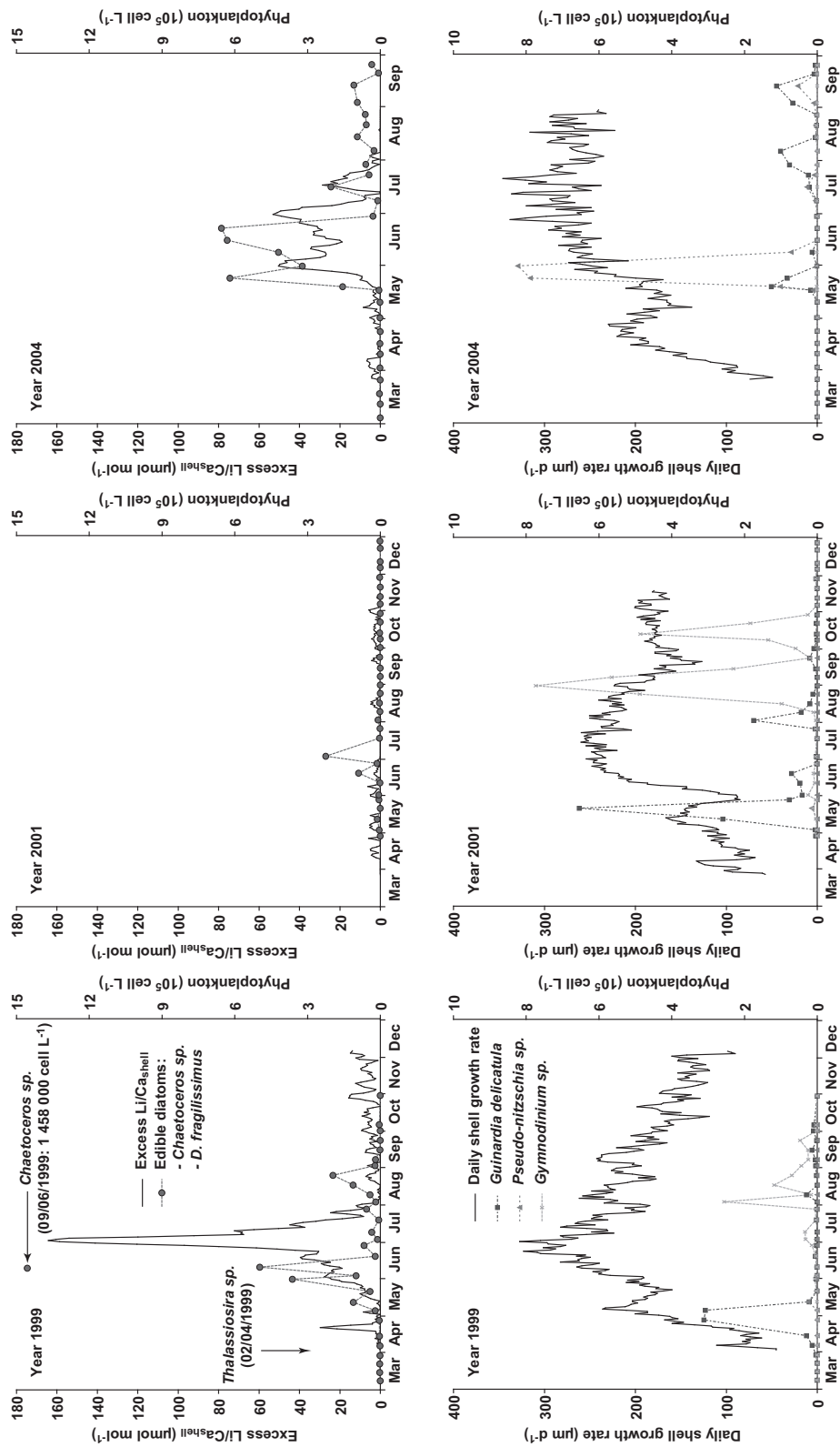


Figure 8: Upper panels: time series of $\text{Li}/\text{Ca}_{\text{excess}}$ (black line) and counts of edible diatoms measured at SOMLIT-Brest (solid circles; *Chaetoceros* spp. + *Dactyliosolen fragilissimus*), for years 1999, 2001, and 2004. Lower panels: time series (1999, 2001, and 2004) of average daily shell growth rate (black line) and abundances of growth-reducing diatoms (solid squares = *Guinardia delicatula*; solid triangles = *Pseudo-nitzschia* spp.) and dinoflagellates (light gray crosses = *Gymnodinium* spp.).

only known study on Li/Ca ratio in bivalve mollusc shells was conducted on juvenile *Arctica islandica* shells from northeast Iceland (Thébault et al., 2009b). Given the very low inter-individual variability in Li/Ca_{shell} for a given season of growth (Figures 5 and 6), it is likely that this ratio responds either to variations of one (or several) environmental parameter(s), and/or to variations of a physiological process synchronized within a given population. Previous studies put forward several hypotheses to explain variations of Li/Ca ratio in calcite: influence of calcification temperature, salinity, dissolved Li concentration in seawater, river inputs of Li-rich silicate particles, calcification rate and seawater carbonate ion (CO₃²⁻) concentration. In the following paragraphs, we discuss the merits of these hypotheses to explain temporal variability of Li/Ca_{shell} in *Pecten maximus*. A new hypothesis, related to phytoplankton blooms, will address the formation of Li/Ca_{shell} peaks.

4.1. Calcification temperature

Many authors highlighted inverse relationships between calcification temperature and Li/Ca in coralline aragonite (Marriott et al., 2004a; Montagna et al., 2006), in foraminifera (Hall and Chan, 2004; Marriott et al., 2004b), in brachiopods (Delaney et al., 1989), as well as in inorganic calcite (Marriott et al., 2004a). Surprisingly, these results are in contradiction with thermodynamic calculations stating that Li content in calcium carbonate should increase with increasing temperature (Hall and Chan, 2004). Conversely, recent studies on foraminifera and aragonitic bivalve shells found a positive dependence of Li/Ca_{shell} on temperature (Hendry et al., 2009; Thébault et al., 2009b). Simple and multiple linear regressions performed on the whole dataset (1999–2007) indicated that seawater temperature alone explained only 6.2% of the Li/Ca_{shell} variability ($r^2 = 0.062$; $p = 0.004$; slope = 2.73; Table 2). In addition, no thermal anomaly, either positive or negative, was observed synchronously with abrupt Li/Ca_{shell} increases, suggesting that temperature did not induce Li/Ca_{shell} peaks (Figure 6). In 2001, ie. a year without Li/Ca_{shell} peaks, temperature appeared quite strongly related with Li/Ca_{shell} ($r^2 = 0.552$; $p < 0.001$) but thorough observation of Figure 6 indicated that this statistical relationship was not obvious (e.g. in May 2001). It is clear from our results that seawater temperature in the bay of Brest was not the primary factor explaining variations of Li/Ca_{shell} between 1999 and 2007. Therefore, we conclude that calcification temperature has only a weak positive influence on Li incorporation in *Pecten maximus* shell calcite precipitated between 8 and 18°C, thus confirming observations by Thébault et al. (2009b) on juvenile *Arctica islandica*.

4.2. Salinity and dissolved lithium concentration

Salinity was put forward as a possible explanation for variations of Li/Ca in inorganic calcite; a salinity decrease, induced by dilution, from 50 to 10 led to a four-fold decrease in Li/Ca_{calcite} (Marriott et al., 2004b). A similar influence of salinity was also highlighted on Na/Ca_{calcite} and might be general for all alkali metals (Ishikawa and Ichikuni, 1984; Marriott et al., 2004b). Indeed, alkali metals are known to be incorporated in an interstitial location

in calcite, while they are incorporated in the crystal structure of aragonite in substitution of Ca, leading to formation of Li₂CO₃ crystals (Okumura and Kitano, 1986). Consequently, it is their concentration in the calcifying fluid that controls the amount of alkali metals incorporated interstitially within calcite, while there is a competition between alkali metals and Ca to enter aragonite so that it is the Li/Ca ratio in the solution which controls Li/Ca_{aragonite}. Because Li concentration is approximately one order of magnitude lower in rivers than in seawater (rivers: 0.012 ppm; seawater: 0.180 ppm; Li, 2000), freshwater inputs leading to salinity decrease therefore also induce a decrease of Li concentration in seawater. At SOMLIT-Brest monitoring station, salinity variations were very small between 1999 and 2007, ranging between 33 and 35.6 during the season of growth of *Pecten maximus* (salinity minima below 33 occurred in winter, when scallops did not grow). According to Marriott et al. (2004b), and assuming that biogenic calcite has the same sensitivity to salinity as inorganic calcite, a 1 unit salinity decrease would result in a 3% decrease in Li/Ca_{shell} for salinity around 35. Therefore, the salinity range measured at SOMLIT-Brest would be responsible for 8% changes in Li/Ca_{shell}, at most. However, average Li/Ca_{shell} variations ranged from 15 to 40 μmol mol⁻¹ in 2001, ie. when Li/Ca_{shell} variations were the weakest. Therefore, salinity, and consequently Li concentration variations in seawater, cannot be responsible alone for Li/Ca_{shell} variations in *Pecten maximus*. Nevertheless, results of simple and multiple linear regressions, albeit equivocal, suggested that salinity might slightly influence Li/Ca_{shell} variations, in addition to another factor (Table 2).

4.3. Weathered Li-rich particles

In their study on Li/Ca_{shell} in juvenile *Arctica islandica* from northeast Iceland, Thébault et al. (2009b) observed that seasonal variations of the closest river discharge roughly followed the same pattern as Li/Ca_{shell}, with maximum values in June. A direct relationship was highlighted by Gislason et al. (2009) between river discharge and mechanical weathering of Icelandic basaltic rocks that have a high Li content. Consequently, Thébault et al. (2009b) hypothesized that high loads of Li-rich suspended basaltic particles probably flow to the sea with Icelandic rivers as soon as snow melts. Direct ingestion of these particles, or their weathering on the seafloor after deposition, may be responsible for significant increases in Li content in shells. Could such an hypothesis explain variations of Li/Ca_{shell} time series in shells of *Pecten maximus*? No data are available on lithium concentration in shales and sandstones composing Aulne and Elorn rivers catchments. Assuming that these rocks have a high Li content and that they are highly susceptible to mechanical weathering, then high concentrations of Li-rich particles could occur in the bay of Brest when river flows are at their annual maximum, ie. in January (see figure 4 in Chauvaud et al., 1998). Conversely, Li-rich particles concentration would be lowest during low water periods, ie. from June to October. Given that highest Li/Ca_{shell} values were recorded during these low river levels, it is unlikely that mechanical weathering of river catchments could explain variability of Li/Ca_{shell} in

Pecten maximus. This possible explanation can therefore likely be ruled out.

4.4. Calcification rate

Our results distinctly highlighted a statistically significant positive relationship between $\text{Li}/\text{Ca}_{\text{shell}}$ and DSGR measured along the axis of maximum growth (Figure 7). This was particularly obvious in 2001 when no $\text{Li}/\text{Ca}_{\text{shell}}$ peak occurred (Figures 6 and 7). For years with periods of Li enrichments in shells (1999, 2004, and to a lesser extent 2007), this relationship was still present but partially concealed by the presence of these $\text{Li}/\text{Ca}_{\text{shell}}$ peaks. A similar relationship between $\text{Li}/\text{Ca}_{\text{shell}}$ and shell growth was observed in *Arctica islandica* (Thébault et al., 2009b). It is worth noting that the slope of the $\text{Li}/\text{Ca}_{\text{shell}}$ -DSGR relationship is very similar in both study (0.098 d m^{-1} for aragonitic *Arctica islandica* vs. 0.107 d m^{-1} for calcitic *Pecten maximus*; Figure 7), suggesting that the control of this physiological factor on Li incorporation within bivalve mollusc shells may be general and ubiquitous. This control of shell growth is supported by results of the elemental analyses performed on three different growth axes of shell #6 collected on 5 November 2007. $\text{Li}/\text{Ca}_{\text{shell}}$ ratios displayed very similar temporal variations whatever the growth axis (Figure 4). Nevertheless, average $\text{Li}/\text{Ca}_{\text{shell}}$ ratios were significantly higher on the central axis (ie. axis of maximum growth). These differences could likely be explained by the lower daily shell growth rates on lateral ribs in comparison to the median one.

At this point, a clarification must be made about the difference between daily shell growth rate and absolute calcification rate. DSGR is not equal to absolute calcification rate (or crystal growth rate) because it does not take into account ontogenetic changes in shell thickness and enlargement. A problem is that crystal growth rate is hardly measurable. Lorrain et al. (2004) tried to estimate it more precisely during the second year of growth of *Pecten maximus* shells from the Bay of Brest by measuring their daily carbon precipitation rate (DCPR). It appeared that DSGR and DCPR slightly differed. Therefore, it must be kept in mind that DSGR is only an approximation of absolute calcification rate.

Beside bivalves, several studies also suggested that changes in calcification rate, that could in turn reflect long-term changes in CO_3^{2-} concentration and carbonate saturation state, may be responsible for variations of Li/Ca in foraminiferal calcite (Hall and Chan, 2004; Lear and Rosenthal, 2006; Hendry et al., 2009). The mechanisms involved in these physiological effects have barely been studied. The influence of calcification rate on Li incorporation in biocarbonates might be related to the presence of calcification anomalies. Indeed, Busenberg and Plummer (1985) suggested that the amount of Na incorporated in calcite may be highly dependent on the number of crystal defects, which is in turn favoured by faster growth rates. By analogy, and because Na and Li are both situated in interstitial positions in the calcite crystals (Okumura and Kitano, 1986), it is reasonable to hypothesize that the same effect controls $\text{Li}/\text{Ca}_{\text{shell}}$. The faster a shell grows, the more defects there are in the crystal structure, and the more interstitial

spaces are available for Li inclusions. Concurrent measurements of $\text{Li}/\text{Ca}_{\text{shell}}$ and scanning electron microscope observations of crystal fabrics in the same shell might help confirming this hypothesis. In any case, our results suggested that $\text{Li}/\text{Ca}_{\text{shell}}$ was probably controlled by calcification rate (as estimated by DSGR) most of the year (ie. outside peak periods).

4.5. Phytoplankton blooms

Once the influence of shell growth on $\text{Li}/\text{Ca}_{\text{shell}}$ has been removed, $\text{Li}/\text{Ca}_{\text{excess}}$ showed very distinct peaks which may be explained by phytoplankton dynamics (Figure 8). Indeed, a striking similarity and proportionality was highlighted between $\text{Li}/\text{Ca}_{\text{excess}}$ and abundance of *Chaetoceros* spp. and *Dactyliosolen fragilissimus*, ie. diatoms that are known to be eaten by scallops in the bay of Brest with no detrimental influence on physiology. An exception is *Chaetoceros sociale* that can form large aggregates and alter scallop growth (Chauvaud et al., 1998) but this species was not observed between 1999 and 2004 (except one occurrence on 23 September 2003 with 8720 cell L^{-1}). Important shell growth retardation occurred only a few days after every large bloom of the diatom *Guinardia delicatula*. This confirms observations of Chauvaud et al. (1998) and Lorrain et al. (2000) who suggested that sedimentation of large aggregates of this species affected food intake and/or respiratory activity of the scallops by gill clogging or oxygen depletion, thus strongly hampering shell growth. Therefore, although this species does not produce toxins, it can definitely not be classified as an edible diatom.

Many species of the diatom genus *Pseudo-nitzschia* are known to produce a powerful neurotoxin named domoic acid (DA), that can generate serious trouble and amnesia (Amnesic Shellfish Poisoning ASP) in human populations feeding on marine resources (Bates et al., 1989). Lithium is known to be an element significantly stimulating production of DA by *Pseudo-nitzschia* spp. (Subba Rao et al., 1998). As DA is a powerful chelating agent, synthesis and release of large quantities of this neurotoxin might be an attempt to sequester lithium (Stewart and Subba Rao, 1995). Given that many marine bivalve species, especially *Pecten maximus*, are known for their capability of accumulating high DA levels (James et al., 2005), it could be hypothesized that peaks of $\text{Li}/\text{Ca}_{\text{excess}}$ were produced (i) after direct ingestion of DA-enriched *Pseudo-nitzschia*, and/or (ii) after ingestion of dissolved DA released in seawater following blooms of toxin-producing *Pseudo-nitzschia*. Only two large blooms of *Pseudo-nitzschia* were recorded at SOMLIT-Brest between 1999 and 2004 (July 2000 and May 2004). Therefore, most of the $\text{Li}/\text{Ca}_{\text{excess}}$ peaks cannot be attributed to such blooms. An exception may be the $\text{Li}/\text{Ca}_{\text{excess}}$ peak recorded in early June 2004, ie. a few weeks after high *Pseudo-nitzschia* concentrations at SOMLIT-Brest. However, there are some uncertainties about the exact timing of this bloom at Roscanvel. Indeed, a shell growth retardation was recorded in early May 2004. Concentrations of *Guinardia delicatula* and *Gymnodinium* spp. were definitely too low to explain this growth reduction. We suppose that the latter was induced by *Pseudo-nitzschia* and that the bloom recorded in late May at SOMLIT-Brest actually occurred 2–3 weeks earlier at Roscanvel. Indeed, blooms of

Pseudo-nitzschia are known to display an especially high spatial variability and they can occur at a very local scale even in a small-size ecosystem such as the bay of Brest (H. Hégaret, pers. comm.). Rines et al. (2002) also highlighted the possibility of *Pseudo-nitzschia* populations to be concentrated into thin horizontal layers, from centimetres to a few metres within the water column or near to the bottom due to the physical transport of water masses. Moreover, most members of the *Pseudo-nitzschia* genus are elongated diatoms that are known for their ability to form chains (Hasle, 1994), thus possibly hampering shell growth by gill clogging. And, finally, Liu et al. (2008) found negative impacts on growth rate and survival of juvenile *Pecten maximus* when exposed to food previously enriched with DA.

Consequently, we suggest (i) that shell growth retardations were induced by blooms of either chain-forming diatoms (*Pseudo-nitzschia* spp.), aggregate-forming diatoms (*Guinardia delicatula*), and/or toxic phytoplankton species (*Pseudo-nitzschia* spp. and dinoflagellate *Gymnodinium* spp.), and (ii) that occurrence and amplitude of Li/Ca_{excess} peaks were probably related to timing and magnitude of edible diatom blooms (especially *Chaetoceros* spp. and *Dactyliosolen fragilissimus*). Nevertheless, a question remains: what is the exact relationship between edible diatoms and Li in shells?

It has previously been estimated that biogenic carbonate and biogenic opal production were two of the main removal processes of lithium from the ocean (Coplen et al., 2002). However, while marine carbonates contain 2 ppm of lithium on average, Quaternary radiolarian and diatomaceous oozes are one order of magnitude more enriched in lithium (about 30 ppm; Coplen et al., 2002). Biogenic opal originating from diatom frustules was assumed to be a major source of Li in diatomaceous sediments of the Gulf of California, based on a Li concentration maximum in pore fluids within a zone of active silica diagenesis (Gieskes et al., 1982). It could therefore be assumed that dissolution of *Chaetoceros* spp. and *Dactyliosolen fragilissimus* frustules in the stomach of *Pecten maximus* led to an increase in lithium concentration in the internal fluids and, ultimately, in the shell. Unfortunately, no data are available about dissolution rates of diatom frustules in digestive tract of molluscs. Nevertheless, the residence time of biogenic silica in sediments of the bay of Brest has previously been estimated to be on the order of 1 month (Chauvaud et al., 2000). Similarly, Laruelle et al. (2009) found that the benthic recycling flux of dissolved silicon to the water column of the bay of Brest follows the diatom deposition pulse with a time lag of 1 to 2 months. These data are consistent with laboratory experiments indicating that opal dissolution is quite slow (2.9–6.6 % d⁻¹, ie. frustules are entirely dissolved after 15–34 days; Moriceau et al., 2007). Assuming that these rates are of the same order of magnitude in scallop stomach, then these data give strength to our hypothesis as it provides an explanation for the ca. 3 week time lag between edible diatom blooms and Li/Ca_{excess} peaks.

5. Summary and conclusions

This first study on Li/Ca_{shell} ratio in calcitic bivalves provided promising and definitely very interesting information. First of all, individuals from a given population presented very similar time series of Li/Ca_{shell}, which suggests that incorporation of this element responds to variations of environmental parameters affecting simultaneously all specimens in a given area. Secondly, a strong and significant linear relationship has been found between daily shell growth rate and variations of Li/Ca_{shell} outside Li enrichment periods, thus confirming previous results obtained on shells of *Arctica islandica* (Thébault et al., 2009b). Interestingly, the slopes of these shell growth–Li/Ca_{shell} relationships are very similar for both species (about 0.1 d m⁻¹). Thirdly, seawater temperature had only a weak positive influence on Li incorporation in *Pecten maximus* shell calcite growing over the range 8–18°C. And finally, we provided *prima-facie* evidence towards an influence of diatom blooms on Li/Ca_{shell} enrichments.

To conclude, we suggest that Li/Ca_{shell} ratio may be used as a proxy for timing and magnitude of diatom blooms in coastal ecosystems. Hence, this proxy would be very useful to assess (i) importance of past phytoplankton blooms as diatoms were dominant in pre-industrial “pristine” coastal ecosystems due to higher Si/N ratios than today (Smayda, 1990), and (ii) magnitude of recent shifts from diatoms to non-siliceous phytoplankton in areas affected by anthropogenic activities (e.g., N-enriched freshwater inputs). A limit of this proxy would be that variations of abundance of non-edible diatoms could likely not be reconstructed using this proxy. However, these species represent only a small fraction of coastal diatom communities. Undoubtedly, Li should therefore be added in the list of elements commonly analysed by ICP-MS in the framework of sclerochemical studies.

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