A review on bivalve shell, a tool for reconstruction of paleo-climate and paleo-environment

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Abstract   Environmental information can be extracted from bivalve shell geochemistry. In this review, the latest research progress and the existing problems as well as the focus of future research on stable oxygen and carbon isotopic composition and trace elemental ratios of bivalve shell were investigated. Oxygen isotopic signatures of bivalve shell have been proved precipitate in equilibrium with their host water and used as a robust tool to reconstruct ancient water temperature. In order to reconstruct quantitative paleo-temperature information, the future research on bivalve shell oxygen isotope should combine with the study of ancient water oxygen isotope. Metabolic effect prevents the direct application of stable carbon isotopic composition of bivalve shell from extracting dissolved inorganic carbon information. The contribution of metabolic carbon to bivalve shell is species specific. Stable carbon isotopic composition of dissolved inorganic carbon could be reconstructed if the metabolic contribution could be accounted for. Explore ways to remove contribution of metabolic effects to bivalve shell is the future focus of the research. There is no consensus on the effect of temperature on bivalve trace element ratios, which may be also species specific, each proxy should ideally be validated and calibrated for each species before being used to interpret past climate and environmental conditions. Future research needs to pay attention to the bivalve shell biomineralization process, which controlled bivalve shell trace element ratios. Cultivation experiment is an important way to obtain the relevant conclusions.

Key words   oxygen and carbon isotopes; trace element; metabolic effect; bivalve shell

1 Introduction

Bivalve shells possess a great potential as environmental proxies. Bivalves are beneficial in the following reasons. They can provide high-accuracy resolution records of environmental conditions (annual, seasonal and even weekly) due to their high growth rate. Their high temporal resolution profiles can easily be obtained (Su et al., 2005; Sano et al., 2012; Yan et al., 2013). And they have a wide geographical distribution, which generally occur in almost all types of aquatic ecosystems (e.g. marine, estuarine, rivers, lakes, and deep ocean vent), from tropics to poles (Gillikin et al., 2005). In addition, bivalve shells are well represented in the fossil record since the Cretaceous, potentially allowing records of environmental conditions to be extended into the past (Chang et al., 2007; Wang et al., 2011; Wanamaker et al., 2011).

The research of modern bivalve shells is to confirm the potential and significance of being environmental proxies. According to the theory of uniformitarianism, i.e., past is equal to present. This will not merely be applied to modern shell itself. Its principle and equations might use in fossil shell. Therefore, modern shell research is the foundation and prerequisite to use the fossil shell to recognite and extract paleo-climate and paleo-environmental information.

The research in this field has developed fast in recent years. In this review, the latest research progress and the existing problems as well as the focus of future research of stable oxygen and carbon isotopic composition and trace elemental ratios of bivalve shell

were investigated to provide a theoretical basis and some research ideas for the bivalve shell geochemistry proxies study.

2 Stable oxygen isotopic composition of bivalve shell

The geochemical parameters of bivalve shell have served as a source of paleo-climatic and paleo-environmental information. Variations in $\delta^{18}O$ of bivalve shells ($\delta^{18}O_S$) reflect oxygen isotope ratios of ambient water ($\delta^{18}O_w$) and temperature during biomineralization. As bivalves have been proved precipitate in oxygen isotope equilibrium with their surroundings, the oxygen isotopic signatures of bivalve shell are used to reconstruct both water temperature and salinity (Dettman et al., 1999; Surge et al., 2001; Elliot et al., 2003; Aucour et al., 2003; Kaandorp et al., 2003; Chauvaud et al., 2005; Wanamaker, 2009; Yan et al., 2009). However, some mollusk display an offset attributed to metabolic processes (e.g. vital effects) (Wefer and Berger, 1991; Fenger et al., 2007). Therefore, modern and living species must be examined to verify isotopic equilibrium before interpreting past climate and environmental conditions preserved in their fossil shells. Examination accomplished through so called marked-recatch project. $\delta^{18}O$ of shell samples that precipitated during the project and host water $\delta^{18}O_w$ were analyzed in the study. To investigate whether bivalve precipitates its shell in equilibrium with ambient water, $\delta^{18}O_S$ was compared with calculated isotopic equilibrium values. The oxygen isotopic equilibrium values can be calculated with several temperature equations (Epstein, 1953; Emiliani, 1955; Grossman and Ku, 1986).

As the absent oxygen isotopic signatures of ancient water that bivalve shell deposited, reconstructed water temperature is qualitative. In order to obtain quantitative data of water temperature, researchers often suppose the oxygen isotopic of ancient water equal to modern water. This assumption is usually wrong (Veizer, 1976), especially for freshwater (Fritz and Poplawski, 1974). So obtain $\delta^{18}O$ of the ancient water have become the key factor to reconstruct quantitative paleo-temperature, which also is a hot issue of paleoclimate and paleoenvironment research.

Sauer et al. (2001) raised aquatic moss in different $\delta^{18}O_w$. Their results suggested that $\delta^{18}O_{cellulose}$ of the new growth mosses showed very good linear correlation with $\delta^{18}O_w$, $\delta^{18}O_{cellulose}=0.882\delta^{18}O_w + 28.3$ ‰. Therefore, $\delta^{18}O_{cellulose}$ of aquatic plant can be use to indicate $\delta^{18}O_w$. Zhu et al. (2011) restored the quantitative lake water oxygen isotope profiles using Caohai sediment organic cellulose oxygen isotope composition, and combined it with the oxygen isotope composition of the carbonate reconstruct over past 500 years water temperature series of Caohai. Shen et al. (2001) reconstructed quantitative paleosalinity values through Sr/Ca ratio of ostracod shells (*Limnocythore cf. inopinata*), and then studied the quantitative relationship between the salinity and oxygen isotope ($\delta^{18}O_w=13.49 \ln_{salinity}-111.33$, $R^2=0.995$), which established through the laboratory simulation test to reconstruct the ancient water $\delta^{18}O_w$. Carrol et al. (2006) found the relationship between the hydrogen and oxygen isotopes of freshwater bivalve shell, and suggested this relationship is useful for quantitative paleo-temperature reconstruction because the hydrogen values of the organic matrix can serve as an independent proxy for the $\delta^{18}O$ of the ancient water.

Thus, the future research of bivalve shell oxygen isotope should involve the study of water oxygen isotope, so as to reconstruct quantitative paleo–temperature data.

As bivalves have been proved precipitate in oxygen isotope equilibrium with their surroundings, $\delta^{18}O_S$ have also been used to establish a time scale of the shell, and then provide the condition for researches of other parameters (Dettman et al., 1999; Kaandorp et al., 2003; Yan and Chen, 2010). Bivalve shell was identified of two growth was patterns by examining variation in $\delta^{18}O_S$: continuous and seasonal. Continuous growth throughout the year was exemplified by a sinusoidal curve, while, seasonal growth corresponded to a sinusoidal curve with truncated peaks, representing winter months or growth cessation (Dettman et al., 1999; Fan et al., 2012). According to the date of bivalve shell specimens collected, from ventral margin to umbo, the first negative excursion in the measured $\delta^{18}O_S$ profile must have precipitated during the lastest summer. The measured $\delta^{18}O_S$ profile was matched to the calculated $\delta^{18}O_{equil}$ by comparing both absolute values and the shape of the profiles (Klein et al., 1996; Freitas et al., 2006). Therefore, bivalve shell provides reliable records of paleoclimate and paleoenvironmental conditions.

3 Stable carbon isotopic composition of bivalve shell

The stable carbon isotopic composition of bivalve shell ($\delta^{13}C_S$) varies in a more complex manner. Some earlier works suggested that bivalves deposited in isotopic equilibrium with the dissolved inorganic carbon (DIC) (Mook and Vogel, 1968; Fritz and Poplawski, 1974; Turner et al., 1983). If $\delta^{13}C_S$ can be used as the proxy to investigate the $\delta^{13}C$ of DIC ($\delta^{13}C_{DIC}$) in ancient water, we can use bivalve shell to obtain the information of paleo-primary production, land use change, bedrock geology, and paleo-atmospheric CO_2 levels (Dettman et al., 1999; Gillkin et al., 2009; Zhou et al., 2010). However,

many recently researches found that bivalves deposited not in isotopic equilibrium with DIC and suggested that both kinetic and metabolic effects play important roles (Keith et al., 1964; Tanaka et al., 1986; Klein et al., 1996; McConnaughey et al., 1997; Veinott and Cornett, 1998; Dettman et al., 1999; Lorrain et al., 2004; Gillikin et al., 2006; Gillikin et al., 2007; Gillikin et al., 2009). Kinetic effects generally affect both $\delta^{18}O_S$ and $\delta^{13}C_S$ and result in a good relation (McConnaughey, 1989). As bivalves generally precipitate in oxygen isotope equilibrium with their surroundings, kinetic effects should be minimal and the disequilibrium should be mainly due to metabolic effects.

In fact, previous studies have reached a consensus that metabolic carbon effects both marine and freshwater bivalve shell carbonate. Tanaka et al. (1986) suggested that up to 85% of mollusk-shell carbonate is composed of metabolic C, but McConnaughey et al. (1997) found that the former study overestimated the metabolic contribution partly because it erroneously included the enrichment factor between carbonate and aqueous CO_2, and McConnaughey et al. (1997) gave the best standing model to calculate the amount of metabolic C:

$$M*(\delta^{13}C_R)+(1-M)*\delta^{13}C_{DIC}=\delta^{13}C_S-\varepsilon_{ar\text{-}b} \qquad (1)$$

Where M is the percentage of metabolic C contribution, $\varepsilon_{ar\text{-}b}$ is the enrichment factor between aragonite and bicarbonate (2.7‰ in Romanek et al., 1992), and $\delta^{13}C_R$ is $\delta^{13}C$ of metabolic C and approximated from $\delta^{13}C_{tissue}$. Using the above equation, McConnaughey et al. (1997) found that in most bivalves the amount of metabolic C in shell is typically less than 10%. Gillikin et al. (2009) found much higher values of 5%–37% for *Mercenaria mercenaria* and of 15%–35% for the freshwater mussel *Pyganodon cataracta*, in both cases associated with strong ontogenic decreases in $\delta^{13}C_S$. Yan et al. (2012) sampled water DIC, shell, and soft tissues from freshwater bivalve *Corbicula fluminea* collected in Guizhou Province, China, to assess the contribution of metabolic C to the shell. The result demonstrates that $\delta^{13}C_S$ of *Corbicula fluminea* were negative than expected equilibrium and a large amount of metabolic C (as much as 19.8%–26.8%) present in *Corbicula fluminea* shell.

This metabolic effect, however, does not exclude $\delta^{13}C_S$ in bivalve shells as useful environmental proxies. Lorrain et al. (2004) suggested that $\delta^{13}C_S$ may provide information about metabolic rates for different population of mollusks. Gillikin et al. (2006) found that $\delta^{13}C_S$ shifted to lower value when a mussel was transplanted from marine into estuarine conditions, which reflects freshwater inputs to the ocean and provide a proxy for salinity. Goewert et al. (2007) found

that shells had clearly different $\delta^{13}C_S$ values between a corn (C4) dominated and soybean (C3) dominated watershed despite metabolic effect still exist and result an ontogenic decrease in $\delta^{13}C_S$. They even proposed that quantitative $\delta^{13}C_{DIC}$ could perhaps be reconstructed from bivalve shells if the metabolic contribution could be accounted for.

Recently, many studies reported the ontogenic decreases in $\delta^{13}C_S$ of bivalve shell and set up the regression equation between M (percent of metabolic C) and H (shell height) for different bivalves (Lorrain et al., 2004; Gillikin et al., 2007; Yan et al., 2012). Lorrain et al. (2004) showed that the ratio of respired to precipitated carbon, which represents the amount of metabolic C available relative to the carbon requirements for calcification, increases through ontogeny. This suggests that the decrease of $\delta^{13}C_S$ through ontogeny is actually caused by increasing utilization of metabolic C to satisfy carbon requirements for calcification.

Yan et al. (2012) reported a strong relationship between *Corbicula fluminea* shell height and M, M=0.39*H+17.36 (R^2=0.74). Gillikin et al. (2007) study *Mercenaria mercenaria* shells from Jarrett Bay and Johnson Creek in eastern North Carolina.

The linear relationship for Johnson Creek is M=0.190(±0.035)*H+7.65(±2.25)   (R^2=0.48).   The Jarrett Bay relationship is M=0.187(±0.092)*H+18.92 (±5.65) (R^2=0.64). The difference in intercepts and slopes between regressions suggests that there is no general relationship between shell height and M for different species or different population of the same species. Thus, there is too much unexplained variability in metabolic rates between sites and species, making M predictions difficult and back calculating $\delta^{13}C_{DIC}$ highly uncertain.

In a word, explore ways to remove contribution of metabolic effects to $\delta^{13}C_S$ is the future focus of research that use bivalve shell to reconstruct quantitative $\delta^{13}C_{DIC}$. However, Gillikin (2005) and other researchers found that $\delta^{13}C_S$ of *S. giganteus* and several other bivalves shell becomes slightly more positive through ontogeny, and proposed that ontogenic decreases in $\delta^{13}C_S$ may not be a general model for all bivalves, which indicates that it will be more complex to use those bivalve shells to reconstruc quantitative $\delta^{13}C_{DIC}$. More recently, Schöne et al. (2011) and Butler et al. (2011) found that long-lived bivalves, *Arctica islandica*, probably forms its shell with a constant offset from expected equilibrium, this suggests that $\delta^{13}C_S$ of this long-lived bivalves can be used as a measure of $\delta^{13}C_{DIC.}$

4 Trace elements in bivalve shell

Like stable isotopes, elemental ratios reported in

bivalve shells can also leave records of environmental and ecological information. Although there have been many studies of high resolution elemental proxies (mainly Sr/Ca and Mg/Ca) in bivalve shells (Klein et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003; Richardson et al., 2004; Gillikin et al., 2005; Strasser et al., 2008; Freitas et al., 2008; Schöne et al., 2010; Yan et al., 2013). The results have been inconclusive, and quite different from research on coral and sclerosponges, which Sr/Ca and Mg/Ca have been proved as the most promising paleo-temperature proxies (Beck et al., 1992; Wei et al., 2000; Rosenheim et al., 2004). For example, Dodd (1965) found a strong negative correlation between temperature and Sr/Ca ratios in *Mytilus edulis* aragonite. Klein et al. (1996) reported that Mg/Ca ratio in mussel shells are a robust SST proxy, Mg/Ca×1000=0.30(±0.04)×T+2.25(±0.63) (R^2=0.74). Hart and Blusztajn (1998) also found a positive relationship between Sr/Ca ratios and temperature in *Arctica islandica* and applied this relationship to derive SST from hydrothermal vent clams (*Calyptogena magnifica*). Dutton et al. (2002) found a negative correlation between Sr/Ca ratios and $\delta^{18}O$ in bulk shell samples of extinct aragonitic bivalve *Cucullaea* sp. Yan et al. (2013) reported that the high-resolution ICP-OES derived Sr/Ca ratios of *T. gigas* had significantly negative correlation with sea surface water (SST), and had the potential of providing a good proxy of historical SST. While, many studies also suggest that trace element ratios in bivalve shell are primarily controlled by physiological factors (Purton et al., 1999; Takesue and van Geen, 2004; Gillikin et al., 2005; Strasser et al., 2008; Freitas et al., 2008; Schöne et al., 2010). Vander Putten et al. (2000) illustrated that Mg/Ca ratios do not track SST in different species of the same genus. Gillikin et al. (2005) found strong biological controls on Sr/Ca ratios in marine bivalve shells, *Saxidomus giganteus* and *Mercenaria mercenaria*, and suggested that Sr/Ca ratios can not be used as a reliable temperature proxy in these species. Elliot et al. (2009) indicated that both Mg/Ca and Sr/Ca profiles of giant long-lived *Tridacna gigas* bivalves reflect a combination of biological and environmental controls, which will need to be disentangled before using these proxies in paleoclimatic studies.

It is clear that there is no consensus on the effect of temperature on bivalve trace element ratios, which may be species specific. Thus, each proxy should ideally be validated and calibrated for each species.

Future research needs to focus on the bivalve shell biomineralization process. Biomineralization in bivalves takes place in the extrapallial fluid (EPF), a thin film of liquid between the calcifying shell surface and the mantle epithelium. Cations, such as Ca^{2+}, Sr^{2+}, and Mg^{2+} move into the EPF through the epithelial mantle cells via intracellular or intercellular transport ways (Klein et al., 1996), which control the bivalve shell trace elements ratios. The mode and flux of cations move into the EPF are different between species and water conditions (Klein et al., 1996; Gillikin et al., 2005). More knowledge about this process will be helpful for understanding the environmental significance of bivalve shell trace element ratios. Sano et al. (2012) found that light can enhance calcification and elemental transportation processes, and that Sr/Ca ratio exhibits striking diurnal variations in a cultivated giant clam shell, reflects the daily light cycle, suggesting the possibility to develop the Sr/Ca ratio as an effective proxy for parameters of daily light cycle.

To sum up, cultivation experiment that under different environmental conditions (such as different temperature, concentration of trace elements and light conditions, etc.) is an effective way to obtain the relevant conclusions.

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