High-Resolution Isotopic Records of Pennsylvanian Appalachian Basin Mollusk Shells

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By
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Introduction

The fractionation of oxygen isotopes between calcium carbonate and the water from which it precipitated is temperature dependent and can be used as a paleothermometer (Urey, 1947; Grossman and Ku, 1986). However, deep time investigations of environmental conditions are complicated by uncertainty in the oxygen isotopic composition of the seawater (δ\textsubscript{18}O\textsubscript{w}) and the potential for diagenetic alteration. These concerns become particularly important when considering oxygen isotope values from Paleozoic marine carbonates (δ\textsubscript{18}O\textsubscript{carb}), which show a general depletion with increasing age (Jaffres et al., 2007; Veizer et al., 1997; Figure 1). Competing explanations for this trend include increasing alteration with age, evolution of seawater δ\textsubscript{18}O through time, and increasing ocean temperatures with age (Veizer, 1999). Successfully proving original mineralogy, thereby eliminating diagenesis as a factor, is a primary hurdle in deconvolving potential causes and thereby interpreting proxy data.

The highly fossiliferous marine units of the Kendrick and Magoffin shales, Middle Pennsylvanian Breathitt Group, in the Appalachian Basin record significant interglacial transgressions and have been suggested to preserve the original calcite and aragonite of marine mollusks (Brand, 1981a-b, 1983). Mollusks are ideal taxa for oxygen isotope paleothermometry because they precipitate their shells in isotopic equilibrium with their environment (Grossman and Ku, 1986) and they grow through accretion, providing a record of intra-annual variations in temperature. Since these fossils are from an interglacial period comparable to conditions today, I would expect a similar range of temperatures and degree of seasonality as experienced in modern equatorial shallow seas. Therefore, I hypothesize that intra-annual equatorial conditions during Pennsylvanian interglacial periods were variable enough to be recorded in accretionary carbonates and that this regular variability, if exhibited in the oxygen isotopes, can rule out diagenesis. I propose to test this hypothesis by serially sampling rigorously screened mollusk carbonate from these units in an attempt to recover primary δ\textsubscript{18}O variation over ontogeny and, if present, thereby rule out diagenesis. Preservation of intra-annual variations in the oxygen isotope records will provide further confirmation of original mineralogy and allow a better understanding of seasonal variation at low latitudes during Pennsylvanian interglacial periods.

Oxygen isotope paleothermometry
Oxygen isotope paleothermometry stems from pioneering work of Harold Urey (1947), and colleagues (Epstein et al., 1953), who demonstrated that the ratio of $^{18}$O to $^{16}$O in calcareous fossils is directly related to the temperature of precipitation. Since then, various oxygen isotope paleotemperature equations for different materials have been experimentally determined (e.g., Grossman, 2012a; Figure 2). The oxygen isotope proxy works on the assumption that the shells were precipitated in equilibrium with the surrounding seawater. Thus, differences in $\delta^{18}$O$_{\text{carb}}$ in a stratigraphic sequence of shells, or within a shell itself, reflect changes in the seawater composition and/or temperature (Epstein et al., 1953). This paleothermometer has been essential in identifying large scale environmental changes during the Cenozoic, including transitions into and out of ice ages and climate variations independent of ice volume.

Application of the oxygen isotope paleothermometer in deep-time is complicated by uncertainty in the oxygen isotopic composition of the seawater. Temporally, $\delta^{18}$O$_{\text{w}}$ varies as a function of ice volume, whereby the oceans become $^{18}$O-depleted when there is little to no ice coverage, and enriched during glacial periods. Additionally, $\delta^{18}$O$_{\text{w}}$ values are spatially heterogeneous, varying with latitude, water depth, proximity to freshwater input sources, and evaporation/precipitation dynamics (Bowen & Wilkinson, 2002). Without direct access to ancient seawater, deep-time studies require an assumption of $\delta^{18}$O$_{\text{w}}$. In principle, an educated assumption of the isotopic composition of the seawater can be made on the basis of an in-depth understanding of a fossil’s age and depositional environment.

An accurate estimation of the oxygen isotopic composition of seawater is particularly important when considering $\delta^{18}$O$_{\text{carb}}$ data throughout the Phanerozoic. Veizer and colleagues (Veizer et al., 1999; Prokoph et al., 2008; Veizer & Prokoph, 2015) have compiled an extensive global database that documents a long-term decrease in $\delta^{18}$O$_{\text{carb}}$ values with age. However, it is unclear whether this trend represents a primary signal or post-depositional alteration (Jaffres et al., 2007). If these data represent a primary signal, the trend indicates an evolution of $\delta^{18}$O$_{\text{w}}$ through time or increasing ocean temperatures with age. Alternatively, if the trend is due to diagenetic alteration, the application of oxygen isotope thermometry to the Paleozoic carbonates would have limited value. Therefore, screening for diagenesis and establishing primary mineralogy in Paleozoic carbonates is crucial to addressing this issue.

**Screening for diagenetic alteration**
Preservation of a specimen is an important factor when attempting to apply the oxygen isotope paleothermometer in deep-time. Alterations to the chemical composition of the specimens can result in changes to the inferred temperature of formation by overprinting of the original isotopic signature by diagenetic waters. Taxa that precipitate low-Mg calcite, such as brachiopods, have long been favored over those that precipitate aragonite or high-Mg calcite, as low-Mg calcite is more stable and resistant to diagenetic alteration (Corfield, 1995). Since the preservation potential of aragonite decreases with age, its occurrence is highly suggestive of an unaltered chemical composition. The presence of primary aragonite further suggests that the co-occurring calcite is also unaltered. However, independent assessments must be implemented in screening specimens for diagenesis (Grossman, 2012a).

There are a variety of techniques used to screen for diagenetic alteration (Figure 3). Standard screening for alteration in accretionary carbonates begins with the inspection of textural preservation at the hand sample level. Samples exhibiting extensive damage to the shell texture such as fracturing, cementation, pitting, and boring should be avoided. Microstructural examinations by scanning electron microscopy (SEM) can help identify secondary growth structures associated with dissolution, reprecipitation, and cementation. Additionally, powder X-Ray Diffraction (XRD) can determine the mineralogy of a specimen; retention of an aragonitic mineralogy is strongly suggestive of primary shell material. However, if the primary mineralogy of the organism is low-Mg calcite, as is the case with brachiopods, further steps must be taken to assure retention of the original isotopic signal (Figure 3). Trace-element abundances can help distinguish between biogenic carbonates and diagenetic calcite since their elemental chemistries are dissimilar. In particular, Mn and Fe concentrations are generally elevated during precipitation from pore waters during diagenesis (Brand & Morrison, 1987).

Following successful screening for diagenetic alterations, sequential microsampling of accretionary carbonate along the growth axis can further demonstrate primary mineralogy while providing a record of intra-annual δ¹⁸O_carb variations (Ivany and Runnegar, 2010). Serially sampled δ¹⁸O_carb values through ontogeny reflect changes in seawater temperature and salinity experienced during shell accretion. The regular, cyclical variation in oxygen isotopes is indicative of primary seasonal variation in environmental conditions and therefore retention of the original primary isotopic composition. If diagenetically altered, a shell would exhibit δ¹⁸O_carb values reflecting the composition and temperature of the diagenetic fluids and any primary
variation would be lost. Once primary composition is established, δ\(^{18}\)O\(_{\text{carb}}\) values can be used as high-resolution archives of paleoenvironmental conditions.

**Geologic and climatic setting**

The Carboniferous represents a dynamic geologic and climatic period in Earth history, marked by declining CO\(_2\) levels and the transition into the late Paleozoic icehouse (Royer, 2014). The most continuous records of oxygen isotope variation for the Carboniferous come from brachiopods from the U.S. midcontinent and the Russian Platform (Grossman, 2012b). During interglacial highstands, the present U.S. midcontinent was situated at tropical latitudes and covered by an epeiric sea that extended eastward into the Appalachian Basin and opened westward into Panthalassa (Figure 4). The Kendrick and Magoffin shales (Figure 5) record significant interglacial transgressions in the Appalachian Basin. Brand (1981a-b, 1983) demonstrated that the fauna of the Kendrick Shale retains its original mineralogy, chemistry, and structures. If original aragonite is preserved, then a geochemical investigation can elucidate the environmental dynamics of this tropical Pennsylvanian epeiric sea.

A high-resolution study of the type proposed below, using Late Pennsylvanian brachiopods from the Conemaugh Group in the Appalachian Basin (~05° N paleolatitude; Roark et al., 2016), found essentially no intra-annual variation in δ\(^{18}\)O\(_{\text{carb}}\) values. On the basis of these results, the authors inferred stable equatorial conditions at the time, both in terms of temperature and precipitation/salinity, suggesting that the late Paleozoic interglacial tropics were characterized by non-monsoonal, humid conditions (Roark et al., 2016). However, constant values within shells is also consistent with alteration of the carbonate and hence of any primary environmental signal. Here, I will expand on their work by analyzing multiple mollusk taxa at high spatial/temporal resolution to assess the potential for intra-annual variation and therefore retention of primary chemistry and to test the hypothesis of stable equatorial conditions.

Published Carboniferous δ\(^{18}\)O\(_{\text{carb}}\) values show a range from 0 to -12‰ (Figure 1); this would result in temperatures as high as 60°C if seen as a pure temperature signal. However, Grossman (2012b) reduced this range in δ\(^{18}\)O\(_{\text{carb}}\) values to 0 to -6‰ (Figure 6) by rejecting data deemed suspect (Grossman et al., 2008). They further argue that this range reflects regional differences in both temperature and salinity within epicontinental seas. A series of studies (Flake, 2012; Joachimski & Lambert, 2015; Roark et al., 2017) investigated this hypothesis by sampling
from several Mississippian and Pennsylvanian localities across the U.S. (Figure 4). All studies reported an enrichment trend in $\delta^{18}O$ from modern-day east to west, which they interpreted as reflecting the proximity of the localities to the Panthalassic Ocean and the concomitant reduced influence of freshwater influx on $\delta^{18}O_w$. If this reported trend is a product of a salinity gradient across the epicontinental sea, values from the Appalachian Basin should consistently exhibit the most depleted and seasonally variable values for a given time slice.

**Proposed Work**

**Acquisition of Specimens**

Specimen suitability for paleotemperature investigations are determined by taxonomy and preservation. The Kendrick and Magoffin shales preserve shallow-marine assemblages containing bivalves, gastropods, cephalopods, and corals. In this study, I will target bivalves and gastropods, as they are known to precipitate their shells in isotopic equilibrium with the ambient seawater (Grossman & Ku, 1986) and their benthic and relatively sedentary nature reduces the possibility of retrieving oxygen isotope data that reflect lateral migration or vertical movement through the water column.

I have access to several specimens previously collected from the Prestonburg and Hazard, KY, localities for preliminary sampling, including the small bivalve *Nucula* and gastropods belonging to the order Archaeogastropoda (Figure 7A-D). I plan to visit various outcrops along routes 80 and 119 between Prestonsburg, KY, and Hazard, KY, in the summer of 2017 to collect additional specimens. Fieldwork in the Breathitt Group will allow me to sample the specimens with the best preservation and acquire multiples of the same taxa. I plan to use multiple specimens of different taxa (e.g., gastropods, bivalves) for this study to better constrain the variation in environmental signals. Demonstrating a seasonal cycle in multiple taxa is essential for demonstrating that the setting is variable and that the original signal is preserved.

**Screening for diagenesis**

All specimens will be screened for diagenetic alteration prior to sampling. Textural evaluation will be done through standard and scanning electron microscopy to evaluate the preservation of the microstructure. To ensure the specimens preserve their original aragonite, multiple microsamples of shell carbonate will be used for powder XRD analysis (Figure 8). If the
mineralogy of the specimens is calcite, trace element ratios (Fe/Ca, Mn/Ca) will be used to indicate the likelihood of dissolution and reprecipitation.

**Isotopic analyses**

The sampling for isotopic analyses will be conducted using both a hand drill and a MicroMill. The hand drill, although less precise, is necessary for gastropod specimens with coiling (Figure 7A) and torsion (Figure 7B). Sampling will be conducted along growth increments in the outer shell layers of specimens. Isotope analyses ($\delta^{18}O_{\text{carb}}, \delta^{13}C_{\text{carb}}$) will be performed at the Keck-NSF Paleoenvironmental and Environmental Laboratory at Kansas University on a Thermo Finnigan Mat 253 Isotope Ratio Mass Spectrometer coupled to a Finnigan Kiel automated preparation device. If oxygen isotope values exhibit a cyclic variation, indicating seasonal variation of temperature or salinity, over multiple annual increments, it can be assumed that these shells retain their original isotopic composition. Values from this study will also be compared to data from previous isotopic studies of Pennsylvanian biogenic carbonates (e.g., Popp et al., 1986; Adlis et al., 1988; Grossman et al., 1993, 2008; Veizer et al., 1999).

Initial sampling has already generated 105 samples from a single gastropod shell (Figure 7A); smaller specimens (e.g., Figure 7C, D) may yield only 40 samples each. Preliminary data show promising results (Figure 9) with both $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values showing regular variation.

**Reconstruction of paleoenvironment**

Knowledge that the original mineralogy is preserved allows us to confidently interpret stable isotope data. Isotope-derived temperatures will be calculated using the empirically derived paleotemperature equation of Grossman and Ku (1986), modified by Dettman et al. (1999):

$$T(\degree C) = 20.6 - 4.34(\delta^{18}O_{\text{carb}} - \delta^{18}O_{w} + 0.20)$$

Since these data are from an interglacial period during a time with a continental ice sheet, similar to conditions today, it would seem practical to assume modern seawater compositions ($\delta^{18}O_{w} = 0\%$). However, using this assumption, values yield temperatures high enough to be suspect (Figure 9) when compared to SST ranges from various modern equatorial locations.
(Figure 10). If we consider these data in a geographic context, as did Roark et al. (2017), values from Kentucky should exhibit the most depleted values of the region. Highlighting the middle Pennsylvanian data (Figure 6), although scarce, and comparing them to the preliminary results from this study, roughly shows that this trend holds. If results from this study remain consistent, we can confirm that the low $\delta^{18}\text{O}$ values, at least pertaining to the USA, are a function of reduced salinity as opposed to a diagenetic signal or an evolving global $\delta^{18}\text{O}_w$.

The Pennsylvanian, with relatively low CO$_2$ levels and ice house conditions (Royer, 2014), is analogous to the present climate, and so conditions could have been similarly variable in places. Modern high-resolution intra-annual data from low latitude locations (Figure 10) can show substantial variation due to both temperature and salinity arising from changes in freshwater input and/or upwelling (Tao et al., 2013). Large amplitude variations will likely be driven by salinity, while small amplitude variation could be temperature-driven. Variations in salinity should be annual, while variation in temperature should be biannual, reflecting the passage of the sun overhead twice a year in the tropics (Figure 11). If so, records of skeletal $\delta^{18}\text{O}$ should be able to capture those variations if they are present and if sampling is done at a high enough resolution.

Conclusions

The utility of the oxygen isotope paleothermometry in deep time is obfuscated by concerns over the increased potential for diagenetic alteration of primary isotopic signals and uncertainty of the isotopic composition of ancient seawater. Standard screening for diagenesis has not changed the observed enrichment of Phanerozoic $\delta^{18}\text{O}_w$ values with decreasing age. Based on the earlier work by Ivany and Runnegar (2010), I propose that the recovery of oxygen isotope variation through ontogeny can be used as an affirmative confirmation of primary isotopic composition. This hypothesis will be tested using carefully screened specimens from the Pennsylvanian Breathitt Group, which has been argued to preserve the primary mineralogy of its marine fauna. The resulting data will provide paleoenvironmental information that will improve our understanding of intra-annual variation in ancient tropical paleoenvironments during the Paleozoic icehouse, test an earlier hypothesis of equatorial climate stability, and help shed light on the significance of ubiquitously low Paleozoic $\delta^{18}\text{O}_{\text{carb}}$ values.

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Timeline

*Fall 2016* acquisition and preparation of preliminary specimens

*Spring 2017* preliminary sampling of gastropod BPHK-01 (XRD and oxygen isotope analyses)

*Summer 2017* field work in July 2017; sampling of remaining specimens

*Fall 2017* data analyses and comparison; draft of manuscript

*Spring 2018* finish thesis and submit manuscript
References


Figures

**Figure 1.** Phanerozoic marine oxygen isotope compilation (from Veizer and Prokoph, 2015).
Figure 2. Experimentally derived relationships between the oxygen isotope fractionation of aragonitic mollusks and the temperature of formation (modified from Grossman and Ku, 1986). Solid black line shows the calcite temperature relationship from O’Neil et al. (1969).
Figure 3. Schematic flow chart illustrating the steps required to adequately test for diagenesis (from Grossman 2012a)
Figure 4. Paleogeography of the North American continental seas during the late Pennsylvanian with sampling locations and average δ¹⁸O_carb values for the Virgilian. Red stars denote the Middle Pennsylvanian localities from this study. Modified from Roark et al. (2017).
Figure 5. Stratigraphic position of the marine units Magoffin and Kendrick shales of the Breathitt Group. Grey bands mark the time slices studied in Roark et al. (2016, 2017). Modified from Roark et al. (2017).
Figure 6. Select oxygen isotope data (Grossman, 2012b; Roark et al., 2016 & 2017) from the Pennsylvanian plotted with data from this study. Middle Pennsylvanian data are highlighted. Data from this study are shifted by -0.8‰ (Kim et al., 2007) to account for fractionation differences between aragonite (this study) and calcite (published data). KS = Kansas, AR = Arkansas, IA = Iowa, MO = Missouri, IL = Illinois, OH = Ohio, KY = Kentucky, WV = West Virginia, PA = Pennsylvania.
Figure 7. Fossil mollusks from the Kendrick Shale. A) *Bellerophon euphemites* (specimen BPHK-01) with 105 sampling paths (orange line), taken along the growth axis (yellow line). B) *Worthenia tabulata*. C) Pelecypod *Nuculopsis*. D) *Trepospira depressa*. Scale bars: 10mm.
Figure 8. XRD spectra data from specimen BPHK-01 compared to aragonite and calcite standards. Alignment with the “twin” peaks around 28 degrees (2θ) confirms that the original aragonitic mineralogy is preserved.
Figure 9. Oxygen and carbon isotope data from specimen BPHK-01 (*Bellerophon euphemites*) sampled along the growth axis. Isotope data are converted into temperature assuming $\delta^{18}O_w = 0.0\%$. Both oxygen and carbon data exhibit 1.5-2\% overall variation throughout ontogeny. Assuming the broad, oscillatory trend in the oxygen data is annual, this dataset records ~2.5 years of paleoenvironmental data.
Figure 10. Average monthly sea surface temperatures (SST) and sea surface salinities (SSS) for various tropical locations (from NOAA/NASA satellite records). A. The Java Sea (yellow, an open shallow shelf) data show minimal variations in SST while also exhibiting a biannual temperature signal. The Gulf of Carpentaria (orange, an epicontinental sea) at a latitude further from the equator shows the highest degree of variation within a year with the lowest temperatures between June and August. The equatorial Pacific (blue) open ocean locality shows an annual signal having an amplitude in variation attributed to upwelling. B. While there is little variation in the SSS of the eastern equatorial Pacific and the Gulf of Carpentaria, the Java Sea shows a decrease in salinity between November and April related to high rainfall during the NW Monsoon.
Figure 11. Annual variation in the proportion of maximum solar energy by latitude. At equatorial latitudes, variation of solar insolation is biannual but has a smaller amplitude. (Ivany, 2012)