

Synchronous barium peaks in high-resolution profiles of calcite and aragonite marine bivalve shells

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Abstract

Barium/Calcium profiles of bivalve shells are characterized by flat background signals periodically interrupted with sharp peaks, with the background signals correlated with water Ba/Ca. To test if the peaks are an environmental signal related to productivity, we analyzed high resolution Ba/Ca profiles in bivalve shells that grew adjacent to one another. Two aragonitic *Saxidomus giganteus* show remarkable similarity over a decade of growth, clearly indicating an environmental forcing. Four calcitic *Pecten maximus* shells also record synchronous Ba/Ca peaks, again indicating an exogenous control. The Ba/Ca peaks, however, start ~40 days after the crash of the bloom, while sedimentation takes place immediately following the bloom. Barite formation in settling phytoplankton flocs, as has been previously proposed, is clearly not the cause of these peaks. Other possible causes such as dissolved Ba in ambient water, spawning, shell organic matter content and kinetic growth rate effects are also discussed, but none provide satisfactory explanations. Background shell Ba partition coefficients ($Ba/Ca_{\text{carbonate}} / Ba/Ca_{\text{water}}$) for both the calcitic shells (0.18) and aragonitic shells (0.16) are similar to that previously reported for the calcitic *Mytilus edulis* (~0.1). We suggest that Ba/Ca peaks in bivalve shells are caused by an as of yet undetermined environmental forcing, while background Ba/Ca levels are a good indication of dissolved Ba/Ca in the water; both are independent of shell mineralogy.

Introduction

Elemental signatures in biogenic carbonates such as corals and foraminifera are well known proxies of climate change and past environmental conditions (see Lea, 2003 for review). However, elemental signatures in bivalve shells are generally not well correlated with environmental conditions due to strong vital effects (e.g., Purton et al., 1999; Takesue and van Geen, 2004; Freitas et al., 2006; Gillikin et al., 2005a; Lorrain et al., 2005; Carré et al., 2006; Surge and Walker, 2006). On the other hand, Ba/Ca ratios do seem to have potential as an environmental proxy. There is a nearly ubiquitous Ba/Ca signal in all bivalve shells: a more or less constant Ba/Ca background that is interrupted with sharp episodic peaks (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003; Carré et al., 2006; Gillikin et al., 2006). The $Ba/Ca_{background}$ has been shown to be a reliable proxy of Ba/Ca_{water} in *Mytilus edulis* (Gillikin et al., 2006) and the sharp peaks seem to be reproducible between different shells growing in the same location indicating an environmental forcing (Vander Putten et al., 2000; Carré et al., 2006). Stecher et al. (1996) first noted these peaks in the aragonite shells of two marine clam species. They postulated that these peaks may represent periods of barite ($BaSO_4$) formation immediately following phytoplankton blooms. Barite is believed to form in organic-rich decaying phytoplankton flocs, where $BaSO_4$ saturation conditions might prevail (Dehairs et al., 1980; Bishop, 1988). Vander Putten et al. (2000) suggested that the Ba/Ca peaks in calcite mussel shells provide excellent markers for spring phytoplankton blooms, but noted there was no direct relationship between peak height and chlorophyll *a* (Chl *a*) concentrations. Lazareth et al. (2003) also postulated that the Ba/Ca peaks in a tropical calcitic bivalve were related to phytoplankton blooms. Other potential causes of these peaks could be short increases of dissolved Ba, biological partitioning of Ba to calcification sites (such as during spawning), or differences in shell micro-structure (see Gillikin et al., 2006 for review). In bivalves, these peaks are not generally considered to be correlated with riverine discharge (see discussion), as they can be with in corals (e.g., McCulloch et al., 2003; Sinclair and McCulloch, 2004).

The aim of this study is to compare Ba/Ca profiles between shells grown at the same location and then to compare shell data with environmental parameters. We also look at

shell background Ba/Ca data from these species to determine if they are potentially a proxy of water Ba/Ca as Gillikin et al. (2006) proposed for *Mytilus edulis*. In order to determine if these Ba/Ca peaks are reproducible between specimens growing in the same locality, which would suggest an extrinsic cause, we sampled two aragonitic *Saxidomus giganteus* shells from Puget Sound (Washington, USA) which provided a 10 year Ba/Ca record and four calcitic *Pecten maximus* shells from the Bay of Brest (France) that provide precisely time resolved Ba/Ca profiles. Several environmental parameters recorded during shell growth were also available from these sites such as temperature, salinity and Chl *a* concentrations.

Materials & Methods

We chose *Saxidomus giganteus* (Fig. 1a) and *Pecten maximus* (Fig 1b) for analysis for several reasons. *Saxidomus giganteus* provides 1) a long term record (~10 years) from a single shell allowing ontogenic effects on peaks and background Ba/Ca ratios to be determined and 2) is an example of an aragonitic bivalve. The calcitic *Pecten maximus*, although only providing a short record (< 1 yr), allows precise matching between shell and environmental variables. Shells of both of these species have been studied extensively (e.g., Chauvaud et al. 1998, 2005; Lorrain et al., 2000, 2005; De Ridder et al., 2004; Gillikin et al., 2005a, b; Gillikin 2005; Freitas et al., 2006; Kingston et al., 2008).

The two *S. giganteus* shells were collected from intertidal sediments of Puget Sound (Washington, USA), and have been described in detail elsewhere (Gillikin et al., 2005a, b). Shells were sampled in cross-section along the axis of maximum growth, thus providing a high-resolution elemental profile spanning ~10 years. To compare data between shells and environment, the $\delta^{18}\text{O}$ profiles were used (presented in Gillikin et al., 2005b). Briefly, the $\delta^{18}\text{O}$ signal was fit between the two shells (x-axis of one shell scaled to the other). Then the $\delta^{18}\text{O}$ signal was converted to a temperature (SST) signature using a constant $\delta^{18}\text{O}_{\text{water}}$ and the paleotemperature equation of Böhm et al. (2000). This modeled temperature was then fit to environmental SST (scaling the x-axis only) using the algorithm described in De Ridder et al. (2004) (see Gillikin et al. (2005b) for

complete details; this resulted in a correlation coefficient (R^2) of ~ 0.8). Considering we did not account for variability in water $\delta^{18}\text{O}$, this is a fairly good correlation, but nevertheless does lead to an unknown error in determining the exact timing of the samples taken from the shell. Shell Ba/Ca ratios were determined using laser-ablation ICP-MS (Fisons-VG frequency quadrupled Nd-YAG laser (266 nm) coupled to a Fisons-VG PlasmaQuad II+ ICP-MS) as described in Gillikin et al. (2005a) and (2006). Data from LA-ICP-MS were calibrated using both the NIST 610 (values from Pearce et al. (1997)) and the USGS MACS1 (values from S. Wilson, USGS, unpublished data, 2004). The laser was shot directly in the drill holes used to generate the $\delta^{18}\text{O}$ data allowing a precise alignment between the two methods (see Gillikin et al., (2005a) and (2006)). Environmental SST and Chl *a* data are from the Washington State Department of Ecology (<http://www.ecy.wa.gov/>).

The *P. maximus* shells (three age class I, with one winter growth check, and one age class II, with two winter growth checks) were collected from 30 m depth in the Bay of Brest (France) in 2003; the age class I shells are the same shells presented in Lorrain et al. (2005). Daily growth rate was determined by measuring distances between successive daily growth striae (external growth increments; Fig 1c) as described in Chauvaud et al. (1998). The method used to assign a precise date to each increment has already been well developed in several papers (e.g., Lorrain et al., 2004; Chauvaud et al. 2005). Each year, the date of growth restart is calculated by counting and measuring the daily increments from the edge of the shell to the first winter mark on 50 juveniles from the same cohort sampled at different moments during the growth season. Dates are thus assigned by backdating from the collection date. A mean profile is obtained by minimizing the sum of the differences between the different growth profiles (Walter and Pronzato, 1994). This mean curve is then used as a reference to assign dates to the striae from any new specimen. A potential error can come from the fact that some individuals may experience a short growth hiatus of a couple of days as a result of a disturbance. An additional source of error may be that a few striae can be broken from manipulation at the ventral edge of the scallop. The error is on the magnitude of a few days; from approximately 1 to 7 days depending on the scallop. The excellent correlation ($R^2 = 0.92$) found between $\delta^{18}\text{O}$ and

temperature in *P. maximus* from this same location (Chauvaud et al., 2005) confirms that the backdating is in fact very precise. Furthermore, a maximum error of one week would in fact not change any of our interpretations.

Carbonate powders representing ~1–6 days growth (covering the 2003 growth season) were milled from the *P. maximus* shells and were acid digested before being analyzed on an HR-ICP-MS (Finnigan Element2) as described in Lorrain et al. (2005).

Reproducibility of an in-house calcite bivalve shell reference material was 6.4% ($\text{Ba/Ca} = 1.21 \pm 0.08 \mu\text{mol mol}^{-1}$). Water was continuously monitored over the lifetime of the scallops for SST and Chl *a* (fluorescence) with a Sea-bird 19 sonde. In the same location and year, reproductive activity of three-year old scallops was assessed by fortnightly sampling of twenty individuals. Three-year-old individuals were used because their larger gonads allow more precise sampling; however, previous studies show high reproductive synchronism between age group in this species (Paulet and Fifas, 1989). For each date, a gonad index was calculated as the dry weight of the gonad divided by the shell weight and multiplied by 1000 (see Paulet et al., 1992 for details).

Results & Discussion

Ba/Ca Peaks

The inter-individual synchronicity of peaks in the shells of the two species is clearly evident in Figures 2 - 4. The very large, sharp peaks in 1993 (2 peaks), 1994 and 1999 are timed exactly in both *S. giganteus* shells (red arrows, Fig. 2; Fig 3a). Ba/Ca was independently fit using $\delta^{18}\text{O}$ cycles (Gillikin et al., 2005b), so the exact peak match is strong evidence of a good time base reconstruction. However, the offset in the 1996 peaks (red circle, Fig. 2; Fig 3b) could be due to improper $\delta^{18}\text{O}$ alignment between the two shells, as this was the most difficult section of the shells to date (see Gillikin et al., 2005b). This offset approximates 80 days, which is considered the maximum error on the fit between shells. However, it should be kept in mind that the other regions of the shell seem to be fit more precisely (e.g., Fig 3a). The smaller peaks ($<10 \mu\text{mol/mol}$) are generally more variable in shape, but still seem to be somewhat reproducible between shells. For the more precisely timed *P. maximus* data, the apexes of the large peaks all

fall within seven days of each other (this is a combined error of backdating striae and time averaging several striae in each carbonate sample milled from the shell) (Fig. 4). Nevertheless, the reproducibility between the shells strongly suggests that these peaks are a response to an exogenous factor in both species, or, if not, the result of a very well timed endogenous process.

There are several possible hypotheses that can be put forward regarding the cause of these Ba/Ca peaks. The link with primary production mentioned in the introduction, variations in dissolved Ba/Ca in the water in which the bivalve is growing, variability in shell organic matter content, kinetic growth rate effects, and the consequence of a precisely timed and synchronous physiological process such as spawning are all plausible hypotheses. With the evidence at hand, we will discuss each of these possibilities.

In corals, Ba/Ca peaks have been shown to coincide with flood plumes which bring lower salinities and higher dissolved barium to the coastal zone (McCulloch et al., 2003; Sinclair et al., 2004). There is generally a linear inverse relationship between salinity and dissolved barium concentrations (Coffey et al., 1997; Sinclair et al., 2004; Gillikin et al., 2006). Variability in dissolved barium concentrations as a source for the Ba/Ca peaks in *P. maximus* is highly unlikely, as the Bay of Brest is a rather stable environment with marine salinities year-round (Chauvaud et al., 2005). Additionally, if the background and peak incorporation mechanism were the same, the Ba/Ca ratio of the water would need to increase 5 to 10 times, which is highly improbable considering salinity only varies a few units over the year (Lorrain et al., 2005). Salinity slowly increases from 33.1 to 35.6 from March to September and can therefore not explain the Ba/Ca peaks measured in the shells (salinity mimics the temperature profile shown in Fig. 4; see Fig. 2 in Lorrain et al., 2005).

In bivalve shells, the Ba/Ca peaks are generally believed to be related to primary productivity (Stecher et al., 1996; Vander Putten et al., 2000; Lazereth et al., 2003). Phytoplankton decay, sedimentation, and release of barium should happen quickly after a bloom in an estuary ends (Stecher and Kogut, 1999; Ganeshram et al., 2003). Most of the

barium released after a bloom is labile and only a minor fraction forms barite crystals (Ganeshram et al., 2003). Therefore, if labile barium, either in phytoplankton or released into the dissolve phase, was the cause of the Ba/Ca peaks, these peaks should form near the end of the bloom or very shortly thereafter. The Ba/Ca peaks are not systematically occurring near the end of the Chl *a* peaks in *S. giganteus* shells; however, due to possible errors in aligning the shell and environmental data we cannot conclude a lack of correlation. Nevertheless, it is clear that Chl *a* amplitude is not related to Ba/Ca peak amplitude (also noted by Vander Putten et al. (2000) in *Mytilus edulis*); despite the large Chl *a* peaks in 1997, 1998 and 2000, there are only minor Ba/Ca peaks during these years (Fig 2). Considering the errors associated with the fit between shell and environmental data, we rely more heavily on the *P. maximus* shells which are much more precisely timed.

The four *P. maximus* shells also show a high correlation between Ba/Ca peaks (Fig. 4). All shells exhibit a double peak, with the first large peak and second smaller peak synchronizing between all shells including both age classes, which illustrates that there is no ontogenic effect on these Ba/Ca profiles in *P. maximus*. There is a remarkable similarity in the Chl *a* and Ba/Ca peak shapes (i.e, the presence of a large peak followed by a smaller peak), however, they are offset by about 40 days. The phytoplankton bloom crashed on the 12th of May, while the Ba/Ca peak started about the 21st of June. Moreover, the sedimentation of phytoplankton occurs around the end of the bloom as is evidenced by a sharp reduction in growth rate (Fig. 5). This phenomenon has been previously described in Chauvaud et al. (1998) and in Lorrain et al. (2000); briefly, the growth reduction is caused by the sedimentation clogging the gills of the scallops and/or a reduction in oxygen at the water-sediment interface as a result of the decaying phytoplankton. Barite formation in settling phytoplankton flocs, or the Ba-rich phytoplankton itself, is clearly not the cause of these peaks, since the growth reduction and Ba/Ca peaks should then have coincided, which is not observed (Figs. 4 and 5). However, Ganeshram et al. (2003) found that barite formation can take several weeks to reach its maximum after the decay of phytoplankton starts. Perhaps barite is formed at the sediment surface and is ingested by the scallops several weeks after the phytoplankton

bloom ends. Although only a small amount of barium is converted to barite, the barite could provide a high concentration of Ba if it dissociates in the gut of the bivalve. It is convenient to suggest that there is indeed a link between phytoplankton and Ba/Ca peaks due to the synchronicity of the *S. giganteus* Ba/Ca profile and the similarity in the peak shapes in *P. maximus*. However, it would be surprising that the double peak is persevered in *P. maximus*. If there was a biological filtering or delay in barite formation in the sediments, the signal in the shell would most likely be averaged and would not show the discreet double peak. Detailed time-resolved experiments are needed to determine if this is the case. If barite is the cause, it should be visible in the gut of bivalves at the time of Ba/Ca peak formation. Experiments over several years following the complete Ba cycle in the water and in the bivalve (e.g., different tissues, gut and shell) are needed.

An alternative hypothesis could be that Ba residing in the animal's tissues is remobilized by the bivalve during spawning, as was proposed by Gillikin et al. (2006); however, *P. maximus* spawns at the beginning of the spring before the shell Ba/Ca peak, as attested by the gonadosomatic index (Fig. 4) (Paulet et al., 1997). It is possible that Ba is used for reproduction and is sequestered to the shell during non-reproductive periods, which would result in low shell Ba/Ca during reproduction and high shell Ba/Ca during non-reproductive periods as seen here. Preliminary data show that gonads are rich in Ba when compared with muscle tissues (Lorrain, unpublished). The fact that shell Ba/Ca peaks exactly when gonad development is at its lowest (Fig. 4) gives support to a Ba-reproduction link hypothesis. However, it seems unlikely that this would lead to similar variations in shell Ba/Ca peak amplitudes between individuals (Fig. 2). This again illustrates the need for further research involving the relationship between ecophysiology and proxy incorporation.

There are other potential causes of the Ba/Ca peaks in these shells. For example, if Ba was to bind to organic matter in the shell, then an enrichment in shell organic matter would result in a high Ba/Ca ratio. However, neither Hart et al. (1997) nor Sinclair (2005) found a relationship between organic matter and Ba concentrations in other biogenic carbonates (i.e., corals), and Rosenthal and Katz (1989) suggest that Ba is bound to the

crystal phase rather than the organic phase in mollusc shells. Moreover, the slower growing tip of the *S. giganteus* shells would be expected to have higher organic matter concentrations (Rosenberg et al., 2001), while higher Ba/Ca ratios are generally observed in the faster growing back sections of the shells (Fig. 2). Thus it is unlikely that the Ba peaks are associated with shell regions containing higher organic content. There has been one report of barite crystals in bivalve shells, but these shells came from a freshwater environment with extremely high barium concentrations (Fritz et al., 1990), so this is also an unlikely cause of the peaks. Alternatively, the Ba/Ca peaks could be a kinetic growth rate effect. Such effects have been noted in both abiogenic calcite and aragonite (Tesoriero and Pankow, 1996; Gaetani and Cohen, 2006), but this is also not supported by our data. The double peak in *P. maximus* (Fig. 4) cannot be explained in terms of changing growth rates as daily growth rates are fairly constant during peak formation (Fig. 5). Moreover, despite growth slowing from about 18 mm/yr in 1993 to about 4 mm/yr in 1999 in the *S. giganteus* shells (See Gillikin et al., 2005a), there are still large Ba/Ca peaks in these years (up to ~25 $\mu\text{mol/mol}$; Fig. 2). Therefore, there is no satisfactory variable that can be used to explain these ubiquitous Ba/Ca peaks in bivalve shells. Interestingly, Sinclair (2005) also found well synchronized Ba/Ca peaks in corals, which could not be correlated to several environmental and biological processes.

Ba Partition coefficients and shell Ba/Ca background

The partitioning of trace elements (Me) between water and carbonate is typically defined in terms of a partition coefficient: $D_{\text{Me}} = (\text{Me/Ca})_{\text{carbonate}} / (\text{Me/Ca})_{\text{water}}$, where Me/Ca are typically given as molar ratios (see Mucci and Morse 1990). Interestingly, abiogenic calcite and aragonite behave rather differently in regards to Ba partitioning (D_{Ba}). Typically, abiogenic calcite D_{Ba} is precipitation rate dependent and is low, usually < 0.5 (Mucci and Morse, 1990; Tesoriero and Pankow, 1996). Abiogenic aragonite D_{Ba} is strongly temperature dependent and is usually > 0.5 (Dietzel et al., 2004; Gaetani and Cohen, 2006). However, both the aragonite (*S. giganteus*) and calcite (*P. maximus*) shells presented here have similar baseline values (*S. giganteus* ~ 1.0 and *P. maximus* ~ 0.7 $\mu\text{mol/mol}$). Considering a seawater Ba/Ca ratio of 3.8 $\mu\text{mol/mol}$ for the Bay of Brest

(Lorrain, unpublished) and a background Ba/Ca ratio of 0.7 $\mu\text{mol/mol}$ for *P. maximus*, a D_{Ba} of 0.18 can be calculated. Similarly, *S. giganteus* has a D_{Ba} of 0.16 using Ba/Ca ratios of 1.0 $\mu\text{mol/mol}$ for the shell and 6.2 $\mu\text{mol/mol}$ for the water (Gillikin, 2005). These are both close to the D_{Ba} that Gillikin et al. (2006) report for *M. edulis* (~ 0.1). In addition, similar partition coefficients for both mineralogies are evident from the peaks. Aragonite shells had higher peaks in this study, but previous studies presented even higher peaks in calcite shells (e.g., *M. edulis* up to 70 $\mu\text{mol/mol}$; Vander Putten et al. (2000)). Thus, despite different mineralogies, these species have very similar barium partition coefficients.

While most research has focused on the Ba-peaks, Gillikin et al. (2006) found that the background Ba/Ca level in the shells of another bivalve species (*Mytilus edulis*, calcite shell) could be used as an indicator of dissolved Ba/Ca ratios in estuarine water and hence provide an indication of salinity (salinity inversely varies with dissolved Ba/Ca ratios in most estuaries). However, in the two *S. giganteus* shells analyzed here, the background Ba/Ca levels are higher near the umbo (Fig. 2). Considering that the $\delta^{18}\text{O}$ data do not suggest a reduced salinity when the clams were younger (see Gillikin et al., 2005b) and the salinity record does not indicate reduced salinities in the Sound, this is probably an ontogenic effect. Unfortunately, this complicates the use of Ba/Ca backgrounds in this species, but does highlight the point that species specific differences in elemental incorporation are important and must be taken into consideration. Nevertheless, despite the ontogenic effect, large temporary salinity changes may still be recorded in this species' shells; especially if shell regions of similar age are compared. Considering that the D_{Ba} for aragonitic corals (1.27; Lea et al. (1989)) and aragonitic coralline sponges (0.86; Rosenheim et al. (2005)) is much closer to the abiogenic end-member, it can be postulated that these aragonitic bivalves are strongly regulating Ba incorporation into their shells. This is also evidenced by the fact that Dietzel et al. (2004) report aragonite D_{Ba} to be 2.0 at 10 °C and 1.5 at 25 °C. This temperature dependence in aragonite has also been demonstrated in larval molluscs (Zacherl et al., 2003), coralline sponges (Rosenheim et al., 2005) and corals (Lea et al., 1989), while it is obviously not evident in the shells used in this study (if it were we would expect to see a sinusoidal

curve in the *S. giganteus* data). Therefore, barium incorporation into bivalve carbonate is not similar to abiogenic carbonate, but does still seem to record some environmental signal.

In conclusion, this study suggests that Ba/Ca peaks in bivalve shells are caused by an environmental forcing regardless of mineralogy, albeit with a biological filter. The exact timing between animals growing in the same environment attests to this. Clearly more work is needed to decipher this potential proxy.

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Figure legends

Figure 1. Pictures of the bivalve species used in this study: *Saxidomus giganteus* (1a; scale bar = 1 cm) and *Pecten maximus* (1b; scale bar = 1 cm). A detail of the daily striae on *P. maximus* shells are also shown (1c; scale bar = 1 mm).

Figure 2. Ba/Ca ratios in two *Saxidomus giganteus* shells that grew side by side in Puget Sound (solid and open circles). The solid green line is chlorophyll *a* and the dotted line is water temperature. Arrows indicate the synchronous sharp peaks noted in the text and red circle highlights the mis-matched section of the profile. Note that each year mark denotes the first day of that year. One Chl *a* peak extends beyond the chart axis (labeled as 35.4 $\mu\text{g/L}$).

[Note to production editor: This Figure (Figure 2) should be as large as possible to show all features of the figure. Please set it to be as wide as the page width.]

Figure 3. An enlargement of two sections of the *Saxidomus giganteus* data presented in Figure 2. The left panel (a) shows the first three large Ba/Ca peaks which correlate very well between the two shells and the right panel (b) shows the section of shell with the poorest match between the two shells. The difference in background levels though ontogeny is also more visible in these panels (i.e., they are higher in the right panel).

Figure 4. Ba/Ca ratios in three age class I (open symbols) and one age class II (crosses) *Pecten maximus* shells that grew in the Bay of Brest (France). The solid green line is chlorophyll *a* and the dashed grey line is water temperature. The dashed black line and solid black symbols are the gonad index (dry weight of the gonad divided by the shell weight (x1000)). Note that each month mark denotes the first day of that month.

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green line is chlorophyll *a*. The red circles highlight the growth minima during the growth dip. Note that each month mark denotes the first day of that month.

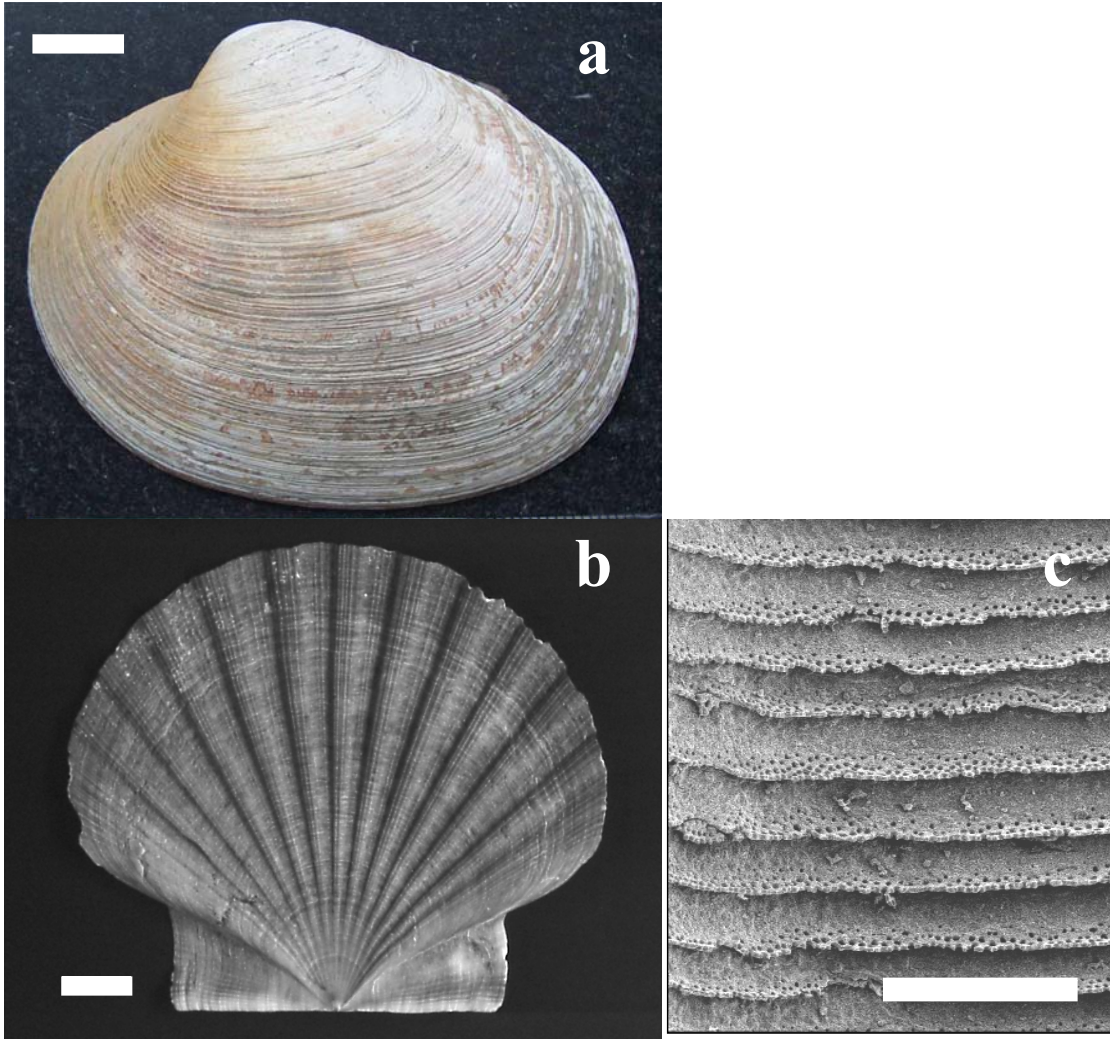


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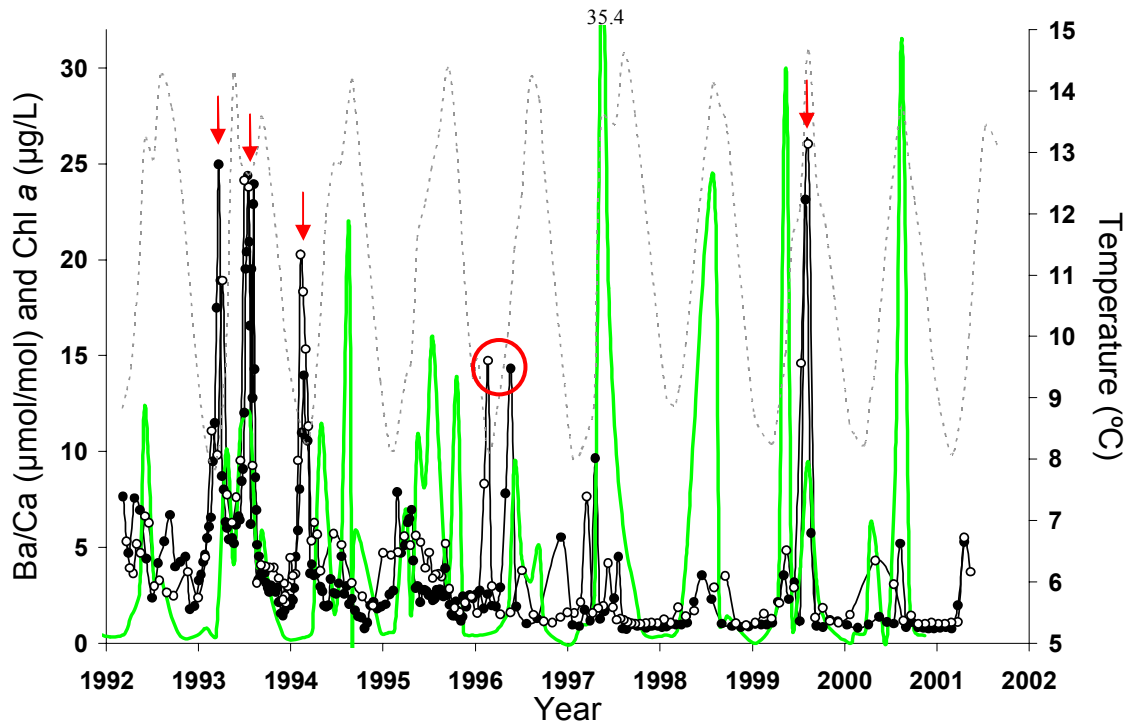


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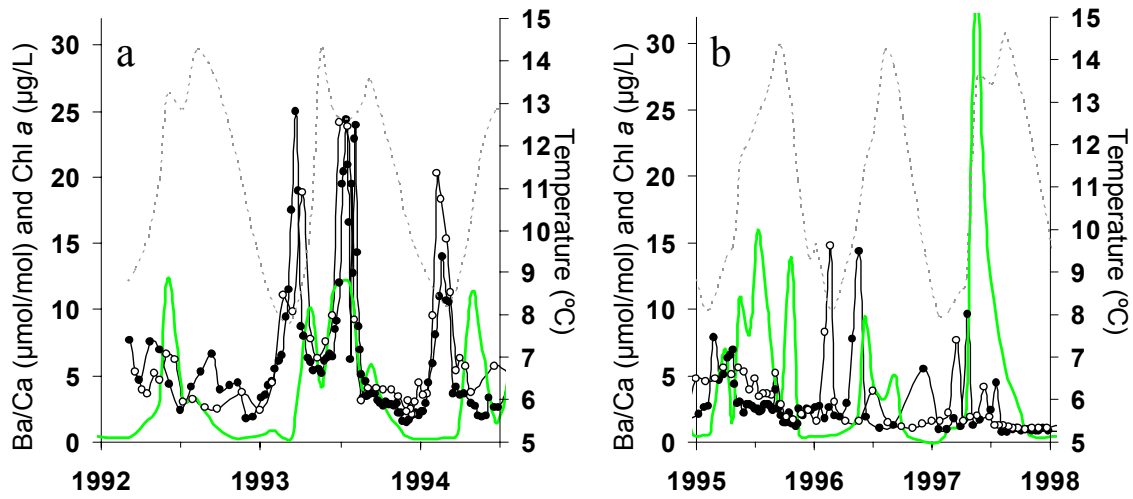


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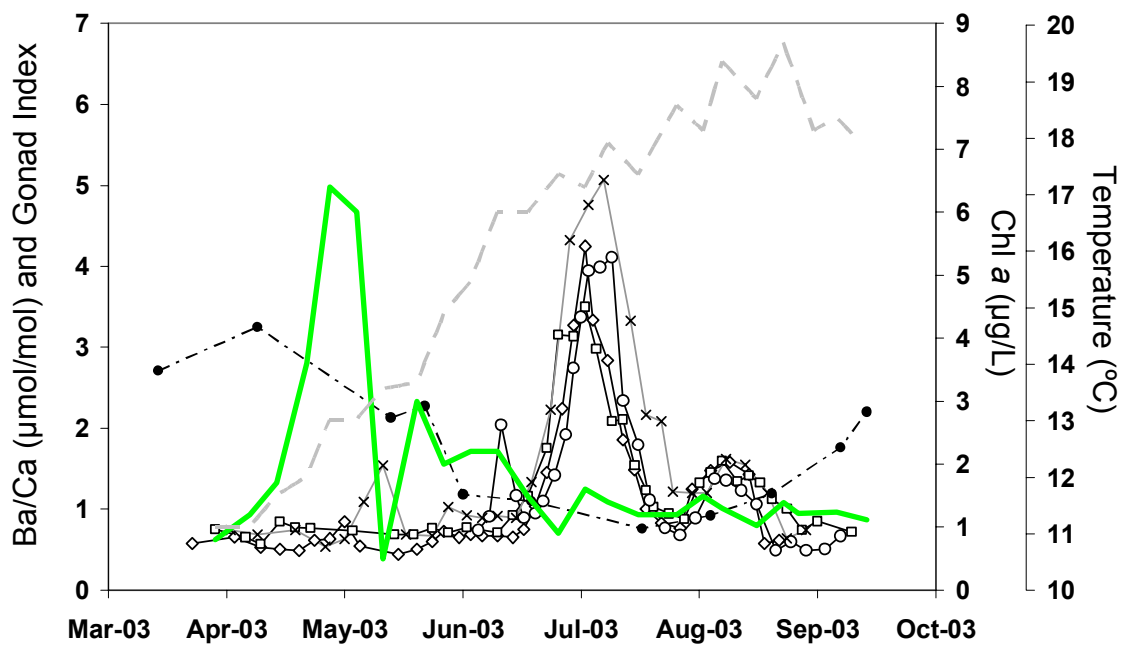


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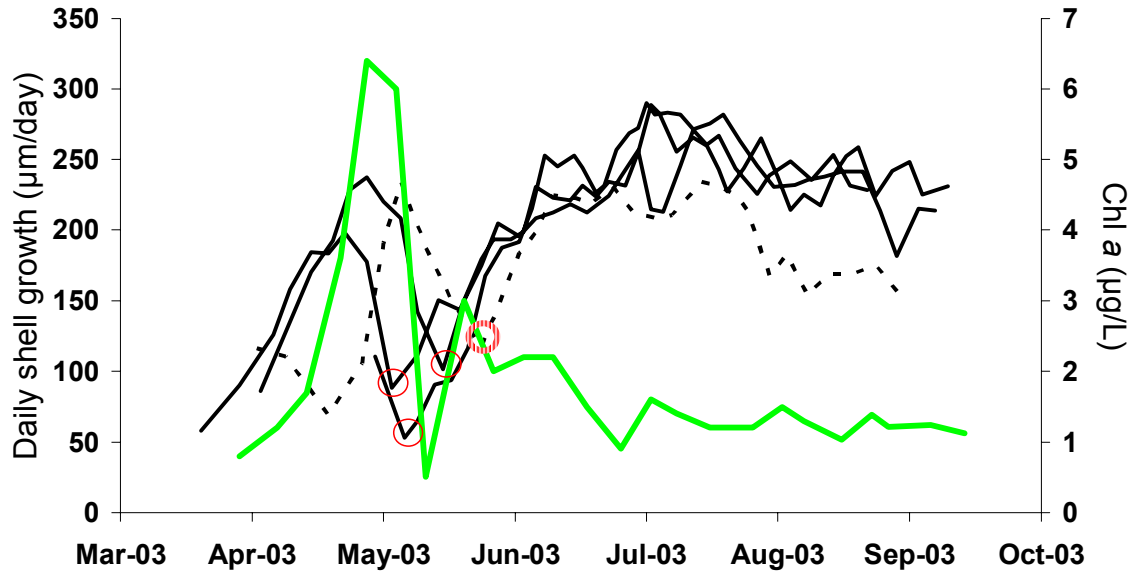


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