

Carbon and oxygen isotope analysis of modern freshwater mollusk shells: applications for climate reconstruction

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ABSTRACT

Modern freshwater mollusk shells record climatic trends across the lifespans of individual organisms. In this study, we analyze growth bands in the carbonate shells of *Lampsilis* sp. and *Potamilns alatus* from the Cannon River in southeastern Minnesota for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ content. Growth band $\delta^{18}\text{O}$ signatures in the *Potamilns* shell show persistent variation on a seasonal timescale and a larger-magnitude variation over multiple years. $\delta^{13}\text{C}$ signatures show less variation and offer no coherent paleoclimate information. We argue that changes in growth band $\delta^{18}\text{O}$ in *Potamilns alatus* reflect variations in water temperature as well as changes in Cannon River geochemistry, so that the mollusk may serve as a high-resolution paleoclimate proxy.

INTRODUCTION

Mollusks are useful as paleoclimate indicators because stable isotope ratios in their shells record environmental conditions. Because mollusks generally precipitate their shells in isotopic equilibrium with the surrounding water, the $\delta^{18}\text{O}$ signature of calcium carbonate they precipitate to form their shells at any one time reflects water temperature and geochemistry (Gillikin et al., 2005). Additionally, $\delta^{13}\text{C}$ values of marine mollusk shells have been shown to replicate that of surrounding water dissolved inorganic carbon (DIC), which provides information regarding productivity and climate (Dettman et al., 1999), and it is possible that freshwater mollusk shells could similarly serve as DIC proxies. Due to this sensitivity to environmental changes and the rate of calcium carbonate secretion, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures of freshwater mollusk shells serve as a high-resolution record of the environment in which they precipitated.

Seasonal to annual precision sampling of shell isotopic signatures is possible because mollusk shells show alternating light and dark growth bands (Fig. 1). These bands occur because shell growth rate in freshwater mollusks is primarily controlled by water temperature, although organism age, reproductive cycle, salinity, and nutrient availability also play a role. Thus, wide light bands develop during the summer when growth rate is maximized, and narrow dark bands precipitate in the winter, so that a light-dark couplet corresponds to one full year of growth (Jones and Quitmyer, 1996; Brey and Mackensen, 1997; Goodwin et al., 2003).

In this study, we analyze the stable isotopic composition of growth bands from shells of two different species of freshwater mollusk from the Cannon River in southeastern Minnesota: *Lampsilis sp.* and *Potamilns alatus* (Fig. 2). The Cannon River



Figure 1. Example of light and dark growth banding on a cross-section of the shell of *Potamilns alatus* (holes and tracks are from samples drilled).



Figure 2. Image of the shell of *Potamilns alatus*, a mussel prevalent in the Cannon River (photograph is laterally compressed; adapted from Carleton College Cannon River website).

Watershed has experienced climatic fluctuations over the last few hundred years as well as environmental change due to industrial and commercial development during the twentieth century. We investigate the possibility that growth band $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ can provide a high-resolution record of seasonal to inter-annual environmental variability, showing the utility of freshwater mollusks as paleoclimate indicators.

GEOLOGIC SETTING

The Cannon River is located in southeastern Minnesota (Fig. 3). It is 120 miles long, running from Shields Lake to the Mississippi River, and has nine dams along its length (Anderson, 2000). The Cannon River watershed encompasses Blue Earth, Dakota, Freeborn, Goodhue, Le Sueur, Rice, Scott, Steele, and Waseca Counties, running through residential, commercial, agricultural and undeveloped land.

METHODS

During the summer of 1993, Professor Gary Wagenbach collected shell remains of *Potamilns alatus* and *Lampsilis* sp. from the Cannon River near the Faribault Dam. Although the exact dates of the mollusks' deaths are unknown, it was inferred from shell condition that the animals most likely died during droughts in the late 1980s (G. Wagenbach, personal communication 2007).

Shell sections from both species were mounted on glass slides as thick sections (~300 μm). Using a Merchantek Leica GZ6 MicroMill, shell sections were drilled along growth banding in transects that were approximately 50 μm in width, 100 to 150 μm in depth and 3 to 6 mm in length, and powder was collected from these transects (Fig. 4). Both light and dark bands were milled from the interior margin of the shell. A Dremel

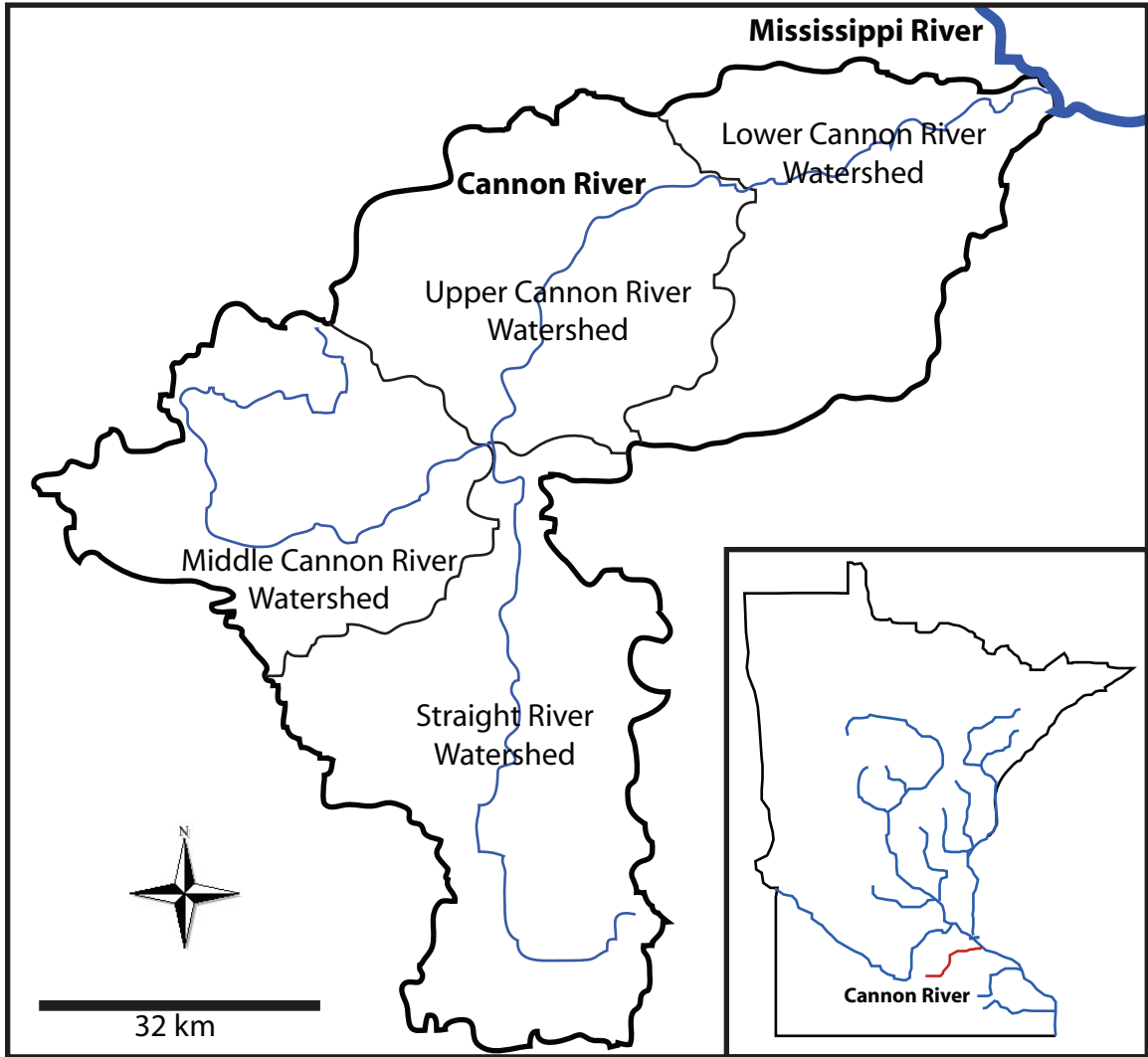


Figure 3. The Cannon River is located in southeastern Minnesota and is a tributary to the Mississippi River. Both *Potamilns alatus* and *Lampsilis* sp. live in the Cannon.

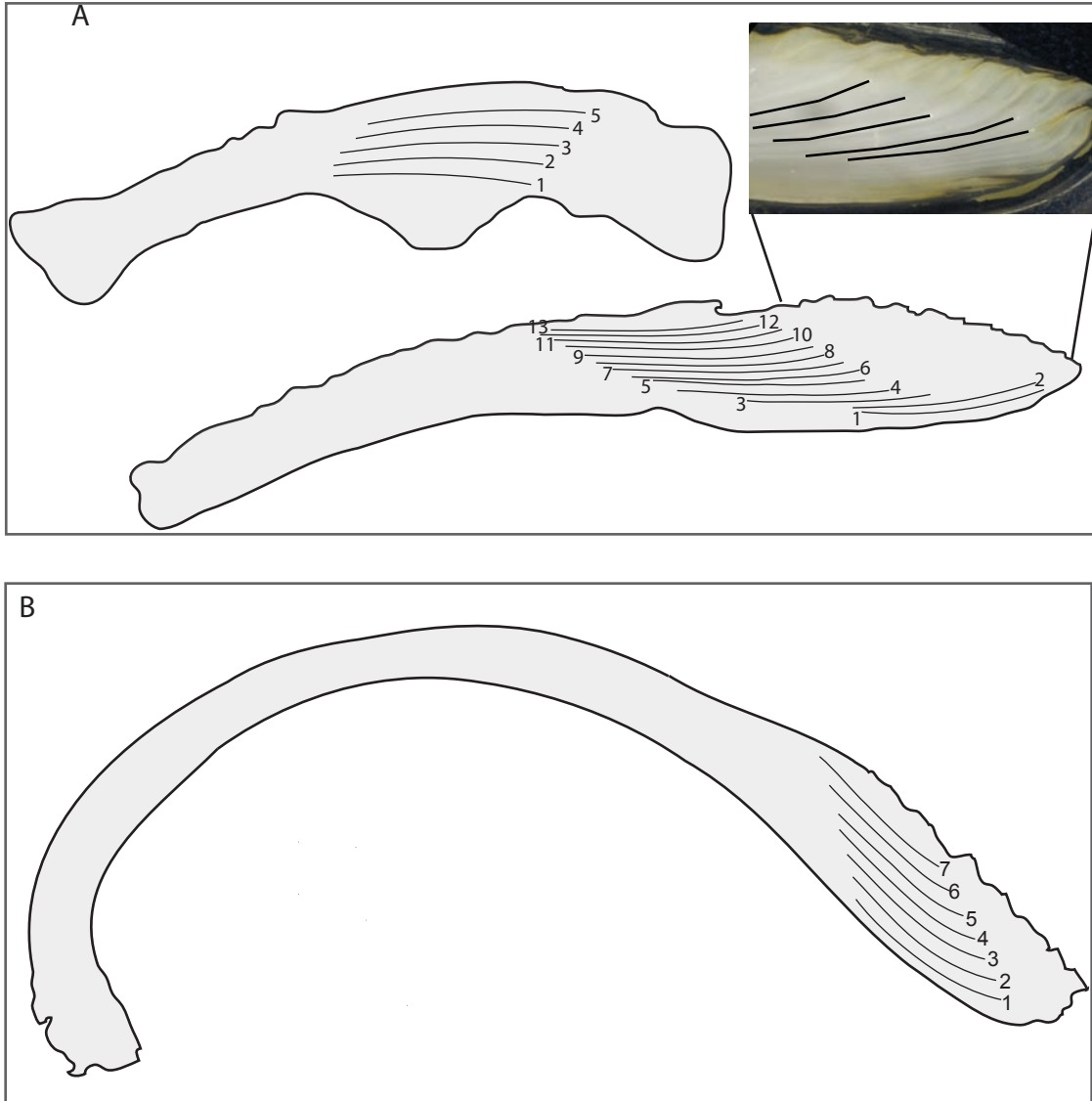


Figure 4. A: *Potamilns* sample locations; note upper, small valve and lower, large valve. Photo of sampled shell is inset with sampling locations marked in black. B: *Lampsilis* sample locations.

MultiPro hand-drill was used to collect bulk samples from the surface of both shell sections (the *Potamilns* bulk sample included material from both small and large valves of one shell).

Powder from each transect was weighed to between 30-90 micrograms (μg) using a Mettler Toledo AX 26 DeltaRange Microbalance, and put into silver capsules. Samples were baked at 300°C for one hour in order to remove organic material, and then analyzed with a Finnigan MAT 252 dual inlet mass spectrometer (a.k.a. “Big Dog”) at the University of Utah in Salt Lake City. Samples were reacted with phosphoric acid (H_3PO_4) under positive He pressure, and run through two cryogenic traps under a vacuum system to isolate CO_2 from the reaction, which was then analyzed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition. Samples were compared to the UU - Carrara (> 140 mesh) carbonate standard.

RESULTS

$\delta^{18}\text{O}$ signatures from growth bands in the large and small *Potamilns* shell valves show some variability both between light and dark bands and a greater-magnitude variability over multiple bands. Trends in $\delta^{13}\text{C}$ signatures mimic $\delta^{18}\text{O}$ variability, though to a lesser extent (Figs. 5 and 6). The *Lampsilis* shell shows almost no variability between individual bands, and little variability across multiple bands (Fig. 7).

Comparison of $\delta^{18}\text{O}$ signatures in both mollusk species’ light and dark growth bands demonstrates, again, more variability in the *Potamilns* shell than in the *Lampsilis* shell (Fig. 8). The small *Potamilns* valve shows a significant difference in $\delta^{18}\text{O}$ between light and dark bands ($p=0.04$), while the large valve does not ($p=0.37$), and bands in the

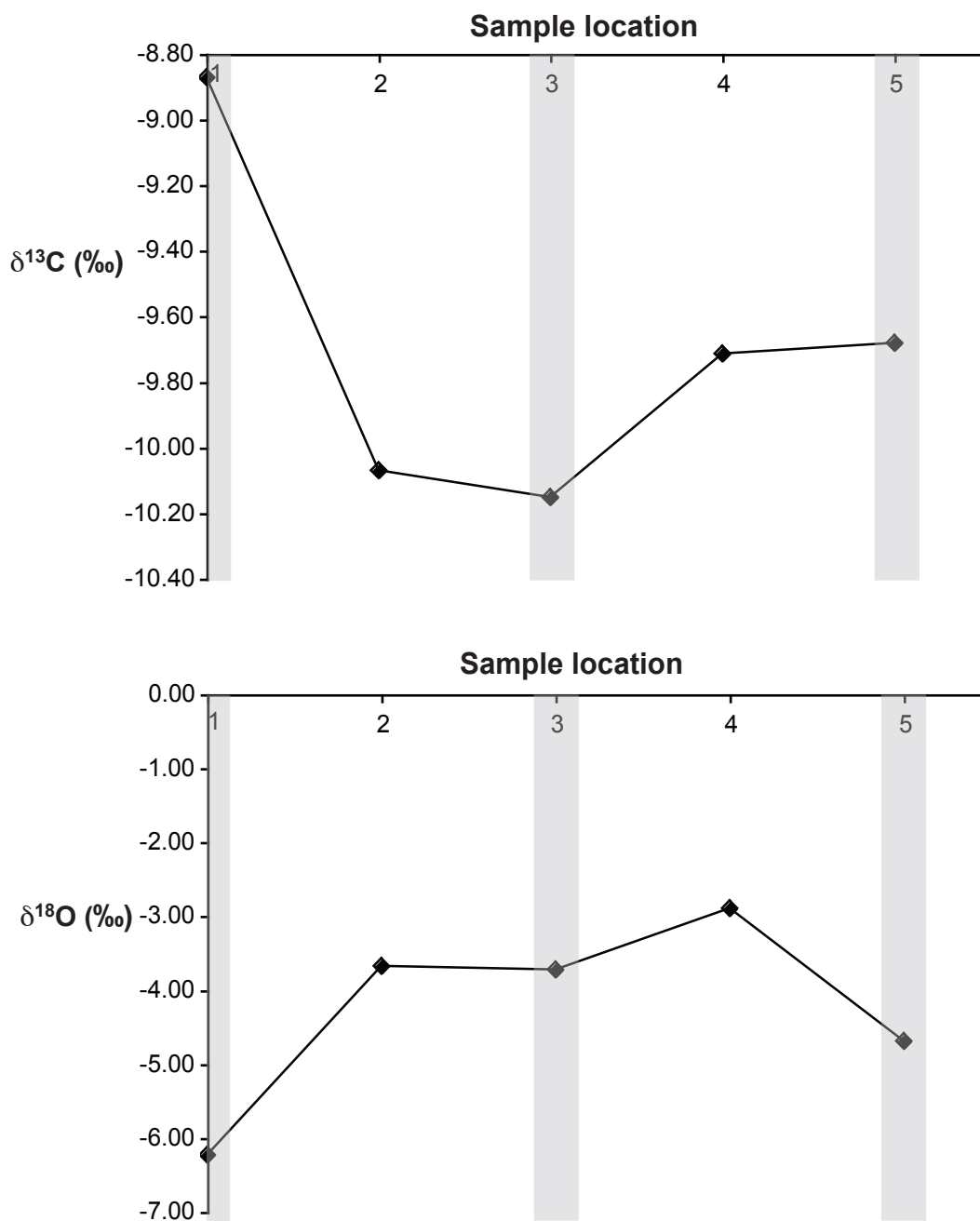


Figure 5. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of growth bands from the small *Potamils* valve; sample numbers begin at the youngest part of the shell and increase towards its edge, and gray bars indicate dark growth bands. Note that variability over multiple bands is of greater magnitude than between light and dark bands.

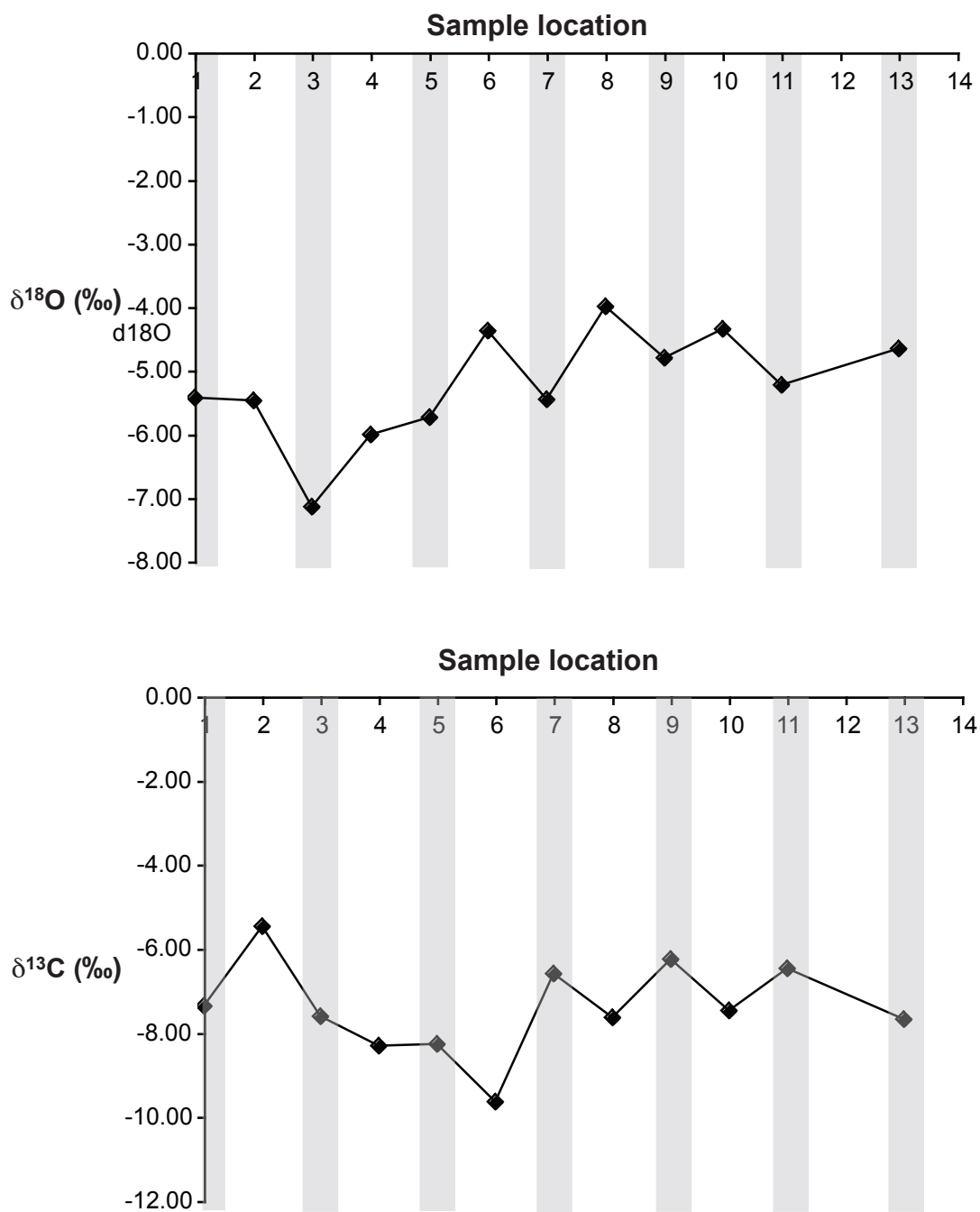


Figure 6. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures of growth bands from the large *Potamilns* valve; sample numbers begin at the youngest part of the shell and increase towards its edge, and gray bars indicate dark growth bands. Note fluctuation in isotopic signature between light and dark bands and larger trend over multiple bands.

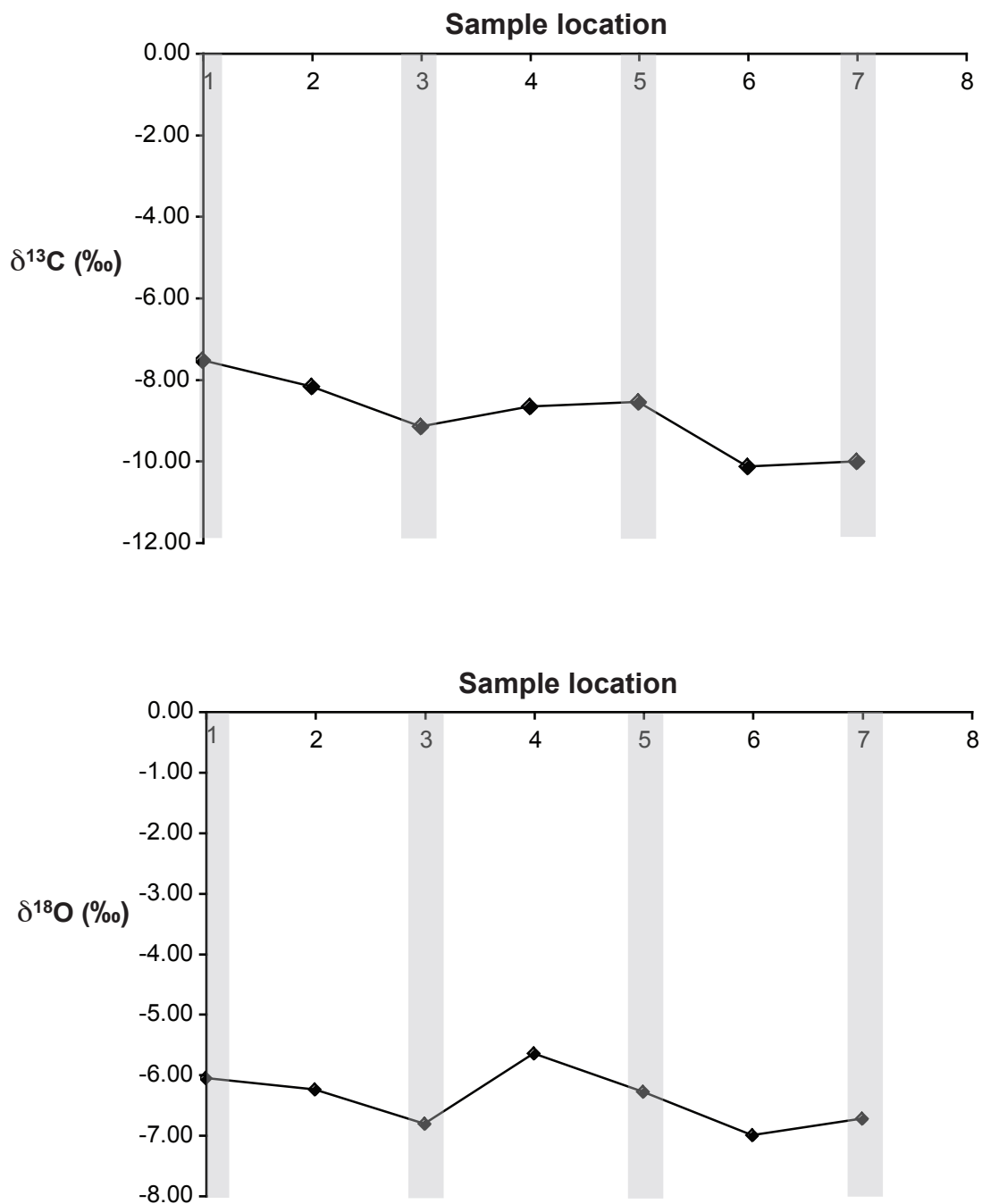


Figure 7. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures of growth bands from the *Lampsilis* shell; sample numbers begin at the youngest part of the shell and increase towards its edge, and gray bars indicate dark growth bands. Note a minor trend over multiple bands but few distinct changes between light and dark bands.

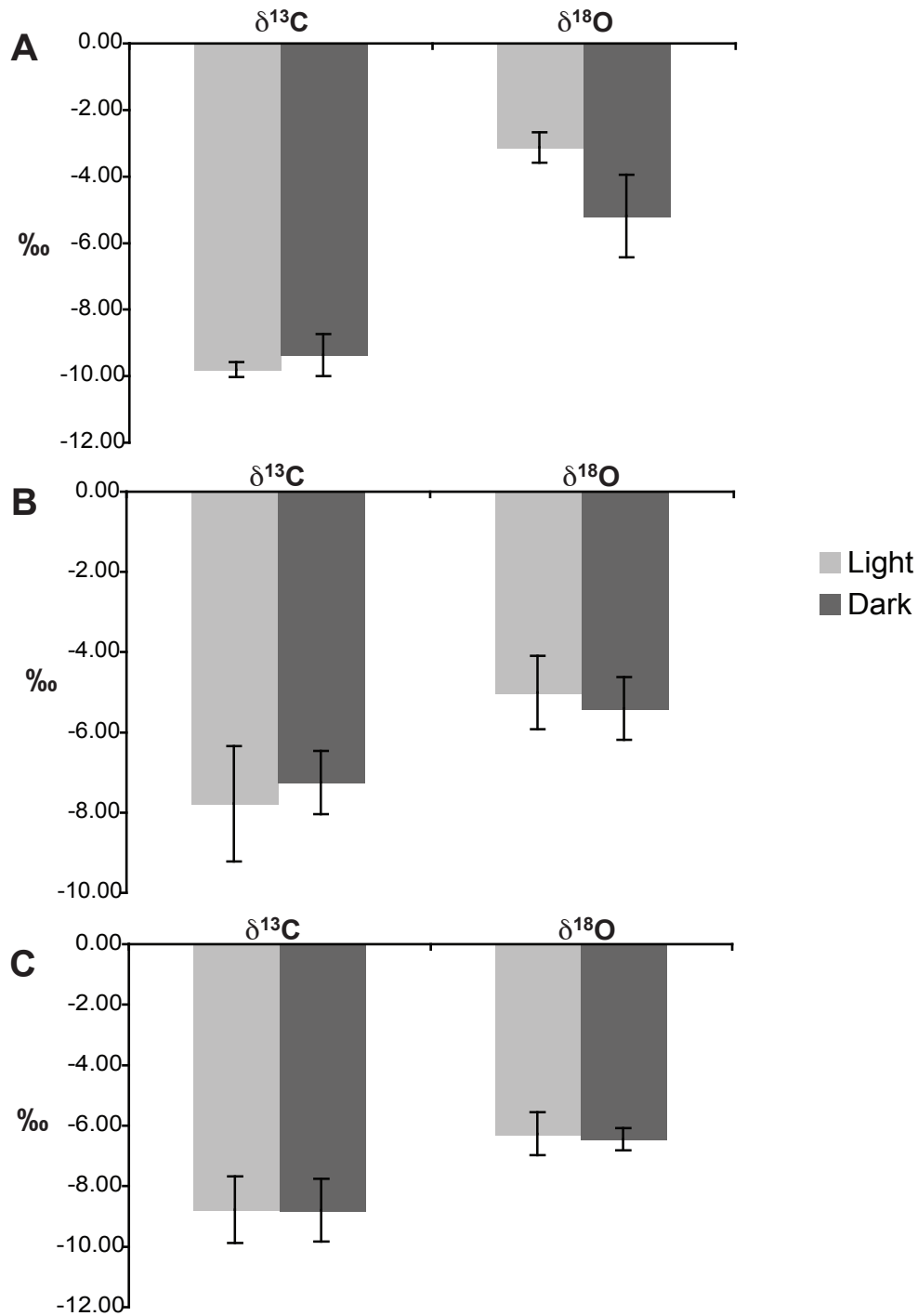


Figure 8. Variation in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures between light and dark growth bands. A: For the small *Potamilns* shell, there is a significant difference ($p=0.04$) between the $\delta^{18}\text{O}$ signature of light and dark bands but not between the $\delta^{13}\text{C}$ signatures ($p=0.31$). B: Variation between light and dark bands in the large *Potamilns* shell is not significant for either $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ ($p=0.37$ and 0.36 , respectively). C: The *Lampsilis* shell shows no significant variation in $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ between light and dark bands ($p=0.66$ and 0.98 , respectively).

Lampsilis shell similarly have little variability in $\delta^{18}\text{O}$ signature ($p=0.66$). $\delta^{13}\text{C}$ signatures show no differentiation between light and dark bands in any of the shells ($p=0.31$, 0.36 , and 0.98 for the small and large *Potamilns* valves and the *Lampsilis* shell, respectively).

In general, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of bulk samples from both the *Lampsilis* and *Potamilns* shells were different from the signatures of sampled locations. *Lampsilis* bulk samples had significantly different $\delta^{13}\text{C}$ signatures from individual samples ($p=0.04$) and $\delta^{18}\text{O}$ signatures tended to be different ($p=0.12$). For both the small and large *Potamilns* valves, bulk sample $\delta^{13}\text{C}$ values showed significant variation from the $\delta^{13}\text{C}$ values of sampled locations ($p<0.01$ and $p=0.03$, respectively). However, bulk sample $\delta^{18}\text{O}$ signatures showed no variation compared to samples taken from the small *Potamilns* valve ($p=0.92$), but were significantly different from large valve *Potamilns* samples ($p=0.10$). Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures varied significantly between samples from the small and large *Potamilns* valves ($p<0.01$ and $p=0.06$).

DISCUSSION

Growth band $\delta^{18}\text{O}$ signatures

Analysis of $\delta^{18}\text{O}$ signatures in both valves of the *Potamilns* shell shows high-resolution variation both between bands and over a series of bands (Figs. 5 and 6). This variation corresponds to published variation in mollusk band $\delta^{18}\text{O}$; accordingly we assume that variation in light and dark band $\delta^{18}\text{O}$ corresponds to seasonal changes in water temperature, with a cyclical variation between ^{18}O -depletion (winter) and ^{18}O -enrichment (summer) (cf. Jones and Quitmyer, 1996; Brey and Mackensen, 1997). Thus, both *Potamilns* valves show variability on a seasonal and inter-annual timescale, with the

inter-annual variability having a greater magnitude (Figs. 5 and 6). In contrast to the *Potamilns* valves, *Lampsilis* shell $\delta^{18}\text{O}$ showed little variation between seasons or inter-annually (Fig. 7).

Light and dark growth bands in the small valve of the *Potamilns* shell had significantly different $\delta^{18}\text{O}$ signatures. Light growth bands were depleted in $\delta^{18}\text{O}$ while dark bands were enriched, supporting our assumption that these bands represent seasonal variation (Fig. 8). However, we did not find similarly significant differences between $\delta^{18}\text{O}$ signatures of light and dark bands in the large *Potamilns* valve and the *Lampsilis* shell (Fig. 8). The lack of difference between light and dark bands in the large *Potamilns* valve may be due to the longer range of time represented by the samples analyzed, so that larger-scale temperature variability recorded in $\delta^{18}\text{O}$ signatures obscures seasonal distinction between light and dark bands. This possibility is supported by the trend of greater inter-annual than seasonal variability observed in growth band $\delta^{18}\text{O}$ (Fig. 6). In contrast, the *Lampsilis* shell did not show significant variation between light and dark bands, or on either seasonal or inter-annual timescales (Fig. 7). This lack of variability may be an artifact of the range of time sampled (perhaps temperatures were unusually similar over those years); another conclusion is that this *Lampsilis* species may record temperature variation with less accuracy than *Potamilns alatus*.

The $\delta^{18}\text{O}$ signatures of bulk samples combining both *Potamilns* valves also suggests that water temperature variation over the mollusk's lifetime was greater than seasonal variation. Bulk sample $\delta^{18}\text{O}$ tended to be different from the $\delta^{18}\text{O}$ signatures of the locations sampled from the large *Potamilns* valve ($p=0.10$), implying that water temperatures during the mollusk's life did not vary within a narrow and consistent

seasonal range, but rather record larger-scale climatic variability. Interestingly, bulk sample $\delta^{18}\text{O}$ values were essentially indistinguishable from the $\delta^{18}\text{O}$ of growth bands from the small *Potamilns* valve ($p=0.92$), but given that few growth bands were sampled on the small valve, it seems likely that the samples analyzed happened to record median temperatures for the organism's life. In addition, the $\delta^{18}\text{O}$ signatures of bands from the large and small valves differed significantly ($p=0.06$), suggesting that the bands sampled record different periods of time with different climatic conditions.

Similarly, although the *Lampsilis* shell showed little variation in $\delta^{18}\text{O}$ over the bands sampled, these samples also tended to differ from the bulk samples ($p=0.12$). Again, this difference implies that the variation in water temperature the mussel experienced over its lifetime was greater than seasonal variation.

In general, $\delta^{18}\text{O}$ signatures in mollusk shells probably record changes in water temperature caused by climate variation as well as seasonal variance in the inputs to the Cannon River. It is clear from the $\delta^{18}\text{O}$ of growth bands in *Potamilns* valves that the Cannon River is subject to seasonal changes in water temperature. However, the lack of a systematic pattern in $\delta^{18}\text{O}$ over the organisms' lifespans indicate that seasonal water temperature is not constant from year to year, and responds to longer term climatic fluctuations. Because of the lack of data regarding sample age and paleo-water chemistry, it is impossible to identify paleo-water temperatures or to correlate the patterns observed in this study with large-scale climate changes. However, our results show that freshwater mollusks, particularly *Potamilns alatus*, record water temperatures at high resolutions through $\delta^{18}\text{O}$ signatures in growth bands.

Growth band $\delta^{13}\text{C}$ signatures

$\delta^{13}\text{C}$ ratios in growth bands of the *Lampsilis* shell and the large and small *Potamilns* valves tend to mimic the pattern of $\delta^{18}\text{O}$ ratios (Figs. 5-7). However, there was no significant difference in $\delta^{13}\text{C}$ in light and dark bands in any of the shells studied (Fig. 8). Thus, it is unlikely that comparison of mollusk shell $\delta^{13}\text{C}$ signatures across seasonal or annual timescales reveals any salient information about the paleoenvironment of the Cannon River.

This conclusion is not surprising in the context of previous work: Hereid et al. (2005), working with the same *Lampsilis* shell, also found no significant difference in $\delta^{13}\text{C}$ between light and dark bands. Further, Geist et al. (2005) finds that different individuals within a population demonstrate unique patterns of growth band $\delta^{13}\text{C}$. These patterns cannot be explained by environmental variables, and are rather the result of fractionation of metabolic carbon dioxide. With such a strong influence by individual metabolic signals, the $\delta^{13}\text{C}$ of growth bands in freshwater mussels are incoherent paleoclimate indicators (Geist et al., 2005).

CONCLUSIONS

Shells of the freshwater mussel *Potamilns alatus* from the Cannon River offer a high-resolution record of temperature variation on seasonal and multi-year time scales based on growth band $\delta^{18}\text{O}$ signatures. In contrast, the *Lampsilis* sp. shell studied shows little variation on any time scale and may be less useful as a paleoclimate indicator. Our results agree with the generally-held conclusion that growth band $\delta^{13}\text{C}$ signatures do not correlate to any specific paleoenvironmental trends because freshwater mollusks

fractionate carbon as a result of metabolic processes that do not correspond to DIC signatures (cf. Geist et al., 2005). While we cannot estimate historical Cannon River temperatures from our data due to the lack of data on stable isotopes of the water during the sampled mollusks' lifetimes, it is clear from this study that temperature variations between summer and winter growing seasons, as well as over multiple years, were recorded by Cannon River mollusks.

FUTURE WORK

In order to further understand the relationship between carbonate shell precipitation in freshwater mussels, water temperature, and isotopic fractionation, it is necessary to better constrain the fractionation factor for ^{18}O . An experiment in which water temperature, isotopic composition of the water, and the isotopic composition of mussels are measured concurrently would allow better definition of the fractionation factor for specific species of freshwater mussels and thus would provide an accurate prediction of paleo-water temperature from fossils of those species.

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