Seasonal-Scale Paleoclimate Reconstruction of the Mid-Pliocene Warm Period Using High-Resolution Stable Isotope, Trace Element, and Clumped-Isotope Analysis of Fossil Molluscan Carbonate from the Yorktown Formation, Virginia

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23 April 2024

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Senior Honors Thesis

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Abstract

The mid-Pliocene Warm Period (mPWP) is an interval in Earth's climatic history characterized by warm conditions and atmospheric CO_2 concentrations comparable to the present. Because of this, the mPWP offers a critical analogue for understanding future global warming. This study examines the paleoclimate of the mPWP on a seasonal-scale by employing high resolution isotopic and trace element analysis of the marine bivalve *Mercenaria* from the mid-Pliocene age Yorktown Formation in Virginia. $\delta^{18}O$ and $\delta^{13}C$ records show seasonal variation and act as a proxy for past sea surface temperatures. A reduction in seasonal temperature variations is observed in the mPWP (10.6°C) compared to present (21.1°C), accounted for by warmer winter and cooler summer conditions. Further analysis of trace elements (Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca, Fe/Ca, and Zn/Ca) provide additional constraints on paleoenvironmental reconstructions and suggest the potential influence of upwelling. Preliminary clumped-isotope analyses contrast with the upwelling hypothesis and are suggestive of riverine input of freshwater. Future work will continue to make use of clumped-isotope analysis to better constrain paleotemperatures and $\delta^{18}O_{sw}$ values for the mid-Pliocene.

Introduction

Earth's past has been punctuated by numerous intervals in which climate conditions have been warmer than during the pre-industrial Holocene. The mid-Pliocene Warm Period (mPWP, about 3.3-3.0 Ma) represents the most recent period in which atmospheric CO_2 levels (360-400 ppm) naturally reached levels comparable to modern times (Raymo et al., 1996). In 2007, the Intergovernmental Panel on Climate Change (IPCC) identified the mPWP as an analogue for future warming and the potential consequences of anthropogenically forced climate change (Jansen et al., 2007).

Temperatures in the mPWP are estimated to have been ~2-3°C above present and sea levels ~20m higher than present, largely due to the reduction of sea and continental ice (Jansen et al., 2007; Raymo et al., 1996). This interval in Earth's climate history (see Figure 1) has been the subject of both regional and global paleoclimate reconstructions and is evidenced by numerous geologic proxies for temperature (Poore and Sloan, 1996; Raymo et al., 1996; Dowsett et al., 1999, 2004, 2013, 2016). However, questions remain regarding the precision of climate estimates in this period, and relatively few studies have focused on seasonal scale paleoclimate reconstructions.

Analysis of the δ^{18}O of benthic foraminifera has provided evidence for an interval of higher average global temperatures during the mid-Pliocene prior to the onset of northern hemisphere glaciation (Lisiecki and Raymo, 2005). This is based on the premise that the presence of ice at high latitudes maintains bottom water temperatures, meaning changes in δ^{18}O reflect changes in ice volume and thus changes in global temperatures (Shackleton et al., 1984; Prell, 1984).

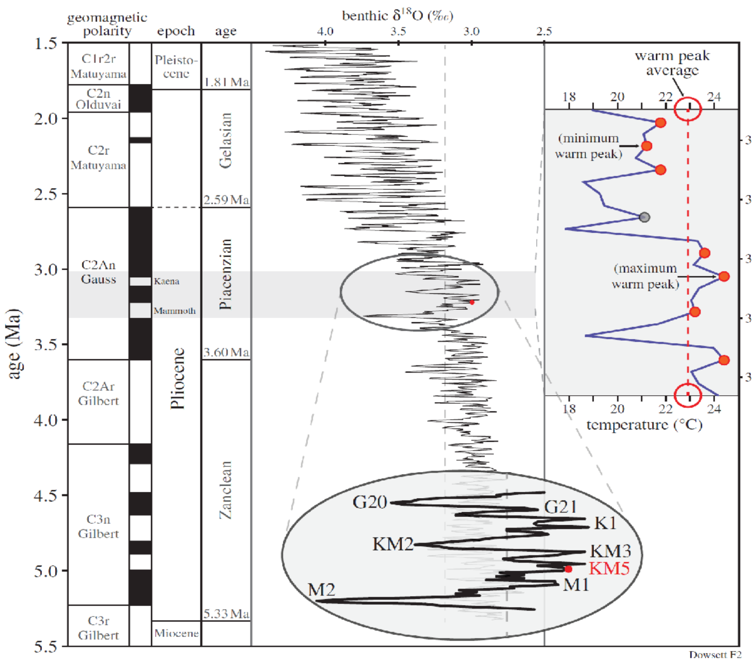

Figure 1: Benthic foraminifera δ^{18}O stacked record from Lisiecki and Raymo (2005) showing overall early and mid-Pliocene warming prior to the initiation of northern hemisphere glaciation. Figure from Dowsett et al., 2003.

The large-scale *Pliocene Research, Interpretation, and Synoptic Mapping* project (PRISM) has focused on the time interval between 3.3 to 2.97 Ma to reconstruct environmental conditions in the Mid-Atlantic Coastal Plain (MACP) of the Southeastern United States (Dowsett et al., 1999, 2004, 2013, 2016). The approach taken in the PRISM project was to quantitatively relate the composition and relative abundance of taxa in biofacies assemblages to reconstruct environmental conditions. Results from PRISM indicate that subtropical assemblages replaced temperate assemblages during the mPWP in response to the overall warming of sea temperatures in the region at this time (Dowsett et al., 2013, 2016).

Krantz (1990) used isotopic ratios from fossil scallop shells for mPWP paleoclimate reconstructions and suggested that hydrographic conditions during the mPWP are similar to the modern Middle Atlantic Bight with significant seasonal river input and relatively little influence from the Gulf Stream. Winkelstern et al. (2013) used isotope ratios from fossils of the molluscan bivalve *Mercenaria* to compare paleoclimate conditions from the mPWP and early Pleistocene. They proposed that warmer winter temperatures may have been the result of increased meridional heat transport and paleogeography which allowed the Gulf Stream to exert a greater influence farther north along the coast than today. Johnson et al. (2017) used oxygen isotope ratios from fossil scallop shells to reconstruct seasonal temperature variations during the mPWP. The authors attribute the warmer conditions to general climate warming rather than a change in Gulf Stream influence. Braniecki (2022) used isotope ratios from both modern and fossil *Mercenaria* shells to compare seasonal temperatures from the mPWP, early Pleistocene, and today. They concluded that warmer winters and reduced seasonal temperature amplitudes may be attributed to an increase in warm-water transport by the Gulf Stream.

Materials

Mercenaria Ecology

Despite extensive mPWP paleoclimate investigations, analysis of seasonal-scale variations is relatively limited. Studies that focus on molluscan carbonates can provide a higher resolution analysis capable of resolving sub-annual changes in the environmental conditions. In effect, changes in seasonality can be reconstructed utilizing the growth-banded structure preserved in their shells. Moreover, by examining near coastal settings, it is potentially possible to more accurately record sea surface temperatures given the shallow water setting of these environments. This approach, however, also has its drawbacks as marginal marine environments may be subject to changing salinity due to freshwater runoff or periodic deeper water upwelling that can bias temperature estimates. Nevertheless, these provide additional constraints for reconstructing paleo-environmental conditions during this time interval.

Shells from the genus *Mercenaria* provide a high-resolution archive of seasonal variability due to their high growth rates. *Mercenaria* shells show a growth-banded structure with alternating light and dark bands, also described as translucent and opaque bands (Lowell et al., 2022). Light and dark bands are thought to represent periods of relatively fast and slow growth, respectively (Lowell at al., 2022). It has been suggested dark bands form when temperatures fall outside the threshold for growth, determined by Ansell (1968) to be between 9-31°C (Lowell et al., 2022). Growth rates are fastest around 20°C (Ansell, 1968).

Figure 2: *Mercenaria sp.* (shell YT-2) that was collected from the Yorktown Fm. near York, VA. and obtained from UMMP. Sampling occurred on the exterior of the shell beginning near the umbo and terminating near the end of the shell. The length of the sampling traverse is 5.6 cm.

Stratigraphic Setting

The Yorktown Fm. outcrops in the Carolinas and Virginia. It is composed of four members corresponding to three separate transgressive events bound by unconformities. In stratigraphic succession from lowest to highest these include the Sunken Meadow, Rushmere, Morgarts Beach, and Moore House Members (Krantz, 1990; Williams et al., 2009). The Yorktown Fm. is estimated to have been deposited between 4-3 Ma representing approximately 1 Myr of deposition (Dowsett and Wiggs, 1992). The Rushmere and Morgarts Beach Members represent a single transgression and represent the deepest transgression of the Yorktown Fm. (30-40m depth; Krantz, 1991). Ward et al. (1991) roughly constrained this depositional event to ~3.4-3.0 Ma coinciding with the mPWP (Krantz, 1991). The Yorktown Fm. consists of fine-grained sandy clays and shell marls and a faunal assemblage consistent with warm-temperate conditions (Krantz, 1990; Ward et al., 1991; Williams et al., 2009; Blackwelder, 1981).

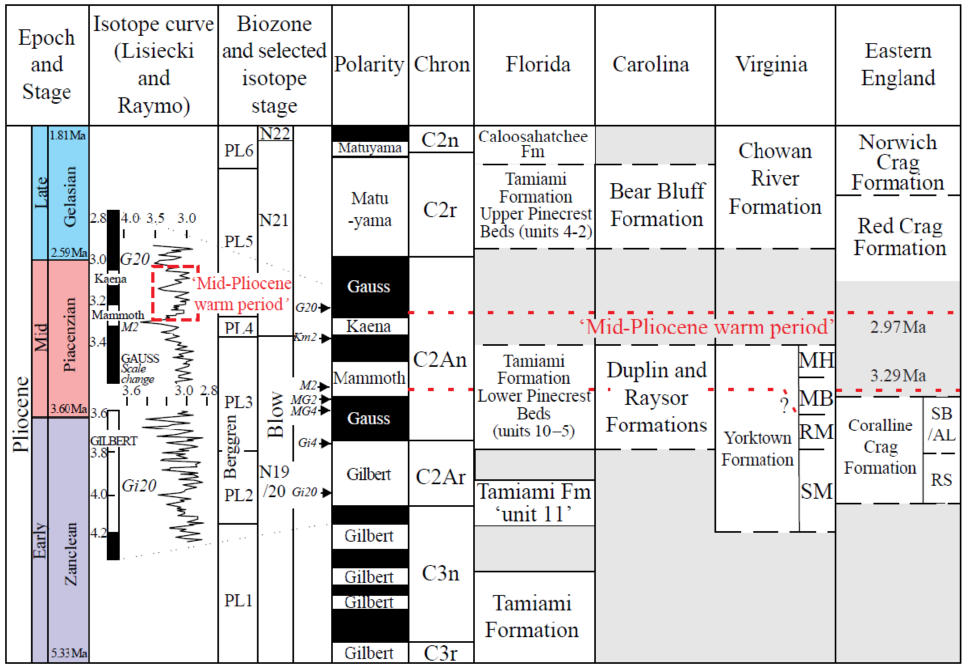

Figure 3: Chronostratigraphic correlation of Pliocene strata along the Atlantic coast of the US including Virginia (from Williams et al., 2009). The Yorktown Fm. in Virginia is coincident with the mPWP.

This study employs high resolution seasonal-scaled sampling of a bivalve Mollusca (*Mercenaria*) from Virginia currently representing temperate conditions. Results obtained will be compared with existing datasets to validate prior findings. Samples will be analyzed for $\delta^{18}O$ and $\delta^{13}C$ isotopic variation, trace element compositions, and clumped-isotope compositions. The $\delta^{18}O$ values obtained provide a proxy for sea temperature conditions throughout the lifespan of the shell. The results of trace elemental analyses can be compared with $\delta^{18}O$ and $\delta^{13}C$ isotopic data to further constrain environmental signals such as upwelling and the input of freshwater. Clumped-isotope analysis provides an independent measure of the temperature during precipitation of the carbonate, and thus allows for the calculation of the composition of the precipitating water. Knowledge of possible changes in water composition will allow discrimination of factors, such as upwelling and terrestrial freshwater runoff, that may have biased temperature estimates in prior studies.

Methods

One fossil bivalve Mollusca shell of the genus *Mercenaria* is analyzed in this study. The shell (ID: YT-2) is of mid-Pliocene age from the Yorktown Fm. of Virginia and has been obtained from the University of Michigan Museum of Paleontology (UMMP). Shell YT-2 contains both dark and light growth bands. Dark bands correspond to sample numbers 1-8, 12-21, 25-40, and

45-52. Light bands correspond to sample numbers 9-11, 22-24, and 41-44. *Mercenaria sp.* YT-2 was used by Boswell (2019) in a prior paleoclimate study in which 52 serial samples were taken for isotopic analysis.

Figure 4: *Mercenaria sp.* (YT-2) with labeled sample IDs 1-52. Each ID corresponds to a layer of growth, with IDs increasing from the umbo (1) to the end of the shell (52).

Before microsampling for analysis, each shell was washed and scrubbed to remove any remaining sand and external contamination. Microsamples were obtained from the polished surface using a microscope-mounted drill assembly outfitted with 0.5mm dental bur. Samples of YT-2 were taken from the exterior of the shell along successive growth bands to obtain a long time series using the sampling apparatus described above.

Stable Isotope Analysis

The typical size of samples taken for isotopic analysis was approximately 50 micrograms of powdered carbonate. The powdered samples were analyzed on a Thermo Delta V ratio gas mass spectrometer with an attached automated Kiel IV carbonate reaction-extraction system. Measured isotopic enrichments were converted to VPDB through a calibration employing international standards NBS-19 and NBS-18. Analytical precision was maintained at better than .01 per mil for both carbon and oxygen measurements.

Trace Element Analysis

This study also examines seasonally scaled trace element data (Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca, Fe/Ca, and Zn/Ca) preserved in the *Mercenaria* sample shell YT-2. The size of samples taken for trace elemental analysis ranged from approximately 400-600 micrograms of powdered carbonate. We measured elemental concentrations of Sr, Ca, Mg, and Ba using a Thermo iCAP 7400 inductively coupled plasma optical emission spectrometer (ICP-OES) in the PACE lab at the University of Michigan's Earth and Environmental Science department using established methods (Cantarero et al., 2016; Schrag, 1999). For each carbonate sample split, 400-600 g samples were diluted to [Ca] ~ 80 ppm in 3.5 ml of 5% trace metal grade HNO 3. Six calibration solutions spanning the expected elemental concentrations were analyzed at the start of each day of analysis. A reference solution was measured every 3rd sample to correct within-run drift, another reference solution (MCP-L) was measured 10 times per day to correct for day-to-day offsets, and two powdered internal standards were analyzed each day of analysis to monitor long-term elemental values. Long-term analytical precision (1-) of the first internal standard (MCP-P) 8 was Sr/Ca = 0.018 mmol/mol, Mg/Ca = 0.055 mmol/mol, and Ba/Ca = 0.24 mol/mol (1-, n=114). The long-term average values of the second powdered coral standard (JCp-1) were Sr/Ca = 8.861±0.026 mmol/mol, Mg/Ca = 4.141±0.091 mmol/mol, and Ba/Ca = 6.70±0.41 mol/mol (1-, n=136), within 1-stdev of previous measurements (Cantarero et al., 2016; Hathorne et al., 2013; Dyez, 2024).

Clumped-Isotope Analysis

The clumped-isotope composition of powdered carbonate samples was determined using a NuCarb automated sample preparation device connected to a Nu Perspective gas-sourced isotope-ratio mass spectrometer in the University of Michigan SCIPP Lab. Approximately 400 micrograms of powdered carbonate was collected from samples for clumped-isotope analysis. The powdered carbonate samples were reacted with phosphoric acid in individual vessels at 70°C. This technique is based on the tendency of heavy oxygen and carbon isotopes to bond within a carbonate molecule at lower temperatures. Excess carbonate molecules containing both heavy isotopes, relative to a random distribution, is measured as a Δ_{47} value. Typically, Δ_{47} is only dependent on the water temperature in which the shell forms. The simultaneous measurement of Δ_{47} and $\delta^{18}O$ gives a temperature estimate that allows for the calculation of the oxygen isotopic composition of the water in which the shell formed ($\delta^{18}O_{sw}$).

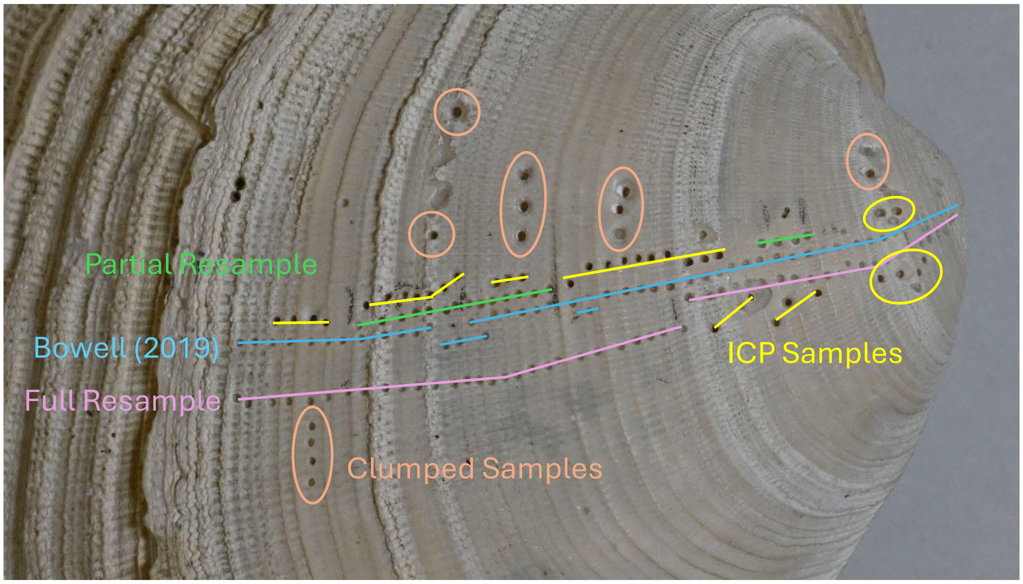

Figure 5: *Mercenaria sp.* (YT-2) with the different samples labeled and color coded. Samples colored blue correspond to samples taken in a prior study (Boswell 2019), samples colored purple and green correspond to samples taken for isotopic analyses, samples colored yellow correspond to samples taken for ICP-OES trace element analyses, and samples colored orange correspond to samples taken for clumped isotope analyses.

Temperature Calculations

The following equilibrium fractionation equation for aragonite from Dettman et al. (1999) was used to estimate expected $\delta^{18}\mathrm{O}$ shell values:

$$1000\ln(\alpha) = 2.559(10^6 T^{-2}) + 0.715$$

where T is temperature in Kelvin and α is the fractionation factor between water and aragonite described by the following equation:

$$\alpha \frac{aragonite}{water} = \frac{(1000 + \delta^{18}O_{aragonite(VSMOW)})}{(1000 + \delta^{18}O_{water(VSMOW)})}$$

Values of $\delta^{18}\mathrm{O}_{aragonite}$ are relative to VSMOW and were therefore converted to VPDB, as reported in this study, using the following equation:

$$\delta^{18}\mathrm{O}_{aragonite(\mathrm{VSMOW})} = 1.03091(1000 + \delta^{18}\mathrm{O}_{aragonite(\mathrm{VPDB})}) - 1000$$

Ocean-atmosphere general circulation model results provide a $\delta^{18}\mathrm{O}_{sw}$ value of 1.1‰ (VSMOW) for Virginia in the mPWP (Williams et al., 2009). This model incorporates regional precipitation, evaporation, and decreased global ice volumes (Williams et al., 2009). This value has previously been used by Winkelstern et al. (2013), Johnson et al., (2017), and Braniecki (2022) to reconstruct seasonal SSTs.

Results

Stable Isotope Results

A total of 96 isotopic analyses were performed on samples of *Mercenaria* shell YT-2 in this study. Samples cover a total of 52 individual growth bands. Numerous growth bands have been sampled and analyzed multiple times to further constrain measured isotopic values. This replicate data produced similar trends for both oxygen and carbon isotope values. The high sample resolution allows for examination of seasonal variation in isotopic data. This data can be employed to estimate environmental conditions such as paleotemperature ranges, variability in salinity, and the possible effects of freshwater runoff or upwelling. In this study, changes in $\delta^{18}O$ are used as the primary means of identifying summer versus winter growth. More positive $\delta^{18}O$ corresponds to cooler conditions while more negative values are representative of warmer summer temperatures. The coupled changes in $\delta^{13}C$ can then be examined to elucidate the seasonal variation in the carbon isotopic composition of seawater and of potential riverine input.

The mid-Pliocene $\delta^{13}C$ and $\delta^{18}O$ values in *Mercenaria* shell YT-2 show a quasi-sinusoidal trend following three seasonal growth cycles (Figure 6). Carbon isotope ratios range from 0.51‰ to 1.84‰ VPDB while oxygen isotope ratios range from -0.24‰ to 2.20‰ VPDB. Dark increments within the shell growth pattern occur when $\delta^{18}O$ values are most negative and $\delta^{13}C$ are most positive. Dark increments have an average $\delta^{18}O$ value of 0.54‰ VPDB and an average $\delta^{13}C$ value of 1.34‰ VPDB. Light increments have an average $\delta^{18}O$ value of 1.36‰ VPDB and an average $\delta^{13}C$ value of 0.99‰ VPDB.

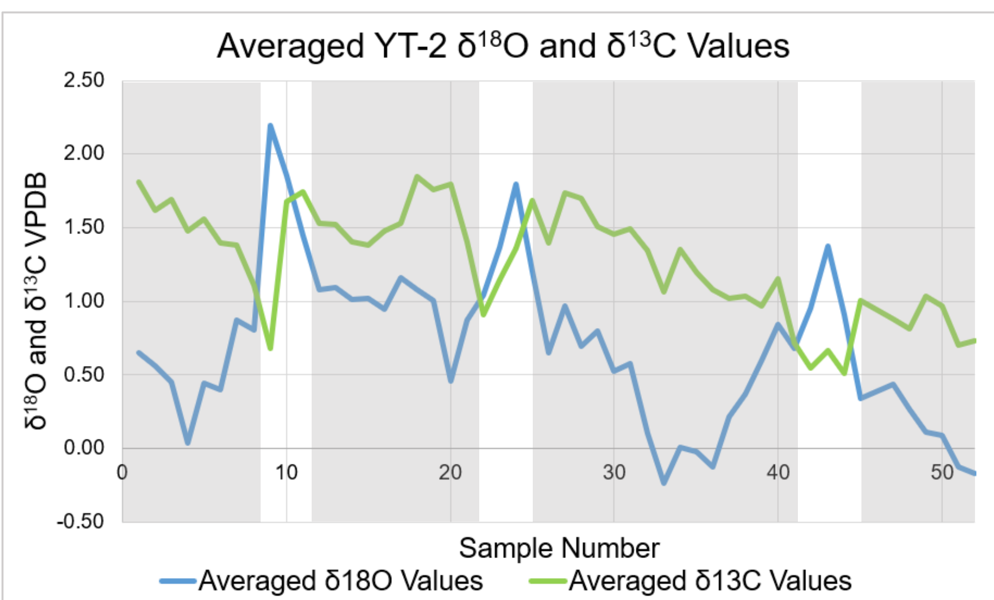

Figure 6: Oxygen and Carbon isotope variation in shell YT-2. Three seasonal signals are observed. Areas shaded gray correspond to dark increments of shell growth, while unshaded areas correspond to light increments of shell growth occurring in sample numbers 9-11, 22-24, and 41-44.

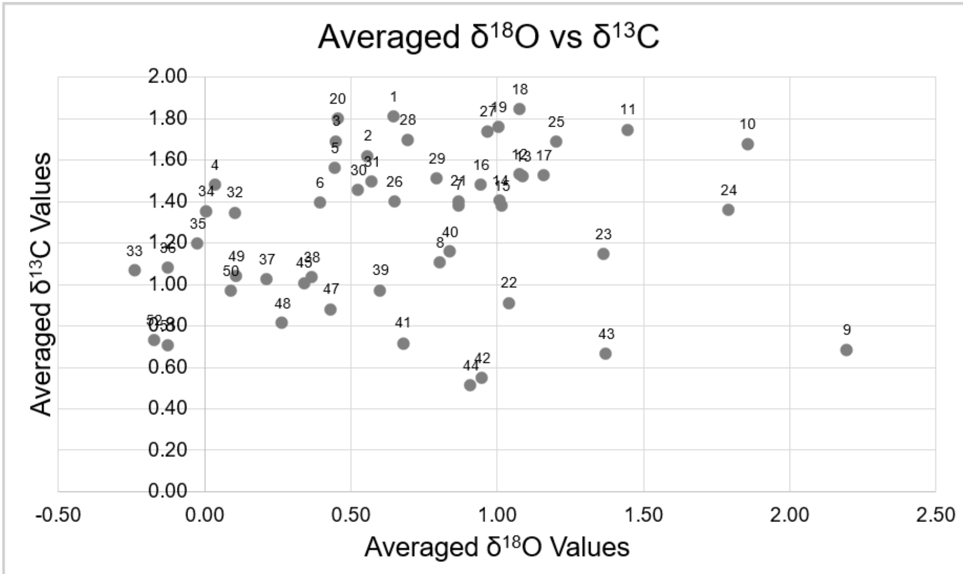

Figure 7: Oxygen and Carbon isotope data from *Mercenaria* shell YT-2. The x-axis displays averaged $\delta^{18}O$ values and the y-axis displays averaged $\delta^{13}C$ values for each band averaged across all samples taken. Data points are labeled corresponding to their sample numbers.

Trace Element Results

A total of 29 trace elemental analyses were performed across samples taken from 27 unique growth bands for *Mercenaria* shell YT-2 in this study. Concentrations of Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca, Fe/Ca, and Zn/Ca were measured. Analyses were performed on a variety of samples to capture a range of $\delta^{18}O$ and $\delta^{13}C$ values. Trace element incorporation into foraminiferal shells is controlled by physical and chemical conditions of the surrounding marine environment, and therefore provides a means for paleoenvironmental reconstructions. Trace elemental data can be compared with $\delta^{18}O$ and $\delta^{13}C$ isotopic data to further constrain environmental signals such as upwelling and the input of freshwater.

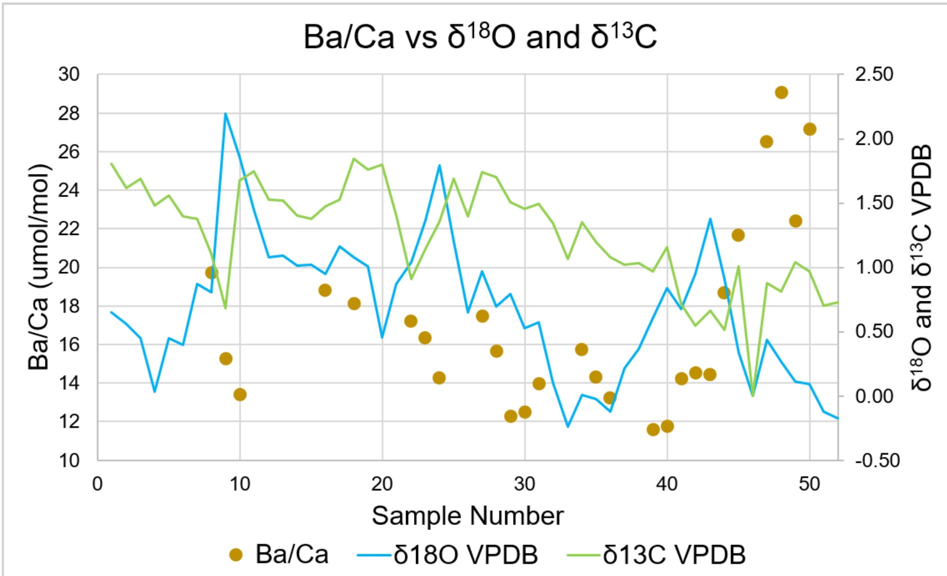

Figure 8: Measured Ba/Ca values (brown points), averaged $\delta^{18}O$ values (blue line), and averaged $\delta^{13}C$ values (green line) from *Mercenaria* shell YT-2 plotted by sample number.

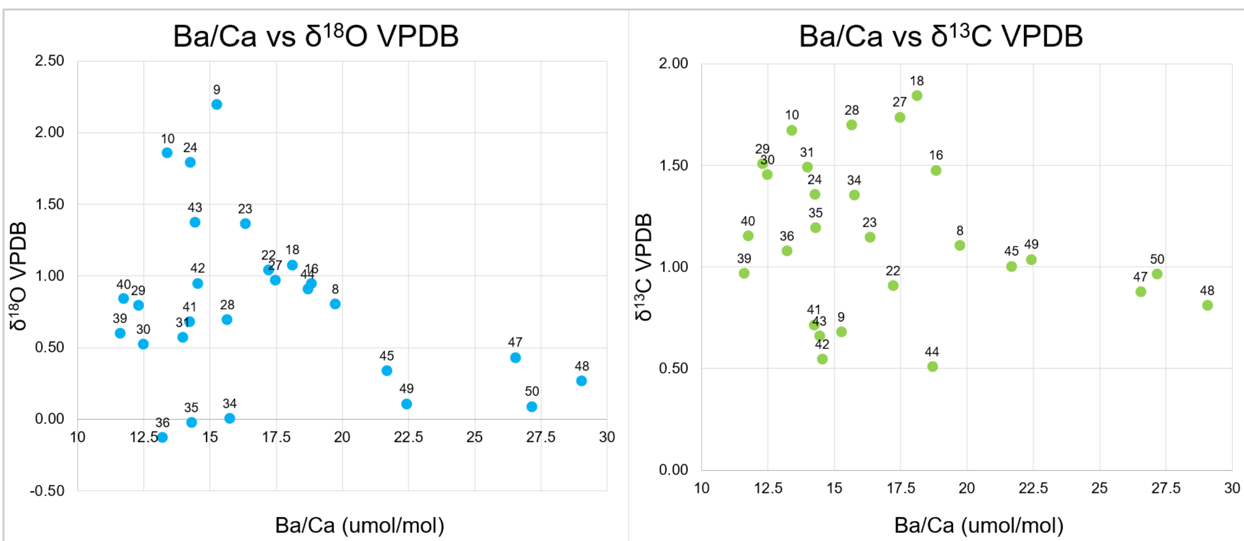

Figure 9: Measured Ba/Ca values from *Mercenaria* shell YT-2 plotted against $\delta^{18}O$ (blue) and $\delta^{13}C$ (green) averaged sample values and labeled corresponding to their sample number.

Several trends were observed when comparing trace element concentrations and isotopic data. Ba/Ca values varied from ~11.5-29 umol/mol. The highest Ba/Ca values were measured between sample numbers 45-50 near the end of the sampling traverse (Figure 8). Increments of shell growth measured to contain high Ba/Ca values were found to coincide with low $\delta^{18}O$ and $\delta^{13}C$ values. The highest $\delta^{18}O$ and $\delta^{13}C$ values were found alongside low measured Ba/Ca values (Figure 9).

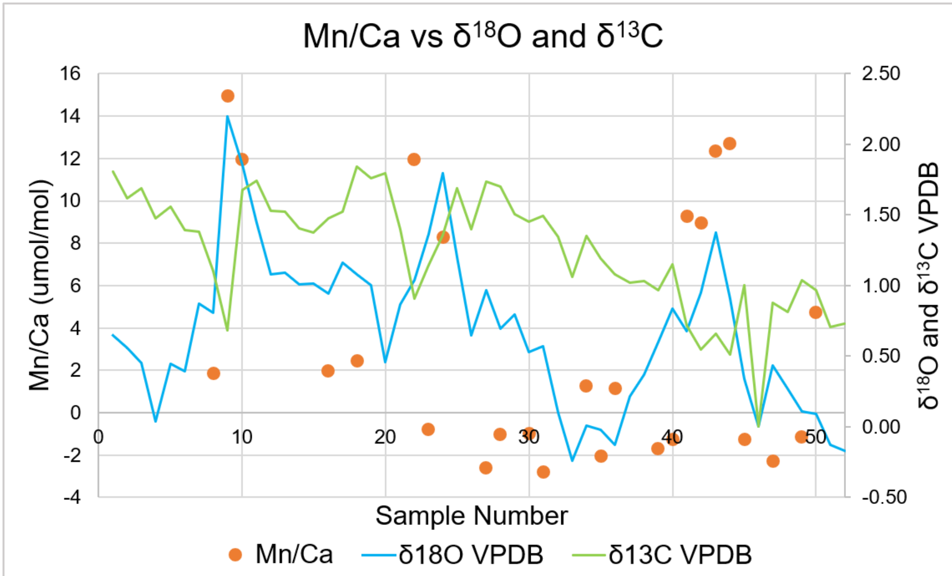

Figure 10: Measured Mn/Ca values (orange points) and averaged $\delta^{18}O$ values (blue line) from *Mercenaria* shell YT-2 plotted by sample number. Negative Mn/Ca values should be treated as samples with negligible concentrations of Mn.

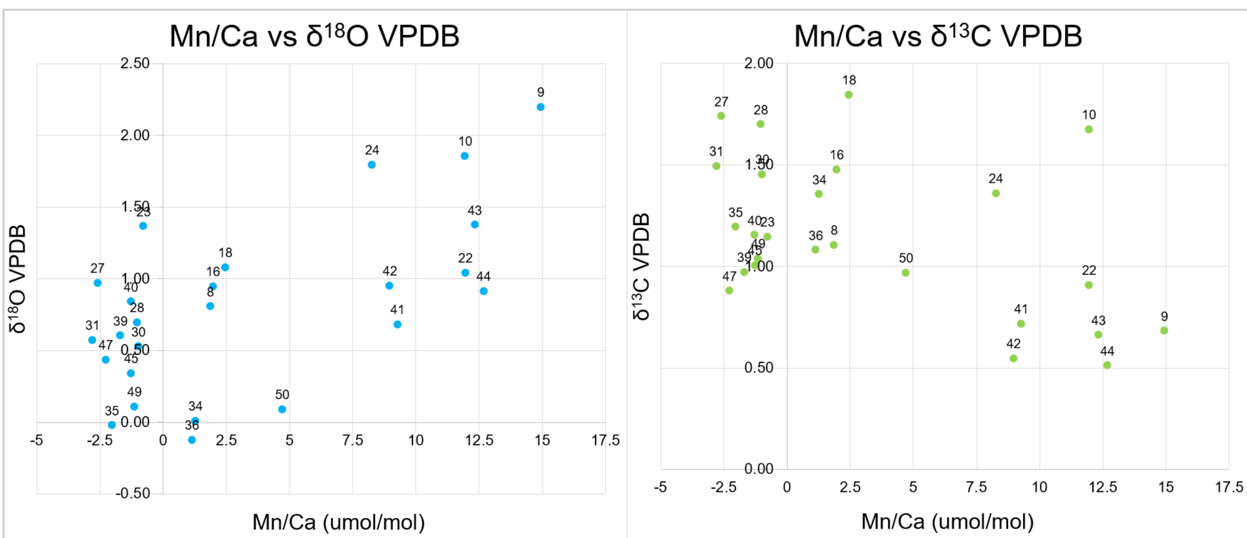

Figure 11: Measured Mn/Ca values from *Mercenaria* shell YT-2 plotted against $\delta^{18}O$ (blue) and $\delta^{13}C$ (green) averaged sample values and labeled corresponding to their sample number. Negative Mn/Ca values should be treated as samples with negligible concentrations of Mn.

Measured Mn/Ca values varied from ~-2.5-15 umol/mol. Several analyses resulted in negative Mn/Ca values. Negative values are not possible and are a result of negligible (below instrumental detection limits) Mn concentrations in the sample. A positive covariance is observed between Mn/Ca values and $\delta^{18}O$ values, while a negative correlation is observed between Mn/Ca values and $\delta^{13}C$ values. Increments of shell growth measured to contain high Mn/Ca values were found to coincide with high $\delta^{18}O$ and low $\delta^{13}C$ values. Increments of shell growth measured to contain low Mn/Ca values were found to coincide with low $\delta^{18}O$ and high $\delta^{13}C$ values (Figure 11).

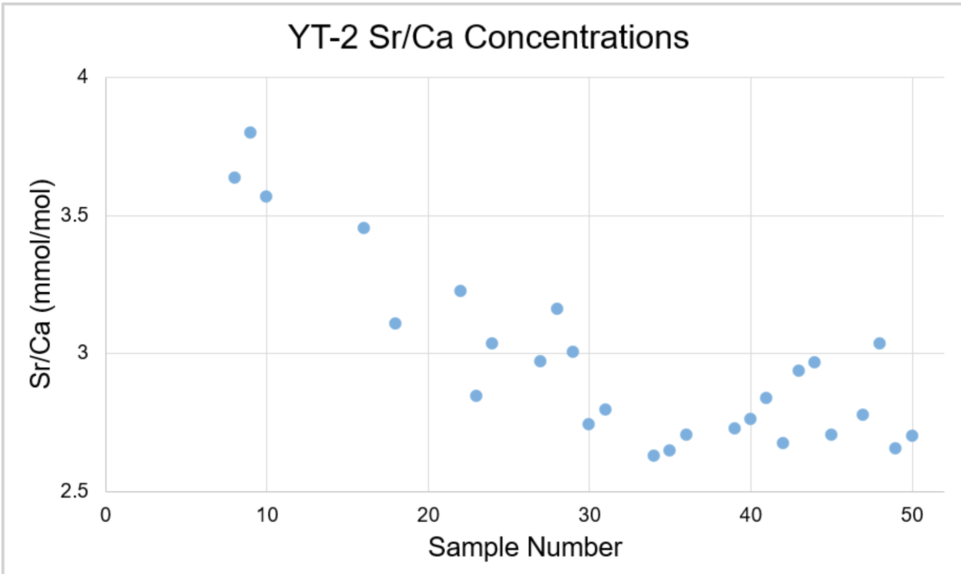

Figure 12: Measured Sr/Ca concentrations plotted against sample number.

Measured Sr/Ca concentrations varied from ~2.6-3.8 mmol/mol. A progressive decrease in Sr/Ca concentrations was observed with age of shell growth, however no covariations with $\delta^{18}O$ and $\delta^{13}C$ were observed (Figure 12). Few trends were observed with measured Mg/Ca, Fe/Ca, and Zn/Ca concentrations throughout shell growth.

Clumped-Isotope Results

A total of 5 clumped-isotope analyses were performed on samples of *Mercenaria* shell YT-2 in this study. The 5 samples taken for clumped-isotope analysis correspond to sample numbers 9, 28, 34, 41, and 48 on shell YT-2 (Table 1). The carbonate clumped-isotope thermometer is useful for paleoclimatic applications because it enables the temperature of shell formation to be measured without assuming $\delta^{18}O_{sw}$ values as required in conventional $\delta^{18}O$ thermometry.

Sample Number	Mean T	Mean d18O	Mean d13C	Mean d18Ow	1SE d18Ow
9	20.3	1.53	1.00	1.6	1.2
28	23.5	1.46	0.89	2.2	1.1
34	36.7	1.34	0.42	4.2	2.4
41	11.9	0.82	0.83	-0.4	2.2
48	14.9	1.14	0.27	-0.3	1.5

Table 1: Results of clumped-isotope analyses taken for sample numbers 9, 28, 34, 41, and 48. Clumped-isotope results for sample number 34 produce extreme estimates for temperature and $\delta^{18}O_{sw}$ and should be considered with caution.

Preliminary clumped-isotope results from shell YT-2 provide a seasonal temperature range of ~11.5°C. Minimum temperatures are estimated to be ~12°C, corresponding to YT-2 sample number 41, and maximum temperatures are estimated to be ~23.5°C, corresponding to YT-2 sample number 28. These results contain a standard error of ~4°C. A range of 2.6‰ is observed for $\delta^{18}O_{sw}$ values calculated in these analyses. Estimated $\delta^{18}O_{sw}$ is as low as -0.4‰ in sample number 41 and as high as 2.2‰ in sample number 28. Clumped-isotope results produced for sample number 34 produce extreme temperature and $\delta^{18}O_{sw}$ estimates and should thus be considered with caution. The temperatures and $\delta^{18}O_{sw}$ values discussed above do not take these results into consideration. Further samples covering a broader range of shell growth intervals is necessary to place more constraints on temperature estimates and $\delta^{18}O_{sw}$ values.

Discussion

Reconstruction of Paleotemperatures

Paleotemperatures from the mid-Pliocene were reconstructed based on the $\delta^{18}O$ values of *Mercenaria* shell YT-2 from the Yorktown Fm. of Virginia. To estimate the temperatures of shell growth from $\delta^{18}O$ carbonate, it is necessary to constrain the $\delta^{18}O_{sw}$ of seawater. This study uses the estimate of 1.1‰ $\delta^{18}O_{sw}$ (VSMOW) provided by Williams et al. (2009) which has been used in prior paleoclimate studies of this time period and region (Winkelstern et al., 2013, Johnson et al., 2017, Braniecki, 2022). Shell YT-2 shows a seasonal temperature range of 10.6°C with a minimum temperature of 11°C and a maximum temperature of 21.6°C. Applying the estimate of -0.6‰ $\delta^{18}O_{sw}$ (VSMOW) used by Krantz (1990) and Boswell (2019), shell YT-2 shows a seasonal temperature range of 9.8°C with a minimum temperature of 4.2°C and a maximum temperature of 14°C. The work of Ansell (1968) constrained the minimum temperature for *Mercenaria* shell growth at 9°C, and thus we find the estimate of 1.1‰ $\delta^{18}O_{sw}$ (VSMOW) provided by Williams et al. (2009) to be more favorable in this study.

Modern day temperatures in coastal Virginia range from 4.4-25.5°C while estimated paleotemperatures range from 11-21.6°C, suggesting a reduced seasonal range (10.6°C vs 21.1°C) accounted for by warmer winter temperatures and cooler summer temperatures in this region during the mPWP.

Study	Sample Location	$\delta^{18}O_{sw}$ Used (‰)	Minimum Temperature Estimate (°C)	Maximum Temperature Estimate (°C)	Estimated Temperature Range (°C)
Krantz (1990)	Yorktown Fm., VA	-0.6	7.9	22.9	15
Boswell (2019)	Yorktown Fm., VA	-0.6	7.7	19.3	11.6
Williams et al. (2009)	Yorktown Fm., VA	1.1	13.6	29.7	16.1
Winkelstern et al. (2013)	Yorktown Fm., VA	1.1	15.3	29.2	13.9
Johnson et al. (2017)	Yorktown Fm., VA	1.1	12.5	29.3	16.8
Braniecki (2022)	Duplin Fm., NC	1.1	14	24	10
This Study	**Yorktown Fm., VA**	**1.1**	**11**	**21.6**	**10.6**
This Study	**Yorktown Fm., VA**	**-0.6**	**4.2**	**14**	**9.8**

Table 2: Minimum and Maximum temperature estimates based on measured $\delta^{18}O$ values across paleoclimate studies. Temperature was calculated using the aragonite-water temperature fractionation relation of Dettman et al. (1999). A seawater $\delta^{18}O_{sw}$ value of 1.1‰ was used in these calculations for mid-Pliocene (Williams et al., 2009). These data are compared to the minimum and maximum temperature estimates from Krantz (1990), Boswell (2019), Williams et al. (2009), Winkelstern et al. (2013), Johnson et al. (2017), and Braniecki (2022).

Comparison to Prior Paleoclimate Studies

Differences are observed when comparing mPWP seasonal temperature estimates with prior paleoclimate studies of this region. Krantz (1990) reported a seasonal temperature range of 15°C and minimum and maximum temperatures of 7.9°C and 22.9°C, respectively. Boswell (2019), using the same Mercenaria shell YT-2 as in this study, reported a seasonal temperature range of 11.6°C and minimum and maximum temperatures of 7.7°C and 19.3°C, respectively. However, both Krantz (1990) and Boswell (2019) used $\delta^{18}O_{sw}$ value of -0.6‰ in temperature calculations, making comparisons difficult. Studies by Winkelstern et al. (2013), Johnson et al. (2017), and Braniecki (2022) use a $\delta^{18}O_{sw}$ value of 1.1‰ in their calculations and therefore provide more meaningful results when making comparisons. Winkelstern et al. (2013) reported a seasonal temperature range of 13.9°C and minimum and maximum temperatures of 15.3°C and 29.2°C, respectively. Johnson et al. (2017) reported a seasonal temperature range of 16.8°C and minimum and maximum temperatures of 12.5°C and 29.3°C, respectively. Using samples from the coeval Duplin Fm. of North Carolina, Braniecki (2022) reported a seasonal temperature range of 10°C and minimum and maximum temperatures of 14°C and 24°C, respectively.

Temperatures calculated in our study suggest a reduced seasonal temperature range (10.6°C) than Krantz (1990), Winkelstern et al. (2013), and Johnson et al. (2017), who all reported a range of ~15°C. Estimates of temperature variability by Boswell (2019, 11.6°C) and Braniecki (2022, 10°C) are more in line with our study. Temperature estimates in our study suggest generally cooler summers and winters than prior studies using a $\delta^{18}O_{sw}$ value of 1.1‰ (Winkelstern et al., 2013, Johnson et al., 2017, and Braniecki, 2022). Estimates by Boswell (2019) suggested generally cooler temperatures year-round, though this is likely due to the $\delta^{18}O_{sw}$ value of -0.6‰ used in calculations in that study. Krantz (1990), also using a $\delta^{18}O_{sw}$ value of -0.6‰, found cooler winter temperatures but comparable summer temperatures. Uncertainties regarding estimated $\delta^{18}O_{sw}$, which is treated as constant year-round, may influence temperature estimates in this study as well as prior studies.

Interpretation of Results

The apparently cool temperature estimates that are derived from oxygen isotope measurements in this study require further examination. To explain high mPWP paleotemperatures (~14-29°C), Winkelstern et al. (2013) and Braniecki (2022) proposed increased Gulf Stream heat transport in this region of the MACP. This hypothesis is not supported by the cooler temperatures estimated from *Mercenaria* shell YT-2.

Trends observed between $\delta^{18}O$, $\delta^{13}C$, Ba/Ca, and Mn/Ca allow for further constraints to be placed on paleoenvironmental reconstructions. A negative correlation is observed between $\delta^{18}O$ and $\delta^{13}C$, whereby an increase in $\delta^{18}O$ values is seen alongside a decrease in $\delta^{13}C$. High Mn/Ca values are found alongside high $\delta^{18}O$ values and low $\delta^{13}C$ values. Upwelling of cold bottom waters would be reflected in more positive $\delta^{18}O$ values and more negative $\delta^{13}C$ values in shell carbonate. Moreover, these waters are sourced from below the oxygen minimum zone where elevated Mn concentrations would be expected. Mn concentrations in normal oxygenated marine waters would not be high enough to be incorporated in precipitated molluscan carbonate. Though not conclusive, it is possible that deep water upwelling could explain the unusually heavy oxygen and light carbon analyses observed alongside increases in Mn/Ca.

Preliminary clumped-isotope results are not compatible with the upwelling hypothesis. The more positive $\delta^{18}O$ values correspond with the highest calculated temperatures. Interestingly, the coldest clumped-isotope temperatures correspond to the cooler carbonate precipitation temperatures as well as the most negative $\delta^{18}O_{sw}$ values. Together, these results may be suggestive of the input of riverine freshwater. The covariance of negative $\delta^{13}C$ and $\delta^{18}O$

are also compatible with a freshwater source. Rivers transport Ba into coastal waters; thus, Ba/Ca values preserved in shell growth are often used as a tracer for freshwater input from rivers and streams (Alibert C, et al., 2003; Elliot et al., 2009). It is possible that the notably elevated Ba/Ca values observed in the trace element analyses, and which coincide with the low $\delta^{18}O_{sw}$ values measured in clumped-isotope analyses, provide further evidence of terrestrial runoff. Though these initial clumped-isotope results are not supportive of an upwelling origin for the most positive $\delta^{18}O$ carbonate values, additional high resolution clumped isotope analysis would further our understanding of climate dynamics during the inferred mid-Pliocene warming.

Conclusions

This study reconstructed paleoenvironmental conditions in the mPWP on a seasonal scale using isotopic and trace element data collected from the marine bivalve *Mercenaria*. Temperatures calculated from oxygen isotope data result in a seasonal temperature range of 10.6°C which is reduced from the present range of 21.1°C recorded by instruments. Minimum temperatures (11°C) estimated in this study are greater than modern (4.4°C), while maximum temperatures (21.6°C) estimated in this study are lower than modern (25.5°C). Temperature estimates were calculated using a $\delta^{18}O_{sw}$ value of 1.1‰ predicted by climate models (Williams et al., 2009). We find this $\delta^{18}O_{sw}$ value to be more favorable than the $\delta^{18}O_{sw}$ value of -0.6‰ used by Krantz (1990) which resulted in temperatures estimates below the growth range of *Mercenaria* shells. The temperature estimates in this study contrast with previously published reconstructions of this period and region which found greater temperature variability (~15°C), and higher minimum (~14°C) and maximum (~29°C) temperatures (Williams et al., 2009; Winkelstern et al., 2013; Johnson et al., 2017).

The examination of trace element data suggests the influence of upwelling along coastal Virginia during the mPWP. The correlation among increased $\delta^{18}O$ values with decreased $\delta^{13}C$ values and increased Mn/Ca may record seasonal periods of upwelling of colder deep waters which may bias temperature estimates. Preliminary clumped-isotope analyses are suggestive of riverine input whereby the coldest estimated clumped-isotope temperatures correspond more negative $\delta^{18}O_{sw}$ values and an increase in Ba/Ca values. Accurate paleoclimate reconstructions of the mPWP will remain difficult until further studies employing high resolution analyses provide more conclusive results.

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