

EVALUATION OF LAND SNAILS FOR CLUMPED ISOTOPE PALEOTHERMOMETRY: A CASE STUDY OF THE PLEISTOCENE OF BERMUDA

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ABSTRACT

With the advent of clumped isotope analyses, sources of data that were previously not of use in determining paleoenvironment may become valuable proxies for the reconstruction of past earth surface temperatures. Land snails, for example, may prove to be useful paleothermometers. It was found that clumped isotope analyses of land snails of the genus *Poecilozonites* in Bermuda do yield reasonable paleoclimate estimates for that region at the time of shell formation during interglacial stage 5e (~125 kyrs). One factor that must be further investigated, however, is the degree to which the ecology of the snails may bias temperature estimates because of differences between ambient conditions and the internal body temperature and water composition of the land snails. An independent estimate of paleotemperature, consisting of clumped and standard $\delta^{18}\text{O}$ analyses, were completed on a coeval marine snail, *Cittarium pica*, collected from Stage 5e coastal carbonates. This individual snail provides an excellent record of annual seasonality. Moreover, based on combined $\delta^{18}\text{O}$ and clumped isotope analyses, this specimen suggests considerably lower Stage 5e surface temperatures (~ 8°C cooler) than recorded today. While temperature estimates based on land snail carbonates are in close agreement with prior reconstructions, their reliability in recording ambient temperature remains unproven.

INTRODUCTION

Land snail shells have historically been useful sources of data in the study of vegetation, soil conditions, environmental temperature, and rainfall (Goodfriend 1992). The experimental methods for extracting such data have included analyzing faunal assemblages, shell morphology, and stable isotope composition of both organic matter and shell carbonate (Goodfriend 1992). In investigation of paleoenvironments, carbonates have been and continue to be an especially useful proxy for both ambient temperature and water isotopic composition. Land snail shells, however, have been a particularly difficult and unreliable proxy due to the complexity of terrestrial environments. While lacustrine and marine environments maintain relatively stable conditions under which carbonates can form, the terrestrial habitats of land snails can vary considerably, with large seasonal and daily variations in both temperature and water composition.

This variability is an obstacle for traditional $\delta^{18}\text{O}$ analyses of carbonate since they require an independent knowledge of either temperature or water isotopic composition during precipitation of the carbonate to completely solve the equation. The shells form at isotopic equilibrium with the surrounding water according to temperature, so an understanding of one is

necessary for the extrapolation of the other (Epstein et al. 1953). However, the advent of clumped isotope analysis (Δ_{47}) has the potential to circumvent this issue because the formation of molecules with two or more heavy isotopes is not dependent on water isotopic composition (Eiler 2007). One can independently estimate the temperature of formation, and then based on the $\delta^{18}\text{O}$ of the carbonate, it is possible to calculate water composition. In regard to the use of land snail shells, the utility of clumped isotope methods remains to be seen.

In 2011, Zaarar et al. (2011) carried out a series of experiments similar to those that I have conducted. In sum, they found that the shells reflect a higher temperature of formation than the known temperatures of those locations from which they were collected. This discrepancy is not unexpected because of the recognized complexities inherent in using land snails. Land snails precipitate their carbonate shells from the bicarbonate in their body water (Goodfriend 1992), and they acquire this body water primarily through the absorption of ground water through their foot (Prior 1985). The absorbed ground water most likely originated as rainwater, but almost certainly would have undergone processes which would have caused isotopic fractionation, such as evaporation or evapotranspiration. Compounding those effects, most land snail species rapidly lose their body water through evaporation and other processes, which would further fractionate their body water composition (Prior 1985). As a result, the snail body water may not accurately reflect rainwater composition. The second difficulty concerns the other variable involved in carbonate isotopic composition: temperature. The carbonate in the shells forms according to the body temperature of the snails, which is problematic because, while land snails are cold-blooded, and do not regulate their body temperature in the traditional sense, their shell morphology and color can affect their temperature (Heath 1975). This would mean that the shell carbonate may not necessarily reflect ambient temperature. Zaarar et al. (2011) concluded that the useful application of clumped isotope analysis to land snail shells is a matter of correlating body water composition and temperature with ambient water composition and temperature.

In this study, the snails being tested are from a different environment, one with less seasonal variability, than those tested by Zaarar et al. (2011). The snail species, *Poecilozonites*, is different as well, which will contribute to an understanding of species-specific effects on isotopic data. The particular land and marine snail shells that I analyzed for this thesis are all from the Quaternary period in Bermuda. Temperature and water isotopic composition data from the land snails are extrapolated from $\delta^{18}\text{O}$ and Δ_{47} values, and are then compared to the coexisting marine snail, *Cittarium pica*. This comparison is valuable because it permits one to evaluate the potential for using clumped isotope analyses of land snails as paleoenvironmental indicators through a comparison with proxies that are better understood. As clumped isotopes techniques are a new technique, this kind of investigation into possible applications is necessary for discovering their full potential.

SAMPLING LOCATIONS AND ANALYTICAL METHODS

Localities where snail samples were collected are shown in Figures 1 and 2. These were chosen to provide a record of terrestrial conditions for time periods coincident with marine isotope stages 1 (Holocene), 5a (85 ka), 5e (~125 ka), 9 (334 ka), and 11+ (>400 ka). Marine snails were collected from the Rocky Bay Formation of Stage 5e, at the Rocky Bay locality, to allow direct comparison between the record derived from a marine coastal environment and that from the coeval land snails present in protosols in adjacent land areas. At this locality, marine beach deposits of the Belmont Fm. (Stage 7, ~425 ka) are unconformably overlain by marine and terrestrial facies of the Rocky Bay Fm. (Figures 3A and 3B). Above this unconformity, marine limestones comprising coarse rubble beds of the Devonshire Mbr. fill an erosional cut within older beach limestones. These beds contain abundant marine snails of the genus *Cittarium*, a taxa restricted to the very shallow, hard bottomed, coastal zone. These sediments grade upwards into protosols of the Harrington Mbr. which contain land snails and record the transition to terrestrial environments.

Sample	Genus	Stage	Location	Sample	Genus	Stage	Location
Bierman	<i>Otala lactea</i>	1	Bierman Quarry	RB7E	<i>Poecilozonites</i>	5e	Rocky Bay
BQ8	<i>Poecilozonites</i>	1	Bierman Quarry	WB4J	<i>Poecilozonites</i>	5e	Whalebone Bay
SH8C	<i>Poecilozonites</i>	11+	Shore Hills Quarry	WB4B	<i>Poecilozonites</i>	5e	Whalebone Bay
SH8A	<i>Poecilozonites</i>	11+	Shore Hills Quarry	WB4I	<i>Poecilozonites</i>	5e	Whalebone Bay
SH8B	<i>Poecilozonites</i>	11+	Shore Hills Quarry	RB10A	<i>Poecilozonites</i>	5e	Rocky Bay
AP1C1	<i>Poecilozonites</i>	5a	Astwood Park	WB4E	<i>Poecilozonites</i>	5e	Whalebone Bay
AP1A	<i>Poecilozonites</i>	5a	Astwood Park	WB4C	<i>Poecilozonites</i>	5e	Whalebone Bay
AP1C2	<i>Poecilozonites</i>	5a	Astwood Park	RB10B	<i>Poecilozonites</i>	5e	Rocky Bay
WB4H	<i>Poecilozonites</i>	5e	Whalebone Bay	BQ4A	<i>Poecilozonites</i>	9	Bierman Quarry
RB10B	<i>Poecilozonites</i>	5e	Rocky Bay	BQ4C	<i>Poecilozonites</i>	9	Bierman Quarry
RB7D	<i>Poecilozonites</i>	5e	Rocky Bay	RB1	<i>Cittarium pica</i>	5e	Rocky Bay
RB7A	<i>Poecilozonites</i>	5e	Rocky Bay				

Figure 1. Genus identification, location, and age.



Figure 2: Map of Bermuda showing locations where samples were collected.

The land snail shell samples of the genus *Poecilozonites* were first cleaned of all attached sediment, and organic matter in the case of modern shells, through a combination of sonication, scraping with a stainless steel precision knife, and the application of 103% phosphoric acid or very dilute hydrochloric acid. After cleaning, the shells or shell fragments were bulk sampled using an agate mortar and pestle. A single specimen of the marine snail *Cittarium* was cross-sectioned and polished to reveal the annual and sub-annual growth structure of the shell. These growth bands were subsequently sampled under a microscope utilizing a 0.5 mm drilling bur. These microsamples of the marine snail and the bulk samples of the land snails were analyzed for their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition utilizing an automated Kiel IV carbonate system coupled directly to a Thermo Finnigan MAT 253 mass spectrometer. All analyses are reported relative to VPDB and analytical precision is maintained at better than 0.1 per mil based on replicated analysis of NBS 18 and NBS 19 standards.

For clumped isotope analyses, approximately 5 mg of shell powder of each sample was reacted with 103% phosphoric acid at 75°C. The CO_2 produced by this reaction was then subjected to two stages of cryogenic separation in cold traps kept at approximately -90°C by liquid N_2 . These traps served to remove water vapor that may have been present along with the CO_2 . Each CO_2 sample was further purified to remove additional organic contaminants through the use of a PoraPak Q column. The PoraPak was kept at approximately -30°C by cooled n-propanol. The gas was then drawn through the PoraPak by a U-trap cooled by liquid N_2 on the opposite side. This precluded the need for a carrier gas, such as helium. The purified CO_2 was held in a sealed glass tube until it was analyzed on the mass spectrometer.

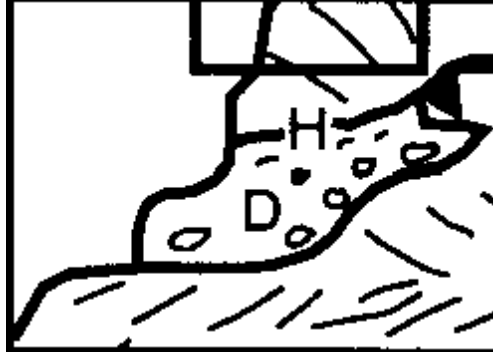


Figure 3A: showing generalized stratigraphic column of Rocky Bay. The lowest unit is the Belmont Formation which is of Stage 7 age (~240 ka). This is overlain by the Devonshire (D), the Harrington (H), and the Pembroke of the Rocky Bay Formation which is of Stage 5e (~125 ka). From Vacher et al. (1995).



Figure 3B: Outcrop photo of sample locality at Rocky Bay, Bermuda. The lowest unit (B) is the Belmont Fm. comprised of beach facies. Above this, across an erosional disconformity, rubble and conglomerate facies of the marine Devonshire Mbr. (D) grades upwards into terrestrial protosols of the Harrington Mbr (H) and eolianites of the Pembroke Mbr (P). All of these are within the Stage 5e (~125 ka) Rocky Bay Formation.

Sample CO₂ was analyzed on a Thermo Finnigan MAT 253 mass spectrometer that had been customized with three extra Faraday collectors to measure masses 44-49, as discussed in Huntington et al. (2009). $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Δ_{47} were measured simultaneously. The mass spectrometer operated in dual inlet mode with a pressure balance of 16 V on mass 44 for both sample and standard gases. Each replicate was measured for 80 acquisitions (8 cycles of 10 acquisitions). The integration time for each replicate was 8 seconds per acquisition with a 16 second changeover time, for a total integration time of 640 seconds for each replicate.

A variety of heated CO₂ standards (at 25°C and 1000°C) were run interspersed with the sample gases to correct for non-linearities in the source. To correct for possible scale compression, CO₂ standards equilibrated with water at 25°C were also measured, as this Δ_{47} fractionation relative to the randomized 1000°C gases is both theoretically predicted and empirically well known. Data was standardized through the use of an empirical transfer function as described by Dennis et al. (2011). Briefly, a regression of the clumped isotope composition Δ_{47} and bulk isotopic composition δ^{47} data of the gases heated to 1000°C and equilibrated at 25°C is plotted with a common slope but differing intercepts. In this experiment, this regression was completed using the R statistical package (www.Rproject.org) and the function 'lm.' Using the common slope, the experimentally determined intercepts were plotted with those calculated by Dennis et al. (2011). This final regression is the empirical transfer function, which places the experimental data into the universal reference frame (URF). For each sample to be placed in the URF, it was corrected to common bulk isotopic composition using the 1000°C heated gas line, and that Δ_{47} value was put through the empirical transfer function above in order to be expressed in the URF. A detailed explanation of this process can be found in Dennis et al. (2011). Acid fractionation effects were corrected for by applying an empirically determined offset (Hren, Defliese, and Lohmann, in prep). Finally, the published empirical temperature calibrations of Ghosh et al. (2006) and Dennis and Schrag (2010), as updated in Dennis et al. (2011), were used to extrapolate temperature from the URF Δ_{47} data. Both calibrations were applied, due to the significant potential variation between the two in final temperature results.

RESULTS

The land and marine snail samples that were analyzed for clumped isotopes were all collected at Rocky Bay, Bermuda, and fall into the 5e interglacial stage. The other land snail samples were gathered at other locations, as marked on Figures 1 and 2 above. Locations for each sample can be found in Figure 2. Stages as interpreted from Vacher et al. (1995).

The bulk $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analysis was completed on 22 land snails, and showed little correlation between the values from samples of the same stage or between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ within one sample. For instance, within stage 5e the $\delta^{18}\text{O}$ values ranged between 0.02‰ and -1.70‰ VPDB. The $\delta^{13}\text{C}$ varied dramatically as well, ranging between -7.82‰ and -11.43‰ VPDB for

stage 5e. All $\delta^{18}\text{O}$ and all $\delta^{13}\text{C}$ values are reported according to the VPDB standard. This data is plotted in Figures 4-6 below. The Shore Hills samples that are stage 11 or older were plotted as stage 11 for simplicity.

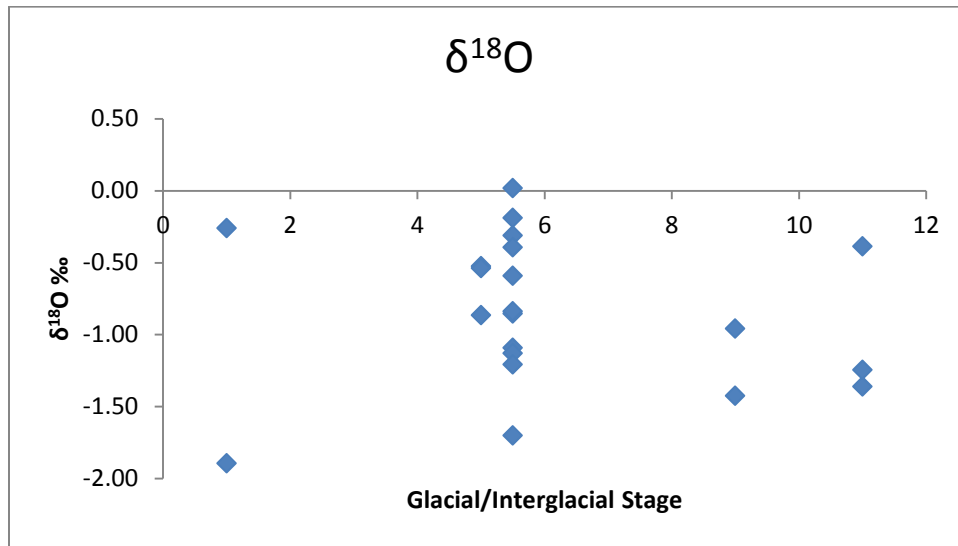


Figure 4: showing bulk $\delta^{18}\text{O}$ values for land snails from various interglacial stages

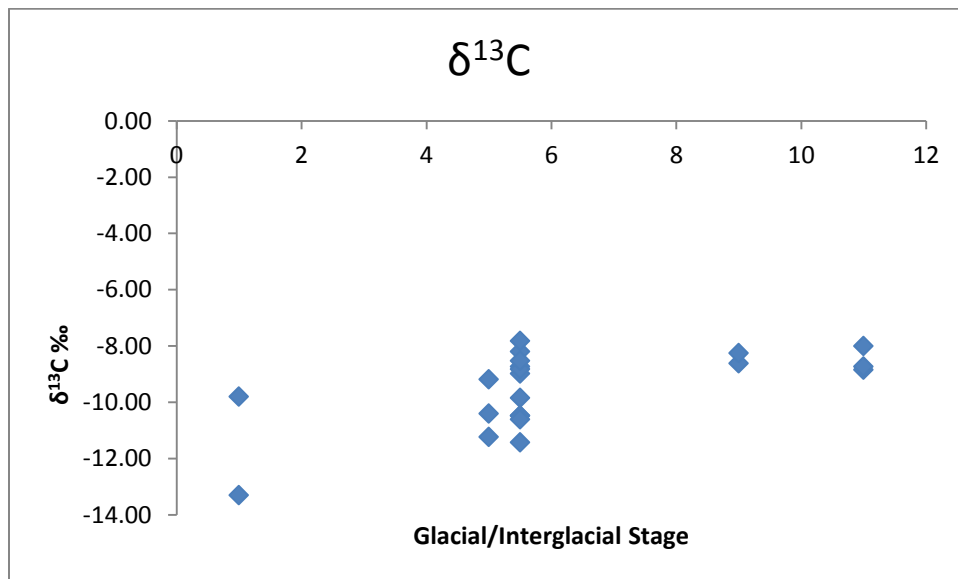


Figure 5: showing bulk $\delta^{13}\text{C}$ values for those same land snails.

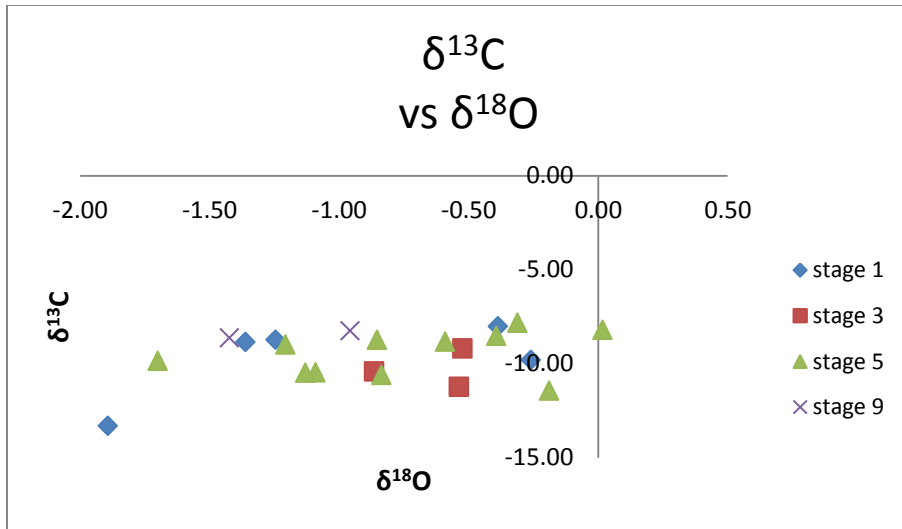


Figure 6: showing $\delta^{18}\text{O}$ plotted against $\delta^{13}\text{C}$.

The large marine snail shell, *C. pica*, that was drilled at high resolution intervals across its growth bands to test for the possibility of seasonal variation in $\delta^{18}\text{O}$ is shown in Figure 7. The results show a clear, nearly harmonic, oscillation in the $\delta^{18}\text{O}$ of each growth band, showing that there is indeed seasonal variation recorded within the shell (Figure 8). Samples collected between the growth band sites 15-18 show the highest $\delta^{18}\text{O}$ values of approximately 1.64‰. Samples collected between the growth bands sites 25-29 show $\delta^{18}\text{O}$ values between approximately 0.2 and 0.4‰. The range between the minimum (0.2‰) and maximum (1.64‰) $\delta^{18}\text{O}$ values is 1.44‰. The higher values likely correspond to winter, and the lower values to summer, and they will be described as such in the following figures.



Figure 7: Photograph showing marine snail shell drilled for high resolution $\delta^{18}\text{O}$ to measure seasonal variation. The holes drilled can be seen on the lower right portion of the shell. Shell is approximately 3 inches across at its longest dimension.

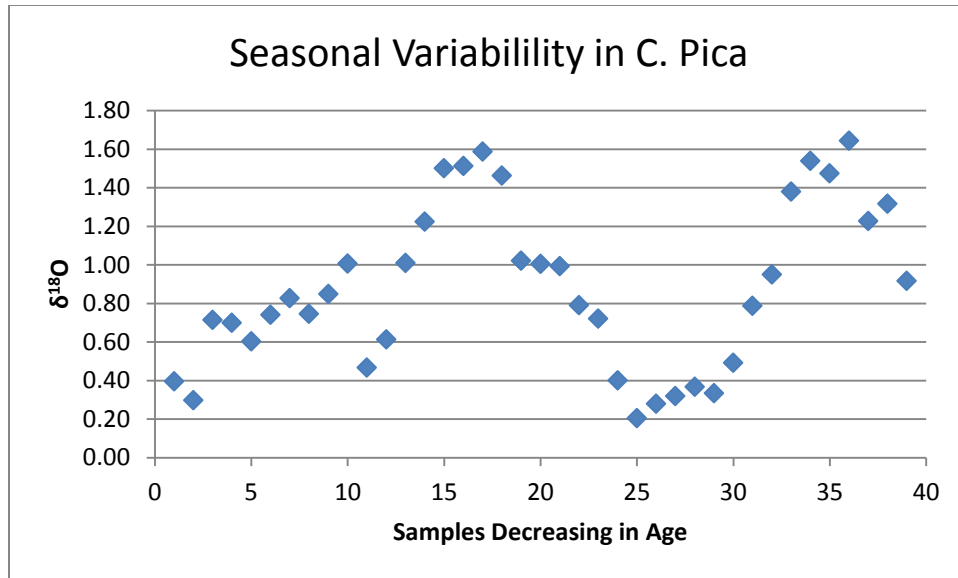


Figure 8: showing seasonal variability of $\delta^{18}\text{O}$ in sample RB1.

Having run this standard $\delta^{18}\text{O}$ analysis, one maxima and one minima within the curve were sampled for clumped isotopes. This data is shown in Figure 8 above. Only two replicates of each sample were analyzed due to a lack of sample material. The $\Delta 47$ values for each replicate are shown below in Figure 9.

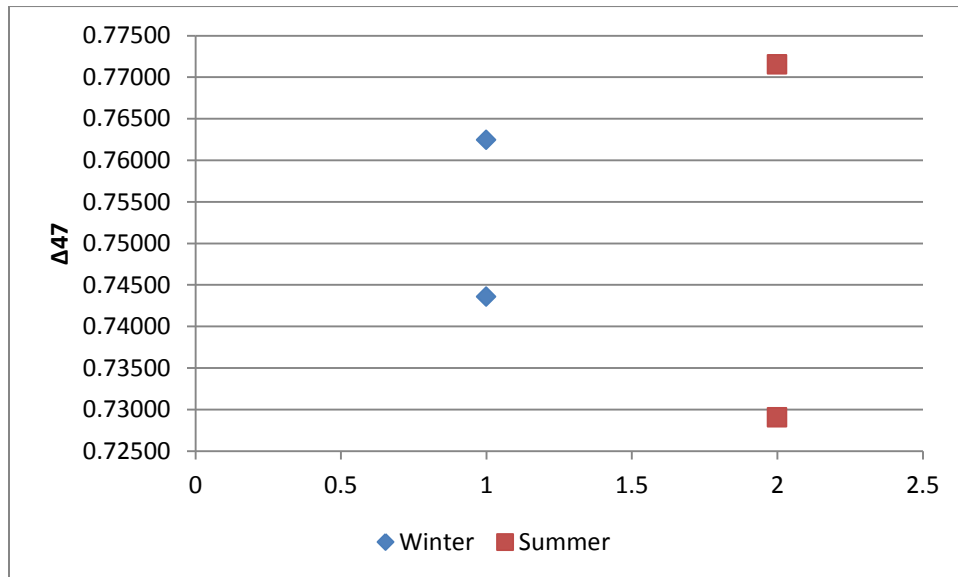


Figure 9: showing the $\Delta 47$ data for the two replicates run for each sample from the marine snail. The Winter $\delta^{18}\text{O}$ sample corresponds with samples 15-18 in Figure 8, while the Summer $\delta^{18}\text{O}$ sample corresponds with samples 25-29.

The variation between the replicates of each sample is clearly very large especially in the case of Summer $\delta^{18}\text{O}$. Winter $\delta^{18}\text{O}$ ranges between 0.762‰ and 0.744‰, while Summer $\delta^{18}\text{O}$

ranges between 0.729‰ and 0.772‰. The temperatures calculated according to these values of course vary as widely as the data that they are based on (Figures 10 and 11).

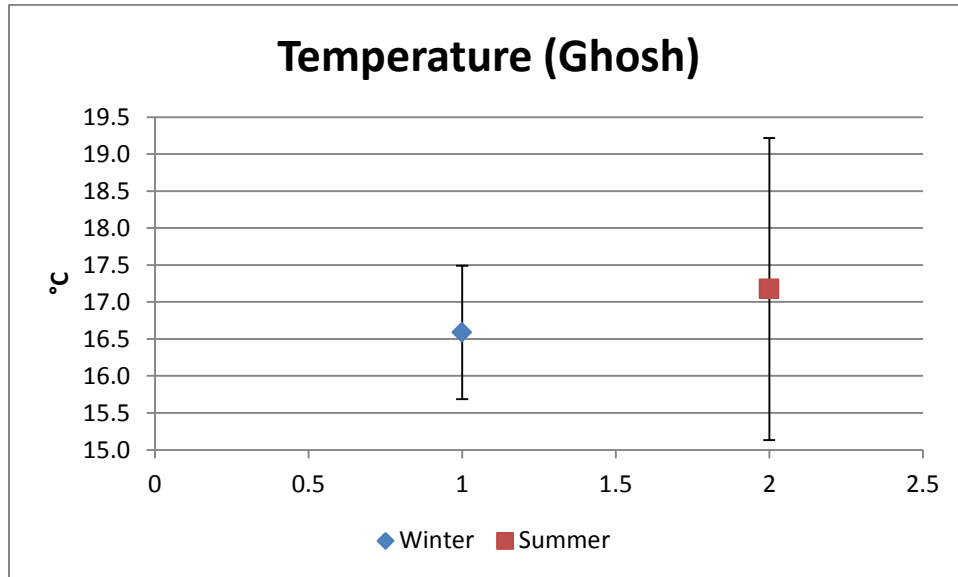


Figure 10: showing calculated temperatures for the marine snail at certain seasons using the Ghosh et al. (2006) calibration.

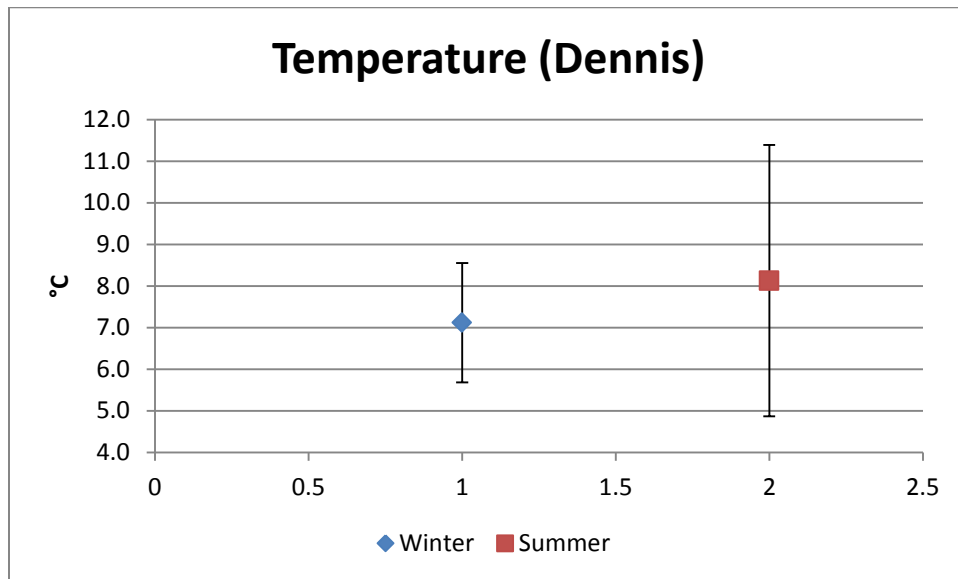


Figure 11: showing calculated temperatures for the marine snail at certain seasons using the Dennis and Schrag (2010) calibration.

Using the Ghosh et al. (2006) calibration, the temperature between seasons varied between 16.6°C and 17.2°C, a difference of 0.6°C. Using the Dennis and Schrag (2010) calibration, the temperature between seasons varied between 7.1°C and 8.1°C, a difference of 1°C. However, the standard errors are fairly high, especially for minima $\delta^{18}\text{O}$, exceeding 3.2°C

in the case of the calibration of Dennis and Schrag (2010), and 2°C in the case of the calibration of Ghosh et al. (2006).

Four land snail samples (*Poecilozonites*) from Rocky Bay were analyzed for clumped isotopes. Four replicates from each sample were tested. The $\Delta 47$ values between replicates of one sample varied by a maximum of 0.0603‰, as seen in sample RB7A. The average values for RB7D, RB7E, RB7A, and RB10B were 0.7112‰, 0.7181‰, 0.7104‰, and 0.6974‰, respectively (Figure 12). Using these average $\Delta 47$ values, temperature was calculated using the calibrations from both Ghosh et al. (2006) and Dennis and Schrag (2010). These calibrations are:

$$\text{Ghosh et al (2006): } \sqrt{\frac{0.0636 \cdot 10^6}{\Delta 47 + 0.0047}} - 273.15 = \text{Temp (}^\circ\text{C)}$$

$$\text{Dennis and Schrag (2010): } \sqrt{\frac{0.0362 \cdot 10^6}{\Delta 47 - 0.292}} - 273.15 = \text{Temp (}^\circ\text{C)}$$

This data is plotted in Figures 13 and 14 respectively. One standard error for the four samples ranged between 0.63 and 1.29 for the calibration of Ghosh et al. (2006), and between 1.08°C and 2.17°C for the calibration of Dennis and Schrag (2010). The calculated temperatures for the calibration of Ghosh et al. (2006) were between 27.82°C and 23.47°C, while the calculated temperatures for the calibration of Dennis and Schrag (2010) were between 25.66°C and 18.31°C. The average temperature indicated by these four samples was approximately 25.3°C according to the calibration of Ghosh et al. (2006) and approximately 21.4°C according to the calibration of Dennis and Schrag (2010).

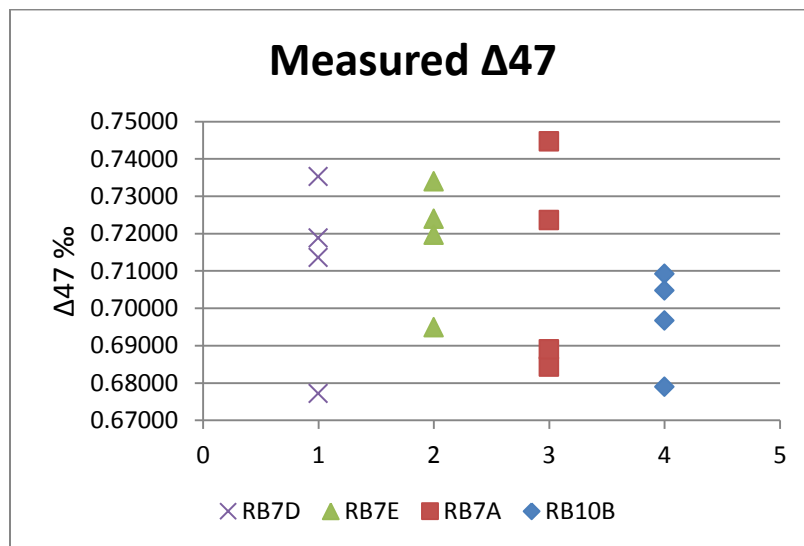


Figure 12: showing measured $\Delta 47$ values for each of the four replicates of four Rocky Bay land snails.

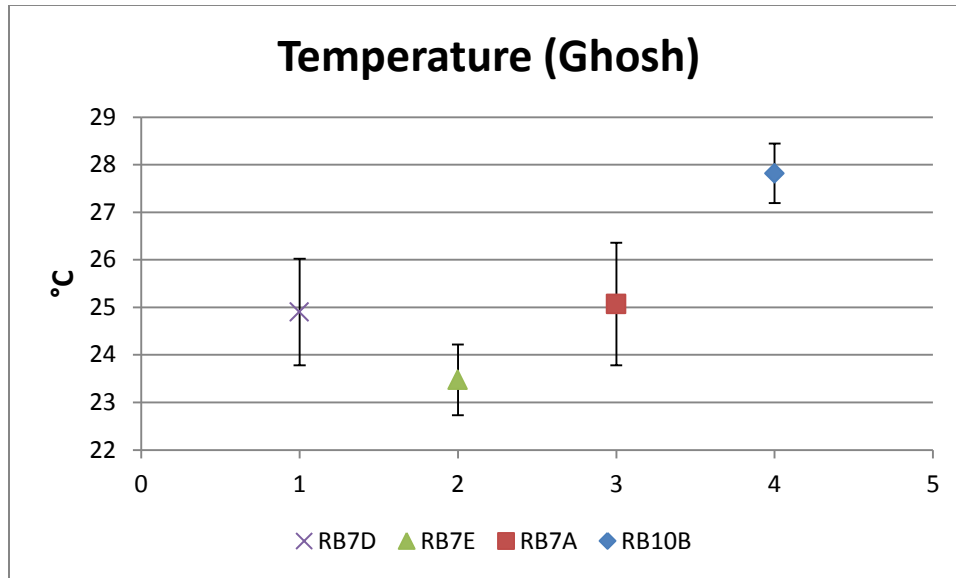


Figure 13: showing calculated temperatures during shell formation for each land snail (*Poecilozonites*) using the calibration of Ghosh et al. (2006). The error bars represent one standard error.

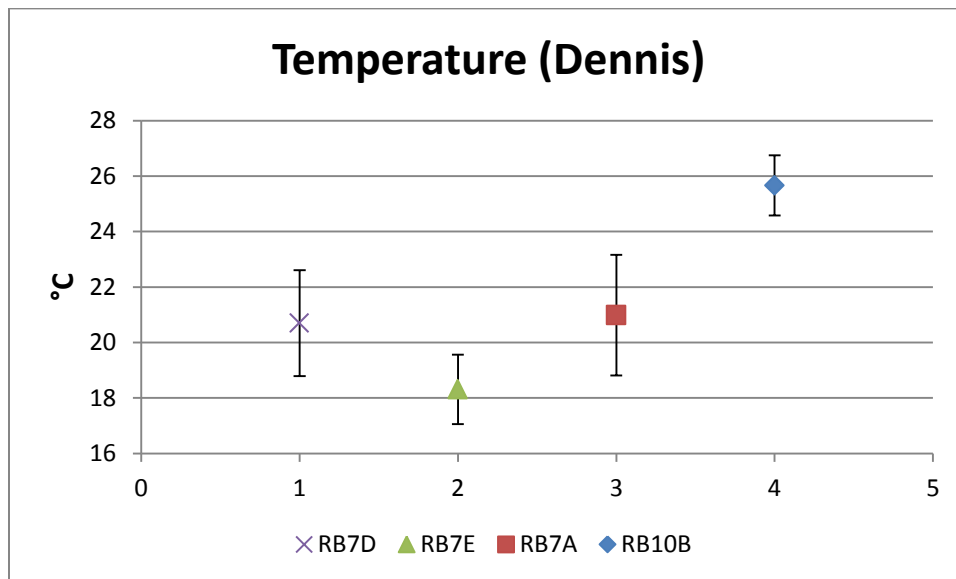


Figure 14: showing calculated temperatures during shell formation for each land snail (*Poecilozonites*) using the calibration of Dennis and Schrag (2010). The error bars represent one standard error.

DISCUSSION

Prior work has suggested that standard $\delta^{18}\text{O}$ analyses (as opposed to clumped analyses) of land snails provide very little information about paleoenvironment (Zaarar et al. 2011). The analysis completed for this thesis confirms that conclusion. As one can see from the data above, there is little or no apparent relation between both the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for shells within the

same stage. This avenue of investigation has resulted in no real conclusions beyond the difficulty in using land snails as indicators of paleoenvironment.

The analyses of seasonal variability, however, have yielded interesting results. The marine snail that was tested for $\delta^{18}\text{O}$ at a high resolution within individual growth bands did contain regular fluctuations in $\delta^{18}\text{O}$, which would correspond to seasonal differences. In order to calculate the temperatures that correspond to these changing $\delta^{18}\text{O}$ values, the water isotopic composition of the ocean water near Bermuda during stage 5e must be calculated. According to Shackleton et al. (1990), the planktonic foraminifera record shows a shell carbonate $\delta^{18}\text{O}$ average of -2‰ during stage 5e. Lehman et al. (2002) used alkenones to show that the sea surface temperature during stage 5e was approximately 22°C at the Bermuda Rise (see Figure 15).

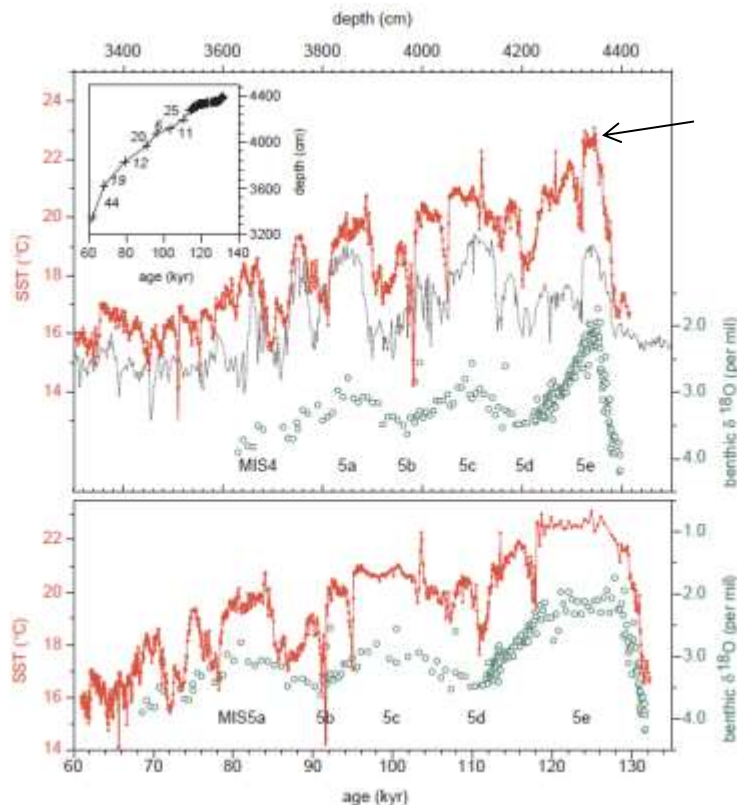


Figure 15: showing alkenone-derived sea surface temperature results (in red) to both age and depth for the Bermuda Rise, shipboard sediment lightness results in grey, and benthic $\delta^{18}\text{O}$ values (in green) to both age and depth. From Lehman et al. (2002).

These two pieces of information can be used with the Kim and O'Neil (1997) calibration for the calcite-water system to calculate the water $\delta^{18}\text{O}$ composition of Bermuda during stage 5e for the calcitic foraminifera value provided by Shackleton et al. (1990). Their calibration is listed below:

$$1000\ln\alpha = 18.03 \left(\frac{10^3}{T(^{\circ}K)} \right) - 32.42$$

Where

$$\alpha = \frac{\delta^{18}O_{calcite} + 1000}{\delta^{18}O_{water} + 1000}$$

Conversion from VSMOW to VPDB was completed through the following conversion:

$$\delta^{18}O_{VPDB} = \frac{\delta^{18}O_{VSMOW} - 30.91}{1.03091}$$

Because the marine snail (*Cittarium*) is composed of aragonite, it is necessary to utilize the aragonite-water fractionation relation (Dettman et al. 1999). With the estimated $\delta^{18}O$ of seawater during Stage 5e and the measured shell aragonite, one can calculate the temperature during shell formation of the marine snail:

$$1000\ln\alpha = 2.559 \left(\frac{10^6}{T^2} \right) + 0.71$$

Where α is defined as:

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

Minimum temperatures were approximately 11.1°C, and maximum temperatures were approximately 17.8°C, giving a seasonal variation of approximately 6.7°C and a mean of 14.7°C.

In this study, the water composition ($\delta^{18}O$ sw) was calculated to be approximately -0.3‰ VSMOW, using the process and data described above. This $\delta^{18}O$ sw estimate is reasonable in light of the known effects of glaciation. Stage 5e (~125 ka) was a period when glacial ice volume was lower than today, so one would expect the $\delta^{18}O$ sw to be more negative compared to the modern standards, which is in accordance with the measured $\delta^{18}O$ sw (see Figure 8). As glacial ice forms, it preferentially takes up ^{16}O , leaving the ocean waters enriched with ^{18}O . As already mentioned, during a period with less glacial ice than today, $\delta^{18}O$ sw would have a more negative value than today's ocean, which has a value of 0‰.

The seasonal variation in sea surface temperature seems reasonable as well. For reference, the sea surface temperature of Bermuda today ranges between 17.6°C in February and 28.2°C in July (Bermuda Weather Service), with a mean annual temperature of approximately 23°C. That range is close to the determined range during stage 5e, although the maximum

temperature is higher today. This data is contrary to that of Lehman et al. (2002) and their conclusion that mean annual sea surface temperature was approximately 22°C on the Bermuda Rise. The calculated temperature data is shown in Figure 16 below.

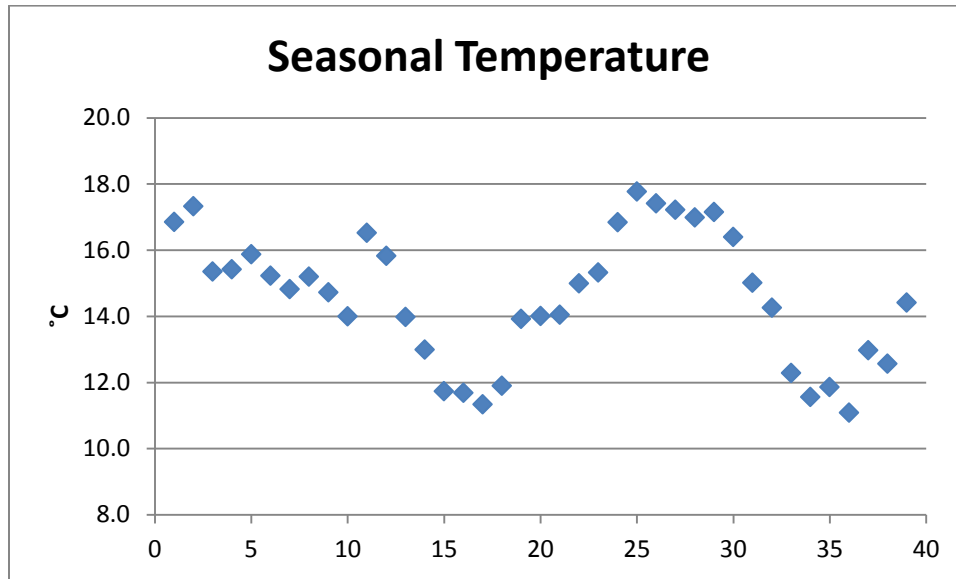


Figure 16: showing calculated seasonal sea surface temperature variation based on the $\delta^{18}\text{O}$ data from the stage 5e marine snail with an estimated $\delta^{18}\text{O}$ sw of -0.3‰.

The calculated temperature range of Bermuda during stage 5e, based on the high resolution $\delta^{18}\text{O}$ analysis of the marine snail *Cittarium*, is substantially colder than the temperature range today. Despite the fact that stage 5e is thought to have been an even warmer period than today, the $\delta^{18}\text{O}$ values obtained for this shell are incompatible with temperatures ranging to warmer values. In order to precipitate the aragonite shell with values of +0.2 to +1.6‰ at the proposed higher temperatures, conditions would require a $\delta^{18}\text{O}$ sw value in excess of +1‰, a value that is more characteristic of an ice-full glacial interval, a condition that is untenable given that Stage 5e was a major interglacial. On this basis, we consider the interpretation of lower mean annual temperatures made in this study to be more compelling than the reconstructions by Lehmann et al. (2002).

One possible explanation for these lower temperatures may be changes in surface water circulation and its effect on the estimated thermal gradient in the region of Bermuda. This difference could conceivably be explained by a change in the behavior of the Gulf Stream, in which Bermuda sits at present. Currently, the Gulf Stream brings warm water north from the equator, making Bermuda warmer than other areas at the same latitude. However, during a warmer period, the temperature gradient between the poles and the equator that drives the Gulf Stream could have been less energetic. This could result in less warm water being transported to the region around Bermuda, or an eastward shift of its pathway, causing the island to be colder

despite the overall planetary warming. For example, today the Gulf Stream impinges on the coastal region of the southeastern United States up to Cape Hatteras and artificially warms this region with mean annual temperatures (MAT) of 18°C and above. Just north of Cape Hatteras, where the Gulf Stream is deflected eastward, for example in Norfolk, VA, temperatures abruptly decline with a MAT of about 14°C.

A test of this hypothesis is to use the clumped isotope analysis data of the marine snail to independently calculate surface water temperature. Despite the large margins of error, the clumped isotope data yield lower temperatures conditions of Bermuda during stage 5e, whether using the calibrations of Ghosh et al. (2006) or Dennis et al. (2011). Additional replicate analyses of the marine snail are necessary to corroborate the initial findings of cooler temperatures during Stage 5e in Bermuda. Moreover, analysis of a living specimen for which the temperature range of growth is known independently would allow for direct calibration of the clumped isotope measurements to temperature for this genus of marine snail.

The clumped isotope data of land snails also had the possibility of providing temperature estimates for this time period, as these snails live on the land surface and should be responsive to temperature shifts between glacial and interglacial times. However, according to Zaarar et al. (2011), the average temperature extrapolated from land snail shells reflects snail body temperature rather than ambient temperature. The results of the clumped analyses of the land snails for this study yielded temperatures (25.3°C and 21.4°C according to the Ghosh et al. (2006) and Dennis and Schrag (2010) calibrations respectively) that roughly agree with the alkenone data from Lehman et al. (2002) and with the extrapolations from the $\delta^{18}\text{O}$ and $\Delta 47$ data from the marine snail. Perhaps this particular genus does not significantly regulate its body temperature, and in this case the data is indicative of ambient temperature. Although these estimates roughly agree with the alkenone data from Lehman et al. (2002), both of these estimates seem particularly high. That difference could perhaps be due to differences in body temperature between the snail and its environment. One would expect the snail body temperature to be higher than ambient temperature if it is exposed to the sun for periods of time during shell growth; however, the snail could also conceivably find shelter during the hot hours, and therefore the body temperature would be less than ambient temperature. A thorough understanding of this snail species' behavior would be vital to making an assessment of the likely biases in body temperature.

The discrepancy in temperature estimates between the two calibrations persists. In this case, the calibration of Ghosh et al. (2006) yielded data with lower standard error (which is always the case); although as already stated, the Dennis and Schrag (2010) temperature values seem more reasonable. It is difficult to determine which calibration indeed provides a more accurate temperature because of the added variable of possible differences between body temperature and ambient temperature. In either case, the results are more in agreement with the higher estimates suggested by Lehman et al. (2002) for the region. However, the lower temperature estimates obtained from the marine snail are compelling, as the calculated $\delta^{18}\text{O}$

values for seawater that would be required to form carbonate with the measured values would be unrealistically high for an interglacial interval.

CONCLUSION

The purpose of this study was to investigate the possible use of clumped analyses of land snails to reconstruct paleoenvironment. The data collected did confirm what is commonly understood: that standard $\delta^{18}\text{O}$ analyses do not provide that information due to the increased number of unknown variables involved in the body temperature and water composition of the land snails. A study of the seasonal variations within one marine snail sample does show clear variation across time that is likely associated with seasonal changes. This raises the important question of whether land snails are subject to such effects. The likely answer is that they are affected, perhaps even more than their marine counterparts, but that was not tested for this thesis. This is an avenue of investigation that should be pursued in the future.

The actual clumped analyses of the land snails provided more reasonable results than were expected. Based on Zaarar et al. (2011) the clumped data should not accurately reflect the environmental conditions of the time, given the number of possible ways for the data to be skewed one way or the other. However, in this study the data was compatible with prior surface temperature estimates from alkenone-based proxies (Lehmann et al. 2002). When temperature estimates based on land snails are compared to those of coeval marine snails, significant differences exist. The marine based record suggests a cooling of the Bermuda region during the Stage 5e interglacial, by as much as 4 to 5°C. Further study of each of these proxies is essential to evaluate which may provide a more accurate reconstruction of paleotemperature.

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