Palaeogeography, Palaeoclimatology, Palaeoecology 472 (2017) 119–127

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Conus Shell $\delta^{13}C$ values as proxies for $\delta^{13}C_{DIC}$ in tropical waters

Lauren E. Graniero [a,*], Ethan L. Grossman [a], John Robbins [a], Jorge Morales [b], Ricardo Thompson [b], Aaron O'Dea [b]

[a] *Department of Geology and Geophysics, Texas A&M University, College Station, TX 77843-3115, United States*
[b] *Smithsonian Tropical Research Institute, P.O. Box 0843-03092, Balboa, Republic of Panama*

ARTICLE INFO

Article history:
Received 23 September 2016
Received in revised form 3 February 2017
Accepted 6 February 2017
Available online 12 February 2017

Keywords:
Mollusk
Gastropod
Dissolved inorganic carbon
Isotopes
Upwelling
Seasonality

ABSTRACT

We use time-series $\delta^{18}O$ and $\delta^{13}C$ data from seawater and live-collected *Conus* shells from Panama's Pacific coast to test the fidelity of the gastropod's $\delta^{13}C$ values as a proxy for the $\delta^{13}C$ of marine dissolved inorganic carbon (DIC), and the potential of $\delta^{18}O$-$\delta^{13}C$ correlations in shell profiles for resolving relative magnitudes of seasonal upwelling and freshening. Water samples were collected from March 2011 to August 2012 from Naos Island Marine Laboratory, and *Conus* specimens were collected from nearby Veracruz Beach in July 2013. In general, patterns corresponded with seasonal changes in rainfall and upwelling on the Pacific coast of Panama. During the long rainy season, the upwelling signal is absent and seawater salinity, $\delta^{18}O$, and $\delta^{13}C_{DIC}$ all decline. During the dry season, the upwelling signal increases and runoff declines increasing salinity, $\delta^{18}O$, and $\delta^{13}C_{DIC}$ values. Shell $\delta^{13}C$ values strongly correlate with measured $\delta^{13}C_{DIC}$ values, but are lower than expected equilibrium for aragonite by approximately +2‰ reflecting the incorporation of light metabolic C. The co-dependences of $\delta^{18}O$ and $\delta^{13}C$ provide reliable indicators of upwelling (negative correlation) and freshening (positive correlation) for nearshore environments, allowing for the study of historical climate change and upwelling based on beach-collected museum specimens.

Published by Elsevier B.V.

1. Introduction

Carbon isotopes ($^{13}C/^{12}C$) potentially provide the best means of studying the linkages between the carbon cycle, climate, and biotic change through Earth history. Carbon isotope analyses on fine-grained carbonate sediments show carbon cycle perturbations associated with Snowball Earth (Hoffman et al., 1998) and the end-Permian extinction event (e.g., Baud et al., 1989). Fossils can provide a more refined carbon isotope signal free of diagenetic and mixing artifacts (Grossman, 1994). For example, researchers have used carbon isotopes in brachiopod shells to explore linkages between carbon burial and Permo-Carboniferous glaciation (Popp et al., 1986; Grossman et al., 2008), and in foraminiferal tests to document productivity collapse at the Cretaceous-Paleogene boundary (Zachos et al., 1989) and Neogene changes in deep sea circulation associated with the rise of the Isthmus of Panama (Keigwin, 1982), among other events. In contrast, surprisingly few studies have used carbon isotopic compositions of mollusk shells to reconstruct past carbon cycle changes despite the rich molluscan fossil record.

Numerous studies have shown that the dissolved inorganic carbon (DIC) $\delta^{13}C$ composition of ambient water is the primary control on shell $\delta^{13}C$ values (e.g., Mook, 1971; Fritz and Poplawski, 1974; Aucour et al., 2003; Beirne et al., 2012), but other studies have shown that molluscan $\delta^{13}C$ values may be influenced by the incorporation of ^{13}C–depleted metabolic carbon and/or kinetic disequilibrium effects (e.g., Wefer and Berger, 1991; Gillikin et al., 2006; Gillikin et al., 2007; McConnaughey and Gillikin, 2008; Poulain et al., 2010). It is commonly observed that around 10% of carbon incorporated into marine bivalve shell carbonate is derived from ^{13}C–depleted metabolic carbon (C_M) (Gillikin et al., 2006; Gillikin et al., 2007; McConnaughey and Gillikin, 2008). The effect of this metabolic component, if not constant, can undermine paleoenvironmental reconstructions. If, on the other hand, C_M is relatively constant, then carbon isotope profiles of mollusk shells could provide high-resolution seasonal records of climate change, ENSO events, and upwelling.

Killingley and Berger (1979) were the first to investigate $\delta^{13}C$ and $\delta^{18}O$ in mollusk shells as an upwelling proxy. Using temperature records and shell $\delta^{18}O$ to develop a chronology, they observed that $\delta^{13}C$ values for the mussel *Mytilus californianus* tended to parallel the Bakun upwelling index and $\delta^{13}C_{DIC}$ estimated from apparent oxygen utilization (AOU). Applying this approach to fossils requires independent evidence for upwelling, leading researchers to explore inverse correlations between $\delta^{13}C$ and $\delta^{18}O$ as a proxy for upwelling of cool, low $\delta^{13}C_{DIC}$ waters (Killingley and Berger, 1979; Kroon and Ganssen, 1989; Geary et al., 1992; Jones and Allmon, 1995; Tao et al., 2013; Dhillon et al., 2015). Freshwater input can also be recorded in the isotopic records of mollusk shells, as revealed by concurrent negative $\delta^{18}O$ and $\delta^{13}C$ spikes (positive correlation) in western North Atlantic bivalves (Krantz et al., 1987).

---

* Corresponding author.
E-mail addresses: graniero@live.unc.edu (L.E. Graniero), e-grossman@tamu.edu (E.L. Grossman), mniproductions@gmail.com (J. Robbins), odeaa@si.edu (A. O'Dea).

http://dx.doi.org/10.1016/j.palaeo.2017.02.007
0031-0182/Published by Elsevier B.V.

Isotope sclerochronology studies of mollusks have attempted to use $\delta^{18}O$-$\delta^{13}C$ (O-C) correlations as upwelling and freshening proxies with mixed success because of oft-seen ontogenetic declines in $\delta^{13}C$, the combined effects of upwelling and freshening (negative versus positive correlation; Geary et al., 1992; Bemis and Geary, 1996; Tao et al., 2013), and the potential influences of reproduction on shell $\delta^{13}C$ values (Wefer and Berger, 1991; Putten et al., 2000; Gillikin et al., 2006). Ironically, the shell studied by Killingley and Berger (1979) did not show a significant inverse $\delta^{18}O$-$\delta^{13}C$ correlation ($R^2 = 0.10$). Tao et al. (2013) attempted to codify the use of O-C correlations as upwelling and freshening indicators using a comprehensive data set for the gastropod *Conus* from the Caribbean and Pacific coasts of Panama. These coasts provide a stark contrast between strongly upwelling and non-upwelling environments. Shells from 10 to 61 m depth in the Gulf of Panama showed a wide range in $\delta^{18}O$ values and no O-C correlation, suggesting contrasting seasons of upwelling and freshening. If this is the case, it should be possible to separate the upwelling and rainy season components of the isotopic record to observe negative and positive O-C correlations, respectively. Alternatively, vital effects associated with metabolism may make the use of carbon isotopes in mollusks problematic.

Most stable isotope sclerochronology studies have focused on bivalve shells, which are spatially and temporally widespread, variety in habitat and environment, and often thick-shelled and long-lived (e.g., Jones and Quitmyer, 1996; Dettman et al., 1999; Surge et al., 2003; Schone et al., 2005; Butler et al., 2013). However, *Conus* shells have many advantages for sclerochronology including widespread occurrence in tropical and subtropical environments since the Eocene, thick and exposed spire for easy sampling, and rapid extension rates providing high resolution; furthermore, *Conus* tends to be stenohaline, slow moving, and can live long than 20 years (e.g., Kohn and Perron, 1994; Kobashi and Grossman, 2003; Gentry et al., 2008; Grossman, unpublished data). Isotopic studies of Cenozoic cone shells have demonstrated warm low-latitude temperatures in the Eocene and cooling throughout the Cenozoic (Kobashi et al., 2001; Grossman et al., in prep.). Despite *Conus*' utility in sclerochronology, no study (including Tao et al., 2013) has compared its $\delta^{18}O$ and $\delta^{13}C$ with time-series data for local seawater $\delta^{18}O$ and DIC $\delta^{13}C$ ($\delta^{13}C_{DIC}$) to rigorously test the fidelity of *Conus* shells to record the environmental signal.

Only a handful of natural system studies have combined time-series data for local water $\delta^{18}O$ (δ_w) and $\delta^{13}C_{DIC}$ with sclerochronological $\delta^{18}O$ and $\delta^{13}C$ values of bivalves to demonstrate an environmental control on shell $\delta^{13}C$ (Dettman et al., 1999; Yan et al., 2009; Versteegh et al., 2010), and none to our knowledge have studied carbon isotope fractionation in marine gastropod shells. Our study compares the $\delta^{18}O$ and $\delta^{13}C$ profiles in four live-collected *Conus mahogani* shells with a 17-month record of concurrent seawater $\delta^{18}O$ and $\delta^{13}C_{DIC}$ measurements for the Pacific coast of Panama to evaluate shell $\delta^{13}C$ values as a proxy for seasonal fluctuations in $\delta^{13}C_{DIC}$. We also examine the utility of O-C correlations within shells as proxies for upwelling and freshwater input.

2. Study area, samples and methods

2.1. Study area

The semi-enclosed Gulf of Panama on Panama's Pacific coast (Fig. 1) experiences rainy and dry seasons. During the rainy season, from May to December, surface water temperatures are relatively stable at 28 °C, while freshening drives declining salinities. In the dry season (January to April), wind jets from trade winds passing over the Isthmus of Panama drive strong upwelling of deep, cool and nutrient-rich waters, lowering surface water temperatures to <18 °C and intensifying chlorophyll-a levels as the thermocline reaches the surface (D'Croz and O'Dea, 2007; D'Croz and O'Dea, 2009). The study site at Veracruz Beach (8°55′00″N, 79°35′49″W), about 8 km southwest of the water collection site at Naos, was chosen because of its accessibility, proximity to Naos, and the known occurrence of live gastropods.

2.2. Oxygen and carbon isotope analyses of water and DIC, respectively

Water samples were collected from early March 2011 to mid-August 2012 from the seawater pumping system at the Naos Island Marine Laboratory (Fig. 1), from which salinity, $\delta^{18}O$ of water (δ_w), and $\delta^{13}C_{DIC}$ were measured. The seawater intake was from 7.6 m depth at high spring tide and 24 m from shore. Samples were collected two to three times a week until May 2012, after which they were collected once every two weeks. Bottles were stored on their side in cool, dark conditions until they could be shipped to Texas A&M University (TAMU) for analysis. For collection of $\delta^{13}C_{DIC}$ samples, evacuated serum bottles with 20 mm blue butyl rubber stoppers (Bellco™ 2048–11,800) and aluminum caps were pre-poisoned with mercuric chloride ($HgCl_2$). A syringe pre-rinsed with the sample water was then used to inject samples into each $\delta^{13}C_{DIC}$ vial. The $\delta^{13}C_{DIC}$ samples were collected one to two times per week for the majority of the sampling period with duplicate vials taken every two to three sampling days (duplicating 20% of samples). These vials were refrigerated until they could be shipped in coolers to TAMU, where they were kept refrigerated until analysis.

Salinity measurements were conducted using an Orion 3-Star conductivity meter. Each sample bottle was measured in triplicate, with an internal precision of 0.08‰. For $\delta^{18}O$ analyses, 2 mL of sample were pipetted into sample vials for analysis on a Picarro cavity ring down spectrometer (L2120-i) in the Stable Isotope Geosciences Facility (SIGF) at TAMU. These samples were run alongside a suite of in-house standards that are periodically calibrated to international standards (VSMOW, GISP, and SLAP). Six injections of 2.1 μL each were used for each sample vial, with the first three removed due to memory effect. External precision for these analyses is 0.1‰.

The $\delta^{13}C_{DIC}$ measurements were performed with a Thermo Finnigan Delta^{PLUS} XP isotope ratio mass spectrometer with a Thermo GasBench II gas analyzer and an A200S auto-sampler in the SIGF at TAMU. 0.5 mL of sample water was acidified for at least 2 h before analysis with ~150 μL of phosphoric acid (specific gravity 1.925) in Exetainers flushed with ultra-high purity helium gas at ~25 °C. These samples were run alongside analyses of NBS-19 and sodium bicarbonate reacted with phosphoric acid at room temperature overnight; additional sodium bicarbonate samples were mixed with degassed ultra-pure water before acidification. Results were standardized based on the NBS-19 analyses ($\delta^{13}C = +1.95‰$), and corrected by +0.2‰ to account for residual CO_2 in solution, as determined by results for powdered and dissolved bicarbonate samples. External precision of replicate analyses was 0.07‰.

2.3. Oxygen and carbon isotope analyses of gastropod shells

Four specimens of the gastropod *Conus mahogani* were live-collected at night during lowest low tide (spring tide) from Veracruz Beach in the Gulf of Panama (Table 1). After collection, gastropod soft-bodies were removed and shells cleaned to remove surface contaminants by lightly sanding and scrubbing with dilute soap and water. Samples for C and O isotopic analyses were drilled around the spire at <0.5 mm depth using a 0.5 mm dental bur and a dental drill at low speed. Samples were drilled at 2 mm intervals. Powdered shell carbonate (40–80 μg) was analyzed for $\delta^{18}O$ and $\delta^{13}C$ on a Thermo Scientific MAT 253 IRMS/Kiel IV instrument at the Stable Isotope Geosciences Facility at Texas A&M University. At least every 5th sample was run in duplicate. Precision was 0.07‰ for $\delta^{18}O$ and 0.03‰ for $\delta^{13}C$ based on replicates of standards.

2.4. Sclerochronology and calculation of predicted $\delta^{18}O$ values of aragonite

To determine the growth chronology and whether the shell $\delta^{18}O$ profiles accurately recorded annual temperature and seawater $\delta^{18}O$ cyclicity, we calculated predicted shell aragonite $\delta^{18}O$ values ($\delta^{18}O_{ar}$ versus VPDB) from water temperatures (T), seawater $\delta^{18}O$ values (δ_w versus VSMOW), and the Grossman and Ku (1986, Eq. (1)) equation