PROCEEDINGS OF THE TWENTY-SIXTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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ROXANNE BANKER, Denison University
Research Advisor: David Goodwin

INTRODUCTION

In recent decades, the analysis of biogenic carbonate geochemistry has become a widely used tool in environmental reconstruction. Numerous authors have shown that chemical variation in bivalve mollusk shell carbonate accurately records environmental conditions experienced during growth (Jones, 1996; Wefer and Berger, 1991; Gillikin et al., 2005). Furthermore, oxygen isotopes in shell carbonate ($\delta^{18}O_{SHELL}$) are precipitated in thermodynamic equilibrium with respect to temperature and the oxygen isotopic composition of the water ($\delta^{18}O_{WATER}$) in which they grew (Jones, 1983). Therefore, their shells contain accurate archives of important environmental parameters (Jones, 1996; Wefer and Berger, 1991).

While bivalve mollusk shell deposition is controlled by numerous biological and physical factors, temperature is the most important abiotic parameter limiting growth (Goodwin et al., 2003; Schöne et al., 2002). Recent work has taken advantage of this relationship to make the link between $\delta^{18}O_{SHELL}$ variation and growth (e.g., Ivany and Wilkinson, 2003; Goodwin et al., 2003; 2009). These studies showed that $\delta^{18}O_{SHELL}$ variation, together with known environmental conditions, can be used to accurately identify growth limiting temperatures and intra-annual growth rates. These studies focused exclusively on marine bivalves, however, the link between growth and $\delta^{18}O_{SHELL}$ variation has not been established in freshwater bivalves. This study builds upon previous work by Paul and Goodwin (2009) who used data from Dettman et al. (1999) to suggest that mathematical models can accurately reconstruct intra-annual growth rates of the freshwater bivalve mollusk *Lampsilis cardium*.

The goal of this study is to reconstruct high-resolution intra-annual growth rates of *L. cardium*. Specimens of *L. cardium* were cultured for one complete year at the Columbus Zoo & Aquarium Freshwater Mussel Conservation & Research Center located on the O'Shaugnessey Reservoir in central Ohio. Temperature and $\delta^{18}O_{WATER}$ were monitored continuously throughout the year. Specimens were sacrificed on three dates during the study period. Shell carbonate deposited during the monitoring interval was sampled. Observed $\delta^{18}O_{SHELL}$ variation was then compared with predicted oxygen isotope values ($\delta^{18}O_{PREDICTED}$) calculated using temperature and $\delta^{18}O_{WATER}$ records. This analysis confirms previous suggestions that intra-annual growth is strongly controlled by temperature. Deviations between observed $\delta^{18}O_{SHELL}$ variation and $\delta^{18}O_{PREDICTED}$ variation were used to infer optimal growth temperatures. Finally, these data suggest growth is also limited by significant reservoir discharge events, especially during cold parts of the year. The findings of this study will shed light on the intra-annual growth of both modern and fossil freshwater bivalves, which may in turn facilitate the interpretation of biogeochemical archives.

METHODS

This Columbus Zoo & Aquarium Freshwater Mussel Conservation & Research Center is located on the O'Shaugnessey Reservoir, Scioto River in central Ohio (40° 10' 12.26" N, 83° 07' 57.87" W). The reservoir is located nine miles northwest of the city of Columbus. The watershed that feeds the reservoir covers ~6,500 square miles and mainly drains agricultural land (http://epa.ohio.gov).

The environmental sampling program began at 1:00 AM on January 1, 2010 and ended on December 31, 2010 at midnight. Onset© HOBO Water Temp Pro V2© loggers collected water temperatures every hour during the study interval. Loggers were attached to the cages where clams grew. Logger accuracy was 0.21°C between 0° and 50°C, and resolution was 0.02°C at 25°C. Average daily temperatures were calculated from hourly records. All calculations were conducted using the open source statistical package R (www.r-project.org).

Water samples were collected at approximately weekly intervals (n=46). Water samples were not collected in the middle of February because the reservoir was frozen. No samples were collected in the first week of November or the last two weeks of the year. Water samples were stored in 125 mL Nalgene© bottles and the caps were sealed with Parafilm©. All $\delta^{18}O_{WATER}$ analyses were conducted using a Picarro© cavity ring-down spectrometer (Earth and Environmental Sciences Isotope Analysis Lab, University of Kentucky). Analytical precision of repeated standards was ~0.2 ‰ SMOW.

Discharge from the O'Shaugnessey Reservoir was monitored daily at a station located on the Scioto River ~0.8 mi below the dam near Dublin, Ohio (USGS 03221000; Hydrologic Unit 05060001; 40° 08' 36" N, 83° 07' 14" W). Discharge measurements are accurate to 0.1 cubic foot per second.

Lampsilis cardium specimens were grown in sediment-laden cages during the study interval. However, they were transferred inside to a flow through facility when water levels were low. Specimens were harvested three times during the study interval and given corresponding IDs: OR2-A1L and OR2-A2R were both sacrificed April 22; OR4-A1L and OR6-A1L were collected September 22 and December 10, respectively. Immediately following collection, specimens were sacrificed and soft tissues were removed.

In the lab one valve from each specimen was adhered to a plexiglass cube. Valves were then wrapped in quick-setting epoxy (J-B KwikWeld©) along the axis of maximum growth to prevent shell fracture during sectioning. Valves were then mounted onto glass slides and cut into ~1 mm thick sections using a low-speed wafering saw (Buehler© IsoMet Low Speed Saw). Thick sections were ground on glass plates using 320 and 600 grit Buehler© Silicon Carbide Powder and polished with Buehler© Metaserv Grinder-Polisher and Buehler© 0.05 micron Alumina MicroPolish. Sections were cleaned between each polishing (Fisher Scientific© FS20 Ultra Sonic Cleaner). High-resolution scans of each polished shell section then were used to identify growth increments (Epson© Perfection 3200).

To collect stable isotope samples thick sections were mounted to a computer controlled x-y-z stage (Newport© Motion Controller ESP301). A stationary microdrill with a cylindrical drill bit (Brasseler© DLT 50K Series 2 Brushless Micro Motor; 300 μm diameter Komet/Gebr. Brasseler© GmbH & Co. KG, model no. H52 003) was used to collect carbonate samples along digitized milling paths parallel to growth lines in the prismatic layer of shells. Sampling began at the commissural margin and worked towards the umbo. Masses of all carbonate samples collected ranged from 50 to 100 μg.

All $\delta^{18}O_{SHELL}$ analyses were conducted using a ThermoFinnigan MAT 252 equipped with a Kiel III automated carbonate sampling device (Environmental Isotope Laboratory, University of Arizona). Powdered carbonates were reacted with dehydrated phosphoric acid under vacuum at 70°C. Analytical precision of repeated standards was 0.1 ‰.

RESULTS

Annual temperature variation shows a strong seasonal cycle. Water temperatures at the beginning of the year remain at or near 0°C. In early March, temperatures increase rapidly to ~10°C and then increase at a slower rate until peak summer temperatures (~30°C) are reached in July. In late August, temperatures decline steadily until the end of the year (Fig. 1).

Figure 1 shows annual $\delta^{18}O_{WATER}$ values and O'Shaugnessey Reservoir discharge. At the beginning of the year, $\delta^{18}O_{WATER}$ values stay near -10 ‰ until March when values drop sharply to a minimum of -13.64 ‰. In late March and early April, $\delta^{18}O_{WATER}$ values rebound to approximately -8.5 ‰. $\delta^{18}O_{WATER}$ values increase gradually through mid November. In late November and early December, $\delta^{18}O_{WATER}$ values

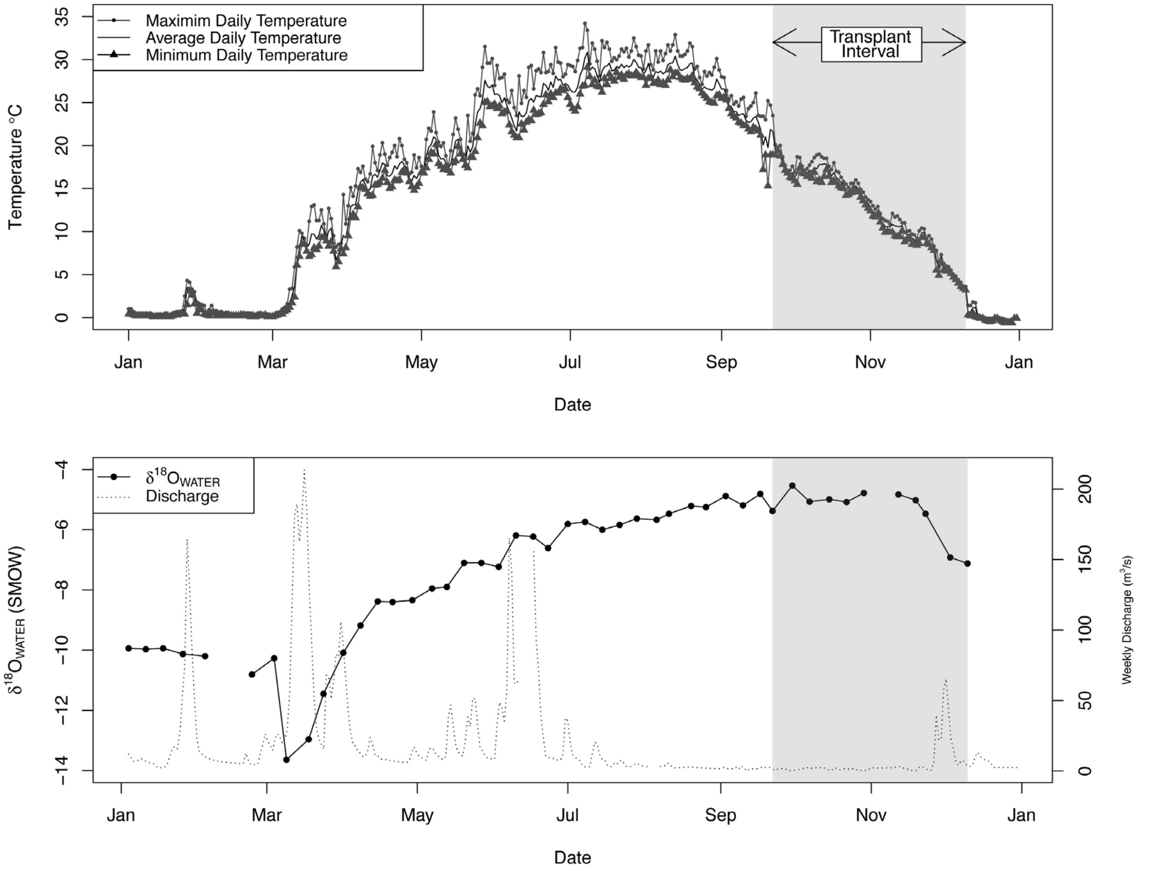

Figure 1. Minimum, maximum, and average daily water temperatures measured for the entire year of 2010 are shown in °C (top panel). Between October and December water level within the reservoir dropped below the level of temperature loggers and sediment cages containing specimens. Individuals were transferred to raceway tanks inside of the Research Center for the duration of this event. Indoor water temperature data was spliced into the outdoor temperature record between October and December so that temperature data would reflect living conditions of specimens. The gray window represents this "transplant" interval. Here approximately weekly values (n=46) of water δ^{18}O (SMOW) are plotted with the daily discharge record from the O'Shaugnessey Dam (bottom panel).

decline rapidly from the most positive values recorded in 2010 (approximately -4.5 ‰) to less than -7 ‰. The discharge record (Fig. 1) illustrates the variable nature of reservoir discharge. Baseline discharges are relatively low, with values generally less than 50 m^3/s. However, in late January, March and April, and June discharge peaked above 150 m^3/s. The largest discharge event occurred in mid March and saw weekly discharges in excess of 213 m^3/s.

Figure 2 shows δ^{18}O$_{SHELL}$ and δ^{13}C$_{SHELL}$ of carbonate samples from the four specimens of *L. cardium* used in this study. In all figures time passes from left to right and the highest sample represents the commissure. The isotope profiles from OR2-A1L and OR2-A2R are strikingly similar with δ^{18}O$_{SHELL}$ values ranging between -5.5 and -6.5 ‰. The most positive values in each specimen are followed by a rapid decline. This is trend is most clearly shown in OR2-A1L.

The δ^{18}O$_{SHELL}$ profile of OR4-A1L follows a similar pattern (Fig. 2). δ^{18}O$_{SHELL}$ values at the beginning of 2010 are ~5.5 ‰ before decreasing sharply. Here δ^{18}O$_{SHELL}$ reaches a minimum of -7.68 ‰. This negative excursion displays two distinct troughs. Values then increase to ~-7.0 ‰ and remain relatively stable until δ^{18}O$_{SHELL}$ begins to increase as temperatures drop at the end of the year. δ^{18}O$_{SHELL}$ values from OR6-A1L display a nearly identical pattern. Values at the beginning of the year are ~-5.5 ‰ before exhibiting a downward trend characterized by two local minima. Here values decrease to -7.86 ‰. δ^{18}O$_{SHELL}$ then increases to ~-7.0 ‰ and does not change appreciably until the end of the year (Fig. 2).

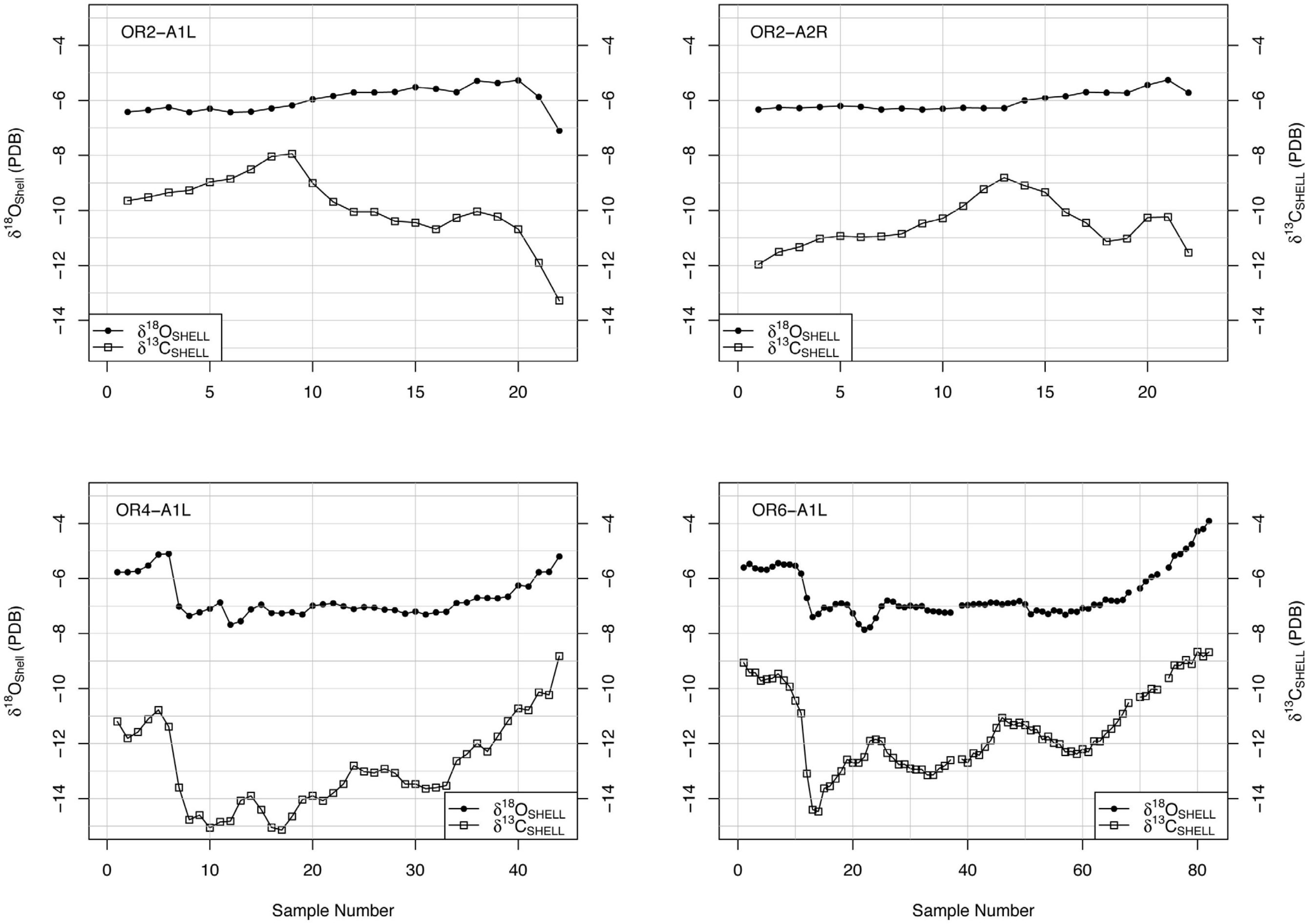

Figure 2. $\delta^{18}O_{SHELL}$ *(PDB) and* $\delta^{13}C_{SHELL}$ *(PDB) of specimens OR2-A1L, OR2-A2R, OR4-A1L, and OR6-A1L are shown. OR2-A1L and OR2-A2R were harvested on April 22 and OR4-A1L and OR6-A1L were sacrificed September 22 and December 10, respectively. Carbon isotope values are shown for completeness, but this study will focus exclusively on the oxygen isotope results.*

DISCUSSION

Previous research shows that $\delta^{18}O_{SHELL}$ variability in bivalves is strongly controlled by temperature as well as by $\delta^{18}O_{WATER}$ (Jones, 1983; Dettman et al., 1999). If specimens grew continuously during 2010, $\delta^{18}O_{SHELL}$ should exhibit a sinusoidal pattern. $\delta^{18}O_{SHELL}$ values from OR2-A1L and OR2-A2R are more positive than $\delta^{18}O_{PREDICTED}$ and do not follow expected trends. This suggests that carbonate samples from OR2-A1L and OR2-A2R represent growth of *L. cardium* at the end of the previous year (2009).

Dettman et al., (1999) suggests that growth of *L. cardium* occurs when temperatures rise above ~12 °C. Water temperatures rise above this threshold on April 1 (Fig. 1). Dates were assigned to OR6-A1L $\delta^{18}O_{SHELL}$ values by comparing patterns to $\delta^{18}O_{PREDICTED}$. These results suggest that growth of specimens resumed on approximately May 16. The time interval between the cessation of growth in 2009 and May 2010 represents a period characterized by little to no growth. A significant reservoir discharge event may have delayed growth onset of *L. caridum* until May 16.

Growth cessation results in missing time from bivalve shells and is characterized by the presence of growth bands (Jones and Quitmyer, 1996). One carbonate sample taken from OR6-A1L has a value of -6.71 ‰ and corresponds to a growth band in the prismatic layer of the shell (circled in Fig. 3). Numerically, this $\delta^{18}O_{SHELL}$ is situated directly between isotopes dated to the end of 2009 and May 2010. It is unlikely, however, that growth occurred during the time of year when this sample corresponds to $\delta^{18}O_{PREDICTED}$ values. This suggests that micromilling resulted in significant time averaging of carbonate material deposited at the end of the previous year and the beginning of the growth season in 2010.

Carbonate removed from the commissure of specimen OR4-A1L represents material deposited just before the animal was sacrificed on September 22 and has a $\delta^{18}O_{SHELL}$ value of -5.2 ‰. The closest value from OR6-A1L is -5.17 ‰ and correlates to $\delta^{18}O_{PREDICTED}$ values calculated for September 22. The most positive $\delta^{18}O_{SHELL}$ value collected from OR6-A1L is ~-3.91 ‰, which corresponds to $\delta^{18}O_{PREDICTED}$ values for September 28.

To assign dates to remaining $\delta^{18}O_{SHELL}$ values, patterns between $\delta^{18}O_{SHELL}$ and $\delta^{18}O_{PREDICTED}$ were assessed; isotopes were fit to the predicted curve and evenly distributed between the dated samples discussed above. Results show deposition beginning ~May 16 at relatively fast rates. This rapid growth continues into early July, but is interrupted by two intervals of diminished growth characterized by elevated temperatures. Growth then continues through the rest of the year at slower rates before experiencing winter shutdown.

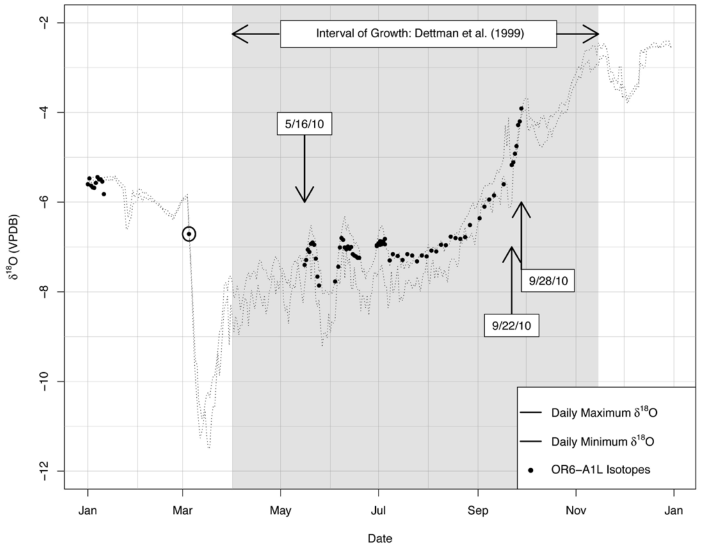

Figure 3. Here observed $\delta^{18}O_{SHELL}$ variation is compared to $\delta^{18}O_{PREDICTED}$ values, which were calculated using temperature and $\delta^{18}O_{WATER}$ data with the alpha (α) version of Grossman and Ku's (1986) paleotemperature equation derived by Dettman et al., 1999. This equation produces $\delta^{18}O_{PREDICTED}$ values in SMOW, which are converted to PDB using $\alpha_{SMOW-PDB} = 1.0309$ (Gonfiantini et al., 1995). Maximum and minimum $\delta^{18}O_{PREDICTED}$ daily values were calculated using minimum and maximum temperatures respectively. The gray window represents anticipated growing season based on temperature constraints of 12°C (Dettman et al., 1999). The circled $\delta^{18}O_{SHELL}$ value likely represents time averaging of carbonate deposited at the end of 2009 and May 2010, not a growth event during March.

Goodwin et al., (2001) suggests that marine bivalve *Chione cortezi* may precipitate carbonate during optimal temperatures. When temperatures calculated from $\delta^{18}O_{SHELL}$ were compared to observed temperatures, Goodwin et al., (2001) found that temperatures were over estimated in the spring and underestimated during peak summer temperatures. Here we find similar results: during cold parts of the year, such as the spring and fall, $\delta^{18}O_{SHELL}$ values occur in the upper range of $\delta^{18}O_{PREDICTED}$. Conversely, during hot parts of the year, $\delta^{18}O_{SHELL}$ occur in the lower range of $\delta^{18}O_{PREDICTED}$. This implies that specimens of *L. cardium* precipitate shell material during the warm parts of cold days and cold parts of hot days, thus displaying growth during optimal growth temperatures (Fig. 3).

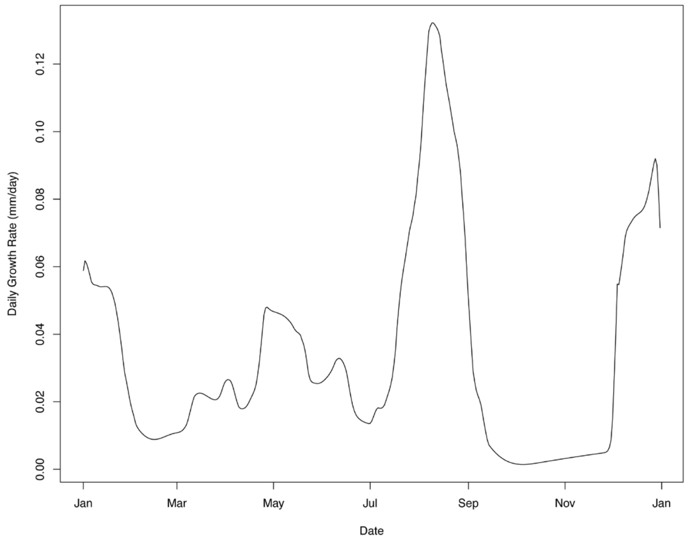

Figure 4. The first step of MoGroFunGen produces continuous functions of temperature and $\delta^{18}O_{WATER}$ vs. time using environmental data. MoGroFunGen then uses a paleotemperature equation to calculate $\delta^{18}O_{PREDICTED}$ and fits $\delta^{18}O_{SHELL}$ to this curve, thus relating $\delta^{18}O_{SHELL}$ to specific dates. MoGroFunGen generates a distance to time curve by assigning sample distance (mm) measurements to dates using the $\delta^{18}O_{SHELL}$ vs. time output. This results in a growth curve output in mm/day. Technique developed by Paul and Goodwin (2009).

Here we evaluate our results using two techniques of calculating intra-annual growth rates of bivalves. The mathematical model MoGroFunGen was used to predict intra-annual growth rates of *L. cardium* (Paul and Goodwin, 2009). Growth rates remain at or near zero until late April or early May. At this time growth rates generally increase but appear to shut down briefly during late May and late June. After a period of rapid growth, rates gradually taper off towards the end of the year before stopping completely (Fig. 4). Daily growth rates were also calculated by dividing average sample interval by time elapsed between deposition of each sample. These predicted growth rates agree well with results in Figure 3 and growth analysis using MoGroFunGen discussed above (Fig. 5).

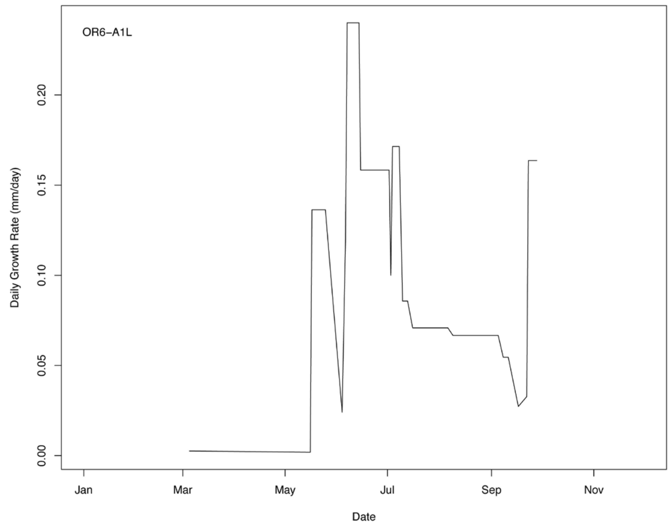

Figure 5. Carbonate was collected by micromilling several consecutive sets of samples from shells, each including ~10 samples. Average sample interval (~0.20 mm) was calculated by dividing micromilled path distance by the number of samples removed in each set. Average sample interval (~0.2 mm) was divided by the number of days between each sample (determined in Fig. 3) to produce daily growth rates in mm/day.

CONCLUSION

Results provide strong evidence that specimens OR4-A1L and OR6-A1L were growing synchronously throughout the year and that these animals are accurate climatic indicators. This study confirms that the growth of bivalves is constrained by temperature. Furthermore, growth of this species may also be limited by other environmental factors such as significant reservoir discharge events. Comparisons between $\delta^{18}O_{SHELL}$ variation and $\delta^{18}O_{PREDICTED}$ variation suggest that *L. cardium* grows during optimal daily temperatures: *L. cardium* precipitates carbonate during the cool parts of hot days and the warm parts of cold days. Additional research is required to substantiate findings discussed in this study. However, these results will provide new insights on the intra-annual growth of modern and fossil freshwater bivalves, which is essential to interpreting biogeochemical archives.

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