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Strong biological controls on Sr/Ca ratios in aragonitic marine bivalve shells

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[1] It is well known that skeletal remains of carbonate secreting organisms can provide a wealth of information about past environments. Sr/Ca ratios have been successfully used as a temperature proxy in corals and sclerosponges. Previous work on aragonitic bivalve shells has not been conclusive but suggests a major control of growth rate on Sr/Ca ratios. As many studies have used bivalve growth rates to determine temperature, we tested if Sr/Ca ratios could predict temperature through its relationship with growth rate. Shells from the two species of clams from the same family (veneroidea) studied here, *Saxidomus giganteus* and *Mercenaria mercenaria*, show vastly different seasonal Sr/Ca profiles. A strong relationship between average annual Sr/Ca ratios and annual growth rate was found in *S. giganteus* shells from both Washington ($R^2 = 0.87$) and Alaska ($R^2 = 0.64$), USA, but not in *M. mercenaria* shells from North Carolina, USA. Furthermore, the Sr/Ca–growth rate relationship was also evident upon a more detailed inspection of subannual growth rates in *S. giganteus* ($R^2 = 0.73$). Although there were significant positive correlations between Sr/Ca ratios and temperature in *S. giganteus* shells, the correlations were weak ($0.09 < R^2 < 0.27$), and thus Sr/Ca ratios cannot be used as a reliable temperature proxy in these species of aragonitic bivalves. It is clear from this study that Sr/Ca ratios are not under thermodynamic

control in either clam species, since thermodynamics predict a negative correlation between Sr/Ca ratios and temperature in aragonite. This points toward dominance of biological processes in the regulation of Sr^{2+}. This is also reflected by the largely differing Sr/Ca partition coefficients (D_{Sr}) in these shells ($D_{Sr} \approx 0.25$), when compared to inorganic, coral, and sclerosponge studies ($D_{Sr} \approx 1$), all of which show a negative dependence of Sr/Ca on temperature. We suggest that caution be taken when using Sr/Ca in any biogenic aragonite as a temperature proxy when the D_{Sr} greatly deviates from one, as this indicates the dominance of biological controls on Sr/Ca ratios.

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1. Introduction

[2] Skeletal remains of carbonate secreting organisms potentially offer a wealth of information about past environments. For example, oxygen isotope ratios ($\delta^{18}O$) in biogenic carbonates are a powerful tool for paleotemperature reconstruction. However, interpretation is complicated since the isotopic composition of carbonates is also dependent on the $\delta^{18}O$ of the water, which in itself is related to salinity [see *Epstein et al.*, 1953]. This can cause severe problems when attempting to obtain paleotemperature records from estuarine bivalves [e.g., *Klein et al.*, 1996; *Gillikin et al.*, 2005] Alternative sea surface temperature (SST) proxies that are independent of other environmental variables would therefore be of great value.

[3] Sr/Ca ratios have been proposed as such a proxy in biogenic aragonite and have been extensively utilized in both corals and sclerosponges with great success [e.g., *Beck et al.*, 1992; *Rosenheim et al.*, 2004]. Sr/Ca ratios in inorganic (or abiogenic) aragonite is a function of the Sr/Ca ratio of the solution, expressed as a partition coefficient, $D_{Sr} = (Sr/Ca)_{aragonite}/(Sr/Ca)_{water}$, where Sr/Ca are typically given as molar ratios [e.g., *Dietzel et al.*, 2004]. The Sr/Ca ratio of the solution is not of major concern, as for many estuaries the Sr/Ca ratio of the water remains relatively constant above a salinity of about 10 [e.g., *Dodd and Crisp*, 1982], which precludes a large salinity effect for many marine and estuarine species. Inorganic precipitation experiments have shown that D_{Sr} in aragonite is inversely related to temperature [*Kinsman and Holland*, 1969; *Dietzel et al.*, 2004] and is independent of precipitation rate [*Zhong and Mucci*, 1989]. Mineralogy also significantly affects Sr incorporation, with aragonite typically containing about one order of magnitude more Sr than calcite due to the differences in the crystal lattice structure and D_{Sr} being strongly precipitation rate dependent in calcite [*Kinsman and Holland*, 1969; *Tesoriero and Pankow*, 1996].

[4] Although many studies have utilized Sr/Ca ratios in corals for paleotemperature reconstruction [e.g., *Beck et al.*, 1992; *McCulloch et al.*, 1999], other studies have illustrated some complications with this proxy. For example, significant differences in Sr/Ca-SST relationships between corals growing at the same site have been reported [*de Villiers et al.*, 1995; *Cardinal et al.*, 2001] and coral Sr/Ca ratios have also been found to be inversely related to calcification or growth rate, indicating that Sr/Ca ratios are not solely dependent on SST in corals [e.g., *de Villiers et al.*, 1995; *Ferrier-Pagès et al.*, 2002; *Cohen and McConnaughey*, 2003].

[5] Sr/Ca ratios in bivalve shells have been less well studied than in corals and there has been much debate over its interpretation. As early as 1956, it was proposed that the Sr/Ca ratio in bivalve shells was dependent on growth rate [*Swan*, 1956]. Later, *Dodd* [1965] found a large negative correlation between temperature and Sr/Ca ratios in *Mytilus edulis* aragonite. *Buchardt and Fritz* [1978] found no correlation with either growth rate or temperature and Sr/Ca ratios in a freshwater aragonitic

gastropod. *Palacios et al.* [1994] found that Sr/Ca ratios were more strongly correlated to age than to growth rate in the chondrophores (an internal shell structure located at the hinge) of extinct and extant populations of *Mya arenaria*. They found an increase in Sr/Ca ratios with age in both populations and a decrease with increasing growth rate in the extinct population, but not in the extant population. On the basis of one shell, *Purton et al.* [1999] concluded that Sr/Ca ratios were metabolically controlled in aragonitic bivalves, since Sr/Ca ratios increased with decreasing growth rate. However, the results of both *Palacios et al.* [1994] and *Purton et al.* [1999] may not be representative because they analyzed the inner layers of the shell, which is known to be repeatedly dissolved and reprecipitated by the animal to buffer internal pH during anaerobic respiration [*Crenshaw*, 1980] and where biomineralization mechanisms can greatly differ [*Wheeler*, 1992]. *Stecher et al.* [1996] found that there was a negative correlation between Sr/Ca ratios and δ^{18}O (therefore positive between Sr/Ca ratios and temperature) in the shell of a modern and a Pleistocene *Mercenaria mercenaria* while there was a positive relationship (negative with temperature) in a *Spisula solidissima* shell, which they attributed to differences in season of maximal growth (i.e., a positive relationship between growth rate and Sr/Ca ratios). *Hart and Blusztajn* [1998] also found a positive relationship between Sr/Ca ratios and temperature in *Arctica islandica* and applied this relationship to derive SST from hydrothermal vent clams (*Calyptogena magnifica*). *Dutton et al.* [2002] found a negative correlation between Sr/Ca ratios and δ^{18}O in bulk shell samples of the extinct aragonitic bivalve *Cucullaea*; however, they could not find a similar relationship in a shell sampled at high resolution. Finally, *Takesue and van Geen* [2004] found that Sr/Ca ratios decreased with decreasing growth rate in the aragonitic shells of *Protothaca staminea*. From this it is clear that there is no consensus on the effect of temperature and/or growth on aragonitic bivalve Sr/Ca ratios, which therefore may be species specific.

[6] Despite the conflicting reports in the literature, interest in Sr/Ca ratios in bivalve shells as a temperature proxy is still high at international congresses [e.g., *Tripati et al.*, 2004; *Watanabe et al.*, 2004].

[7] Although it seems there is no direct relationship between temperature and Sr/Ca ratios in aragonitic bivalves, but rather a relationship between growth rate and/or metabolism and Sr/Ca ratios, the latter may still be a useful environmental proxy. In fact, growth rates in bivalves can be dependent on many factors including salinity, temperature and food supply [e.g., *Lewis and Cerrato*, 1997; *Witbaard et al.*, 2003; *Strom et al.*, 2004]. In particular there is often a strong correlation between temperature and both shell growth and metabolism [*Lewis and Cerrato*, 1997; *Heilmayer et al.*, 2004]. Indeed, there have been many reports using bivalve shell growth increments to determine SST and other environmental parameters [e.g., *Schöne et al.*, 2002, 2003; *Strom et al.*, 2004]. Thus, indirectly, Sr/Ca ratios in bivalve shells may record temperature.

[8] Due to their wide distribution and good preservation, bivalve shells are potentially excellent archives of (paleo)environmental information. Two species that could be particularly suitable for such analyses are *Mercenaria mercenaria* (common along the East coast of North America) and *Saxidomus giganteus* (common along the Northwest coast of North America). These species are well represented in both archaeological and geological deposits [e.g., *Kvenvolden et al.*, 1979; *Stecher et al.*, 1996; *Hetherington and Reid*, 2003] and can live for several decades [*Quayle and Bourne*, 1972; *Peterson*, 1986].

[9] To test if Sr/Ca ratios in aragonitic bivalves can indeed provide environmental information, we used high-resolution sampling techniques to measure both δ^{18}O and Sr/Ca ratios in several specimens of two infaunal clam species from North America, *Mercenaria mercenaria* (from North Carolina, USA) and *Saxidomus giganteus* (from Washington and Alaska, USA), both belonging to the family veneroidea. In particular we aim to determine whether Sr/Ca ratios are controlled by growth rate and if so, whether growth rate and temperature are coupled tightly enough to allow the use of Sr/Ca ratios as an indirect SST proxy.

2. Methods

2.1. Sample Collection and Preparation

[10] Three *Saxidomus giganteus* were collected from Puget Sound, Washington and one from Old Harbor, Kodiak Island, Alaska, USA, and nine *Mercenaria mercenaria* were collected from the Cape Lookout region of North Carolina, USA (i.e., Wade Creek, Johnson Creek and Back Sound; full data are listed in Table 1). All specimens were collected alive. *Elliot et al.* [2003] have shown that *M. mercenaria* precipitate aragonite shells. We

Table 1. Samples and Environmental Data

Species	Shell Name	Location	Sediment	SST Range, °C	Salinity Range	Date Collected	Clam Age, years	Number of Years Sampled
Saxidomus giganteus	B1	Puget Sound, WA	gravely mud	7–17	21–30	18 Sept. 01	11	10
	B2	Puget Sound, WA	gravely mud	7–17	21–30	18 Sept. 01	11	10
	B3	Puget Sound, WA	gravely mud	7–17	21–30	18 Sept. 01	11	5
	OH1	Old Harbor, Kodiak Is., AK	gravely mud	0–13	18–32	28 June 03	21	19
Mercenaria mercenaria	MW1	Jarrett Bay, NC	mud	1–35	23–37	15 Sept. 02	9	4.5
	MW2	Wade Creek, NC	mud	1–35	23–37	20 Aug. 03	7	7
	MB1	Back Sound, NC	sandy	2–30[a]	28–34[a]	23 Aug. 03	4.5	4.5
	MB2	Back Sound, NC	sandy	2–30[a]	28–34[a]	23 Aug. 03	23	22[b]
	MB3	Back Sound, NC	sandy	2–30[a]	28–34[a]	May 1980	16	16[b]
	MB4	Back Sound, NC	sandy	2–30[a]	28–34[a]	May 1980	24	23[b]
	MJ1	Johnson Cr., NC	mud	2–30[a]	28–34[a]	1982	7	7[b]
	MJ2	Johnson Cr., NC	mud	2–30[a]	28–34[a]	1982	28	27[b]
	MJ3	Johnson Cr., NC	mud	2–30[a]	28–34[a]	1982	34	33[b]

[a] Based on *Peterson et al.* [1987].
[b] Sampled at an annual resolution.

conducted X-ray diffraction measurements of powdered samples of a *S. giganteus* shell, which revealed pure aragonite. Sections of the shells were cut with a diamond saw along the axis of maximal growth (dorso-ventral), rinsed with deionized water, air-dried and mounted on microscopic slides. Carbonate powder was milled from the shell cross-sections using a 300 μm drill bit and Merchantek Micromill (a fixed drill and computer controlled micro positioning device), which allows precise sampling. To avoid shell regions that may have been altered (e.g., the inner layer may have been dissolved and reprecipitated (see section 1), while the outermost layer may have exchanged ions with seawater as they were in direct contact), and to be consistent with other studies, samples were taken from the outer shell layer of *S. giganteus* (which have no middle layer), avoiding the outermost part [see *Gillikin et al.*, 2005], and from the middle layer of *M. mercenaria* [see *Stecher et al.*, 1996; *Elliot et al.*, 2003]. Various sampling distances were used (150 μm to 1 mm) depending on growth rate (i.e., fewer samples in regions of high growth). High-resolution Sr/Ca profiles were obtained using a laser ablation system (see Sample Analysis, section 2.3). As the three *M. mercenaria* sampled at high resolution did not show expected results (see Discussion), six more *M. mercenaria* were sampled at low resolution (annual) using the growth lines on the shells, which are formed annually in late August to late September in this region [*Peterson et al.*, 1985]. Annual sampling (low resolution) was carried out by milling lines across the annual growth increment, thus providing average annual Sr/Ca ratios for these six shells.

2.2. Environmental Data

[11] Both SST and salinity data from Puget Sound, Washington (sampled monthly from October 1997 to September 2001) were provided by the King County Environmental Laboratory. Hourly SST data (September 2002 to August 2004) from Kodiak Island, Alaska, are from the National Oceanographic and Atmospheric Administration (data access at http://co-ops.nos.noaa.gov/data_retrieve.shtml?input_code=001000111pan&station=9457292+Kodiak+Island+,+AK, 2004) and salinity is from *Taylor* [2004, and references therein]. SST from Wade Creek, North Carolina, was recorded hourly for one year (September 2002 to August 2003) using a temperature logger (Onset Computer Corporation, StowAway TidbiT), while salinity was measured sporadically over a two year period using a WTW multiline P4 conductivity meter. Data from Back Sound are from *Peterson et al.* [1987]. Although no data were available from Johnson Creek, it probably experiences SST and salinities similar to Back Sound. Average monthly SST data are represented in Figure 1. For all samples, salinity was well above 10 and hence Sr/Ca ratios in the water can be considered constant [*Dodd and Crisp*, 1982; *Klein et al.*, 1996].

2.3. Sample Analysis

[12] Oxygen and carbon isotope analysis was performed using a ThermoFinnigan Kiel III coupled to

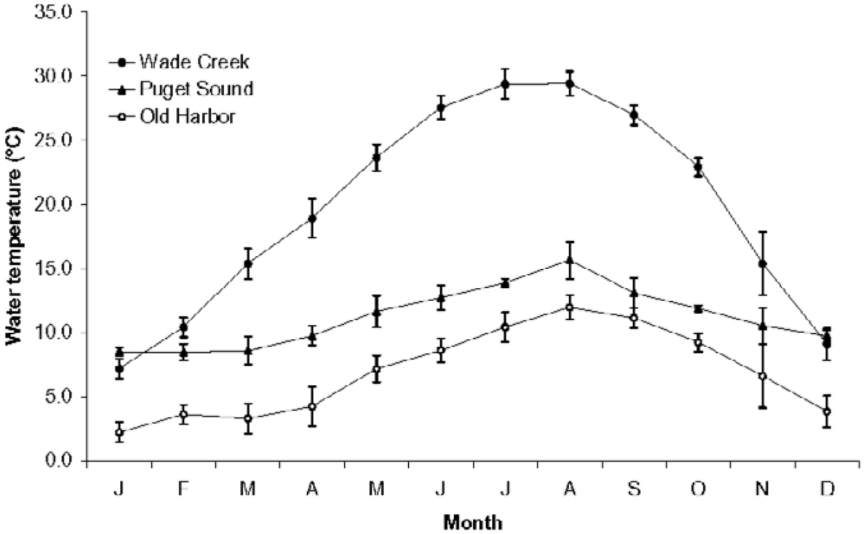

Figure 1. Monthly average SST and standard deviations from the three locations in this study. Data from Puget Sound, Washington, are averages of monthly temperature data collected between October 1997 and September 2001. Data from Old Harbor, Kodiak Island, Alaska, represent averaged data collected hourly between September 2002 and August 2004. Wade Creek, North Carolina, data are averaged hourly temperature data, recorded between September 2002 and August 2003.

a ThermoFinnigan Delta+XL dual inlet isotope ratio mass spectrometer (IRMS). The samples were calibrated against the NBS-19 standard ($\delta^{18}O = -2.20‰$, $\delta^{13}C = +1.95‰$) and data are reported as ‰ VPDB using the conventional delta notation. The reproducibility (1σ) of the routinely analyzed carbonate standard is better than 0.1‰ for both $\delta^{18}O$ and $\delta^{13}C$ (more details are given by *Gillikin et al.* [2005]).

[13] High-resolution Sr/Ca sampling and analysis of all shells was carried out on a laser-ablation inductively coupled plasma-mass spectrometer (LA-ICP-MS) and data 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 (~50 μm spots) directly in the holes of the isotope sampling allowing direct alignment of Sr/Ca and isotope profiles [cf. *Toland et al.*, 2000]. Calibration (including blank subtraction and drift correction) was performed offline following *Toland et al.* [2000]. LA-ICP-MS Sr/Ca reproducibility over the entire sampling period (>1 year) was better than 0.1 mmol/mol (1σ) based on replicate measurements of shell material. Details of LA-ICP-MS operating conditions are given by *Lazareth et al.* [2003]. Briefly, the system consists of a Fisons-VG frequency quadrupled Nd-YAG laser (266 nm) coupled to a Fisons-VG PlasmaQuad II+ mass spectrometer.

[14] LA-ICP-MS data were validated with solution nebulization high-resolution ICP-MS (SN-HR-ICP-MS; Finnigan MAT Element2). SN-HR-ICP-MS sampling was performed by drilling directly beneath the isotope sample, thus removing surface contamination (see section 2.1). Carbonate powders from the high-resolution LA-ICP-MS validation and low-resolution annual samples (~150 μg) were dissolved in a 1 mL 5% HNO_3 solution containing 1 μg l^{-1} of In and Bi, which were used as internal standards. SN-HR-ICP-MS Sr/Ca reproducibility over the entire sampling period was better than 4% (1σ) based on replicate measurements of two reference materials (CCH1, n = 36, Sr/Ca = 0.359 mmol/mol (values from *Govindaraju* [1994]) and MACS1, n = 18, Sr/Ca = 0.255 mmol/mol). Considering the low Sr concentrations in these two standards, an in-house standard produced from a *S. giganteus* shell was also analyzed (approximately 25 mg of milled carbonate was dissolved in 50 mL of 5% HNO_3, diluting this four times at the time of analysis provided similar concentrations to the samples). The higher concentration of the in-house standard provided better reproducibility (2.6% (1σ), Sr/Ca = 1.99 ± 0.05, n = 9) and is more indicative of the reproducibility of our samples. There was a significant linear correlation between LA-ICP-MS and SN-HR-ICP-MS results from the B1 shell, with the slope not significantly different from one (slope = 0.99, $R^2 = 0.90$, $p < 0.0001$, n = 63, intercept not

significant ($p = 0.62$)); note that sample sizes are different, 50 μm for LA vs. 300 μm for micromilling, so this can also include small-scale spatial variability in the sample itself. Therefore our LA-ICP-MS calibration method can be considered robust. Additionally, this illustrates that the sample size difference between drilling (300 μm; SN-HR-ICP-MS and $\delta^{18}O$ sampling) and LA (50 μm) does not influence the Sr/Ca profiles and thus allows direct comparison of Sr/Ca ratios and $\delta^{18}O$ values.

2.4. Data Treatment

[15] To asses the similarity between the Sr/Ca profiles of the three *S. giganteus* shells collected from the same location (Puget Sound), the $\delta^{18}O$ profiles of shell B1 and B3 were fit to shell B2. This was achieved by using a phase demodulation method [see *De Ridder et al.*, 2004]. Briefly, this method models the intraannual variation in growth rate by using Fourier analysis. Once the variation in growth rate of each shell is known, the time axes (x axes) can be scaled accordingly and the $\delta^{18}O$ profiles of the three shells can be fit to one scale. Considering that the Sr/Ca analyses were perfectly aligned with $\delta^{18}O$ analyses (see section 2.3), the fitting of the $\delta^{18}O$ profiles now allows a direct comparison of Sr/Ca profiles between the three shells. Similarly, this method was also used to fit the $\delta^{18}O$ calculated temperature to the instrumental temperature (see *Gillikin et al.* [2005] for full details), which we used here to derive daily growth rates (see section 4.1).

2.5. Terminology

[16] Considering that we discuss our results in the context of calcification processes, the distinction between growth rate and calcification rate should be made. In this study, the term growth rate is defined as the dorso-ventral linear extension of the shell per unit time (or growth increment per time). It must be noted that variations in this growth rate may differ from variations in the calcification rate (or crystal growth rate), which can be difficult to estimate (see *Lorens* [1981] and *Carpenter and Lohmann* [1992] for discussions on this). It is well known that growth rates (i.e., linear shell extension rates) in bivalves decrease through ontogeny [e.g., *Peterson*, 1986; *Schöne et al.*, 2002], and vary within one year [*Peterson and Fegley*, 1986; *Lorrain et al.*, 2004a]. Since decreasing shell growth rate is usually accompanied by a thickening of the shell, variations in the total $CaCO_3$ precipitated by the animal each year and linear shell growth rate may not necessarily correlate [e.g., *Lorrain et al.*, 2004a]. On the other hand, along linear transects, as sampled in this study, we may expect calcification rate and shell growth rate to vary in a similar fashion. Unlike corals, bivalve shell density should not change dramatically along the shell. Therefore differences in linear growth can result either from constant calcification rates and non continuous growth over the year, or varying calcification rates and continuous growth. Considering that both of these species apparently grow for most of the year [*Peterson and Fegley*, 1986; *Gillikin et al.*, 2005], it seems highly unlikely that calcification rates remain constant.

3. Results

[17] Oxygen isotope profiles obtained from all seven shells sampled at a high resolution show a clear, relatively smooth, annual cyclicity (Figures 2 and 3). The $\delta^{18}O$ axes in Figures 2 and 3 are inverted in order to reflect a relative temperature scale. More positive $\delta^{18}O$ values correspond to winter temperatures and more negative $\delta^{18}O$ values to summer temperatures. Sharp, episodic drops in the $\delta^{18}O$ profiles, indicative of short-term freshwater discharge extremes, are absent. As reported by *Gillikin et al.* [2005], the three *S. giganteus* shells from Puget Sound show remarkably similar $\delta^{18}O$ profiles ($0.77 < R^2 < 0.87$) recording the full range of temperatures at this site (i.e., there was no shell growth shutdown temperature); thus the average $\delta^{18}O$ from the three Puget Sound specimens are given in Figure 4. The shell from Alaska has more positive $\delta^{18}O$ indicative of the cooler temperatures this clam experienced (Figure 2d). Growth lines in *S. giganteus* shells were not annual in nature (up to three lines in one year) and were not systematically located in a particular season (data not shown). $\delta^{18}O$ in *M. mercenaria* cover the range of $\delta^{18}O$ measured in the four *S. giganteus* shells (Figure 3), undoubtedly due to the large range of temperatures at the North Carolina sites (see Table 1 and Figure 1). The annual growth lines in *M. mercenaria* shells occurred in late summer as has been previously shown for this location [*Peterson et al.*, 1985].

Figure 2. Sr/Ca ratios (black lines and circles) and $\delta^{18}O$ (gray lines) from the three *S. giganteus* shells from (a–c) Puget Sound, Washington, and (d) the specimen from Old Harbor, Kodiak Island, Alaska. Note that the $\delta^{18}O$ axes are inverted and x axes vary. See Table 1 for more details about each site. Vertical lines indicate the separation of slow and fast growth (see Table 2). The resolution of the $\delta^{18}O$ samples is identical to the Sr/Ca samples.

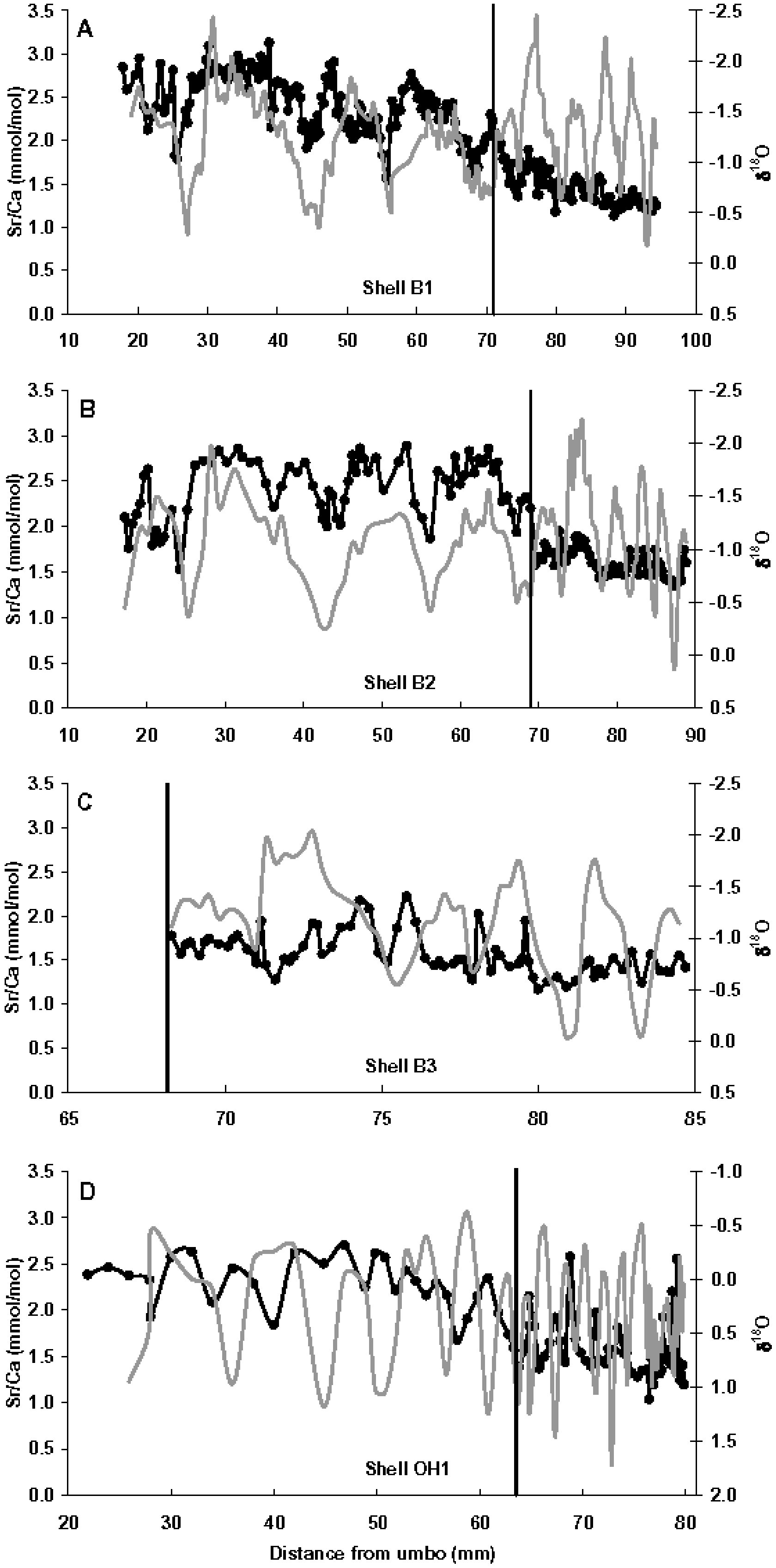
A
Shell B1
B
Shell B2
C
Shell B3
D
Shell OH1
Sr/Ca (mmol/mol)
$\delta^{18}O$
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
10
20
30
40
50
60
70
80
90
100
65
75
85
Distance from umbo (mm)

Figure 2

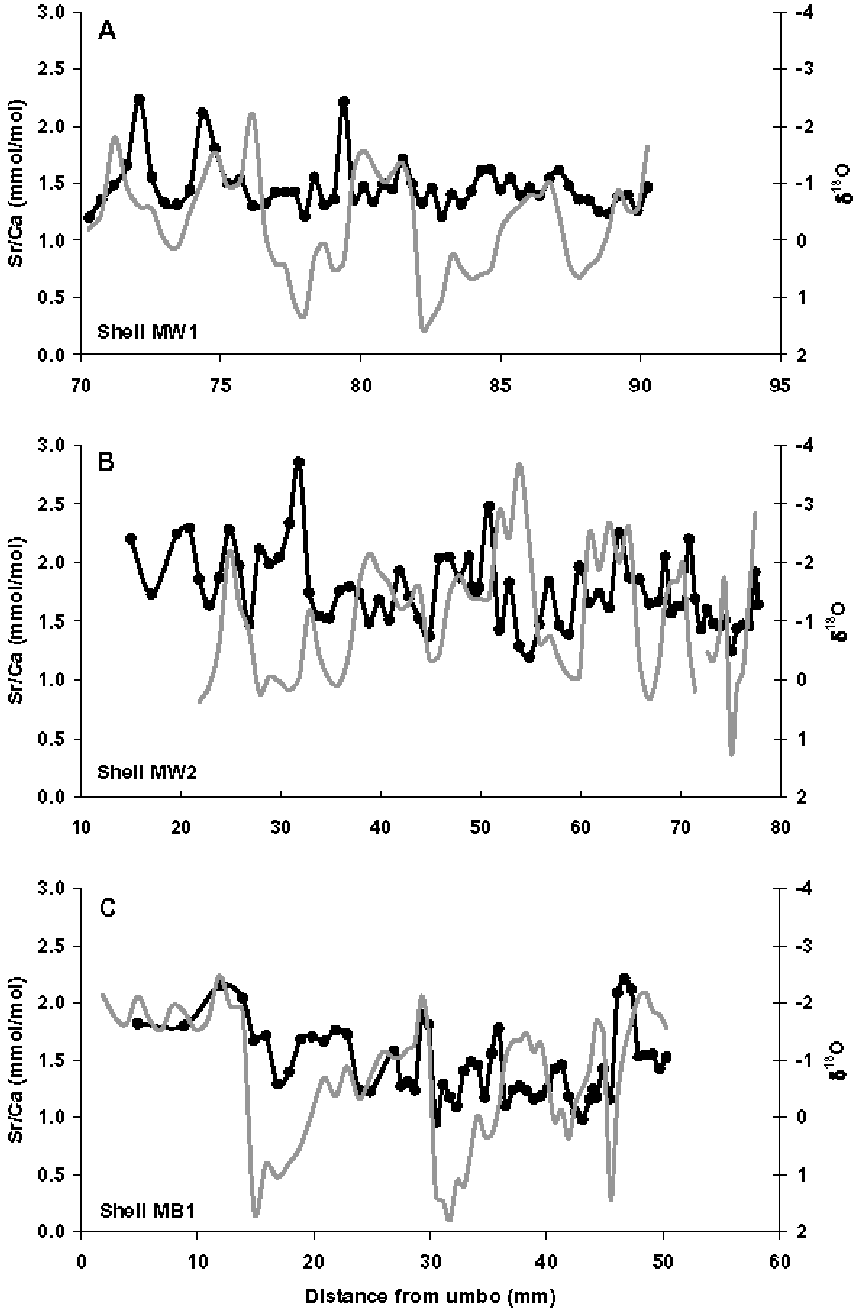

Figure 3. Sr/Ca ratios (black lines and circles) and δ^{18}O (gray lines) from the three *M. mercenaria* shells from North Carolina. (a and b) Shells MW1 and MW2 are from more estuarine sites with muddy sediments, while (c) shell MB1 is from a more marine site with sandy sediments. Note that the δ^{18}O axes are inverted and x axes vary. See Table 1 for more details about each site. The resolution of the δ^{18}O samples is identical to the Sr/Ca samples.

[18] As there is a negligible salinity effect on the δ^{18}O variability in these *S. giganteus* [*Gillikin et al.*, 2005] and *M. mercenaria* [*Elliot et al.*, 2003] shells, δ^{18}O is presumed to be primarily temperature controlled. Using the δ^{18}O profiles as a relative temperature scale, Sr/Ca profiles also show an annual cyclicity near the umbo in shell B1 and B2 (Figures 2 and 4). However, in the slow growing parts of the shell (most recently formed), the cyclicity becomes unclear. This is most easily seen in the Sr/Ca profile of shell B3, in which only the slow growing part of the shell was sampled (Figure 2c; compare x axes). The annual Sr/Ca cyclicity was not observed in the *S. giganteus* shell collected in Alaska, nor in any of the three *M. mercenaria* shells analyzed at high resolution.

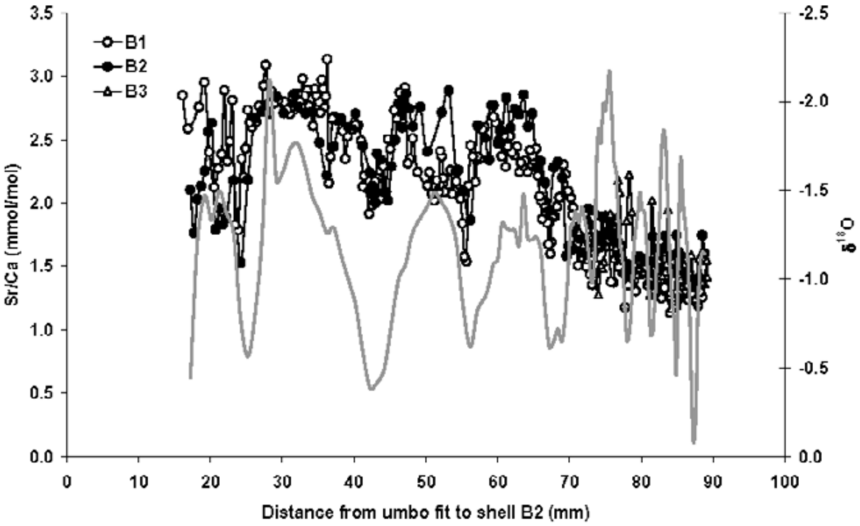

Figure 4. Sr/Ca ratios (black lines with symbols) and average δ^{18}O (gray line) from the three *S. giganteus* shells from Puget Sound, Washington (Figures 2a–2c). Data were fit to the x axis of shell B2 using a phase demodulation method (see section 2). Note that the δ^{18}O axis is inverted.

Detailed inspection of the profiles shows that there is an annual Sr/Ca cycle for both species only in years when annual growth rates were above about 10 mm yr^{-1}, but this is not always the case (Figures 2 and 3). There were no distinct changes in the Sr/Ca profiles in the organic rich regions of shell growth lines for either species.

[19] All *S. giganteus* shells show a clear decrease in Sr/Ca ratios through ontogeny, starting around 2–3 mmol/mol, decreasing to 1–2 mmol/mol as the clams age (Figure 2). Figure 4 illustrates the good correlation between Sr/Ca ratios in the shells from Puget Sound (between B1 and B2: $R^2 = 0.73$, slope not different from one, $p < 0.0001$). As the negative relationship between shell δ^{18}O and temperature is well established [*Epstein et al.*, 1953], the δ^{18}O data were used to delimit annual growth for each shell sampled at high resolution. Simply, the shell δ^{18}O maximum was used as a winter mark and the distance between each of these points was considered as the annual growth rate. The Sr/Ca data between two successive winter marks were then averaged. Combining the 21 years sampled from the three *S. giganteus* shells from Puget Sound resulted in a significant relationship between Sr/Ca ratios and growth rate ($p < 0.0001$) with $R^2 = 0.87$ (Figure 5a). The partially sampled shell (B3) had a lower R^2 (0.69, n = 4) as compared to the other two shells (B1: $R^2 = 0.88$, n = 8; B2: $R^2 = 0.92$, n = 9), undoubtedly due to the small sample size and reduced growth rate range. The shell from Kodiak Island also shows a significant relationship between these parameters, albeit not as strongly as the Puget Sound specimens ($R^2 = 0.64$, $p < 0.0001$, Figure 5a). As can be seen in the high resolution profiles, *M. mercenaria* shells do not show a significant relationship between growth rate and Sr/Ca ratios ($R^2 = 0.04$, $p = 0.56$, Figure 5b). Likewise, the 128 annual growth increments sampled at an annual resolution from six *M. mercenaria* shells do not show a consistent trend with growth rate (Figure 6). Only two of the six shells were found to have a significant positive relationship between annual growth and average annual Sr/Ca ratios; however, growth rate explained only 30 and 56% of the Sr/Ca variation in these two shells (Table 3).

[20] It is clear that the overall relationship between Sr/Ca ratios and δ^{18}O is weak in all shells. There are, however, significant correlations between δ^{18}O and Sr/Ca ratios in *S. giganteus* shells when regions of fast and slow growth are separated (Table 2; see also Figure 2). Although the correlations are weak (maximum $R^2 = 0.27$), the slopes of the fast and slow growing regions were similar between shells B1 and B2 (Table 2). *M. mercenaria* shells on the other hand do not exhibit this trend. There is no discernable relationship between δ^{18}O and Sr/Ca ratios, nor was an ontogenic decrease noted (Figure 3).

4. Discussion

[21] It is becoming increasingly clear that many proposed proxies in biogenic carbonates are complicated by the influence of the physiology of the

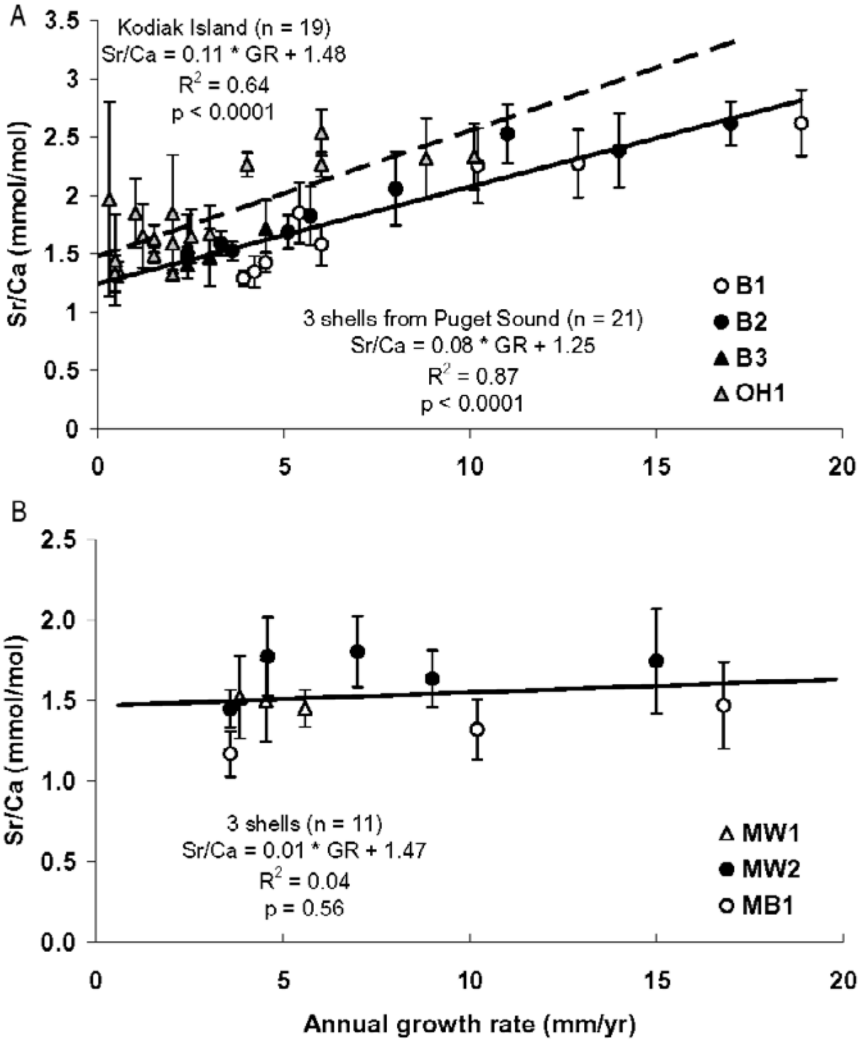

Figure 5. Average annual Sr/Ca ratios versus annual growth rates (GR) (from data in Figures 2 and 3). (a) The three *S. giganteus* shells from Puget Sound, Washington, are included in the same regression (solid line) and are compared with the regression of the 19 year old specimen from Kodiak Island Alaska (dashed line). (b) The three *M. mercenaria* shells are included in the same regression as well. Error bars represent standard deviations; n is the number of annual growth increments included in each regression.

animal precipitating the carbonate [e.g., *Klein et al.*, 1996; *Stecher et al.*, 1996; *Purton et al.*, 1999; *Vander Putten et al.*, 2000; *Zacherl et al.*, 2003; *Lorrain et al.*, 2004a]. However, an animal's physiology is often strongly dependent on the environmental conditions it experiences (see section 1). For elements to reach the site of calcification, they must first pass through biological membranes which can alter the original seawater chemistry [*Wheeler*, 1992], possibly in a predictable manner. Although the elemental contents of the external water may influence the elemental contents of the shell to some degree, it is highly unlikely that variations in the external seawater Sr/Ca ratios are responsible for the approximately 50 to 200% Sr/Ca variations observed in the shells in this study. As previously stated, seawater Sr/Ca ratios should have remained relatively constant in the areas where these bivalves grew. Although some shells experienced low salinities (see Table 1), the δ^{18}O profiles do not show sharp episodic peaks to more negative values as would be expected if the clams were growing during periods of reduced salinity (Figures 2 and 3).

4.1. Are Sr/Ca Ratios Controlled by Growth Rate?

[22] On an annual scale, using δ^{18}O maxima as winter markers, we found that annually averaged Sr/Ca ratios are strongly correlated to annual growth rate in *S. giganteus* shells from Puget

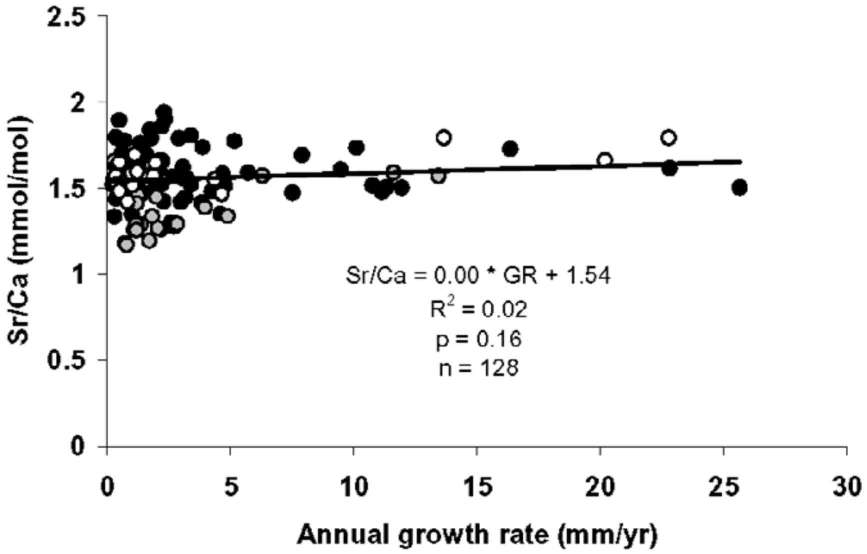

Figure 6. Annual Sr/Ca ratios from the six *M. mercenaria* shells sampled at an annual resolution. Shells MB3 and MJ3, which had significant correlations with growth rate (GR) (see Table 3), are represented by the gray and white symbols, respectively. All data are included in the regression; n is the number of annual growth increments included in the regression.

Sound and to a slightly lesser extent in the *S. giganteus* shell from Alaska (Figure 5a). However, using annual growth rates does not account for subannual variations in growth rate, which is undoubtedly occurring in these shells [*Peterson and Fegley*, 1986; *Elliot et al.*, 2003]. To determine if Sr/Ca ratios are related to growth rate on a subannual scale, which would rule out a purely ontogenic effect [see *Palacios et al.*, 1994], we require subannual growth rate data. This is possible considering that temperature calculated from $\delta^{18}O$ in the shells of *S. giganteus* from Puget Sound covers the full range of instrumental temperature at this site [see *Gillikin et al.*, 2005], indicating these shells very likely grew throughout the year. Therefore calendar dates can be assigned to each sample from these shells with some degree of confidence. This can be done using the method outlined by *Klein et al.* [1996], where the calculated temperature (here using the empirical equation of *Böhm et al.* [2000]) from each sample is fit with the instrumental temperature, for which the calendar dates are known (see section 2.4). Then with the sample distance and the time difference between the samples, a daily growth rate can be calculated. Comparing Sr/Ca ratios and daily growth rates in the three *S. giganteus* shells (B1, B2 and B3) resulted in a significant positive relationship between both factors (Figure 7; $R^2 = 0.73$, $p < 0.0001$, n = 350). The relationship was not as good in the shell where only the slow growing section was sampled (shell B3: $R^2 = 0.31$, $p < 0.0001$, n = 53) as compared to the fully sampled shells (shell B1: $R^2 = 0.73$, $p < 0.0001$, n = 179; shell B2: $R^2 = 0.70$, $p < 0.0001$, n = 118). Thus, even at a more detailed level, growth rate explains much of the variability of Sr/Ca in these *S. giganteus* shells. Therefore the relationship between Sr/Ca ratios and annual growth rate is not caused by an age effect as was noted by *Palacios et al.* [1994].

[23] In opposition, Sr/Ca ratios in *M. mercenaria* shells were not significantly correlated to growth rate in seven of the nine shells analyzed (Figures 5b and 6, Table 3). Two factors may account for the discrepancy between the Sr/Ca patterns in *M. mercenaria* shells in this study as compared to the *M. mercenaria* shells analyzed by *Stecher et al.* [1996]. First, *Stecher et al.* [1996] sampled

Table 2. Regression Data for Sr/Ca Ratios and $\delta^{18}O$ in *S. giganteus*[a]

Shell and Growth	Slope	R^2	p<	n
B1 fast	−0.42	0.21	0.0001	120
B1 slow	−0.11	0.09	0.05	62
B2 fast	−0.44	0.22	0.001	56
B2 slow	−0.16	0.27	0.0001	63
B3 slow	−0.09	0.03	n.s.	54
OH1 fast	0.06	0.01	n.s.	31
OH1 slow	0.23	0.13	0.01	52

[a] Data are separated between regions of fast and slow growth. The separation between fast and slow growth was chosen on the basis of the $\delta^{18}O$ profile (see Figure 2). n.s., not significant at $\alpha = 0.05$. Shells B1-3: Puget Sound, WA; OH1: Kodiak Island, AK.

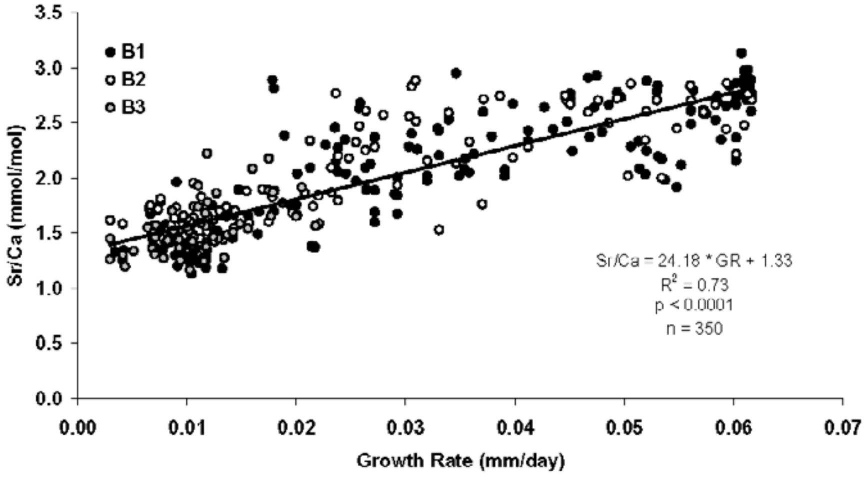

Figure 7. All Sr/Ca data from the three *S. giganteus* shells from Puget Sound, Washington, versus calculated daily growth rate (GR) (see text). All data are included in the regression; n is the number of samples included in the regression.

their modern clam from a marine site with sandy sediment (Delaware, USA), which could imply differences in Sr controls between the same species depending on habitat. However, even though we sampled our nine clams from both estuarine muddy sediments and sandy marine sediments, we did not find anything comparable to *Stecher et al.* [1996] for *M. mercenaria*. A second possibility for the difference may be that growth rates in the shells analyzed by *Stecher et al.* [1996] were generally higher than the growth rates of the *M. mercenaria* analyzed in this study, which could imply that differences in nutrient availability or other site-specific differences could be responsible for the discrepancy. Overall, we could not find a satisfactory explanation based on our current knowledge of Sr incorporation into bivalve shells.

[24] Despite the good correlation between growth and Sr/Ca ratios in *S. giganteus*, the fact that there is no precipitation rate effect in inorganic aragonite [*Zhong and Mucci*, 1989], and that the *M. mercenaria* shells analyzed in this study do not consistently show a relationship between growth rate and Sr/Ca ratios, implies that Sr/Ca ratios are not under direct control of growth rate. Therefore there is no general mechanism that can answer the question of whether Sr/Ca ratios are controlled by growth rate.

4.2. Can Sr/Ca Ratios Be Used as a Temperature Proxy?

[25] The inverse relationship between $\delta^{18}O$ in bivalve shells and temperature is well established [*Epstein et al.*, 1953]. *Elliot et al.* [2003] and *Gillikin et al.* [2005] have shown that variations of $\delta^{18}O$ in the shells of both species used in this study are largely temperature controlled, with temperature explaining most of the $\delta^{18}O$ variability in the *S. giganteus* shells used in this study ($R^2 = 0.83$ [see *Gillikin et al.*, 2005]). Therefore, if Sr/Ca ratios are under thermodynamic control, there should be a negative relationship between Sr/Ca ratios and temperature, and a positive relationship between Sr/Ca ratios and $\delta^{18}O$. However, we did not find any positive correlations between $\delta^{18}O$ and Sr/Ca ratios in either species (correlations between Sr/Ca ratios and $\delta^{18}O$ in these shells are negative), aside from a very weak, but significant positive correlation in the *S. giganteus* shell from Kodiak Island ($R^2 = 0.13$, $p < 0.01$, Table 2). This further stresses that Sr/Ca ratios are not under thermodynamic control and that biological effects on Sr incorporation dominate in these bivalves.

[26] If Sr/Ca ratios are correlated with growth rate, and growth rate is correlated with temperature, then Sr/Ca ratios should correlate fairly well with $\delta^{18}O$.

Table 3. Regression Data of Sr/Ca Ratios and Annual Growth Rate in *M. mercenaria* Sampled at an Annual Resolution[a]

Site	Shell	Slope	R^2	p<	n
Back Sound	MB2	0.00	0.00	n.s.	22
	MB3	0.03	0.56	0.001	16
	MB4	0.02	0.13	n.s.	23
Johnson Creek	MJ1	−0.01	0.03	n.s.	7
	MJ2	−0.01	0.06	n.s.	27
	MJ3	0.01	0.30	0.01	33

[a] n.s., not significant at $\alpha = 0.05$.

However, despite the evidence that Sr/Ca ratios are tightly coupled with growth rate in *S. giganteus* (Figure 7), and growth rate is often following temperature in bivalves (see section 1), Sr/Ca ratios are not very well correlated with $\delta^{18}O$ ($0.09 < R^2 < 0.27$; see Table 2). Therefore, disappointingly, Sr/Ca ratios cannot be used as a reliable temperature proxy in these bivalves. Although the good correlation between Sr/Ca ratios between the different shells of *S. giganteus* that grew in Puget Sound (Figure 4) could indicate an environmental control on Sr/Ca ratios, the correlation is probably the result of the clams having similar ages and growth rate being correlated between them.

[27] The discussion above suggests that there is a biological control on Sr/Ca ratios in bivalve shells. Additional evidence for this is given by comparing the D_{Sr} of inorganic, coral, and sclerosponge aragonite with the D_{Sr} of aragonitic bivalves. The D_{Sr} of inorganic, coral, and sclerosponge aragonite is typically around 1 [e.g., *McCulloch et al.*, 1999; *Dietzel et al.*, 2004; *Rosenheim et al.*, 2004], while in aragonitic bivalves it is around 0.25 [*Palacios et al.*, 1994; *Stecher et al.*, 1996; *Takesue and van Geen*, 2004; this study], indicating a strong biological regulation of Sr in aragonitic bivalves. Although biogenic aragonites with Sr/Ca ratios far from expected equilibrium values (i.e., $D_{Sr} = 1$) may still be faithful recorders of the environment, we stress that care should be taken when using these carbonates due to the high probability of dominating biological controls on Sr/Ca ratios.

4.3. What Controls Sr/Ca Ratios in Aragonitic Bivalves?

[28] Biomineralization in bivalves takes place in the extrapallial fluid (EPF), a thin film of liquid between the calcifying shell surface and the mantle epithelium [*Wheeler*, 1992]. Elements may move into the EPF through the epithelial mantle cells via active (i.e., intracellular transport) or inactive processes (i.e., intercellular (or paracellular) transport through, e.g., "gap" junctions) [see *Crenshaw*, 1980; *Wheeler*, 1992; *Klein et al.*, 1996]. In the marginal mantle epithelium (where the shell areas we analyzed are formed) it is believed that active processes dominate [*Crenshaw*, 1980]. Two enzymes which have been determined to be of great importance in active calcification are Ca^{2+}-ATPase and carbonic anhydrase (CA). Ca^{2+}-ATPase pumps Ca^{2+} to the EPF while removing 2 H^+, and CA catalyses the reaction of bicarbonate to CO_2, which can then easily diffuse through membranes [*Crenshaw*, 1980; *Cohen and McConnaughey*, 2003]. Ca^{2+}-ATPase not only supplies Ca^{2+} to the site of calcification, but helps concentrate CO_3^{2-} at the calcification site by pumping protons away [*Cohen and McConnaughey*, 2003]. It is therefore logical that when Ca^{2+}-ATPase activity increases, so do calcification rates (and presumably shell growth or extension rates increase as well). *Ferrier-Pagès et al.* [2002] found that both Ca and Sr in corals were inhibited by a calcium channel blocker, illustrating that both elements can use similar pathways. However, the enzyme Ca^{2+}-ATPase does have a higher affinity for Ca^{2+} [*Yu and Inesi*, 1995]. Therefore increased Ca^{2+}-ATPase activity increases calcification rate and decreases Sr/Ca ratios by increasing Ca^{2+} disproportional to Sr^{2+}, so Sr/Ca ratios and growth rates should be inversely correlated. This inverse correlation between Sr/Ca ratios and extension rates (and calcification rates) is observed in corals [*de Villiers et al.*, 1995; *Ferrier-Pagès et al.*, 2002], but *S. giganteus* displays the opposite (Figure 7).

[29] *Klein et al.* [1996] also found a positive correlation between Sr/Ca ratios and extension rates in the calcite shell of *Mytilus trossulus*. They proposed a model similar to the Ca^{2+}-ATPase model, where increased metabolic pumping caused lower Sr/Ca ratios. However, to explain the positive correlation between Sr/Ca ratios and extension rates, they used the work of *Rosenberg and Hughes* [1991], which states that growth rate is inversely proportional to mantle metabolic efficiency (measured as glucose consumption). In light of the above discussion, the model of *Klein et al.* [1996] contradicts the logical notion that increased metabolic pumping (which implies increased Ca^{2+}-ATPase activity [see *Cohen and McConnaughey*, 2003]) would increase growth rates and not decrease them. Moreover, in the *Klein et al.* [1996] model, increased metabolic pumping should both decrease Sr/Ca ratios and lead to more negative $\delta^{13}C$ of the EPF and shell (by addition of ^{12}C enriched metabolic CO_2). However, in spite of a threefold Sr/Ca decrease in *S. giganteus* shells (Figure 5a), there was no decrease in $\delta^{13}C$ (data not shown [see *Gillikin et al.*, 2005]). The opposite was true for *M. mercenaria* shells where $\delta^{13}C$ strongly decreased through ontogeny in (up to 4‰ in one shell [see *Meng*, 2004]), but Sr/Ca ratios did not (Figure 5b). Thus a mechanism other than metabolic pumping must control Sr/Ca ratios in bivalve aragonite.

[30] Contrary to the Ca^{2+}-ATPase discussion above, *Wada and Fujinuki* [1976] found that Sr/Ca ratios in the central EPF of two aragonitic

bivalves was higher in summer than in winter and that elemental concentrations were slightly more concentrated during periods of rapid shell growth (summer) and slightly diluted during periods of slow or no shell growth (winter) as compared to the ambient seawater. Although the central EPF is not relevant for this study, this illustrates a biological accumulation of Sr^{2+} in the central EPF during periods of high growth. If this were also the case for the marginal EPF, this could help explain our results from *S. giganteus* shells and other works who found a positive effect of growth rate on aragonitic bivalve shell Sr/Ca ratios [e.g., *Stecher et al.*, 1996; *Dutton et al.*, 2002; *Takesue and van Geen*, 2004]. However, the Sr/Ca ratios of the EPF measured by *Wada and Fujinuki* [1976] did not differ from that of seawater enough to produce aragonite with such low Sr/Ca ratios, which we have more recently confirmed for another aragonitic bivalve [*Lorrain et al.*, 2004b]. This implies that Sr^{2+} discrimination in aragonitic bivalve shells occurs during shell crystallization, at the crystal surface, and not at biological membranes. Indeed, there is strong evidence that there are biological controls on crystal formation [e.g., *Falini et al.*, 1996], which could possibly also regulate Sr/Ca ratios in the shell.

5. Conclusions

[31] It is clear from this study that Sr/Ca ratios are not under thermodynamic control and that biological processes dominate. Growth rate explained much of the variability in *S. giganteus* shells, but there was no discernable pattern in the Sr/Ca profiles of *M. mercenaria* shells. *Stecher et al.* [1996] found a seasonal periodicity in *M. mercenaria* shell Sr/Ca ratios from Delaware Bay which was related to growth rate. Thus either Sr^{2+} is governed by another factor, occasionally correlated to growth rate, or Sr^{2+} incorporation biology is site specific. Although there were significant positive correlations between Sr/Ca ratios and temperature in *S. giganteus* shells ($0.09 < R^2 < 0.27$; using $\delta^{18}O$ as a relative scale of temperature), the correlations were weak and therefore Sr/Ca ratios cannot be used as a reliable temperature proxy in these species of aragonitic bivalves. The strong biological regulation of Sr/Ca ratios can be seen from the deviation of D_{Sr} in these shells ($D_{Sr} \approx 0.25$) from expected equilibrium values (i.e., $D_{Sr} \approx 1$). Inorganic, coral, and sclerosponge aragonite all show a negative dependence of Sr/Ca ratios on temperature, the opposite of what is typically found in bivalves. Considering this strong biological regulation on Sr/Ca ratios, it also seems unlikely that these shells would record changes in seawater Sr/Ca ratios. We suggest that caution be taken when using Sr/Ca ratios in any biogenic aragonite as a temperature proxy when the D_{Sr} greatly deviates from one, as this indicates the dominance of biological controls on Sr/Ca ratios. We strongly believe that if a mechanistic understanding is to be achieved, future research needs to focus on the biochemistry of the elemental pathway through the organs, body fluids, and, most importantly, incorporation into the shell.

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