

Mid-Pliocene Paleotemperature Reconstruction: Evaluation of the Sclerochronologic Isotopic
Record of Molluscan Bivalves from the Pinecrest Beds of the Tamiami Formation, FL and the
Yorktown Formation, VA.

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Abstract

The Mid-Pliocene Climatic Optimum is an interval of natural warming of the Earth's climate from 4.4 to 2.97 Ma that has been based on the synthesis of numerous geologic proxies of temperature (Dowsett et al, 1999, 2004, 2013, 2016, Poore and Sloan, 1996; Raymo, Grant, et al., 1996). However, numerous questions remain regarding the absolute magnitude and extent of this temperature departure as quantification of paleotemperatures remains difficult and imprecise. Prior studies have examined taxa abundance assemblages, numerical climate modeling and oceanographic faunal analysis yet the application of stable isotope analysis of skeletal carbonate preserved in coastal sediments of this age is relatively limited (Jones and Allmon, 1995, Krantz, 1990, and Williams et al., 2009). This study, employing high resolution sampling, extends these studies to evaluate the coherence of existing datasets and validity of prior paleoclimate reconstructions.

This study examined samples of the marine bivalve *Mercenaria* from the Pliocene Pinecrest beds of the Tamiami Fm. (Sarasota, FL) and the Yorktown Fm. (York, VA). High resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records show strong seasonality in most specimens which record possible variation in surface temperature and/or water composition. Temperature estimates from the Pinecrest Beds. range from 10 to 28.4°C whereas, estimates for the Yorktown Fm. show lower winter and summer temperatures, ranging from 7.7 to 19.3°C. Combined variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ was also examined and shows a strong positive covariance in most samples, although significant variation in $\delta^{13}\text{C}$ deviating from this covariance is present in several samples.

Paleotemperature estimates presented here share similarities with prior studies, yet possess some significant differences. When compared to the data of Jones and Allmon (1995) that show a 13.9°C (6.9-20.8°C) seasonal temperature range, we observe a greater seasonal range, 18.4°C (10-28.4°C, winter-summer) when using a $\delta^{18}\text{O}$ seawater value of -0.6‰ for the mid-Pliocene. Our estimates are comparable to Williams et al. (2009) who recalculated temperatures of the Jones and Allmon (1995) data using a $\delta^{18}\text{O}$ seawater value of +1.02‰, a value predicted by numerical climate models. This estimate results in a seasonal range of 18.8°C (6.9 to 25.7°C – winter-summer). For comparison, today's temperature in Florida ranges from 16 to 27°C. Yorktown Fm. temperature estimates for this study show a seasonal range of 11.6°C (7.7 to 19.3°C, winter-summer) in contrast to that of Williams et al. (2009) where they used an adjusted $\delta^{18}\text{O}_{\text{sw}}$ of +1.2‰. The use of such isotopically enriched estimates of $\delta^{18}\text{O}$ of seawater artificially raise their temperature estimates relative to those of this study and of Jones and Allmon (1995). When such high seawater $\delta^{18}\text{O}$ values are applied to our Pinecrest Beds data, unrealistically high temperatures are obtained that lie above the growth limits of *Mercenaria*. In addition, examination of combined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data, that shows a strong positive covariance, suggest that input of freshwater from terrestrial sources may dominate the carbon isotopic composition and may bias estimates to slightly higher temperatures. Non-covariant change in $\delta^{13}\text{C}$ may be recording episodes of upwelling of colder deep waters, which again may bias temperature estimates. Accurate reconstruction of the mid-Pliocene paleoclimate record will remain elusive until independent measures of $\delta^{18}\text{O}$ seawater are made utilizing other geochemical proxies such as clumped isotope paleothermometry.

Introduction

The impacts of the current trajectory of global temperature change suggests significant climate warming is likely. This will be the case unless drastic and immediate steps are taken to mediate the atmospheric inputs of anthropogenic CO₂ from the burning of fossil fuels. Though numerical simulations can provide a glimpse into possible global impacts of Earth's response to warming, such as changes in latitudinal thermal gradients and retardation of ocean circulation, a more accurate picture is possible through the analysis of the geologic record during times of comparably warm periods in Earth's past. It has been proposed by numerous authors that warming to such high levels has occurred naturally during the Mid-Pliocene approximately 4.4 to 2.97 Ma (Poore and Sloan, 1996; Raymo, Grant, et al., 1996). This interval in Earth's climate history (see Figure 1) has been termed the Mid-Pliocene Climatic Optimum (Zubakov and Borzenkova, 1988). The Mid-Pliocene Climatic Optimum has been based on the synthesis of numerous geologic proxies of temperature. However, numerous questions remain regarding the absolute magnitude and extent of this temperature departure as quantification of paleotemperatures remain difficult and imprecise.

Evidence for this interval of global warmth has been supported through analysis of the $\delta^{18}\text{O}$ of benthic foraminifera that shows a marked departure during the early and mid-Pliocene prior to initiation of northern hemisphere glaciation (Lisiecki and Raymo, 2005). This is based on the premise that in a world where ice is present at high latitudes (i.e., Antarctica and Greenland), thermohaline circulation maintains bottom water temperatures relatively constant. This means that changes in measured $\delta^{18}\text{O}$ must reflect changes in ice volume which is responsive to global temperatures. (Shackleton, Blackman, et al., 1984; Prell, 1984). Further evidence lies in an evaluation of sea level during time. Haq et al (1987) suggested significantly higher sea level (up to 60 meters) that also suggests significant warming of the Antarctic region with substantial melting of the ice sheet. It is not until the latest mid-Pliocene (2.5-2.4 Ma) that evidence of the initiation of Northern Hemisphere glaciation is present in the form of IRD – Ice Rafted Debris (Shackleton, et al., 1984; Raymo, 1994; and Hay et al., 2002).

It is in this context that a multi-proxy study was initiated through the USGS – Pliocene Research, Interpretations, and Synoptic Mapping project (PRISM) (Dowsett et al., 1999, 2004, 2013 and 2016). PRISM research has focused on the time interval between 3.3 and 2.97 Ma to reconstruct the surface temperatures and environmental conditions associated with the period of overall warmth. Though subsequent work has synthesized multiple proxies to this end, the primary approach was to construct transfer functions that quantitatively relate the composition and relative abundance of taxa in biofacies assemblages to specific environmental factors such as temperature, salinity, etc. This is akin to the approach utilized in present, Eco-Niche Modelling, which is a current revitalization of biofacies analysis in a context of environmental limiting factors. Results of this work indicate temperate faunas were replaced by subtropical assemblages during the Mid-Pliocene in response to the overall warming of the North Atlantic region (Dowsett et al., 2013, 2016). In addition, the synthesis of multiple proxies supports the contention that during this time the Pole to Equator temperature gradient was reduced in large part due to a decrease in sea-ice extent (Dowsett et al., 2016).

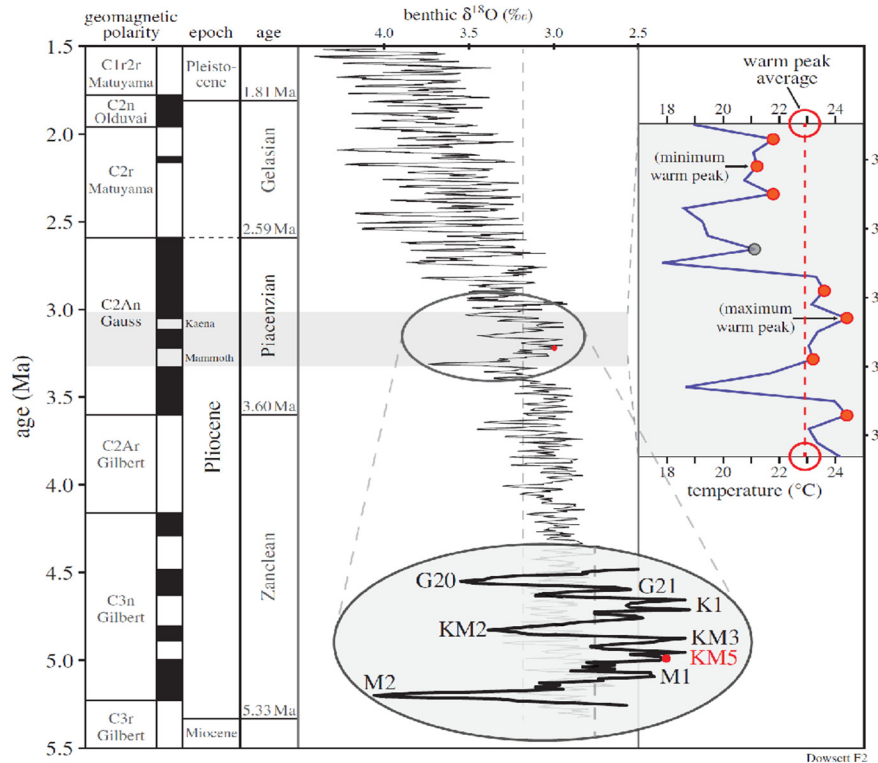


Figure 1: Benthic foraminifera $\delta^{18}\text{O}$ stacked record from Lisiecki and Raymo (2005) showing overall early and mid-Pliocene warming prior to the initiation of northern hemisphere glaciation. Figure from Dowsett et al., 2003.

Despite extensive investigation, including numerous geochemical and biological proxies that show a general increase in global temperature, the application of stable isotope analysis of skeletal carbonate preserved in coastal sediments of this age is relatively limited (Jones and Allmon, 1995, Krantz, 1990, and Williams et al., 2009). Studies that focus on molluscan carbonates have the ability to 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.

This study examines the seasonal-scaled $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic variation preserved in bivalve Mollusca from two disparate geographical sites: Southeast Florida and Virginia –currently representing tropical and temperate conditions, respectively. Results obtained will be compared with existing published datasets to validate prior findings. If comparable temperature ranges and seasonal variation are observed, this will provide the framework for further application of additional paired proxies (clumped isotope analysis). 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 that may have biased temperature estimates of prior studies (i.e., upwelling versus salinity modification).

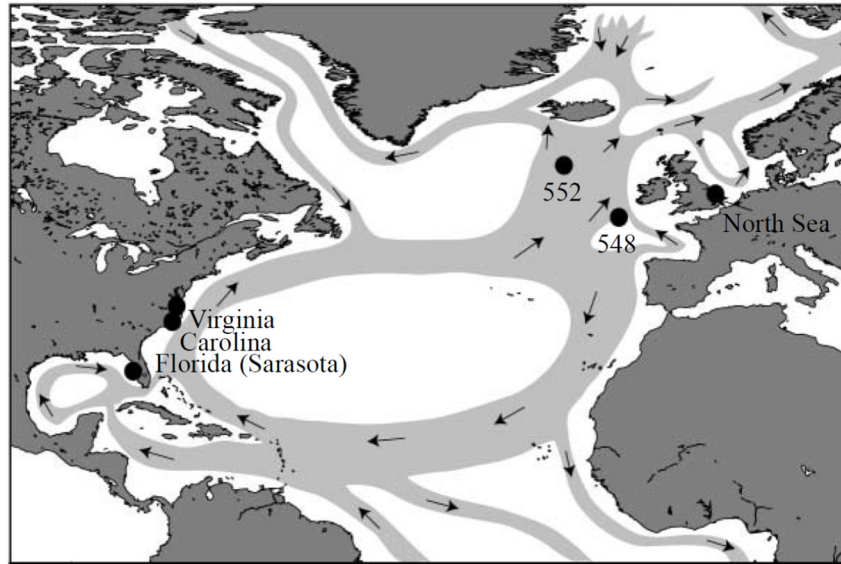


Figure 1: Locality map of the Pinecrest beds of the Tamiami Fm. of Sarasota, FL with its lateral equivalent of the Yorktown Fm. of York, VA. *Figure from Williams et al. (2009)*

Materials and Methods

Stable isotope analysis of marine molluscan (bivalves) carbonate was employed in this study to provide a high temporal resolution of environmental conditions of growth. Numerous previous studies have demonstrated that Mollusca precipitate their shells in isotopic equilibrium, reflecting changes in both water composition and temperature (Elliot et al., 2003; Surge and Walker, 2006; and many others). Given the relatively rapid rate of growth of the shell, incremental banding provides a framework for reconstructing environmental conditions on a sub-annual (seasonal) scale.

Samples used in this study are of mid-Pliocene age from the Pinecrest Beds of the Tamiami Fm. (Quality Aggregates Quarry near Sarasota County, FL) and from the time equivalent Yorktown Fm. (York County, VA – University of Michigan Museum of Paleontology - UMMP). These sites were chosen to provide a spatial context enabling the evaluation of coeval latitudinal temperature difference. In this study, we have concentrated our analysis on *Mercenaria sp.* These taxa are coastal infaunal bivalves occupying marginal marine coastal settings (Elliot et al., 2003). Their shallow water habitat offers a setting capable of recording variation in seasonal temperature, salinity, and nutrient supply.

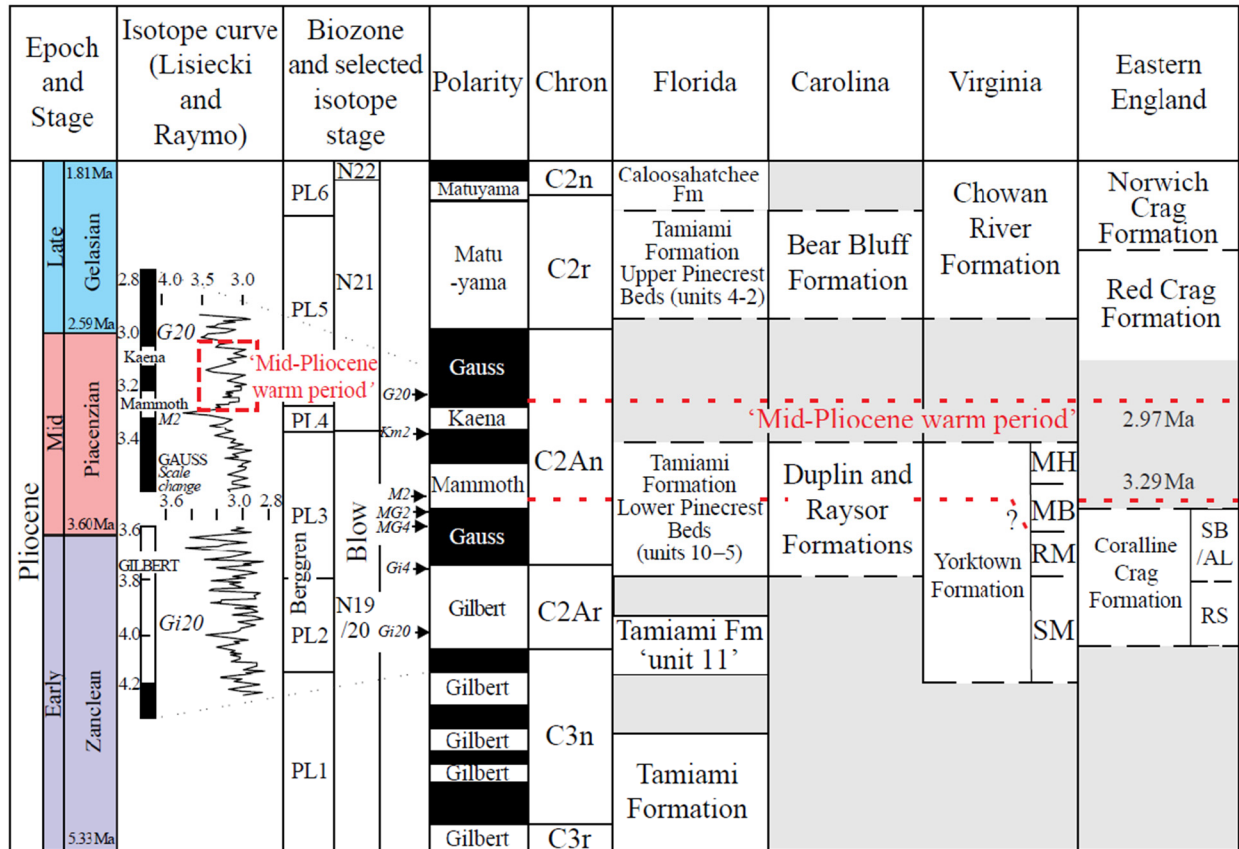


Figure 2: Chronostratigraphic correlation of Pliocene strata along the Atlantic coast of the US including Florida, the Carolinas, and Virginia (from Williams et al., 2009). The Pinecrest Beds of the Tamiami Fm. are temporally equivalent to the upper members of the Yorktown Fm. in Virginia and are coincident with the Mid-Pliocene warm period.

The Pinecrest Beds of the Tamiami Fm. (Fig. 2) lie below the Caloosahatchee Fm. in southwest Florida (Williams et al., 2009). They are composed of fine quartz sand containing abundant fossils and calcareous muds (Williams et al., 2009). The depositional environment represents a major transgression of a beach sequence and is characterized by spectacularly preserved taxa that are largely unaltered. The preservation of their primary aragonite mineralogy and fine internal shell structure make them ideal specimens for this study.

The Yorktown Fm. outcrops in the Carolinas and Virginia. The lower boundary of the formation is unconformable above the Eastover Fm. and it is overlain by the Chowan River Fm. (Williams et al., 2009). This formation comprises fine-grained sandy clays and shell marls that were deposited during a transgressive phase of the Coastal Plain sedimentary sequence (Williams et al., 2009). The Yorktown Formation (Fig. 2) is composed of four members with the middle of the formation being the Rushmere and Mogart’s Beach Members (Williams et al., 2009). It is estimated to represent 1 Ma of deposition.

Before microsampling for isotopic analysis, each shell was washed and scrubbed to remove any remaining sand and external contamination. Samples PC-2, PC-4, and PC-5 were cut along the axis of maximum growth from the umbo to the ventral margin with a water-cooled diamond saw. After cutting, each half of the sample was then highly polished using .05 alpha alumina powder to clearly show the internal growth band structure. Microsamples were obtained from the

polished surface using a microscope-mounted drill assembly outfitted with 0.5mm dental bur. Samples Pc-5, YT-1, and YT-2 were taken from the exterior of the shell along successive growth bands to obtain a long time series, again using the sampling apparatus described above. Typical sample size was approximately 50 micrograms of powdered carbonate. The powdered samples were analyzed on 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.

Sampling of Molluscan Shell Carbonate

Sampling varied among the specimens examined in this study. Initial reconnaissance was performed on polished cuts in an attempt to sample successive growth bands. This was done for sample PC-2 and PC-4 (see Fig. 3 and 4). Because of the fineness of banding, subsequent sampling was performed on the exterior of shells where growth increments were thicker. Sample numbers correspond the sequential analyses in Figures 3 to 6.

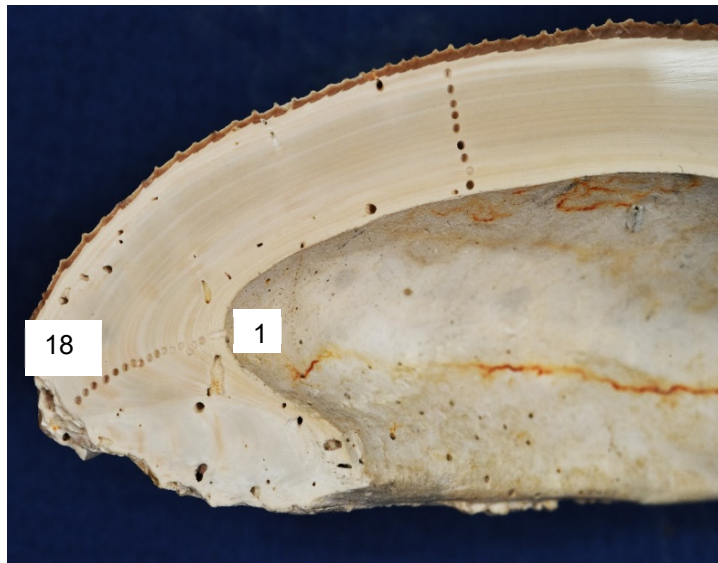


Figure 3: *Mercenaria sp.* (Sample PC-2) that was collected from Pinecrest beds of the Tamiami Fm. near Sarasota FL. Sample numbers begin on the interior of the shell (youngest growth) toward the outer margin (oldest growth). Length of sampling traverse is 13 mm. Sample from K.C. Lohmann.

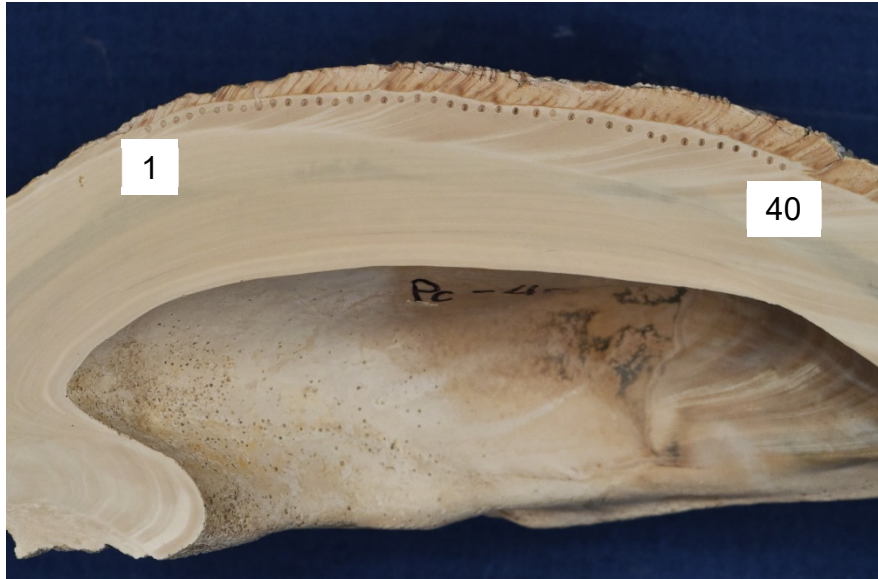


Figure 4: *Mercenaria sp.* (Sample PC-4) from Pinecrest beds of the Tamiami Fm. near Sarasota FL. Specimen obtained from UMMP. Samples follow growth bands on the polished surface beginning from 1 and completing at 40. The length of this traverse is 52 mm.

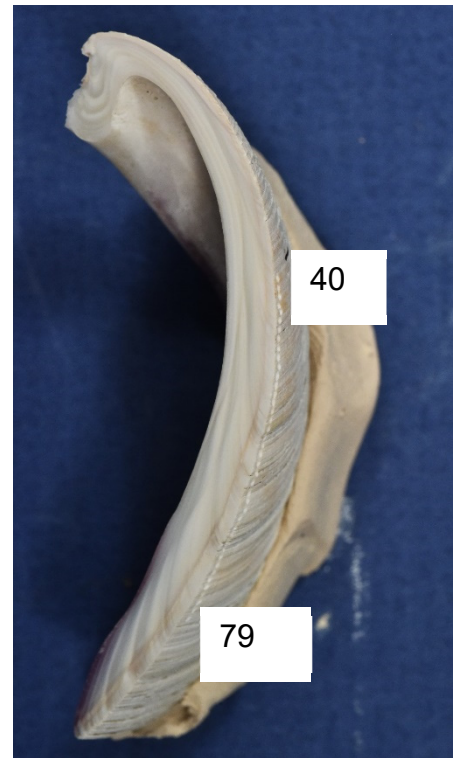
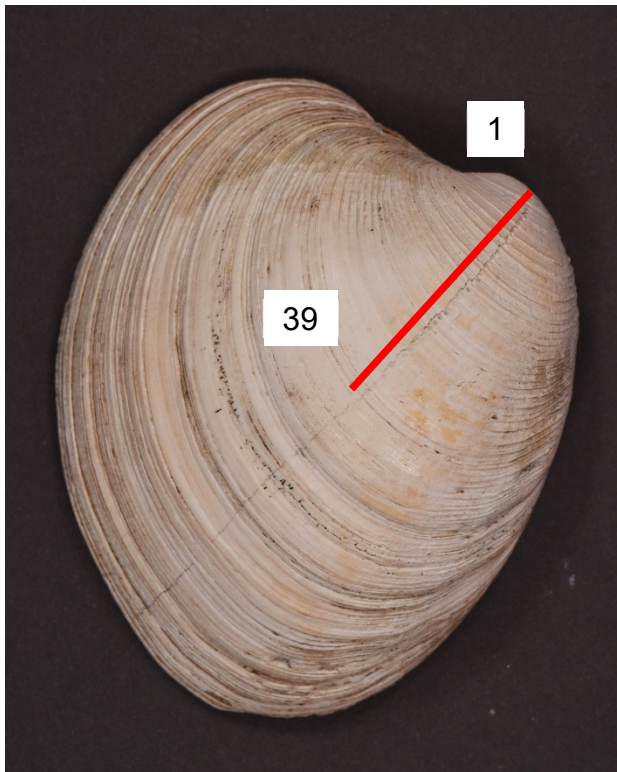


Figure 5: *Mercenaria sp.* (Sample PC-5) that was collected from Pinecrest beds of the Tamiami Fm. Specimen obtained from UMMP. Samples 1 through 39 were taken on the exterior of the shell prior to cutting. Sampling continued along line of cut for samples 40 to 79. Sample is 6.5 cm from umbo to the distal margin.

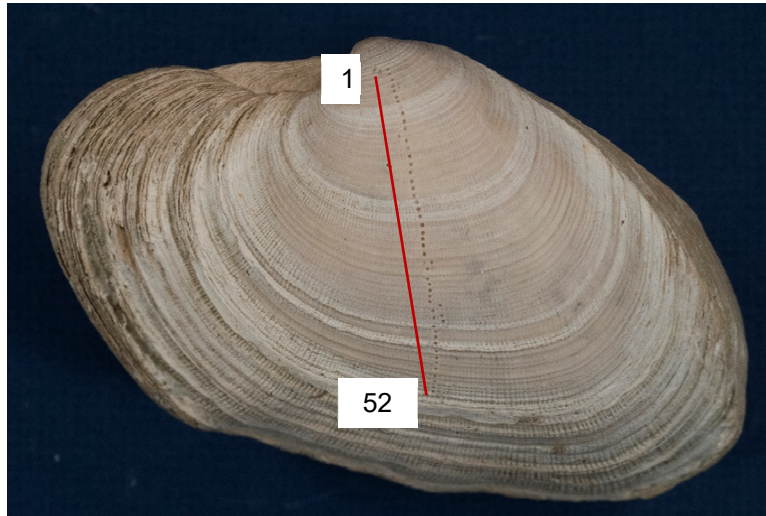


Figure 6: *Mercenaria sp* (Sample YT-2) that was collected from the Yorktown Fm. near York, VA. and obtained from UMMP. Sampling occurred on the exterior of the shell beginning near the umbo and terminating near the end of the shell at 52. The length of the sampling traverse is 5.6 cm.

Results of Stable Isotope Analysis

A total of 221 analyses were performed on four specimens as part of this study. The moderately high resolution serial sampling provides a temporal framework that enables examination of seasonal-scaled variation in the shell carbonate. In turn, these data can be employed to estimate environmental conditions such as seasonal paleotemperature ranges, variability in salinity, and possible effects of freshwater runoff or periodic upwelling. For all of the specimens examined, a seasonal signal was observed, although for one specimen a complete annual record may not be present. In this study, changes in $\delta^{18}\text{O}$ are used as the primary means of identifying summer versus winter growth. More positive $\delta^{18}\text{O}$ corresponds to cooler conditions while more negative values are representative of warmer summer temperatures. The coupled changes in $\delta^{13}\text{C}$ can then be examined to elucidate the seasonal variation in the carbon isotopic composition of seawater.

The most complete and longest record is present in sample PC-5 from the Pinecrest beds that shows four annual cycles. Summer minimum $\delta^{18}\text{O}$ values range from -1.5 to -2.2‰ and winter values range from +1.0 to +1.5‰ (Fig. 7 and Table 1). PC-4 also shows multiple years of record although the seasonal signal is attenuated (Fig. 9) with seasonal variation in $\delta^{18}\text{O}$ ranging from -.3 to +1.17 ‰ VPDB. Sample PC-2 (Fig. 8) exhibits only a partial yearly seasonal signal with $\delta^{18}\text{O}$ ranging from -0.71 to +0.92‰. Replicate sampling near the center of the shell across comparable growth bands produced a similar trend for both carbon and oxygen isotope values.

Seasonal changes in $\delta^{13}\text{C}$ show also exhibit seasonal variation. $\delta^{13}\text{C}$ values for PC-5 vary from +0.9 to -1.0‰, with an overall positive correlation with changes observed in $\delta^{18}\text{O}$ (Fig.7, right panel). This indicates that during summer warm periods, shown by more negative $\delta^{18}\text{O}$ values, seawater $\delta^{13}\text{C}$ composition is shifted toward more negative values. Other specimens

showing a lower seasonal amplitude in $\delta^{18}\text{O}$ variation, also show a similar, though weak, covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Variation in $\delta^{13}\text{C}$ present in these samples, however, is more complicated suggesting that other factors may be in play that influences the seawater carbon isotope composition independent of seasonal temperature effects. For example, sample P-2 exhibits two distinct populations, one that exhibits strong covariance in $\delta^{18}\text{O} - \delta^{13}\text{C}$ (Fig. 8. Field 1) and one that shows variable $\delta^{13}\text{C}$ coincident with relatively invariant $\delta^{18}\text{O}$ values coincident with the more positive $\delta^{18}\text{O}$ compositions (Fig. 8, Field 2). Similar deviations from an overall covariance trend is present in PC-4 (Fig. 9), although not as distinct as is illustrated in specimen PC-2.

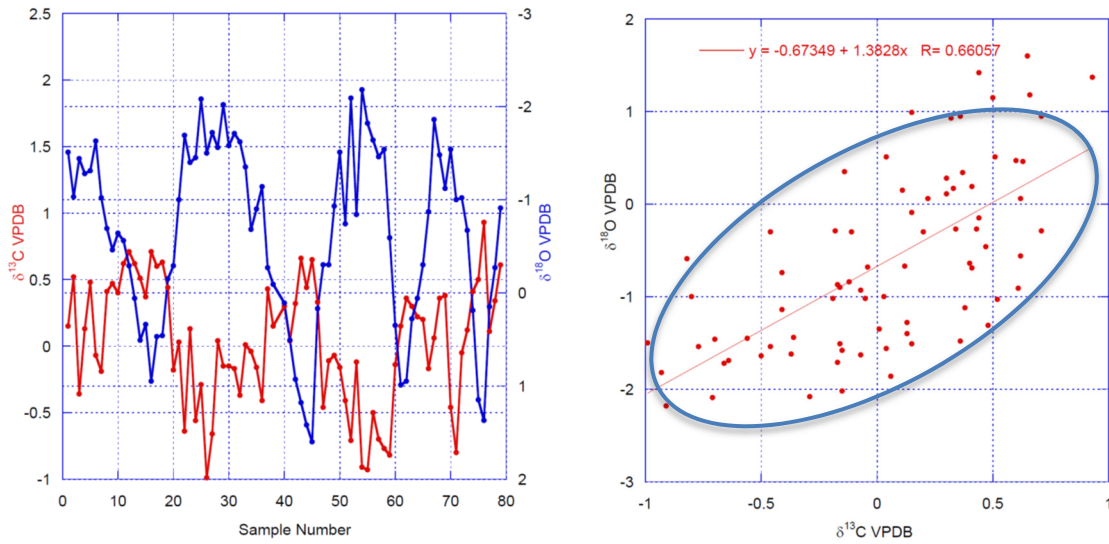


Figure 7: Carbon and Oxygen isotopic variation of Pinecrest 5. Note the seasonal range in oxygen (blue) extending from ~ -2.2 to $+1.6$ $\delta^{18}\text{O}$ VPDB (range 3.8‰). $\delta^{13}\text{C}$ (red) varies from -1.0 to $+0.9$. In the right diagram, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ co-vary with a significant correlation coefficient.

Sample Location	Sample Number	Minimum Temperature estimate ($^{\circ}\text{C}$)	Maximum Temperature estimate ($^{\circ}\text{C}$)	Temperature Range ($^{\circ}\text{C}$)	Maximum $\delta^{18}\text{O}_{\text{‰}}$	Minimum $\delta^{18}\text{O}_{\text{‰}}$	$\delta^{18}\text{O}_{\text{‰}}$ Range
Pinecrest Beds	PC-1A	14.8	17.6	2.8	0.54	-0.06	0.6
Pinecrest Beds	PC-1B	14.5	21.8	7.2	0.59	-0.91	1.5
Pinecrest Beds	PC-2	13.0	20.8	7.8	0.92	-0.71	1.63
Pinecrest Beds	PC-4	11.9	18.8	6.9	1.17	-0.3	1.47
Pinecrest Beds	PC-5	10.0	28.4	18.4	1.6	-2.18	3.78
Yorktown Fm.	YT-1	13.7	19.0	5.3	0.78	-0.34	1.12
Yorktown Fm.	YT-2	7.7	19.3	11.6	2.11	-0.41	2.52

Table 1: Minimum and Maximum temperature estimates based on measured $\delta^{18}\text{O}$ values for each sample. Temperature was calculated using the aragonite-water temperature fractionation relation of Dettman et al. (1999). A seawater $\delta^{18}\text{O}_{\text{SW}}$ value of -0.6 ‰ was used in these calculations for mid-Pliocene (Jones and Allmon, 1995).

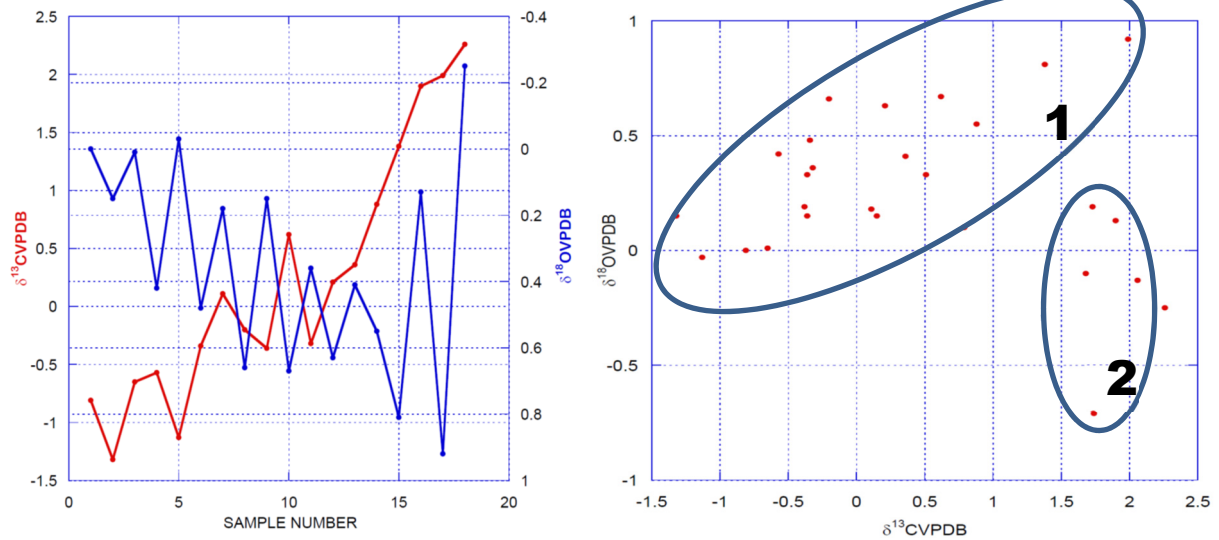


Figure 8: Carbon and Oxygen isotopic variation of Pinecrest 2. Although a much shorter time series is represented here compared to sample PC-5, a partial yearly seasonal signal is still present. Note that in the range in $\delta^{18}\text{O}$ variation is significantly less, exhibiting a range of only 1.6‰. Also, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cross plots show two populations: **Field 1** is positively covariant while **Field 2** exhibits little variation in $\delta^{13}\text{C}$ over a narrow range of positive $\delta^{18}\text{O}$. The linear regression equation for Field 1 is: $y = .3431 + .227x$ ($R = .60$)

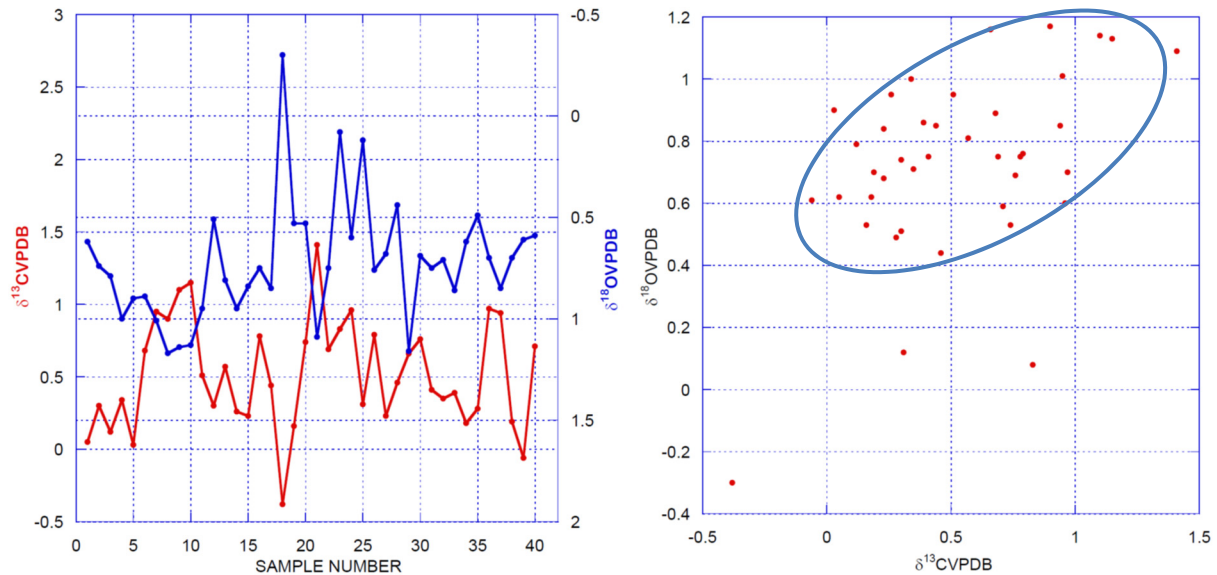


Figure 9: Carbon and Oxygen isotopic variation of Pinecrest 4. Seasonal variation is present with oxygen variation ranging from -0.3 to $+1.17$ $\delta^{18}\text{O}$ VPDB (range 1.47‰). $\delta^{13}\text{C}$ (red) varies from ~ -0.4 to $+1.41$ (range 1.79‰). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ shows a weak positive covariance. The linear regression equation is: $y = .534 + .3721x$ ($R = .47$)

The serial sampling of TC-2, a specimen collected from the Yorktown Fm. exhibits two full summer records (and two partial summers) and three winter records (Fig. 10). This sample yielded $\delta^{18}\text{O}$ results similar to most of the Pinecrest samples, characterized by low amplitude seasonal signals. $\delta^{18}\text{O}$ values range from +2.11 to -.41; $\delta^{13}\text{C}$ values range from +1.81 to +.46. Results for ample YT-1 are not shown here as an inadequate sample traverse length precluded definitive recognition of seasonal cycles. Data for this shell likely captured the summer compositions but a winter maximum was likely not represented in our sampling traverse. Similar to what was observed in the Pinecrest samples, there is a weak positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for much of the data, however, deviation of carbon values from this trend show positive excursions across a large range of $\delta^{18}\text{O}$ values. This is in contrast to the negative $\delta^{13}\text{C}$ deviations observed for those samples.

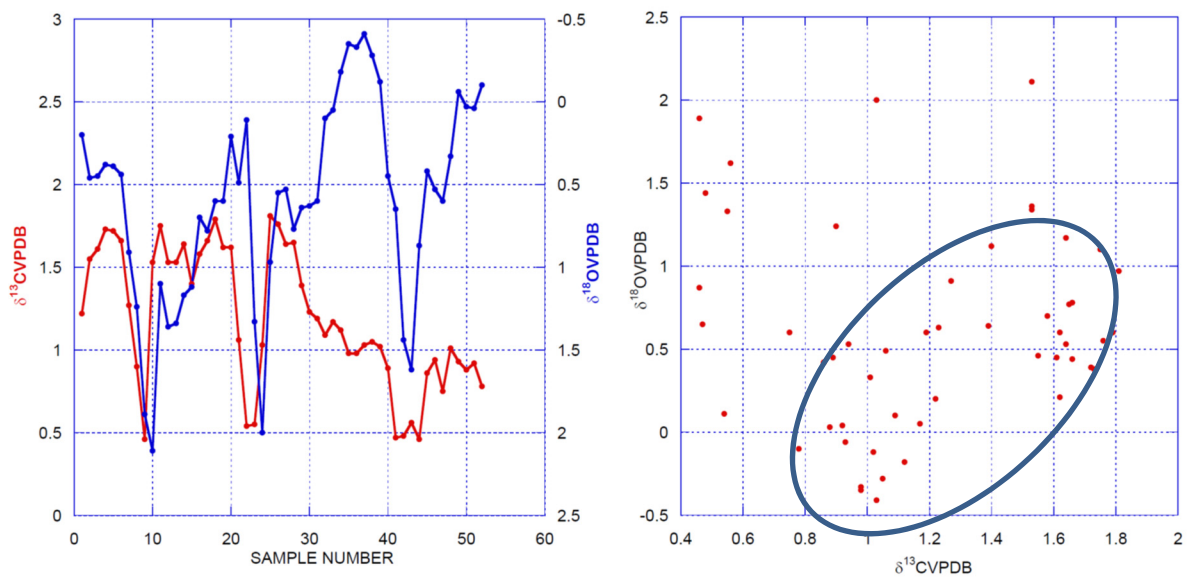


Figure 10: Carbon and Oxygen isotopic variation of YT-2. The $\delta^{18}\text{O}$ trend shows two complete summers (negative excursions) coupled with three winters (positive excursions) and two bounding partial summers. The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ crossplot shows a complicated relationship that may reflect two general populations similar to that observed in samples from the Pinecrest Beds: a weakly correlated field of positively correlated values with deviations occurring as more positive $\delta^{13}\text{C}$ values independent of $\delta^{18}\text{O}$ values.

Study	Sample Location	Sample number	Minimum Temperature Estimate (°C)	Maximum Temperature Estimate (°C)	Estimated Temperature Range (°C)
Jones and Allmon (1995)	Pinecrest	PC-1A	14.8	17.6	2.8
	Pinecrest	PC-1B	14.5	21.8	7.3
	Pinecrest	PC-2	13.0	20.8	7.8
	Pinecrest	PC-4	11.9	18.8	6.9
	Pinecrest	PC-5	10.0	28.4	18.4
	Yorktown	YT-1	13.7	19.0	5.3
	Yorktown	YT-2	7.7	19.3	11.6
	Pinecrest	TA 6	12.6	21.5	8.9
	Pinecrest	TG 1, 2A, 4,5	11.6	18.8	7.2
	Pinecrest	MC 121	11.8	20.3	8.5
	Pinecrest	MC 130	10.9	18.2	7.3
	Pinecrest	TA 056	13	21.6	8.6
	Pinecrest	CE 139	6.9	20.8	13.9
	Williams et al. (2009)	Pinecrest	N/A	6.9	25.7
Yorktown		N/A	8.2	23.9	15.7
Yorktown		N/A	6.8	22.9	16.1

Table 2: Minimum and Maximum temperature estimates based on measured $\delta^{18}\text{O}$ values for each sample. Temperature was calculated using the aragonite-water temperature fractionation relation of Dettman et al. (1999). A seawater $\delta^{18}\text{O}_{\text{SW}}$ value of -0.6‰ was used in these calculations for mid-Pliocene (Jones and Allmon, 1995). Pinecrest PC-5 (highlighted in yellow) provides a multi-year record and is used as the primary estimate of seasonal temperature range. These data are compared to the minimum and maximum temperature estimates from Jones and Allmon (1995) and Williams et al. (2009)

Discussion

Reconstruction of Paleotemperatures

Paleotemperatures from the Mid-Pliocene were reconstructed based on the $\delta^{18}\text{O}$ values of the molluscan carbonate from the Pinecrest Beds of the Tamiami Fm. and the Yorktown Fm. In order to estimate the temperatures of shell growth from $\delta^{18}\text{O}$ carbonate, it is necessary to have a reasonable constraint on the $\delta^{18}\text{O}_{\text{w}}$ of seawater. In this study, we have used an estimate of -0.6‰ $\delta^{18}\text{O}$ SMOW provided by Krantz et al (1990) that considered changes in global ice volume as the primary driver of changes in seawater composition. Calculated temperature ranges varied based on sample and location. The best record for the Florida location is present in sample PC-5 recovered from the Pinecrest Beds. This sample shows a seasonal temperature range of 18.4°C from 10°C to 28.4°C . The average temperature range exhibited by the remaining Pinecrest samples is 6.2°C which is ~ 3 times less than the range exhibited by PC-5. Although other samples retrieved from the Pinecrest beds exhibit a lower amplitude seasonal change between the minimum and maximum temperatures, all fall within the bounds represented by PC-5.

When Pinecrest Bed temperatures are compared to modern temperatures, some differences are observed. Modern day temperature range in South Florida is 16-27°C while PC-5 paleotemperatures range from 10°C to 28.4°C, suggesting slightly warmer summers and cooler winters during the mid-Pliocene than today. In comparison to previous stable isotope studies of the Pinecrest Beds, temperatures estimated in this study show a greater seasonal range than those of Jones and Allmon (1995) with coldest and warmest temperatures approximately 10°C and 22°C, respectively (Table 2). Williams et al. (2009) in his temperature calculations estimated seawater $\delta^{18}\text{O}_{\text{sw}}$ values predicted through numerical simulation models and consideration of the latitudinal balance between precipitation-evaporation that can affect $\delta^{18}\text{O}_{\text{sw}}$ composition. Using a $\delta^{18}\text{O}_{\text{sw}}$ value of 1.02 for the southwest Florida Shelf, his temperature reconstruction shows significantly higher overall temperatures that are seemingly more compatible with faunal assemblage temperature estimates.

This study also examined samples from the coeval Yorktown Fm. from Virginia to determine whether the northward expansion of subtropical faunal assemblages was reflected in temperature reconstructions from *Mercenaria* shell carbonate $\delta^{18}\text{O}$. The seasonal temperature range was determined for the Yorktown Fm. sample YT-2 was 11.6°C with a minimum winter temperature of 7.7°C and a maximum summer temperature of 19.3 °C. This indicates generally colder summer and winter temperatures for the Virginia Shelf relative to Florida during the mid-Pliocene. The present-day temperature ranges from 4.4 to 25.5°C. It should be noted that based on the work of Elliott et al. (1003), it is possible winter temperatures were are possible as shell growth typically ceases below 8-10°C temperatures and no record would be preserved in the shell. These estimates contrast with the 14.1 to 26.3°C range estimated by Williams et al. (2009) that would suggest slightly warmer summers and significantly warmer winters. Such temperature predictions are not compatible with the observations made by this study, again emphasizing the ambiguities that result from various predictions of the $\delta^{18}\text{O}$ composition of seawater at the time of shell growth. Our study uses the ice-volume controlled estimate of -0.6‰, whereas Williams et al. 2009) use a climate model prediction of +1.2‰

The apparently cool temperature estimates that are derived from oxygen isotope measurements compared to inferred temperatures from faunal assemblage data require additional examination. In their evaluation of the Pinecrest Bed data and the need to explain the anomalously cool temperatures observed for a subtropical site, Jones and Allmon (1995) invoke upwelling of deep waters onto the Florida Shelf. Upwelling of deeper and colder waters would bias temperature to lower values. Because some their isotopic data also exhibited negative correlation $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, in contrast to the positive correlation observed in PC-5 of our study, this interpretation could be compatible with upwelling whereby colder temperatures (+ $\delta^{18}\text{O}$ values) would be paired with - $\delta^{13}\text{C}$ values. Again, this is not consistent with the data collected in this study. As shown in Figures 7 through 10, all sites show some component of positive covariance of carbon and oxygen isotope values. An explanation for this phenomenon is an influx of freshwater run off which could be reflected by a depletion in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during warm seasons. Today's rainy season in Florida occurs during the summer months, June through September, during the warm periods. Terrestrially-derived freshwater would serve as a source for - $\delta^{13}\text{C}$ where dissolved inorganic carbon in these waters is derived from decomposition of organic matter within the soil zone. This would also lead to a more - $\delta^{18}\text{O}$ of the marine-meteoric water mixture, which might bias temperature estimates toward higher values (more negative $\delta^{18}\text{O}$ of precipitated carbonate). The degree of biasing of the temperature estimate may not be significant, as meteoric water $\delta^{18}\text{O}$ at low latitude is offset from seawater values by a small amount (~-1 to -2‰; data from IAEA 2001).

In contrast, given the relatively high concentration of dissolved inorganic carbon in freshwaters compared to marine water, the $\delta^{13}\text{C}$ composition would be significantly modified relative to shifts in $\delta^{18}\text{O}$ composition. All of the Pinecrest data show some covariance of carbon and oxygen, but there is variation that cannot be explained by freshwater input. In PC-2, Field 2 shows variation in $\delta^{13}\text{C}$ associated with $+\delta^{18}\text{O}$, in other words, during times of colder temperature. This pattern of variation is compatible with upwelling proposed by Jones and Allmon (1995). This means that upwelling could be one factor that controls the composition of the shell carbonate, however it is a secondary effect preserved in PC-5 and may bias the lower temperature estimates. This same phenomenon may be occurring with the Yorktown data and could explain the observed variability in $\delta^{13}\text{C}$. However this seems to happen throughout the year, across the full spectrum of temperatures ($\delta^{18}\text{O}$ values). This may explain the overall lower temperatures recorded in samples of the Yorktown Fm. as part of this study relative to the higher temperatures expected for the mid-Pliocene climatic optimum.

In the work of Williams et al. (2009), they did not propose upwelling as a hypothesis to explain the lower calculated temperatures proposed by Jones and Allmon (1995) when assuming that the $\delta^{18}\text{O}_{\text{sw}}$ was -0.6‰ , an estimate that is based on ice-volume considerations. When using similar $\delta^{18}\text{O}_{\text{sw}}$ value, Williams et al. (2009) estimates lower mid-Pliocene temperatures for both the Pinecrest and Yorktown locations were also indicating cooler temperatures than would be expected based on taxonomic assemblages. In contrast to the work of Jones and Allmon (1995) and this study, the use of a climate model prediction of $\delta^{18}\text{O}_{\text{sw}}$ values (Pinecrest and Yorktown of 1.02‰ and 1.1‰ , respectively) by Williams et al. (2009) result in significantly higher temperatures overall for both regions. Some problems are apparent when such high values are invoked for Pliocene seawater. For example, using a $+1.02\text{‰}$ $\delta^{18}\text{O}_{\text{sw}}$ value to reassess the temperature estimates calculated for Pinecrest sample PC-5, would indicate a seasonal temperature range of 20°C , from 17°C to 37°C . This estimate is unreasonable based on growth studies of living *Mercenaria*. In the work of , (Elliott et al., 2003), it was determined that *Mercenaria* precipitates its shell over a temperature range from $8\text{--}10^{\circ}\text{C}$ to $30\text{--}31^{\circ}\text{C}$. Temperatures above or below these limits result in a thermal growth shut down that is not recorded in the shell carbonate. Based on this calibration of the temperature growth limits of living *Mercenaria*, the high temperature estimates resulting from a $\delta^{18}\text{O}_{\text{sw}}$ of $\sim 1\text{‰}$ proposed by Williams et al. (2009) are not reasonable. While their approach for constraining $\delta^{18}\text{O}_{\text{sw}}$ may bring temperature reconstructions in line with estimates based on other non-geochemical proxies, i.e., taxonomic assemblage analysis, it emphasizes the inadequacy of uniquely positing water compositions for accurately reconstructing paleoclimates from $\delta^{18}\text{O}$ measures of shell carbonate.

In conclusion, Jones and Allmon's use of -0.6‰ as the $\delta^{18}\text{O}_{\text{sw}}$ estimate is in accord with estimates from oceanographic data and provides a more reasonable temperature for Florida than model estimated $\delta^{18}\text{O}_{\text{sw}}$ values used by Williams et al. (2009). Data collected as part of this study suggest colder winter temperatures for Florida than previous studies. This may reflect the more complete sampling of seasonal growth through our higher resolution sampling that is capable of extracting material for analysis of both the high and low temperature extremes. Additionally, the data from Virginia reconstruct an even colder setting that is significantly offset in absolute temperatures from the reconstruction of Williams et al. (2009). If the lower temperature estimates of this study are correct, it is possible that deep water upwelling could explain the low winter temperatures estimated for Florida and overall lower temperatures for Virginia. Importantly, this study emphasizes that temperature reconstruction is equivocal given that coeval seawater $\delta^{18}\text{O}$

must be known if provide accurate temperature estimates are to be made. This study provides that physical framework for future studies that employ newly developed clumped isotope approaches that will allow for unique determination of paleotemperatures, and likewise, calculate the $\delta^{18}\text{O}$ of seawater. This will enable further discrimination of competing hypotheses regarding biasing of the temperature record due to the effects upwelling or freshwater runoff that may mask the primary record of paleotemperature in geological archives of climate change.

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