

Geochemical variation in microstructural shell layers of the southern quahog (*Mercenaria campechiensis*): Implications for reconstructing seasonality

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Abstract

Shells of the northern and southern quahogs (*Mercenaria mercenaria* and *Mercenaria campechiensis*, respectively) from paleontological and archaeological deposits have been used to reconstruct climate, environmental conditions, and ecological relationships. Seasonal fluctuations in temperature and salinity are recorded in shell carbonate as variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and Sr:Ca ratios; however, these environmental proxies have not yet been calibrated for *M. campechiensis*. Previous geochemical studies of quahog shells focused on the outer prismatic layer as an ecological archive. The outer layer is often not preserved in fossil and archaeological shells. Moreover, recent innovations in microsampling techniques allow high-resolution sampling of the middle cross-lamellar layer. This study tests whether outer prismatic and middle cross-lamellar layers record similar variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and Sr:Ca ratios in modern shells of *M. campechiensis* and whether profiles are similar among individuals.

The last 2 years of shell growth from three individuals (6, 7, and 9 years old) collected alive near Bokeelia, southwest Florida, were microsampled for geochemical analyses. $\delta^{18}\text{O}$ varies seasonally relative to translucent (summer) and opaque (winter) growth increments. Variation of $\delta^{18}\text{O}$ from outer and middle layers are identical within and among shells; however, the oldest individual did not preserve the most positive values represented in the two younger shells. $\delta^{13}\text{C}$ from both layers are similar within shells, although the outer layer is more variable and the range of values varies somewhat among individuals. Sr:Ca ratios from the outer and middle layers within shells do not track each other well, and profiles among individuals are different. To evaluate whether a seasonal signal was present, Sr:Ca ratios were compared to $\delta^{18}\text{O}$ values. There was no co-variation within the outer layer in any of the shells; therefore, this layer should be avoided when using Sr:Ca ratios as a temperature proxy. The middle layer from the 6-year-old shell showed no co-variation, the 7-year-old shell exhibited a moderate negative co-variation ($r^2=0.55$, $p<0.01$), and the 9-year-old shell reflected a strong negative co-variation ($r^2=0.72$, $p<0.01$). These findings suggest that Sr:Ca ratios from the middle layer may serve as a proxy for temperature only in older individuals with slower growth rates. Either shell layer can be sampled for assessing seasonality using $\delta^{18}\text{O}$, and environmental interpretations made using $\delta^{13}\text{C}$ values should be treated with caution.

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1. Introduction

Shells of *Mercenaria campechiensis*, the southern quahog, are common remains found in coastal archae-

ological deposits in subtropical, southwest Florida (Walker, 1992, 2000; Walker et al., 1995). Thus, they can potentially serve as archives of Late Holocene climate change and provide insight into human-climate interactions. However, before past climate can be reconstructed from these carbonate skeletal archives, it is essential to examine modern specimens to understand how geochemical variation in their shells relates to the local environmental conditions. Variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and in Sr:Ca ratios contained in the aragonitic shells of northern and southern quahogs (*Merccenaria mercenaria* and *M. campechiensis*, respectively) from paleontological and archaeological deposits have been used in paleoenvironmental, paleoclimate, and paleoecological studies (Jones et al., 1984, 1989, 1990; Jones and Allmon, 1995; Jones, 1996; Stecher et al., 1996; Quitmyer et al., 1997; Arnold et al., 1998; Elliot et al., 2003), although these environmental proxies have not yet been calibrated for *M. campechiensis*.

Early geochemical studies of quahog shells focused on the outer prismatic layer. Because the outer layer is often not preserved in fossil and archaeological shells and because of innovations in microsampling techniques, recent studies have focused on the middle cross-lamellar layer, providing high temporal resolution. Do both microstructural layers record similar variations in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Sr:Ca data? If not, which layer more faithfully records ambient conditions? Are geochemical variations similar among individuals collected at the same time and place? This study tests the hypothesis that both microstructural layers record similar geochemical information within and among individuals that were collected alive.

2. Materials and methods

2.1. Water sampling

The United States Geological Survey (USGS) measured water temperature and salinity from July 1996 to September 2002 at a locality near the north shore of Pine Island within the Charlotte Harbor estuary (Fig. 1). The monitoring site was closer to the main channel than from where the live quahogs were collected. These data allowed evaluation of the potential seasonal growth given the known temperature and salinity thresholds of *M. campechiensis*. Measurements were made at monthly intervals in 2001 and 2002 and more sporadically before then.

The utility of Sr:Ca ratios as a paleothermometer in aragonitic hard parts assumes that the ratio of Sr to Ca does not vary above salinities of 10 psu because they

are conservative elements. Elemental determination of water samples collected along a salinity gradient allowed us to test this assumption. To characterize variation during the summer wet and winter dry seasons, water chemistry was measured at a site in the north end of Pine Island Sound (adjacent to a location known for its archaeological deposits). This location was selected because a very small number of hard-to-find *M. campechiensis* were found nearby, but were never again recovered as it turned out. Water samples were collected at fortnightly intervals from August 2003 to May 2005 (Fig. 1). Salinity was measured using a refractometer. Understanding the mixing relations and seasonal variability of local waters provided an environmental context in which to evaluate geochemical variation in shells. A companion study employing fortnightly water monitoring at another *M. campechiensis* bed is underway to provide a detailed geochemical calibration of this species.

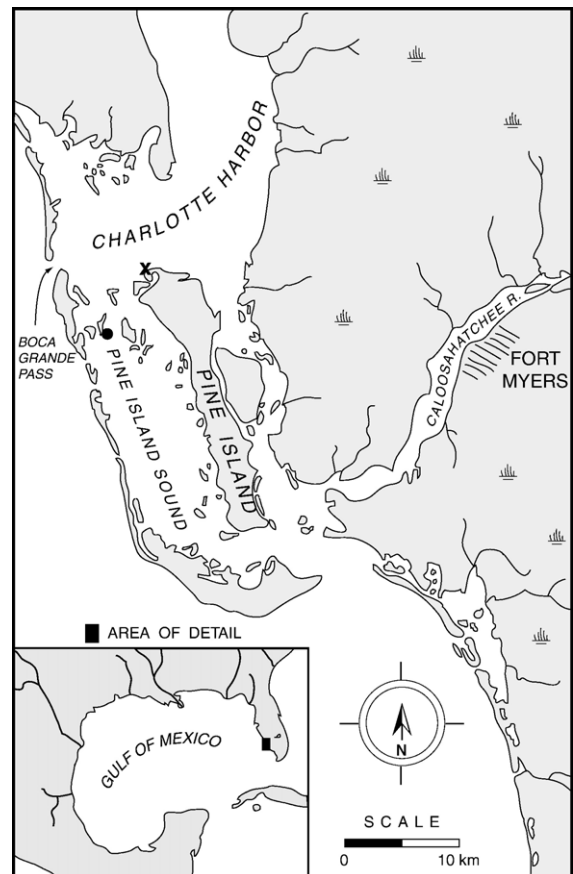


Fig. 1. Map of the study area identifying the location north of Pine Island where live quahogs were collected (marked by an "X"; N26° 42' 31.0", W82° 09' 20.5") and where seasonal variation in Sr:Ca ratios and salinity was monitored (marked by a black circle; N26° 39' 16.0", W82° 12' 42.0"). Gray areas indicate land.

Water samples for elemental analyses were collected 10 cm above the sediment surface using a horizontal point sampler. Thirty milliliters of water was filtered, acidified with HNO₃ to 2 pH, and stored in acid-washed polyethylene bottles. Samples were diluted by one-tenth and analyzed on a JY Horiba Ultima 2C inductive-coupled plasma optical emission spectrometer (ICP-OES). A conductivity standard (IAPSO, seawater at 32 psu) was run every 5 samples. The standards were made gravimetrically from high purity stock solutions. An internal standard, yttrium, was used to correct for any matrix effects. Precision of IAPSO was generally better than 1%, but sometimes fell to ~2%.

2.2. Shell samples

M. campechiensis specimens (BOK1, BOK2, and BOK3) were collected alive near Jug Creek on 10/8/02. Shells were cleaned of soft organic tissue, cut along the axis of maximum growth, and polished to reveal internal growth features (Fig. 2). Accretionary growth patterns in their shells preserve increments that, like tree rings, can serve as annual markers. Translucent increments in *M. campechiensis* form during summer

months when water temperature and salinity approach the maximum and minimum values, respectively, for optimal shell growth (Jones et al., 1990; Jones, 1996) and can be traced across both microstructural layers. Ansell (1968) reported that optimal temperature for growth in *M. mercenaria* ranges from 15–25 °C and growth rate decreases markedly below 9 °C and above 31 °C. Grizzle et al. (2001) report optimal salinity range for *M. mercenaria* between 20–30 psu with marked decrease in growth rate below 17 psu. The upper salinity limit has not been determined. Given their close taxonomic relationship and overlapping geographic range (*M. campechiensis* ranges from south Florida to southern New Jersey and *M. mercenaria* ranges from south Florida to New Brunswick, Canada; Merrill and Ropes, 1967; MacKenzie et al., 2002), these optimal ranges and growth thresholds are assumed to be similar in both species except at temperatures colder than that occurring at the northern most extent of *M. campechiensis*' geographic range. However, *M. campechiensis* is more tolerant of lower salinity water (personal communication of W. Arnold, Florida Marine Research Institute, St. Petersburg, Florida). Fritz (2001) provides a comprehensive review of annual growth increment formation and characteristics of the outer prismatic and middle cross-lamellar microstructural layers contained in shells of *M. mercenaria*. We expect similar characteristics in the middle and outer microstructural layers of *M. campechiensis* based on personal communication from W. Arnold.

Given these growth features, the age of each individual was determined by counting annual growth increments towards the dorsal-ventral margin, and age estimates were cross-checked along the umbonal area to avoid inclusion of disturbance (false, non-annual) increments. Specimen BOK1 was 6 years of age, specimen BOK2 was 7 years of age, and specimen BOK3 was 9 years of age at the time of harvest.

The last 2 years of shell growth were sampled from the prismatic (outer) and cross-lamellar (middle) microstructural layers. Approximately 24 samples per year provided submonthly resolution. High-resolution sampling was achieved using a Merchantek micromill. A series of sampling traverses parallel to shell growth lines was digitized online from a real-time image of a bivalve section cut parallel to growth direction. The exceedingly small amount of carbonate powder produced (50–100 µg) was collected from the polished specimen surface and split for isotopic and elemental determination. Oxygen and carbon isotope compositions were analyzed on a Finnigan MAT 251 isotope ratio mass spectrometer with an automated carbonate



Fig. 2. Photograph of cross-sectioned *M. campechiensis* shells cut along axis of maximum growth. Three specimens (BOK1, BOK2, and BOK3) were collected alive near the mouth of Jug Creek, Bokeelia, Florida. The last 2 years of growth were sampled. The scales are in centimeters.

reaction system (Kiel Device). Analytical precision was better than 0.1‰. Oxygen isotope ratios were corrected for ^{17}O contribution (Craig, 1957). Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are reported in per mil units with respect to the VPDB standard. Sample splits for elemental analysis were dissolved individually in 1.5 ml of dilute Fisher Optima grade $\text{HNO}_3 + \text{HCl}$ spiked with indium as an internal standard. Solutions were analyzed on a Finnigan *Element* inductively coupled plasma-mass spectrometer (ICP-MS) for Ca and Sr content. Given the small sample size, it was not possible to measure accurately the weights of individual carbonate powder splits; therefore, raw solution (ng/g) data are reported as molar Sr:Ca ratios using mmol/mol concentrations. Analytical precision was better than $\pm 1\%$ RSD (raw standard deviation) based on check standards and sample replicates and duplicates.

3. Results

3.1. Physical and chemical water properties

Based on the USGS water property data set, temperature and salinity follow a more or less sinusoidal pattern reflecting seasonal variation (Fig. 3). Temperature ranges from 17–31 °C between winter and summer months. Salinity varies between 19–36 psu with lowest values occurring from July through November.

Sr:Ca ratios (mol/mol) average 0.0085 with a standard deviation of 0.0002 (Table 1, Fig. 4) and is close to the average of low-latitude seawater (0.0084; Taylor and McLennan, 1985). A least-squares regression produces a slope that is not significantly different than zero ($r^2=0.01$, $n=49$) across a salinity range of 23 to 35 psu. Therefore, the assumption that Sr:Ca ratios does not vary significantly in the range of salinity optimal for shell growth is valid.

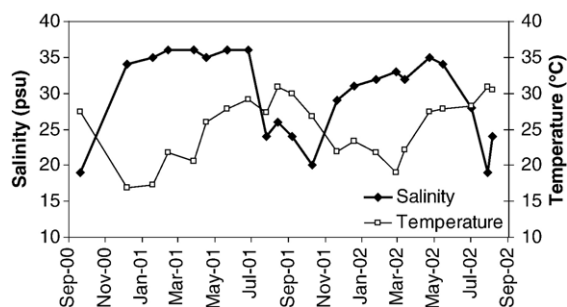


Fig. 3. Salinity and temperature recorded by the United States Geological Survey at Bokeelia, Florida, from September 2000 to September 2002. Heavy, dark line with filled diamonds represents salinity (psu) and thin line with open squares represents temperature (°C).

Table 1

Water property data measured fortnightly from August 2003 to May 2005 in northern Pine Island Sound, Florida, USA, characterizing the seasonal variability from the summer wet to winter dry seasons

Date	Salinity (psu)	Sr:Ca (mol/mol)
4 August 2003	32	0.0089
18 August 2003	28	0.0087
1 September 2003	30	0.0086
16 September 2003	24	0.0089
29 September 2003	30	0.0087
6 October 2003	26	0.0092
13 October 2003	29	0.0085
27 October 2003	31	0.0086
10 November 2003	30	0.0087
25 November 2003	29	0.0087
8 December 2003	33	0.0086
23 December 2003	31	0.0085
4 January 2004	32	0.0085
19 January 2004	32	0.0086
2 February 2004	33	0.0085
16 February 2004	32	0.0086
1 March 2004	31	0.0086
15 March 2004	32	0.0086
29 March 2004	32	0.0085
13 April 2004	32	0.0086
27 April 2004	34	0.0085
11 May 2004	35	0.0086
24 May 2004	35	0.0086
7 June 2004	35	0.0087
21 June 2004	35	0.0087
6 July 2004	35	0.0089
20 July 2004	34	0.0088
2 August 2004	35	0.0086
26 August 2004	30	0.0081
29 August 2004	30	0.0082
7 September 2004	30	0.0082
21 September 2004	23	0.0082
4 October 2004	24	0.0083
19 October 2004	30	0.0082
2 November 2004	30	0.0081
15 November 2004	30	0.0084
28 November 2004	32	0.0082
20 December 2004	34	0.0084
3 January 2005	29	0.0083
17 January 2005	32	0.0084
31 January 2005	34	0.0083
15 February 2005	34	0.0081
28 February 2005	34	0.0085
16 March 2005	33	0.0084
29 March 2005	31	0.0082
11 April 2005	29	0.0082
21 April 2005	28	0.0084
3 May 2005	30	0.0084
16 May 2005	31	0.0084

3.2. Shell microstructural chemistry

The hypothesis that different microstructural layers record the same geochemical information was tested by comparing the isotopic and elemental ratios between

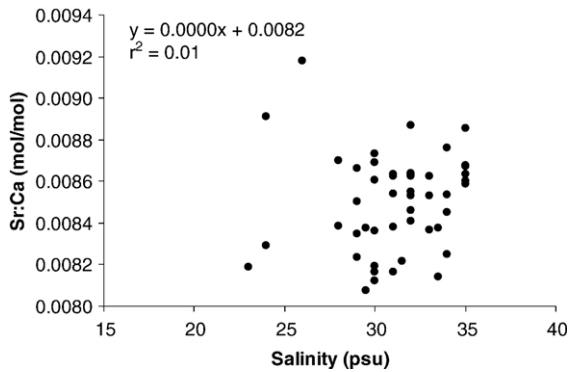


Fig. 4. Cross-plot Sr:Ca ratios (mol/mol) versus salinity (psu) with an inset of the resultant least-squares regression equation and associated r^2 value.

the outer and middle layers from the last 2 years of growth from three individuals (BOK1, BOK2, and BOK3; Figs. 5–7). Paired samples from the outer and middle layers within a shell were aligned using the measured distance at the boundary between the outer and middle layers. Profiles of $\delta^{18}\text{O}_{\text{SHELL}}$ values from outer and middle layers are nearly identical within all three shells and between shells BOK1 and BOK2 (Fig. 5). Shell BOK3 does not preserve the most positive $\delta^{18}\text{O}_{\text{SHELL}}$ values because this individual was the oldest specimen with the slowest growth rate. Slight offsets likely represent the lack of perfect alignment. Values range from -2.42‰ to $+2.10\text{‰}$, from -2.50‰ to $+2.11\text{‰}$, and from -2.21‰ to $+0.54\text{‰}$ in shells BOK1, BOK2, and BOK3, respectively. The most negative values in the outer layer of shell BOK1 in band 2 are not represented because samples during that time interval did not generate sufficient CO_2 for analysis.

Variation in $\delta^{13}\text{C}$ values of microstructural layers are similar within shells, but the outer layer is somewhat more variable. The range of values varies somewhat among shells (Fig. 6). The middle layer in shell BOK1 ranges from 3.83‰ to 1.99‰ , and the outer layer ranges from 3.88‰ to 1.39‰ . (Note that as in $\delta^{18}\text{O}$ values for this shell, the range of values corresponding to Summer 2001 are not represented because of insufficient CO_2 during analysis.) In contrast, $\delta^{13}\text{C}$ values from shell BOK2 are more negative and more variable in the outer layer (ranging from 6.82‰ to 1.07‰) than in the middle layer (ranging from 3.15‰ to 1.05‰). The most negative value in the outer layer cannot be discarded as an analytical artifact.

Profiles of Sr:Ca ratios in both shells reveal different periodic variability and patterns of offset with an apparent age dependence (Fig. 7). The outer layer in shell BOK1 appears to have as many as six cycles and is as much as 1 mmol/mol higher and more variable than the

middle layer. Prominent cycles are not as evident in the middle layer of this shell. Sr:Ca ratios in the outer layer range from 1.50 to 2.55 mmol/mol, whereas those from the middle layer range from 1.44 to 1.84 mmol/mol. In shells BOK2 and BOK3, both layers within the shells appear to have only two cycles and track each other much more closely than the profiles in shell BOK1. The middle layer in shell BOK2 has slightly higher Sr:Ca ratios (by as much as 0.4 mmol/mol) than the outer layer and the reverse is true for shell BOK3. As with

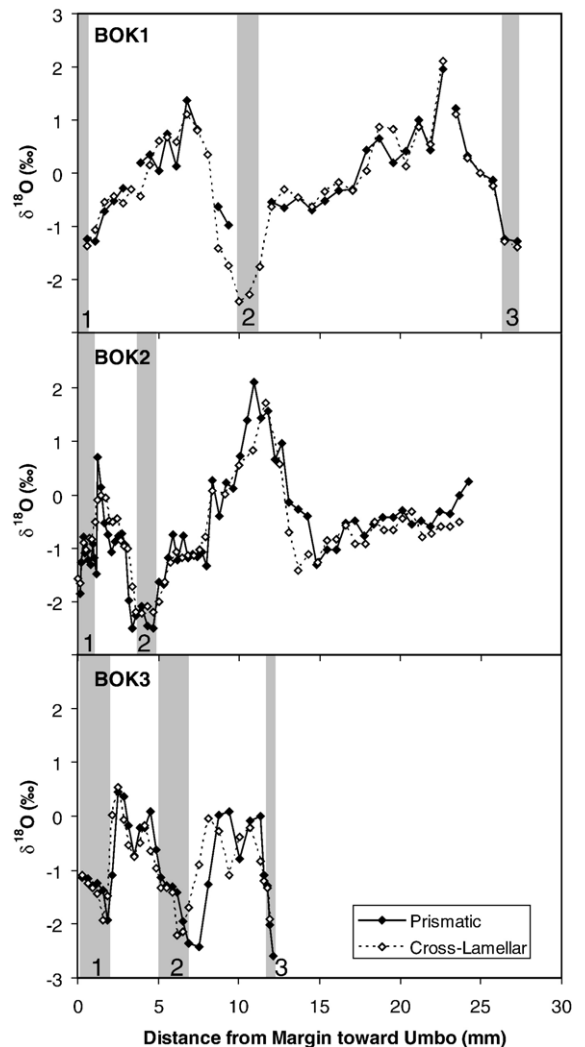


Fig. 5. Variation in $\delta^{18}\text{O}$ (‰) with shell growth. Filled diamonds with the black line are samples from the outer prismatic layers, and open diamonds with the dashed line represent the middle cross-lamellar layer. Vertical gray bars represent the location of translucent (summer) growth increments with numbers identifying specific increments. Distance on x -axis is measured in mm from the growth margin toward the umbo (i.e., age decreases toward the right). Top panel = specimen BOK1. Middle panel = specimen BOK2. Bottom panel = specimen BOK3.

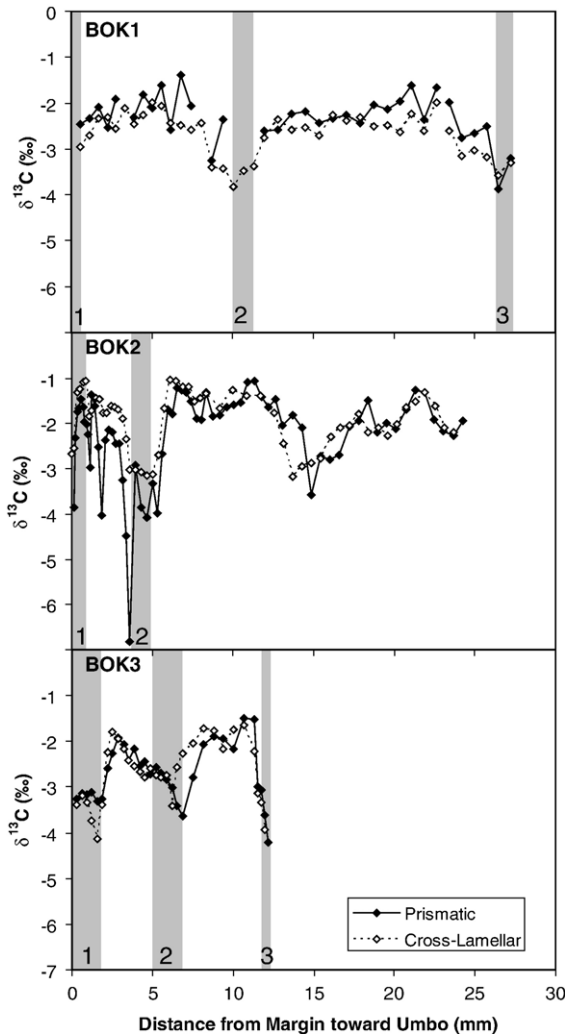


Fig. 6. Variation in $\delta^{13}\text{C}$ (‰) with shell growth. Filled diamonds with the black line are samples from the outer prismatic layers, and open diamonds with the dashed line represent the middle cross-lamellar layer. Vertical gray bars represent the location of translucent (summer) growth increments with numbers identifying specific increments. Distance on x -axis is measured in millimeter from the growth margin toward the umbo (i.e., age decreases toward the right). Top panel = specimen BOK1. Middle panel = specimen BOK2. Bottom panel = specimen BOK3.

oxygen and stable carbon isotope compositions, the highest values of Sr:Ca ratios recorded in shells BOK1 and BOK2 are not preserved in shell BOK3 with ratios ranging from 1.25 to 1.91 mmol/mol.

4. Discussion

4.1. Isotopic composition of shell carbonate

Variation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values from the last 24–27 mm of growth were compared within and among

individuals. Based on nearly identical variation of $\delta^{18}\text{O}$ values between the outer and middle microstructural layers within each shell, either layer is appropriate for oxygen isotope analysis. Specimens BOK1 and BOK2 have similar ranges and variation; however, specimen BOK3 does not preserve the most positive values represented in the other two shells (Fig. 5). This pattern likely reflects the slower growth rate exhibited by the last 2 years of BOK3, the oldest shell. Examination of the range of temperature and salinity recorded at Bokeelia

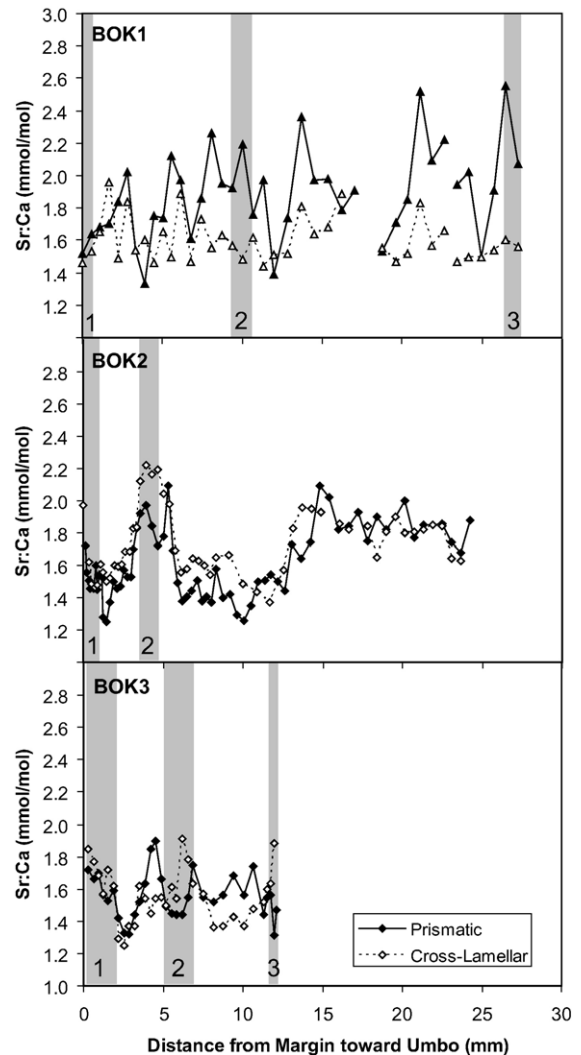


Fig. 7. Variation in Sr:Ca ratios (mmol/mol) with shell growth. Filled diamonds with the black line are samples from the outer prismatic layers, and open diamonds with the dashed line represent the middle cross-lamellar layer. Vertical gray bars represent the location of translucent (summer) growth increments with numbers identifying specific increments. Distance on x -axis is measured in mm from the growth margin toward the umbo (i.e., age decreases toward the right). Top panel = specimen BOK1. Middle panel = specimen BOK2. Bottom panel = specimen BOK3.

by the USGS indicates that these water conditions were within the range for optimal shell growth in *Mercenaria* shells which could allow for incremental shell growth throughout the year. Elliot et al. (2003) report similar results for shells of *M. mercenaria*. In particular, they observe nearly identical variation in $\delta^{18}\text{O}$ values between individuals growing at the same time and place.

Although variation of $\delta^{13}\text{C}$ from the outer and middle layers follows the same general trend within a shell, the difference in variability and direction of variability (more or less negative) between microstructural layers among the three shells suggests this environmental proxy should be treated with caution (Fig. 6). Our findings suggest a vital effect (e.g., metabolically derived CO_2 used in shell formation) influences the $\delta^{13}\text{C}$ of shell carbonate. Other workers have observed that changes in growth rate influenced by ontogenetic and seasonal differences affect the stable carbon isotope composition in shells of other marine bivalves (Krantz et al., 1987; Harrington, 1989; Klein et al., 1996). We attempted to control for ontogenetic and seasonal differences by selecting individuals of similar size (but as it turned out, of not the same age) and sampling across the same period of growth. Elliot et al. (2003) report similar results (a lack of reproducibility among individuals) for shells of *M. mercenaria*. Given the lack of reproducibility between individuals regardless of microstructural layer, interpreting environmental information from $\delta^{13}\text{C}$ shell values remains challenging.

4.2. Shell elemental ratios

Early studies investigating Sr:Ca ratios as a potential paleothermometer in bivalves document a seasonal variation and negative correlation with temperature (Dodd, 1965; Hallam and Price, 1968; Palacios et al., 1994; Klein et al., 1996; Stecher et al., 1996). In addition to a seasonal variation in Sr:Ca ratios, Stecher et al. (1996) report a correspondence in seasonal patterns between Sr:Ca ratios and $\delta^{18}\text{O}$ values for shells of *M. mercenaria*. Moreover, they observed lower Sr:Ca ratios in a shell that grew during the Pleistocene relative to a modern specimen, which is consistent with the colder climatic conditions in the Pleistocene than today. They concluded, however, that the seasonal variation in Sr:Ca ratios is not directly related to temperature change, but rather may reflect kinetic effects due to seasonal changes in growth rate. However, in a more recent study, Gillikin et al. (2005) investigated whether the variation of Sr:Ca ratios in three individuals of *M. mercenaria* (4.5, 7, and 9 years of age) collected off the coast of North Carolina contained environmental and

ecological information. They found no relationship between average annual Sr:Ca ratios and annual growth rate, nor any annual cyclicality in any of the shells analyzed. Does the lack of reproducibility of Sr:Ca ratios between the middle and outer layers and between individuals observed in our study indicate that this proxy cannot be reliably used as a paleothermometer in *M. campechiensis*?

To evaluate whether Sr:Ca ratios preserve a seasonal signal and, hence, provide temperature information, Sr:Ca ratios were compared to $\delta^{18}\text{O}$ values (Fig. 8). The observations reported by Stecher et al. (1996)

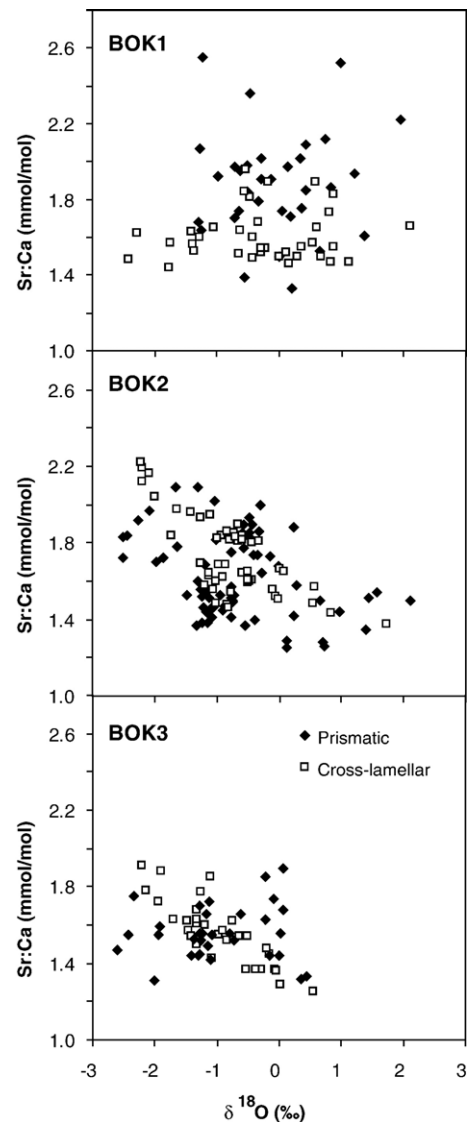


Fig. 8. Covariance of Sr:Ca ratios (mmol/mol) and $\delta^{18}\text{O}$ (‰) of outer prismatic (filled diamonds) and middle cross-lamellar (open squares) microstructural layers. Top panel = specimen BOK1. Middle panel = specimen BOK2. Bottom panel = specimen BOK3.

predict that these two proxies should be correlated. Although the relationships will likely not be perfect (because $\delta^{18}\text{O}_{\text{SHELL}}$ values are also influenced by seasonal variation of $\delta^{18}\text{O}$ values in estuarine water (Surge and Lohmann, 2002), whereas Sr:Ca ratios are not), there should be some covariance between the two variables if temperature has an effect on both proxies. A direct comparison of Sr:Ca ratios of shell carbonate with water temperature was not possible given the coarseness of the USGS data set. There is no co-variant relationship between Sr:Ca ratios and $\delta^{18}\text{O}$ in the outer prismatic layer in all three shells. The middle cross-lamellar layer in shell BOK1 also reflects no covariant relationship between Sr:Ca ratios and $\delta^{18}\text{O}$ values ($r^2=0$, $p<0.001$). In contrast, Sr:Ca ratios and $\delta^{18}\text{O}$ values in the middle cross-lamellar layer of shell BOK2 has a moderate co-variant relationship ($r^2=0.55$, $p<0.001$). Shell BOK3, the oldest shell, has the strongest co-variant relationship between Sr:Ca ratios and $\delta^{18}\text{O}$ values ($r^2=0.72$, $p<0.001$). We conclude that there is a kinetic effect due not only to seasonal changes in growth rate, but also related to age of an individual — the older, the better in this case. However, as shells achieve 9 years of age and older, the seasonal record becomes truncated because of slowed growth. Nonetheless, this method of comparison provides a screening test to evaluate whether Sr:Ca ratios in a particular individual record environmental information or whether there is sufficient metabolic overprinting that obscures an environmental signal.

5. Conclusions

This study shows that seasonal profiles of $\delta^{18}\text{O}$ values preserved in shells of *M. campechiensis* record similar water conditions in outer prismatic and middle cross-lamellar microstructural layers and among individuals. Detailed calibration was not presented here because of the coarseness of the USGS data set and the lack of sufficient proximity to where the quahogs were collected. A calibration study with fortnightly monitoring of water conditions at a quahog locality in Pine Island Sound is currently underway. As observed in a closely related species, *M. mercenaria*, $\delta^{13}\text{C}$ values in skeletal carbonate of *M. campechiensis* likely reflects a combination of environmental and physiological factors incorporated into the shell. Sr:Ca ratios can record temperature information in the middle cross-lamellar layers of older, but not younger, individuals. Comparing Sr:Ca ratios with $\delta^{18}\text{O}$ values provides a screening method for identifying individuals that have the best potential for recording temperature information.

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