Species-specific isotopic oxygen temperature calibrations for three Gulf of Maine bivalves

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Abstract:

Certain species of mollusk are frequently used for paleoclimate reconstructions due to their annual growth patterns and ability to record seawater temperature in their shells. Current paleoclimate reconstructions implement an isotopic oxygen calibration equation derived from multiple species, including foraminifera, gastropods and scaphopods (Grossman & Ku 1986). However, there is uncertainty as to whether all marine calcifiers record temperature similarly, which would highlight the need for species-specific calibration equations to reconstruct paleoclimate. To test this, we grew three Gulf of Maine mollusk species (*Arctica islandica, Mya arenaria, Mercenaria mercenaria*) in controlled temperature treatments (6.21 ± 0.06, 8.91 ± 0.28, 11.83 ± 0.14°C) in a flow-through lab experiment for twenty weeks. We measured the $\delta^{18}O$ of the seawater ($\delta^{18}O_w$) in each tank throughout the experiment and the $\delta^{18}O$ in the growing edge of each shell ($\delta^{18}O_c$) at the conclusion of study ($n_{arctica}$ = 22, $n_{arenaria}$ = 56, $n_{mercenaria}$ = 46). The $\delta^{18}O_c$ values for replicate individuals from the same species and tank agreed within ~± 0.2-0.6‰ (±1 SD, n = 4-10 replicates per species), which is above the analytical uncertainty of ~±0.09‰. We used both $\delta^{18}O_w$ and $\delta^{18}O_c$ to calculate predicted seawater temperature using Grossman and Ku's calibration equation and found that predicted temperatures differed significantly from measured temperatures ($p<0.05$ for *M. arenaria* and *M. mercenaria* for all three temperature treatments). *M. arenaria* $\delta^{18}O_c$ values predicted temperatures that were ~1-4°C cooler than the measured temperatures, while *M. mercenaria* $\delta^{18}O_c$ values predicted temperatures that were ~2-6°C warmer. Temperature calculated from *A. islandica* $\delta^{18}O_c$ values were not significantly different from the measured temperatures. These results suggest the need to investigate why these offsets exist for some species, which is likely a result of "vital effects" occurring within the organism itself.

Project Objectives:

Some marine organisms have the ability to form calcium carbonate ($CaCO_3$) to support their skeletal structure in a process known as calcification; they are known as marine calcifiers. These marine calcifiers use the calcium (Ca^{2+}) and carbonate (CO_3^{2-}) found in their environment to perform calcification. The oxygen embedded in CO_3^{2-} has a certain property that makes it useful for estimating past climates. During calcification, heavier oxygen isotopes (^{18}O) more readily calcify in colder water than lighter oxygen isotopes (^{16}O). In other words, marine calcifiers are more likely to take in ^{18}O when the surrounding temperature is cold, and ^{16}O when the surrounding temperature is hot. Because of this phenomenon, paleoceanographers can analyze the ratio of ^{18}O:^{16}O isotopes in a marine calcifier's structure to approximate historical temperature data; higher isotopic oxygen ratios indicate colder seawater temperatures while lower isotopic oxygen ratios indicate hotter seawater temperatures.

Although we know that oxygen isotopes are sensitive to temperature, in order to quantify these changes, we need a calibration equation that converts isotopic oxygen ratio into temperature. In a previous study, Ethan Grossman and Teh-Lung Ku developed a calibration equation that contemporary paleoceanographers commonly use to convert isotopic oxygen ratios into temperature (Grossman & Ku 1986). To make this equation, Grossman and Ku sampled the $CaCO_3$ present in a few different marine species, including foraminifera, gastropods and scaphopods. The issue with this sampling method is that we do not know if all marine calcifiers record temperature similarly, and if they don't, then it would not make sense to apply Grossman and Ku's equation to all marine calcifiers. Instead, paleoceanographers should develop an equation specific to each species to accurately convert isotopic oxygen ratios to temperature.

We chose to study three species of mollusk – *Arctica islandica, Mya arenaria* and *Mercenaria mercenaria* – because they grow their shells in annual increments and are known to faithfully record the temperature of the surrounding seawater (Witbaard *et al.* 1994; MacDonald & Thomas 1980; Arnold *et al.* 1998). Although these records were accurate, paleoceanographers noticed that the predicted temperature obtained using the Grossman and Ku equation was sometimes off by a few degrees when compared to the measured temperature of the seawater. Using *A. islandica*, *M. arenaria* and *M. mercenaria* shells, we can develop three species-specific isotopic oxygen calibration curves and compare them to the calibration curve determined by Grossman and Ku to test for these offsets between the predicted and measured temperature. This is all possible because the isotopic composition of the seawater used in our experiment is known, allowing us to appropriately apply the Grossman and Ku equation (Wanamaker *et al*. 2008). Specifically, we applied the modified version of the Grossman and Ku equation, which changes minor aspects about the original equation to produce an even better agreement between the predicted and measured temperature values (Dettman *et al.* 1999).

Our research question is, do different species of marine calcifiers record seawater temperature similarly? The answer to this question will refine our current understanding of isotopic oxygen dating techniques in marine calcifiers and help us construct more accurate records of historical temperature, not just in the Gulf of Maine, but for all regions where marine calcifiers are found. This project was designed to provide me an opportunity to develop the skills that every scientist should have. With this in mind, my main objectives throughout the project were (1) to practice safe laboratory techniques relating to isotopic oxygen sampling, (2) organize and interpret data and (3) communicate our results to people outside of the scientific community.

Methods:

We collected three species of mollusk (*A. islandica, M. arenaria, M. mercenaria*) from the Gulf of Maine and divided them amongst sixteen tanks. Each tank was set to a temperature of 6.21 ± 0.06, 8.91 ± 0.28, 11.83 ± 0.14°C, a pH of 7.4, 7.6, 7.8, or 8.0 (ambient pH) and was supplied with seawater from the Harpswell Sound, ME (Fig.1). We stained the mollusks with calcein to differentiate between pre-experimental and post-experimental growth, and they were raised in the tanks for 20 weeks. The $\delta^{18}O$ of the seawater ($\delta^{18}O_w$) was measured throughout the experiment.

At the end of the growth period, we sampled a small amount of shell material from the edge of our samples using a dremel. We measured the $\delta^{18}O$ of each sample ($\delta^{18}O_c$) using a Thermo Scientific Delta V. Plus mass spectrometer in continuous flow mode connected to a Gas Bench with a CombiPAL autosampler. Reference standards (NBS-18, IAEA 603) were used for isotopic corrections and to assign the data to the appropriate isotopic scale. The analytical uncertainty of the autosampler is ≈±0.09‰.

We conducted two rounds of two-sample t-tests assuming unequal variance. First, we tested the measured temperature of the tanks vs the calculated temperatures of the tanks derived from the modified Grossman and Ku equation: Temperature(°C) = $20.60 - 4.34x[\delta^{18}O_c - (\delta^{18}O_w - 0.27)]$ (Whitney *et al*. 2022). Then we tested the $\delta^{18}O_c$ values for the three species at both 6°C and 12°C (*A. islandica* vs *M. arenaria*, *A. islandica* vs *M. mercenaria*, *M. arenaria* vs *M. mercenaria*).

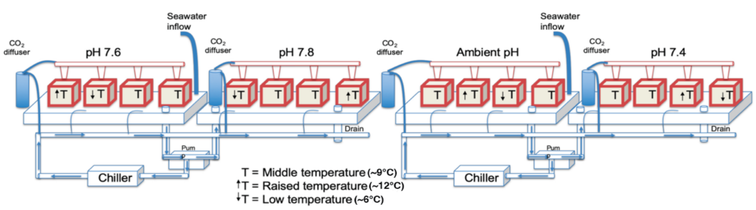
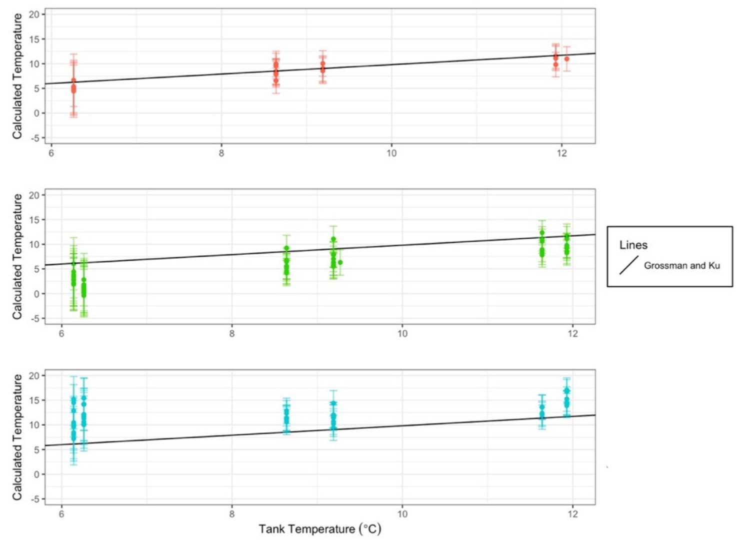


Figure 1: A diagram of our experimental setup.

Results:

Seawater temperatures calculated from *M. arenaria* and *M. mercenaria* $\delta^{18}O_c$ values using the modified Grossman and Ku equation differed significantly from the measured tank temperatures ($p<0.05$ for *M. arenaria* and *M. mercenaria* for all three temperature treatments). *M. arenaria* $\delta^{18}O_c$ values predicted temperatures that were ~1-4°C cooler than the measured temperatures, while *M. mercenaria* $\delta^{18}O_c$ values predicted temperatures that were ~2-6°C warmer than the measured temperatures (Fig.2). Seawater temperature derived from *A. islandica* $\delta^{18}O_c$ values was not significantly different from measured temperature at any of the temperature treatments. Additionally, at the low temperature treatment all three species' $\delta^{18}O_c$ values were different from one another ($p<0.05$) (Fig.3). At the high temperature treatment, the three species' $\delta^{18}O_c$ values were still different ($p<0.05$), but this difference was less pronounced than the low temperature treatment. Additionally, *M. arenaria* had the steepest calibration curve while *M. mercenaria* had the least steep calibration curve, indicating that $\delta^{18}O_c$ is more sensitive to changes in temperature in *M. arenaria* than *M. mercenaria*.



<u>Figure 2</u>: *A. islandica* (top), *M. arenaria* (middle) and *M. mercenaria* (bottom) calculated temperatures vs the measured temperatures in each of the tanks. Calculated temperature was derived using the modified Grossman and Ku equation. Tank temperature was recorded regularly using tidbit data loggers. Error bars represent ±1 SD of $\delta^{18}O_c$ values.

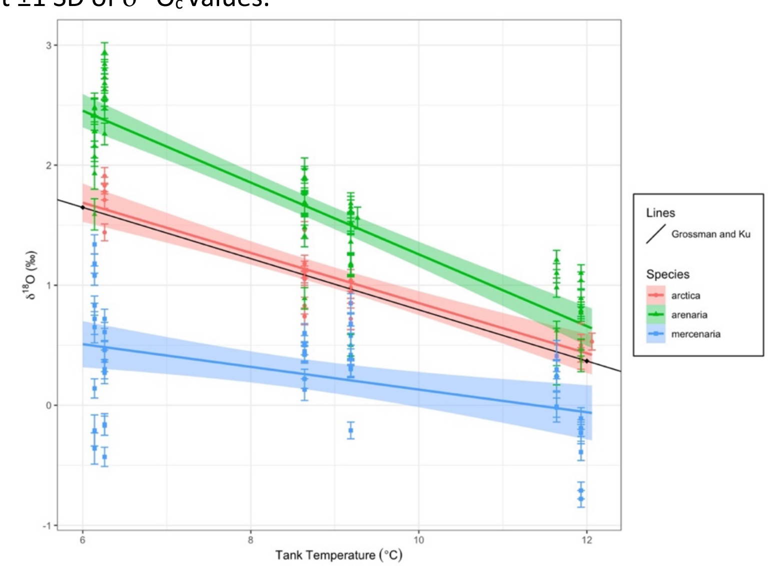


Figure 3: Isotopic oxygen calibration curves for our three species, along with the calibration curve determined by Grossman and Ku. Tank temperature was recorded using tidbit data loggers. Shaded areas represent 95% confidence intervals. Error bars represent the analytical uncertainty of the autosampler.

Discussion:

The offset of the $\delta^{18}O$ of the *M. arenaria* and *M. mercenaria* shell samples from the $\delta^{18}O$ of the seawater is likely due to a number of "vital effects" occurring within the organism itself (Ravelo & Hillaire-Marcel 2007). There are documented effects of $\delta^{18}O$ decreasing with increasing carbonate ion concentrations (Spero *et al*. 1997) and of $\delta^{18}O$ changing as an organism matures from juvenile to adult (Spero & Lea 1996). Offsets of the $\delta^{18}O$ of shells from the $\delta^{18}O$ of seawater have been identified in other organisms as well; for scleractinian corals, increases in pH drives $\delta^{18}O$ of the coral down (due to a shift of the dissolved inorganic carbon speciation toward the ^{18}O-depleted carbonate ion) and kinetic effects also impact $\delta^{18}O$ (Chen *et al*. 2018). An investigation on the impact of vital effects on the $\delta^{18}O$ of these three mollusk species should be conducted in a future study.

The *A. islandica* $\delta^{18}O$ values obtained in this study were nearly identical to the predicted values determined by the Grossman and Ku equation, which is consistent with results from other studies based in Norway (Mette *et al*. 2015) and in the North Sea (Schöne *et al*. 2005). However, other studies have shown an offset of +2.9°C for *A. islandica* from the Faroe Shelf (Bonitz *et al*. 2018). Some possible explanations for these varying results include site-specific variation in calcification processes amongst *A. islandica* populations and/or differences in sampling individuals and curating data (Trofimova *et al*. 2018).

Conclusion:

Moving forwards, it may be good practice to develop species-specific calibration curves when reconstructing paleoclimate records. Although the Grossman and Ku equation was a good fit for *A. islandica*, both *M. arenaria* and *M. mercenaria* had offsets that could be remedied with their own respective calibration curves. Due to the wide range of factors that affect an organism's calcification process – genetic differences, varying ion concentrations, pH differences – species-specific calibration curves may be especially helpful for creating more consistent results across multiple studies. This in turn would produce more accurate paleoclimate records, providing us with an even better baseline to compare modern climate trends to. It is difficult to determine whether previous reconstructions in scientific literature need to be updated, but I would recommend reevaluating these previous reconstructions whenever necessary for a new study.

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