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Ontogenic Decrease of δ^{13}C in Bivalve Shell: Evidence of Vital Effect

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INTRODUCTION

Stable isotope geochemistry of biogenic carbonates, especially the bivalve shell, has become a key tool in paleoclimate and paleoenvironment reconstruction. The oxygen isotopic signatures of bivalve shell have been used to reconstruct both water temperature and salinity. The interpretation of stable carbon isotopic composition of shell ($\delta^{13}C_s$) remains contentious (Gillikin et al., 2007; Dettman et al., 1999).

If $\delta^{13}C_s$ can be related to the δ^{13}C of dissolved inorganic carbon ($\delta^{13}C_{DIC}$), fossil shells could be used to investigate the $\delta^{13}C_{DIC}$ in ancient rivers and thereby to draw conclusions about paleo-productivity, paleo-atmospheric CO_2 composition and concentration (Gillikin et al., 2009). Some studies have shown that $\delta^{13}C_s$ is governed by the $\delta^{13}C_{DIC}$ and therefore records changes in environmental variables such as pH, temperature and salinity (Mook, 1971). On the other hand, shell carbonates were often found not to reflect the predicted equilibrium fractionation, being in general less enriched than predicted δ^{13}C. Most authors explain this offset by a contribution of metabolic effects and suggest that incorporation of metabolic carbon can obscure carbon isotope records of $\delta^{13}C_{DIC}$ (Gillikin et al., 2007; Lorrain et al., 2004; Dettman et al., 1999). Whether $\delta^{13}C_s$ performed vital effect or not, preclude the use of $\delta^{13}C_s$ in bivalve shell to reconstruct the $\delta^{13}C_{DIC}$ in ancient host water.

In the present research, we studied a population of *Corbicula fluminea* in the Huaxi River in Guizhou Province, South China (Fig. 1). *Corbicula fluminea* are freshwater bivalves and common in China. Our aim is to determine if *Corbicula fluminea* incorporate metabolic carbon and how to judge this vital effect.

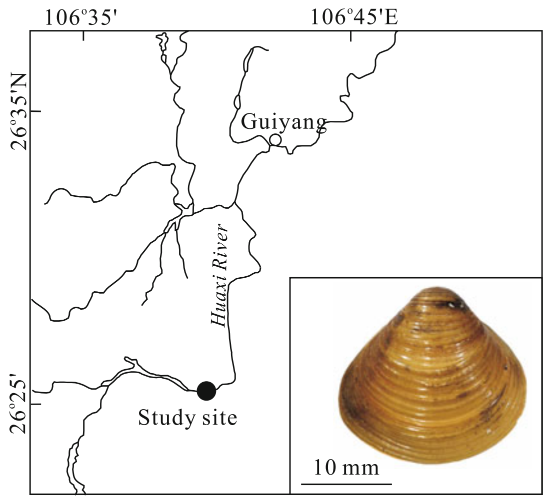

Figure 1. Locality of study site and image of *Corbicula fluminea.*

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MATERIALS AND METHODS

On January 9, 2007, two live *Corbicula fluminea* (Shell 1 and Shell 2) were collected and the shell height was measured by Vernier Caliper. The periostracum was removed with a 50 ℃ solution of hydrogen peroxide, rinsed by demineralised water and air-dried. To acquire high-resolution $\delta^{13}C_s$ profiles of growth increments, we used a scalpel blade to sample the shell (Geist et al., 2005); samples were about 300 to 500 μm in width, 100 μm in depth and 5 to 7 mm in length. Progressively sampling began at the ventral of the shell (portion of the latest growth), and was along the axis of maximum growth, and perpendicular to the growth increment. Seventeen and eighteen carbonate powder samples were respectively recovered from Shell 1 and Shell 2 (Fig. 2a).

On August 10, 2007, eighteen *Corbicula fluminea* samples were further collected and the shell height was measured. Each shell was pre-treated following the above way, and the carbonate on the most recently formed portion was sampled.

The $\delta^{13}C_s$ was performed on Continuous Flow Isotope Ratio Mass Spectrometer at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Results were reported relative to VPDB by calibration to the reference standard GBW04405, GBW04406 and GBW04416, at 1σ precision of 0.1‰ for $\delta^{13}C_s$.

RESULTS AND DISCUSSION

The $\delta^{13}C_s$ values measured ranged from -11.12‰ to -7.45‰ in Shell 1 and from -11.36‰ to -8.42‰ in Shell 2. The $\delta^{13}C_s$ values measured are more negative than predicted (Yan, 2009). The $\delta^{13}C_s$ values of the eighteen different specimens ranged from -11.27‰ to -9.60‰; the shells were about 7.04‰ to 8.71‰ more negative than expected (Yan, 2009).

Kinetic effects can definitely be ruled out as bivalves generally induce the precipitation of carbonate in oxygen isotope equilibrium with their surroundings (McConnaughey and Gillikin, 2008). Therefore, this disequilibrium should be mainly due to metabolic effects.

We found an interesting phenomenon that $\delta^{13}C_s$ showed a trend of more negative $\delta^{13}C$ through ontogeny (Fig. 2a) or a strong significant negative relationship with the shell height (R^2=0.75, Fig. 2b).

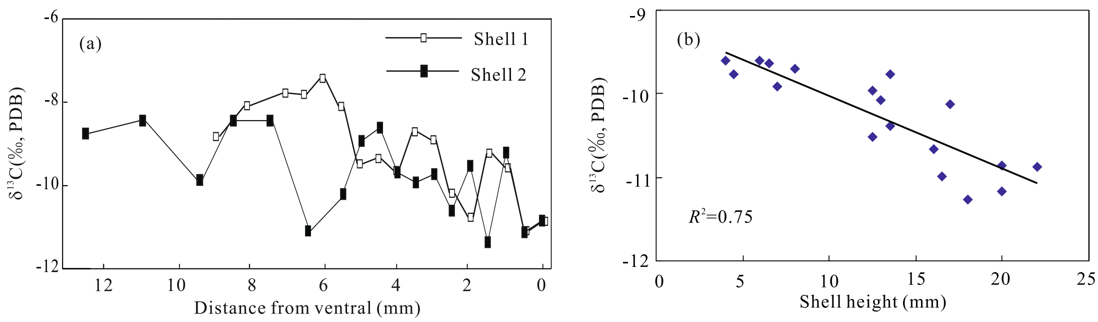

Figure 2. High-resolution $\delta^{13}C_s$ profiles of *Corbicula fluminea* shells (a) and their correlation with the shell height (b).

In fact, ontogenic decreases in $\delta^{13}C_s$ of bivalve shell have been noted before (Gillikin et al., 2007; Lorrain et al., 2004 and many others). Klein et al. (1996) reported high metabolic rate results in an increased intracellular: intercellular ratio, and intracellular transport to the extrapallial fluid (EPF, where the shell precipitated) with metabolic carbon (depleted in ^{13}C), so higher metabolic rate of old individuals leads to a decreased $\delta^{13}C_s$. Lorrain et al. (2004) showed that the ratio of respired to precipitated carbon, which represents the amount of metabolic carbon available relative to the carbon required for calcification, increases through ontogeny. This suggests that the decrease of $\delta^{13}C_s$ through ontogeny is actually caused by increased utilization of metabolic carbon to satisfy carbon requirements for calcification.

Although Gillikin (2005) and others found that $\delta^{13}C_s$ of *S. giganteus* and several other bivalve shells become slightly more positive through ontogeny, and indicated that it may not be a general model for all bivalves, ontogenic decreases of $\delta^{13}C_s$ in bivalve shells can still be used as the evidence of metabolic effects.

CONCLUSIONS

The δ^{13}C values measured in *Corbicula fluminea* shells are more negative than predicted, and all shells followed a trend to the lower δ^{13}C values with the increase in age. This phenomenon is proposed to be caused by the incorporation of more metabolic carbon through ontogeny. Although this character may be not universal, ontogenic decrease of $\delta^{13}C_s$ in bivalve shells used as the evidence of vital effect (metabolic effects) is still feasible.

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