# Carbon and Oxygen Isotope Trends in Freshwater Mussel Species from the Cannon River, MN

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## INTRODUCTION

As bivalves grow, layers of calcite or aragonite form alternating dark and light laminations (Fig. 1). The amount of shell added, resulting from the rate of bivalve growth, is primarily based on water temperature (Goodwin et al. 2003). Freshwater bivalves grow shells between about 12ºC and a peak at 24ºC (Dettman 1999, Schone et al. 2002), resulting in thicker banding during the summer months.

As shell material is added, carbon and oxygen isotopic ratios reflect environmental conditions. The $\delta^{18}O$ recorded in bivalve shells is affected by the surrounding water, based on changes in river water inputs and temperature fractionation. Mollusk shells are more enriched in $^{18}O$ during cold months (Schone 2002, Goodwin 2003, Dettman 1999), and this cyclic $\delta^{18}O$ cycle proves that laminations are annual (Brey and Mackensen 1996). Carbon isotope ratios are based on the isotopic signature of dissolved inorganic carbon in river water (Wurster and Patterson 2001, Veinott and Cornett 1997), which is due to variations in magnitude of carbon sources and sinks (Dettman 1999). However, very negative $\delta^{13}C$ metabolic carbon may be incorporated in shells (Veinott and Cornett 1997), which offsets the water's isotopic signature.

This project sampled shell carbon and oxygen isotope ratios to find large-scale trends from the freshwater mussels Pink Heelsplitter and *Lampsilis*, from the Cannon River, MN. Any trends in $\delta^{18}O$ or $\delta^{13}C$ could reflect a change in river water composition over the life of the mussel, and thus possibly short-term climatic changes.

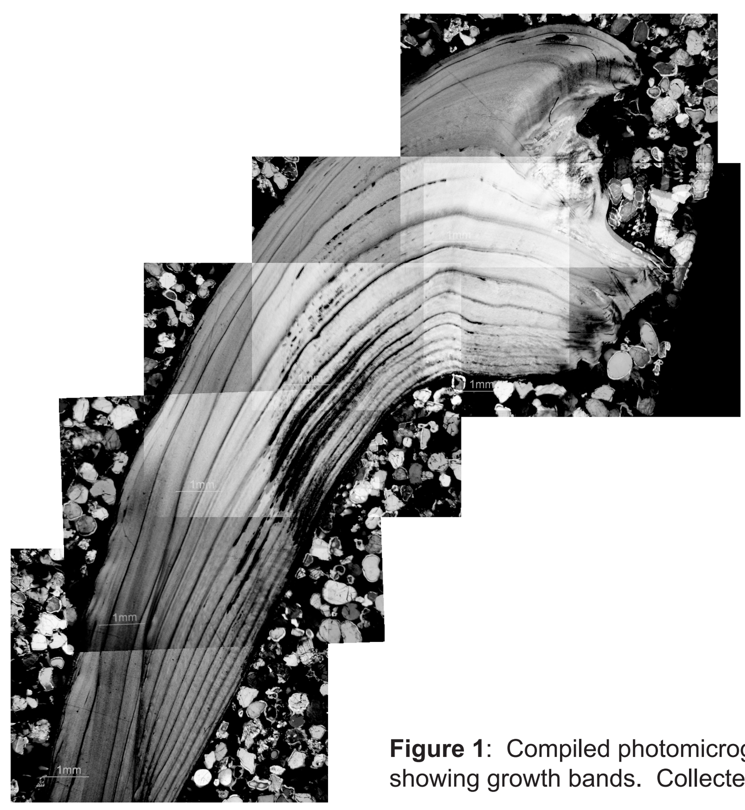

**Figure 1**: Compiled photomicrographs of a Pink Heelsplitter shell showing growth bands. Collected from the Cannon River, MN.

## METHODS

Two mussel shells were collected in the early 1990s from the Cannon River near Northfield, MN (Fig. 2), one *Lampsilis sp.* and one *Potamilus alatus*, known commonly as Pink Heelsplitter. Two thin sections from the *Lampsilis* shell were taken, and one thin section from the Pink Heelsplitter. From thin sections, multiple samples of shell carbonate were extracted using a Dremel MultiPro hand-drill for the Pink Heelsplitter shell. A Merchantek Leica GZ6 MicroMill was used for the *Lampsilis* shell. From the Pink Heelsplitter, 4 samples total were taken (Fig. 3). From the *Lampsilis*, 13 samples from dark bands only were taken along a transect from the first thin section, and 14 samples were taken, alternating light and dark bands, from the other thin section (Fig. 4). Samples were reacted with 100% $H_3PO_4$ under positive He pressure at 90∞C for seven minutes. The resulting $CO_2$ was cryogenically purified. Isotopic analysis for both carbon and oxygen was carried out using a Finnigan MAT 252 dual inlet mass spectrometer. Samples were compared against the UU – Carrara (> 140 mesh) carbonate standard. Results were analyzed statistically by regression analysis, and a t-test paired two samples for means.

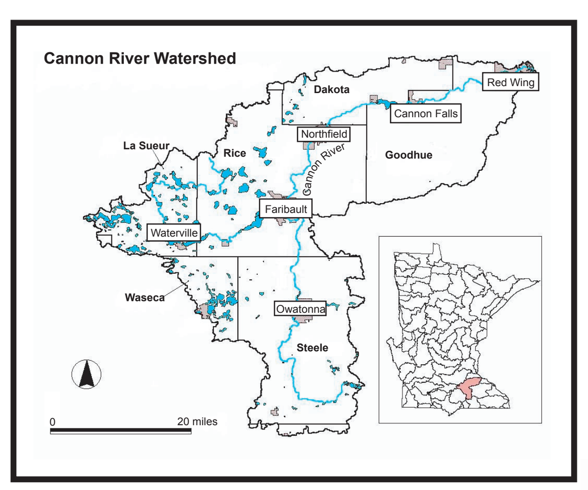


**Figure 2**: A map of the Cannon River and surrounding watershed, the region of mussel collection. Figure courtesy of the Cannon River Watershed Partnership.

**Figure 3:** (a) Digital image of the sampled Pink Heelsplitter shell; (b) Radial section of the shell showing sampling sites. Top segment is overlapped by bottom segment and together represent the entire shell growth. Only 4 samples total were taken from this shell, enough data to compare it to the Lampsilis in Figure 4, but not to discern any trends.

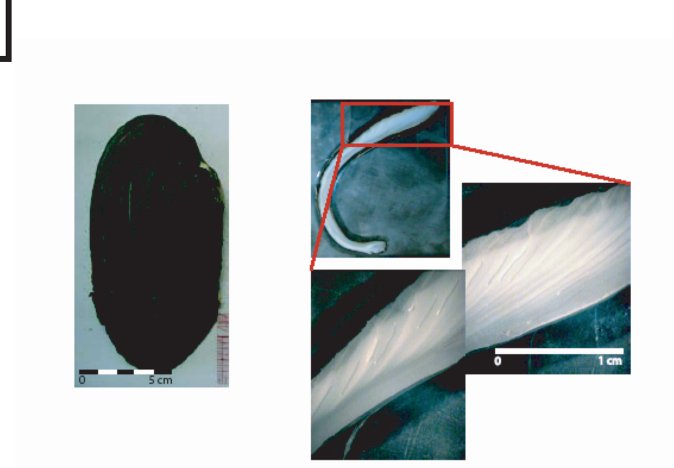

**Figure 4:** (a) Digital image of the sampled Lampsilis shell; (b) Digital image of radial section of shell and drillview image showing sampled sites in light and dark bands. Note that dark layers appear much wider than light ones.

## ABSTRACT

As they precipitate calcium carbonate to make their shells, bivalves record geochemical information on surrounding environmental conditions. Carbon and oxygen isotopic signatures in freshwater mussel shells result from surrounding water chemistry and temperature. This study sampled carbon and oxygen isotope data from growth banding throughout the life of one *Lampsilis* shell and one *Potamilus alatus* (Pink Heelsplitter). Significant differences in $\delta^{18}O$ between the light and dark bands in the *Lampsilis* shell revealed that a light-dark band pair is precipitated annually. A heavier $\delta^{18}O$ signature from the light band is due to cool water temperature and possibly a different source of precipitation to the river during cooler months. No significant variation is observed in $\delta^{18}O$ and $\delta^{13}C$ as the mussel aged. However, *Lampsilis* shells have potential to be good paleoclimate indicators based on isotopic variation within the seasonally-deposited growth bands.

## RESULTS

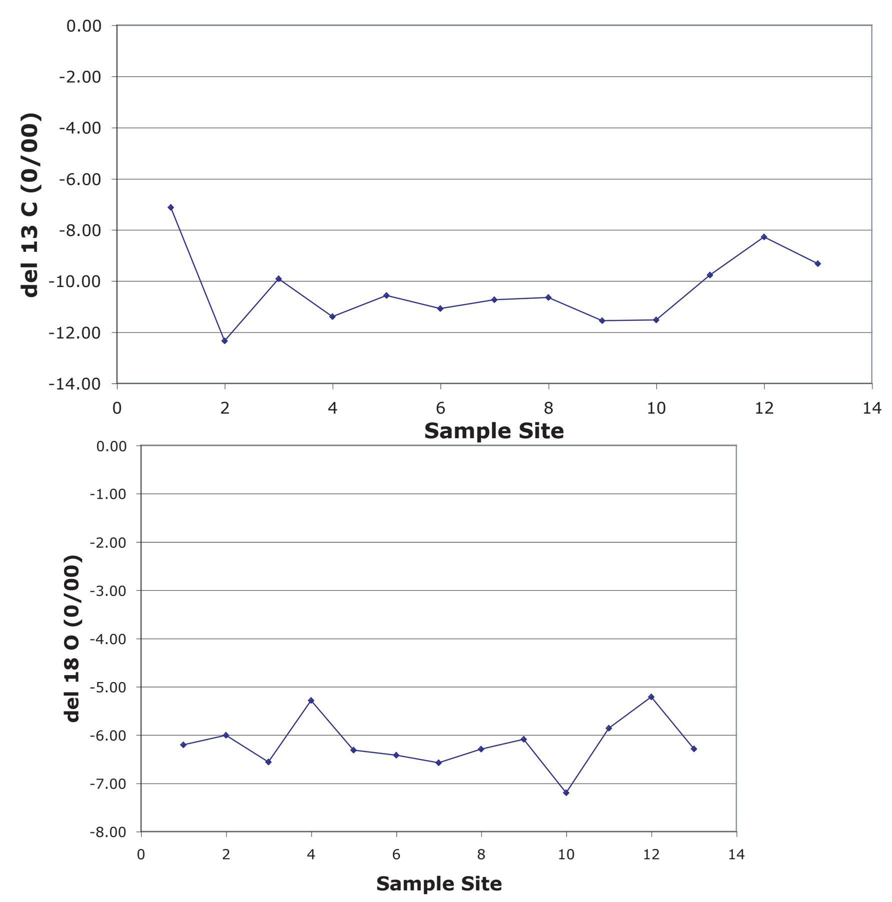


**Figure 5**: Trends in $\delta^{18}O$ and $\delta^{13}C$ from dark bands along the length of the Lampsilis shell. Sample site denotes the band which the carbonate was drilled from, starting from the youngest band. Thus, age is increasing on the x-axis.

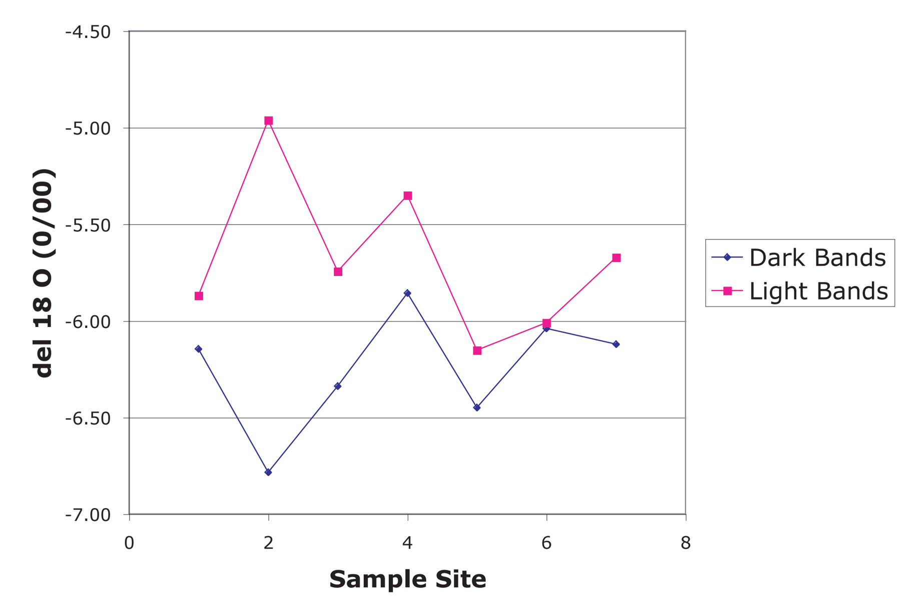


**Figure 7**: A line graph showing $\delta^{18}O$ of light and dark bands. Sample site denotes a light-dark pair, starting from the youngest bands. Thus, age is increasing on the x-axis. Note that dark bands are isotopically lighter on average than the light bands.

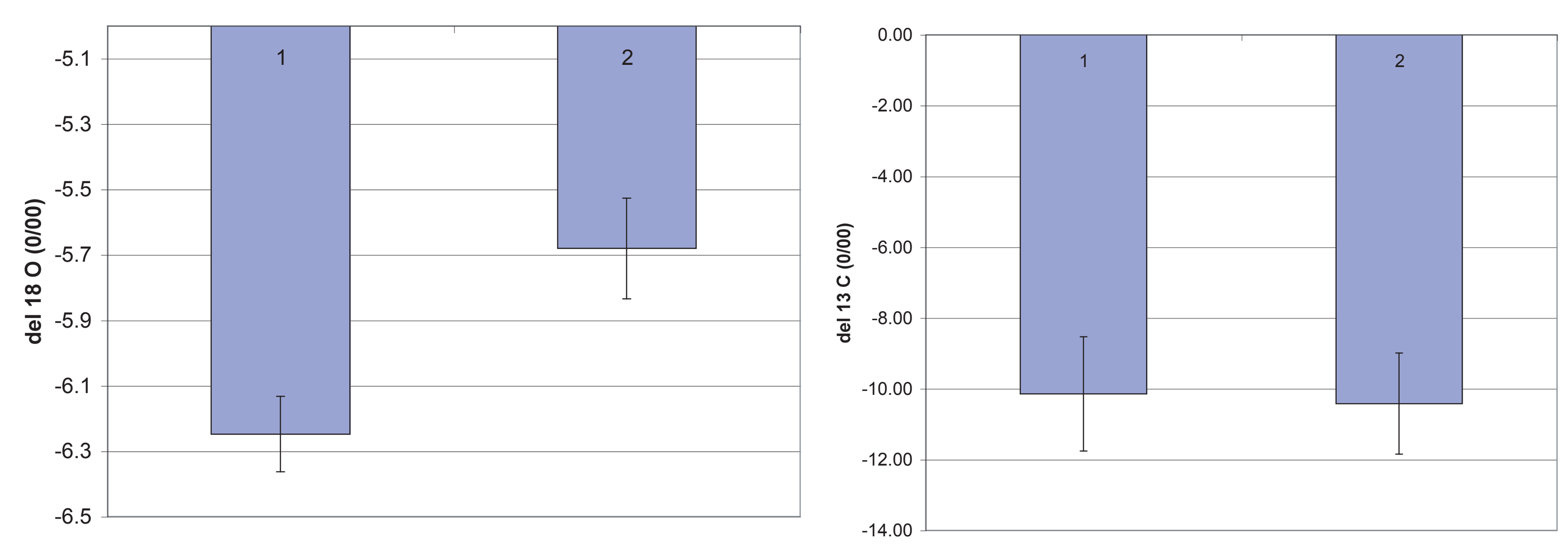


**Figure 6**: A bar graph comparing average $\delta^{18}O$ and $\delta^{13}C$ of light versus dark bands from Lampsilis. The $\delta^{18}O$ between light and dark bands is significantly different by t-test paired means (p=0.02), and the $\delta^{13}C$ is not different.

The average $\delta^{13}C$ of shell carbonate from the *Lampsilis* was -10.33 parts per thousand (standard deviation of 1.44 parts per thousand), and the average $\delta^{18}O$ was -6.18 parts per thousand (standard deviation of 0.53 parts per thousand). $\delta^{18}O$ and $\delta^{13}C$ ratios from *Lampsilis* dark bands did not change significantly with shell age (regression, p=0.78 for $\delta^{13}C$, p=0.89 for $\delta^{18}O$), however, there was some variance (Fig. 5). There was no significant difference between in $\delta^{13}C$ between *Lampsilis* light and dark bands (t-test paired means, p=0.39) (Fig. 6). However, there was a significant difference in $\delta^{18}O$ between light and dark bands from the same *Lampsilis* sample (t-test paired means, p=0.02) (Fig. 6 and 7). Dark bands averaged -6.25â (0.31 parts per thousand standard deviation) and light bands averaged -5.68 parts per thousand (0.40 parts per thousand standard deviation).

The average $\delta^{13}C$ from the Pink Heelsplitter was -8.89 parts per thousand (0.39 parts per thousand standard deviation) and the average $\delta^{18}O$ was -3.46 parts per thousand (1.40 parts per thousand standard deviation). Both the average $\delta^{18}O$ and $\delta^{13}C$ ratios are significantly different from those from the *Lampsillis* (t-test, two sample assuming equal variances, p = .04 for $\delta^{18}O$, p > 0.01 for $\delta^{13}C$).

## DISCUSSION

When examined in cross-section, the *Lampsilis* shell revealed a number of alternating light and dark bands (Fig. 1). Because of repeated cycles in oxygen isotope ratios between light-dark pairs, other studies hypothesized that the one light-dark band pair is one annual cycle (Brey and Mackensen 1997). The *Lampsilis* shell sampled in this study shows a similar repeated cycle; therefore we conclude a light-dark pair of bands represents a year of shell growth.

Goodwin et al. (2001) concluded that bands formed during colder months produce a more positive $\delta^{18}O$ signature as a result of temperature fractionation effects in carbonate deposition; a higher $\delta^{18}O$ was found in the light bands. Because shell growth is discontinued when water temperatures fall below about 12º C, presumably the light band is laid down immediately before and/or after this interruption in $CaCO_3$ deposition. The light bands were thinner, which correlates with the slowing metabolism under cooler temperatures. Correspondingly, the dark bands had a lower $\delta^{18}O$ and appeared to be much thicker than the light bands. It is logical to assume that these bands were added in the summer when warmer temperature would allow for more shell growth.

Studies by Dettman et al. (1999), Goodwin et al. (2001), and Veinott and Cornett (1998) showed a much larger degree of seasonal variation in $\delta^{18}O$, up to 5 parts per thousand. This study yielded an average variation of 0.57 parts per thousand. One explanation for this dampening of seasonal $\delta^{18}O$ variation is that previous studies were much higher resolution than our study. Another possible explanation is that the source of precipitation is different between the winter and summer months due to a weak monsoon cycle that affects Minnesota. Winter precipitation, which originates in the Pacific Ocean, is more depleted in heavy oxygen because it preferentially condenses out $^{18}O$ as it rises over the Rocky Mountains. Summer rainfall sourced from the Gulf of Mexico is comparitively enriched in $^{18}O$ due to a more direct path to the Great Plains. This summer $^{18}O$ enrichment could dampen the decrease in $\delta^{18}O$ that is traditionally seen during warmer temperatures.

## CONCLUSIONS

*Lampsilis* shells in cross section show an alternating light and dark banding pattern that is easily visible to the naked eye. Of these bands, a light-dark pair likely represents one year, based on a $\delta^{18}O$ cycle. In this annual light-dark pair, the dark band likely represents summer calcium carbonate precipitation, and the light band represents precipitation during the spring and late fall when water temperatures are cooler but still warm enough for the mussels to grow. *Lampsilis*, and bivalves in general, have potential as a high-resolution paleoclimate record. The *Lampsilis* sampled in this project recorded isotopic variation throughout its growth period, but no major changes, implying a relatively stable regional climate from the 1970s to the 1990s, when the mussel was alive. *Lampsilis* should be studied in more depth in the future as a potential for paleoclimate information, but more specimens spanning a wider time period will be needed, and data on the river conditions when the mussels were growing will be essential.

## ACKNOWLEDGEMENTS

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## WORKS CITED

1. Brey, T., and A. Mackensen. 1997. Stable isotopes prove shell growth bands in the Antarctic bivalve Laternula elliptica to be formed annually. Polar Biology 17:465-468.
2. Cannon River Watershed Partnership. Accessed: 5/17/2005. Url: http://www.crwp.net
3. Dettman, D. L., A. K. Reische, and K. C. Lohmann. 1999. Controls on the stable isotope composition of seasonal growth bands in aragonitic fresh-water bivalves (unionidae). Geochimica et Cosmochimica Acta 63:1049-1057.
4. Goodwin, D. H., K. W. Flessa, B. R. Schˆne, and D. L. Dettman. 2001. Cross-calibration of daily growth increments, stable isotope variation, and temperature in the Gulf of California bivalve mollusk Chione cortezi: Implications for paleoenvironment analysis. Palaios 16:387-398.
5. Goodwin, D. H., B. R. Schˆne, and D. L. Dettman. 2003. Resolution and fidelity of oxygen isotopes as paleotemperature proxies in bivalve mollusk shells: Models and observations. Palaios 18:110-125.
6. Schˆne, B. R., J. Lega, K. W. Flessa, D. H. Goodwin, and D. L. Dettman. 2002. Reconstructing daily temperatures from growth rates of the intertidal bivalve mollusk Chione cortezi (nothern Gulf of California, Mexico). Palaeo 184:131-146.
7. Veinott, G. I., and R. J. Cornett. 1998. Carbon isotopic disequilibrium in the shell of the freshwater mussel Elliptio complanata. Applied Geochemistry 13:49-57.
8. Wurster, C. M., and W. P. Patterson. 2001. Seasonal variation in stable oxygen and carbon isotope values recovered from modern lacustrine freshwater molluscs: Paleoclimatological implications for sub-weekly temperature records. Journal of Paleolimnology 26:205-218.