

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



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### ABSTRACT

We use time-series  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data from seawater and live-collected *Conus* shells from Panama's Pacific coast to test the fidelity of the gastropod's  $\delta^{13}\text{C}$  values as a proxy for the  $\delta^{13}\text{C}$  of marine dissolved inorganic carbon (DIC), and the potential of  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  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,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}_{\text{DIC}}$  all decline. During the dry season, the upwelling signal increases and runoff declines increasing salinity,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}_{\text{DIC}}$  values. Shell  $\delta^{13}\text{C}$  values strongly correlate with measured  $\delta^{13}\text{C}_{\text{DIC}}$  values, but are lower than expected equilibrium for aragonite by approximately +2‰ reflecting the incorporation of light metabolic C. The co-dependences of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  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.

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### 1. Introduction

Carbon isotopes ( $^{13}\text{C}/^{12}\text{C}$ ) 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)  $\delta^{13}\text{C}$  composition of ambient water is the primary control on shell  $\delta^{13}\text{C}$  values (e.g., Mook, 1971; Fritz and Poplawski, 1974; Acour

et al., 2003; Beirne et al., 2012), but other studies have shown that molluscan  $\delta^{13}\text{C}$  values may be influenced by the incorporation of  $^{13}\text{C}$ -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  $^{13}\text{C}$ -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  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in mollusk shells as an upwelling proxy. Using temperature records and shell  $\delta^{18}\text{O}$  to develop a chronology, they observed that  $\delta^{13}\text{C}$  values for the mussel *Mytilus californianus* tended to parallel the Bakun upwelling index and  $\delta^{13}\text{C}_{\text{DIC}}$  estimated from apparent oxygen utilization (AOU). Applying this approach to fossils requires independent evidence for upwelling, leading researchers to explore inverse correlations between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  as a proxy for upwelling of cool, low  $\delta^{13}\text{C}_{\text{DIC}}$  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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  spikes (positive correlation) in western North Atlantic bivalves (Krantz et al., 1987).

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Isotope sclerochronology studies of mollusks have attempted to use  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  (O–C) correlations as upwelling and freshening proxies with mixed success because of oft-seen ontogenetic declines in  $\delta^{13}\text{C}$ , 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  $\delta^{13}\text{C}$  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  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  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  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  with time-series data for local seawater  $\delta^{18}\text{O}$  and DIC  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{DIC}}$ ) 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  $\delta^{18}\text{O}$  ( $\delta_w$ ) and  $\delta^{13}\text{C}_{\text{DIC}}$  with sclerochronological  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of bivalves to demonstrate an environmental control on shell  $\delta^{13}\text{C}$  (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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  profiles in four live-collected *Conus mahogani* shells with a 17-month record of concurrent seawater  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  measurements for the Pacific coast of Panama to evaluate shell  $\delta^{13}\text{C}$  values as a proxy for seasonal fluctuations in  $\delta^{13}\text{C}_{\text{DIC}}$ . 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,  $\delta^{18}\text{O}$  of water ( $\delta_w$ ), and  $\delta^{13}\text{C}_{\text{DIC}}$  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  $\delta^{13}\text{C}_{\text{DIC}}$  samples, evacuated serum bottles with 20 mm blue butyl rubber stoppers (Bellco™ 2048–11,800) and aluminum caps were pre-poisoned with mercuric chloride ( $\text{HgCl}_2$ ). A syringe pre-rinsed with the sample water was then used to inject samples into each  $\delta^{13}\text{C}_{\text{DIC}}$  vial. The  $\delta^{13}\text{C}_{\text{DIC}}$  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  $\delta^{18}\text{O}$  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  $\mu\text{L}$  each were used for each sample vial, with the first three removed due to memory effect. External precision for these analyses is 0.1‰.

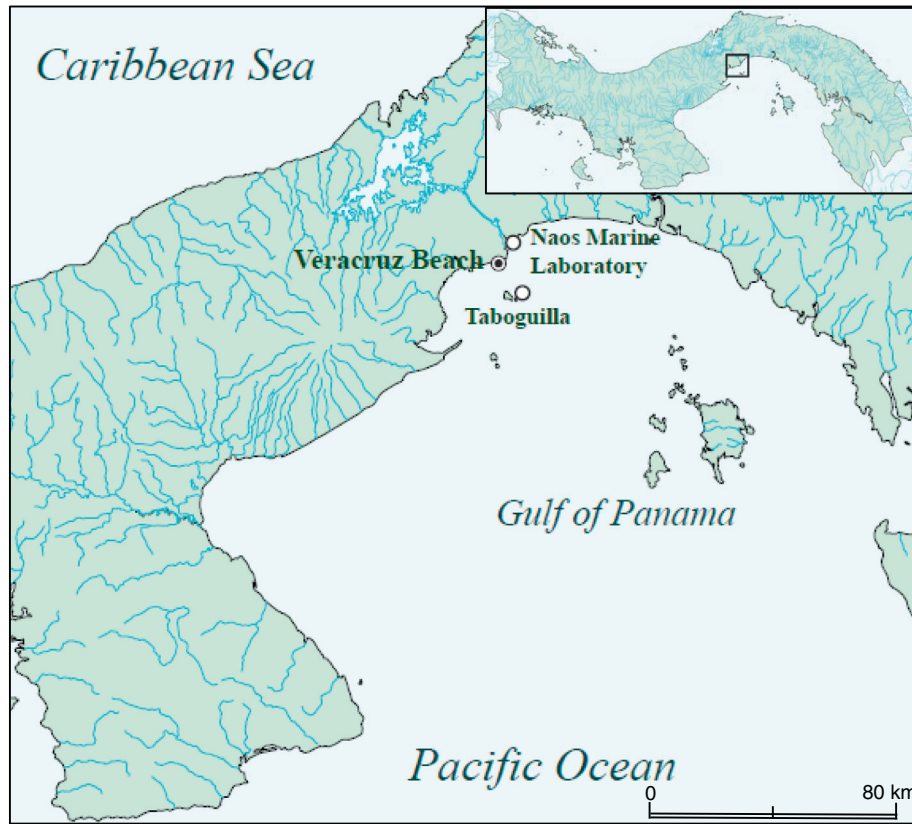
The  $\delta^{13}\text{C}_{\text{DIC}}$  measurements were performed with a Thermo Finnigan Delta<sup>PLUS</sup> XP isotope ratio mass spectrometer with a Thermo GasBench II gas analyzer and an A200S auto-sampler in the SIGF at TAMU. 0.5 mL of sample water was acidified for at least 2 h before analysis with ~150  $\mu\text{L}$  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 ( $\delta^{13}\text{C} = +1.95\text{‰}$ ), and corrected by +0.2‰ to account for residual  $\text{CO}_2$  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  $\mu\text{g}$ ) was analyzed for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  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  $\delta^{18}\text{O}$  and 0.03‰ for  $\delta^{13}\text{C}$  based on replicates of standards.

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

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



**Fig. 1.** Map of study area in Panama. Study site is labeled with black filled dot. Naos Marine Station and Taboguilla are denoted with unfilled circles. Inset map shows study area within the map of Panama.

as modified by Hudson and Anderson (1989) to reference  $\delta_w$  to SMOW/VSMOW instead of “PDB” (see Grossman, 2012, for more details):

$$T (\text{ }^\circ\text{C}) = 19.7 - 4.34 (\delta^{18}\text{O}_{\text{ar}} - \delta_w) \quad (1)$$

Water temperatures were provided by the Smithsonian Tropical Research Institute’s (STRI) Physical Monitoring Program ([http://www.stri.si.edu/sites/esp/mesp/research\\_sites.htm](http://www.stri.si.edu/sites/esp/mesp/research_sites.htm)). Dates were assigned to shell length by matching predicted and measured  $\delta^{18}\text{O}$  minima and maxima as anchor points. Between anchor points, dates were assigned to shell length by matching predicted and measured  $\delta^{18}\text{O}$  values with the understanding that mollusk growth will have periods of growth cessation and growth spurt, especially during seasonal extremes and spawning (e.g., Goodwin et al., 2001; Gentry et al., 2008). For instance, VC04–6 and VC04–8 exhibit a period of growth cessation during the summers of 2011 and 2012, which may be attributed to the seasonal temperature extreme and/or spawning in late summer that has been observed in other *Conus* (Gentry et al., 2008).

### 3. Results

#### 3.1. Oxygen isotopes in seawater ( $\delta_w$ )

Seawater  $\delta^{18}\text{O}$  and salinities for the Pacific coast of Panama from March 2011 to August 2012 show trends expected with seasonal rainfall (Fig. 2). During the dry season (January through April) salinity ranged from 23.6 to 34.6 with monthly averages of 30.6 to 33.8; during the rainy season (May through December) salinities varied from 28.1 to 32.7. Seawater  $\delta^{18}\text{O}$  ranged from  $-2.8$  to  $+0.2\text{‰}$ , with monthly averages of  $-0.8$  to  $-0.1\text{‰}$  in the dry season and  $-1.8$  to  $-0.2\text{‰}$  in the rainy season. Averaging monthly  $\delta^{18}\text{O}_w$  and salinity (*S*) data for the Pacific coast of Panama yields a robust correlation defining the relation:

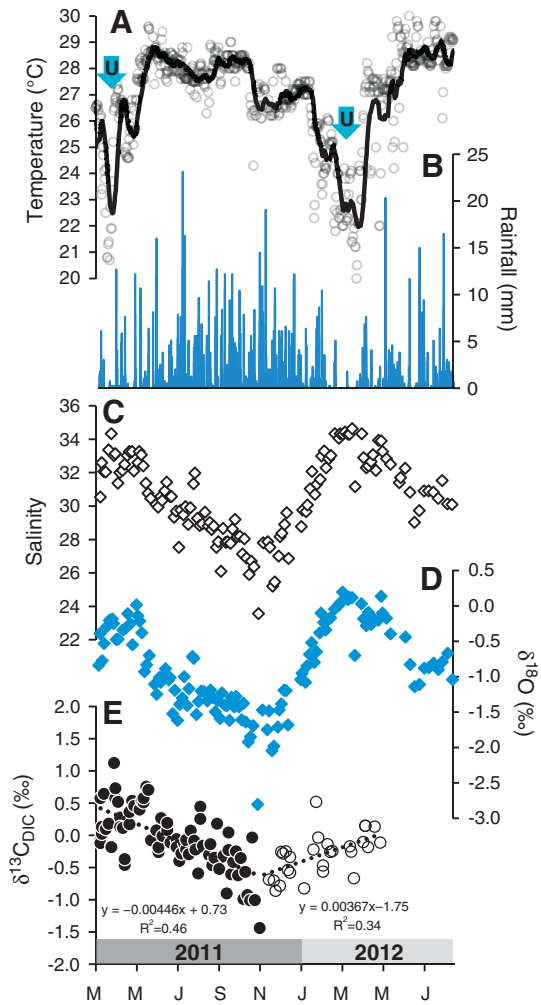
$$\delta_w (\text{‰VSMOW}) = 0.242 (\pm 0.010) S - 8.23 (\pm 0.30) \quad (R^2 = 0.985) \quad (2)$$

with the y intercept approximating runoff on the Pacific side of Panama (Lachniet and Patterson, 2009; Lachniet, 2009). This equation is slightly

**Table 1**

Specimen information, isotopic data, and relationships for *Conus mahogani* specimens collected from Veracruz Beach ( $8^\circ 53' 00''\text{N}$ ,  $79^\circ 35' 49''\text{W}$ ) on July 24–26, 2013. Specimen ages and growth rates are determined from oxygen isotope profiles.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are the range in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively.  $C_m$  is the calculated percentage of metabolic  $\text{CO}_2$  incorporated into the shell (see discussion in text). Statistically significant  $R^2$  values shown as bold.

Identifier	Shell diameter (mm)	Shell height (mm)	Age (yrs)	Mean growth rate (mm/yr)	n	O-C $R^2$	O-C slope	Mean $\delta^{18}\text{O}$ (‰)	Mean $\delta^{13}\text{C}$ (‰)	$\Delta^{18}\text{O}$ (‰)	$\Delta^{13}\text{C}$ (‰)	$C_m$ (%)
$\delta_w$ & $\delta^{13}\text{C}_{\text{DIC}}$					181			-0.9	-0.1	3.0	2.6	
Predicted shell						0.46	1.0	-2.6	2.6	5.0	2.6	
VC04–5	14	29	1.5	45	34	0.03	0.8	-2.1	1.2	2.7	0.8	11
VC04–6	15	35	3	20	30	<b>0.45</b>	1.9	-2.3	0.9	3.2	1.5	13
VC04–7	15	34	2.5	23	30	<b>0.46</b>	1.9	-2.6	0.7	3.4	1.2	15
VC04–8	15	33	3.5	18	32	<b>0.45</b>	1.6	-2.4	1.3	3.4	1.4	11



**Fig. 2.** Naos Marine Station water temperature (A) and rainfall (B) from nearby Culebra, provided by STRI's Physical Monitoring Program ([http://biogeodb.stri.edu/physical\\_monitoring/](http://biogeodb.stri.edu/physical_monitoring/)). Daily temperatures are grey circles and a two-week average is a solid black line. The rainfall diagram shows data collected at 15 min intervals over the study period. Grey arrows with "U" show upwelling intervals. Water salinity (C),  $\delta^{18}\text{O}$  (‰ vs. VSMOW) (D), and  $\delta^{13}\text{C}_{\text{DIC}}$  (‰ vs. VPDB) (E) measurements collected biweekly from the STRI Naos Marine Station from March 2011 to August 2012. Note that  $\delta^{18}\text{O}$  axis (D) is reversed. The  $\delta^{13}\text{C}_{\text{DIC}}$  data (E) defining decreasing (filled circles) and increasing (unfilled circles) trends roughly correlate with rainy and dry seasons.

different from that reported in Tao et al. (2013),

$$\delta_w (\text{‰VSMOW}) = 0.25 (\pm 0.01) S - 8.35 (\pm 0.30) \quad (R^2 = 0.98) \quad (3)$$

Eq. (2) averages monthly data from 2011 and 2012, producing a regression line for the twelve months of the year, whereas the Tao et al. regression (Eq. (3)) is based on monthly data for 18 months (March 2011–August 2012), weighing data for March through August twice as much as that for September through February. Predicted  $\delta^{18}\text{O}$  values prior to 3/2011 and after 8/2012 were estimated based on  $\delta_w$  values calculated using salinity data from STRI's Naos Marine Station ([http://biogeodb.stri.edu/physical\\_monitoring/](http://biogeodb.stri.edu/physical_monitoring/)) and the relation between average monthly  $S$  and  $\delta_w$  (Eq. (2)).

### 3.2. Carbon isotopes in DIC

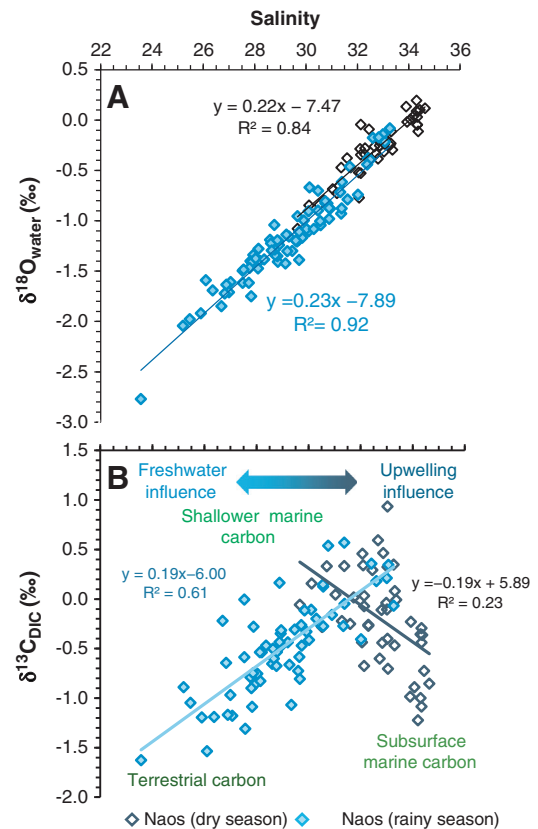
Carbon isotopic compositions of DIC range from  $-1.4$  to  $+1.1$ ‰. Values decrease from  $+0.4$  to  $-0.6$ ‰ (on average) from March to October 2011, spanning the late dry season through most of the rainy

season; values then increase ( $-0.6$  to  $+0.0$ ‰) from November 2011 to April 2012, from the late rainy season through the dry season (Fig. 2B). Comparison between  $\delta^{13}\text{C}_{\text{DIC}}$  and salinity ( $S$ ) shows a more revealing pattern. Dissolved inorganic carbon  $\delta^{13}\text{C}$  was lowest during strong upwelling (high  $S$ ) or freshwater influence (low  $S$ ), and highest during the dry season between intervals of strong upwelling, probably reflecting productivity-driven drawdown of  $^{13}\text{C}$ -depleted DIC (Fig. 3). These processes are responsible for a negative  $\delta^{13}\text{C}_{\text{DIC}}-S$  (and  $\delta^{13}\text{C}_{\text{DIC}}-\delta^{18}\text{O}_w$ ) relationship ( $R^2 = 0.23$ ) during the dry season. Conversely, during the rainy season there is a positive  $\delta^{13}\text{C}_{\text{DIC}}-S$  relationship reflecting mixing between marine and terrestrial DIC ( $R^2 = 0.61$ ).

### 3.3. Oxygen and carbon isotopes in shells

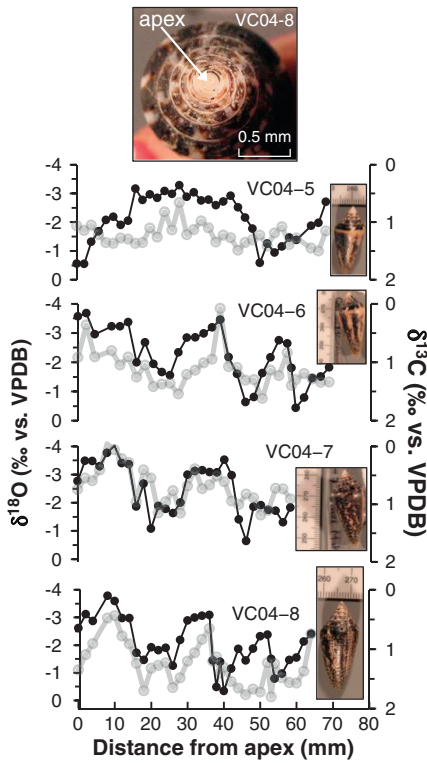
Oxygen isotope values for Veracruz Beach *Conus* show a large 3.7‰ range ( $-4.1$  to  $-0.4$ ‰) with an average of  $-2.3$ ‰. The profiles reveal 1.5 to 3.5 cycles, representing the age of the specimens in years (Fig. 4). Three of the four profiles begin with decreasing values suggesting spawning during the end of the dry (upwelling) season when food availability is presumably greater. The fourth (VC04–6) begins in the middle of the  $\delta^{18}\text{O}$  minima (rainy season). Fig. 5 shows the  $\delta^{18}\text{O}$  chronology established using minima and maxima  $\delta^{18}\text{O}$  values to tie measured and predicted curves. Extension rates based on this chronology vary greatly between specimens, ranging from 45 mm/yr in VC04–5 to 18 mm/yr in VC04–8.

Carbon isotopic values for the four *Conus* shells range from  $-1.6$  to  $+1.8$ ‰ and average  $+0.8$ ‰. There is a weak positive correlation between  $\delta^{13}\text{C}$  and ontogenetic age in all specimens ( $R^2 = 0.08$  to  $0.29$ ; Fig. 4). The oxygen isotope chronologies previously mentioned are used to compare  $\delta^{13}\text{C}_{\text{DIC}}$  to measured shell  $\delta^{13}\text{C}$  values. The shell  $\delta^{13}\text{C}$



**Fig. 3.**  $\delta^{18}\text{O}$  (A) and  $\delta^{13}\text{C}_{\text{DIC}}$  (B) of seawater versus salinity for individual water samples from the Naos Island Marine Laboratory on the Pacific coast of Panama. Separate regressions are determined for dry-season (open diamond) and rainy-season (filled diamond) samples. Extrapolation of data to 0 salinity suggests  $\delta^{18}\text{O}$  values of  $-7.5$  to  $-7.9$ ‰ for river water and a  $\delta^{13}\text{C}$  value of  $-6$ ‰ for river-derived (terrestrial) DIC.





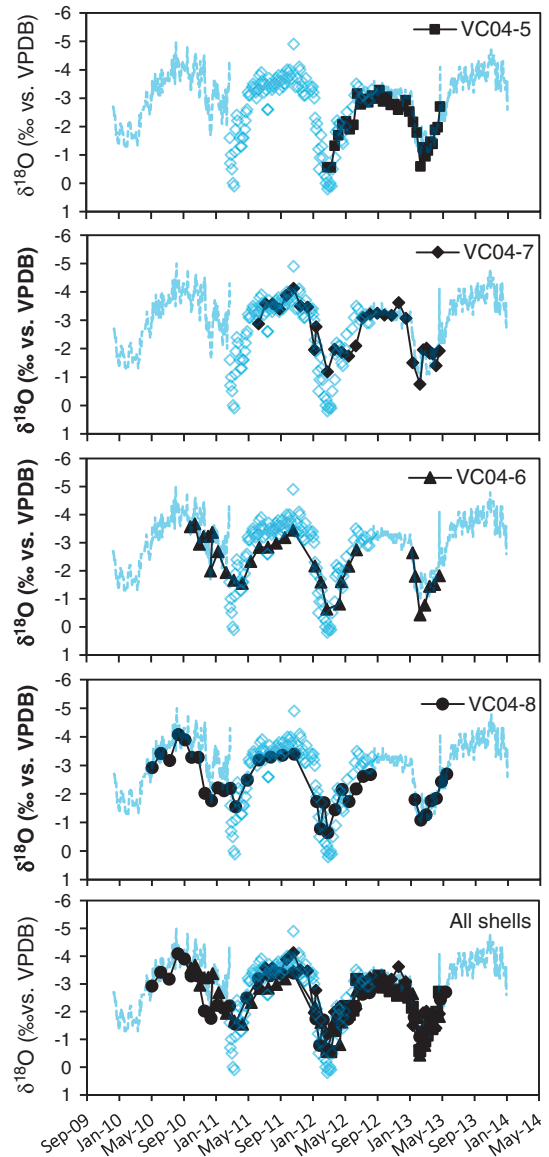
**Fig. 4.** *Conus mahogani*  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  profiles versus distance from apex (mm) in Gulf of Panama samples with corresponding shell photos (major units in scale in cm).  $\delta^{18}\text{O}$  profiles are black lines and  $\delta^{13}\text{C}$  profiles are grey. Note that values are plotted negative up. Top photo shows apex of VC04-8.

values were then matched to their corresponding  $\delta^{13}\text{C}_{\text{DIC}}$  value using the linear relationship shown in Fig. 2E. There is a significant positive correlation between shell  $\delta^{13}\text{C}$  values and  $\delta^{13}\text{C}_{\text{DIC}}$  in all shells ( $R^2 = 0.51$  to  $0.75$ ; Fig. 6).

**4. Discussion**

**4.1. Carbon isotope trends in  $\delta^{13}\text{C}_{\text{DIC}}$**

The decline in  $\delta^{13}\text{C}_{\text{DIC}}$  from March to October 2011, primarily during the rainy season, appears contradictory given that upwelling, which takes place principally from January to March, advects low  $\delta^{13}\text{C}_{\text{DIC}}$  water upwards. However, the change in seawater  $\delta^{13}\text{C}_{\text{DIC}}$  associated with upwelling is less than that from freshwater input. The  $\delta^{13}\text{C}_{\text{DIC}}$  of upwelled waters from 60 to 80 m depth (D’Croz and O’Dea, 2007) will likely be  $\sim 1\%$  lower than surface  $\delta^{13}\text{C}_{\text{DIC}}$  (Quay et al., 2003), whereas  $\delta^{13}\text{C}_{\text{DIC}}$  of freshwater discharge from tropical rivers will be  $-8$  to  $-12\%$  lower (Fig. 2; Moyer et al., 2013). Thus, waters with  $<31$  salinity ( $\sim 10\%$  fresh water) will be  $>1\%$  lower in  $\delta^{13}\text{C}_{\text{DIC}}$ . Restated, waters with  $<31$  salinity will have  $\delta^{13}\text{C}_{\text{DIC}}$  values lower than those of upwelled waters (Fig. 2). Complicating this relationship is the non-conservative behavior of  $\delta^{13}\text{C}_{\text{DIC}}$ . Nutrient delivery from upwelling invokes a positive feedback on  $\delta^{13}\text{C}_{\text{DIC}}$  through preferential uptake of  $^{13}\text{C}$ -depleted DIC during photosynthesis. This general trend may be complicated by a desynchronization between upwelling, the resulting plankton blooms, and the subsequent energy flux into the food chain that eventually impacts shell growth in *Conus mahogani*. For example, Henson and Thomas (2007) identified a 15-day lag between upwelling favorable winds and phytoplankton blooms in the California Current system. Despite the complexities, upwelling and freshwater input are the primary influences on seawater  $\delta^{13}\text{C}_{\text{DIC}}$  values as confirmed by the strong relationship between salinity and  $\delta^{13}\text{C}_{\text{DIC}}$  (Fig. 3)



**Fig. 5.** Measured versus predicted  $\delta^{18}\text{O}$  profiles for Gulf of Panama *Conus*. The predicted shell profiles for 3/2011 through 8/2012 are based on Grossman and Ku (1986) using measured  $\delta_w$  values and water temperatures measured at Taboguilla (STR1’s Physical Monitoring Program; Fig. 1; blue diamonds). Predicted  $\delta^{18}\text{O}$  values for before 3/2011 and after 8/2012 (dashed blue lines) were estimated based on  $\delta_w$  values that were calculated using a relation between average monthly salinity and  $\delta_w$  shown in Eq. (2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**4.2. Environmental resolution of isotopic record**

Comparison between measured and predicted shell  $\delta^{18}\text{O}$  profiles tests the resolution of isotope sclerochronology of *Conus* shells (Fig. 5). For individual shells, the mean measured  $\delta^{18}\text{O}$  value is statistically identical ( $t$ -test) to the predicted value ( $-2.6\%$ ). The mean measured  $\delta^{18}\text{O}$  range ( $\Delta^{18}\text{O} = 3.4\%$ ), however, is less than the predicted ranges for fortnightly averages,  $4.0\%$ . Based on the two-week averages, *Conus* specimens from Veracruz Beach record 85% of the predicted range (Fig. 4). This resolution does not increase with growth rate. Despite the  $<100\%$  resolution, the lower intensity of early 2011 upwelling is clearly seen in the records of longer lived specimens VC04-6 and VC04-8.

The incomplete record of environmental variability may reflect (1) time averaging during drilling, (2) sample resolution, (3) environmental differences between water and shell collection sites, or (4) limited

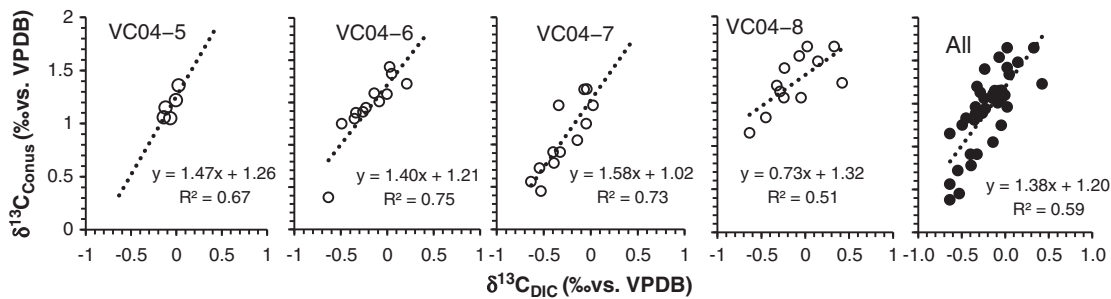


Fig. 6. Carbon isotopic composition of *Conus* shells versus corresponding DIC  $\delta^{13}\text{C}$  value.

growth during lowest temperature or lowest salinity conditions. Sample averaging during drilling is roughly 0.4 to 1.4 weeks based on growth rates and hole diameter. Monte Carlo simulation of fortnightly average temperatures yield resolutions of 91%, 79%, and 72% for 16, 12, and 8 samplings per year, consistent with the observations here. Water collection and shell collection localities are 8 km apart, but we presume they share similar salinity regimes because both receive waters from the same bay and neither are influenced by significant freshwater output. Although the water collection site is 8 km northeast of the shell collection sites, both sites are located on the coast, and are separated by the Panama Canal, which has intermittent and insignificant freshwater output. Consequently, we presume that these localities do not have significantly different salinity profiles. The temperature data were collected from Taboguilla, 12.5 km to the south of the collection sites. The isolated and short-lived nature of upwelling events in the Gulf of Panama temperature data suggest upwelling events have typical durations of one to two weeks (e.g., see Matthews et al., 2008), and therefore could also contribute to the absence of the lowest temperatures recorded in *Conus*  $\delta^{18}\text{O}$ , as discussed by Tao et al. (2013). The same appears to be true for freshening events (Fig. 2B). Similar underrepresentation of environmental variation has been observed in many other studies, including studies of *Conus* shells from the Gulf of Mexico (Gentry et al., 2008) and bivalves shells from Peru (Carré et al., 2005). Thus, modest underrepresentation of environmental extremes likely results from time averaging of drilled samples, sample resolution, moderation of the upwelling signal in nearshore environments, and slow or paused growth. Fortunately, this underrepresentation does not significantly undermine our chronology based on  $\delta^{18}\text{O}$  and our efforts to relate shell  $\delta^{13}\text{C}$  to DIC  $\delta^{13}\text{C}$ .

#### 4.3. Shell $\delta^{13}\text{C}$ as a proxy for DIC $\delta^{13}\text{C}$

*Conus*  $\delta^{13}\text{C}$  profiles from Veracruz Beach reflect changes in  $\delta^{13}\text{C}_{\text{DIC}}$ . Fig. 6 reveals a significant positive correlation between shell and DIC  $\delta^{13}\text{C}$  in all shells. Combining all data yields the equation:

$$\delta^{13}\text{C}_{\text{shell}} = 1.38 \delta^{13}\text{C}_{\text{DIC}} + 1.20 \quad (R^2 = 0.59) \quad (4)$$

The slope is near, but not equal, to one and the y-intercept (+1.20‰) is 1.5‰ lower than expected for aragonite-bicarbonate  $^{13}\text{C}$  equilibrium (Romanek et al., 1992).

As discussed previously, lower-than-equilibrium  $\delta^{13}\text{C}$  values (vital effects) can occur in biogenic carbonates due to kinetic effects and incorporation of  $^{13}\text{C}$ -depleted  $\text{C}_\text{M}$  (e.g., McConnaughey and Gillikin, 2008). Increased availability of  $\text{C}_\text{M}$  in internal fluids may cause the incorporation of more  $^{12}\text{C}$  into shell carbonate (cf. Lorrain et al., 2004; Gillikin et al., 2007; Gillikin et al., 2009). For each shell,  $\text{C}_\text{M}$  can be calculated using the equation described by Gillikin et al. (2009),

$$\text{C}_\text{M} = \left( \delta^{13}\text{C}_{\text{ar}} - \varepsilon_{\text{ar-b}} - \delta^{13}\text{C}_\text{b} \right) / \left( \delta^{13}\text{C}_\text{M} - \delta^{13}\text{C}_\text{b} \right) \quad (5)$$

where  $\delta^{13}\text{C}_{\text{ar}}$  is the shell  $\delta^{13}\text{C}$  value (Table 1),  $\varepsilon_{\text{ar-b}}$  is the enrichment factor between aragonite and  $\text{HCO}_3^-$  (2.7‰; Romanek et al., 1992),  $\delta^{13}\text{C}_\text{b}$  is the bicarbonate  $\delta^{13}\text{C}$  value, and  $\delta^{13}\text{C}_\text{M}$  is the  $\delta^{13}\text{C}$  of metabolic carbon (−15.3‰ for *Conus mahogani* tissues from this study). We calculated  $\delta^{13}\text{C}_\text{b}$  from  $\delta^{13}\text{C}_{\text{DIC}}$  data and the mass balance of aqueous  $\text{CO}_2$ , bicarbonate, and carbonate ion using equilibrium constants (Roy et al., 1993, 1996), carbon isotope enrichment factors (Zhang et al., 1995), and temperature, salinity, pH, and alkalinity data from the study area and region (e.g., Manzello, 2010). The  $\delta^{13}\text{C}$  difference between bicarbonate and DIC is roughly +0.3‰ for the Gulf of Panama for wet and dry season conditions. These calculations yield  $\text{C}_\text{M}$  of  $12 \pm 2\%$  for *Conus*. Other gastropods collected from the same area during the sampling period produced values of  $10 \pm 1\%$  (*Vasum*) and 23% (*Strombus*) (Graniero, 2014). The  $12 \pm 2\%$   $\text{C}_\text{M}$  is consistent with previous studies that estimate incorporation in marine mollusks (e.g., McConnaughey et al., 1997; McConnaughey and Gillikin, 2008; Sadler et al., 2012). The greater  $\delta^{13}\text{C}$  vital effect in Panama *Strombus* has also been observed in fossil specimens (Grossman et al., in prep.).

Feeding habit differences between *Conus*, *Strombus*, and *Vasum* gastropods may impact the incorporation of  $\text{C}_\text{M}$  into shell carbonate. The offset between  $\delta^{13}\text{C}_{\text{DIC}}$  and aragonite shell values are within ranges observed by others (−0‰, Aucour et al., 2003; +1‰, Beirne et al., 2012). Using  $\% \text{C}_\text{M}$  values and  $\delta^{13}\text{C}_{\text{DIC}}$  values, the relationship between mean  $\delta^{13}\text{C}_\text{s}$  and  $\delta^{13}\text{C}_\text{b}$  values for *Conus*, *Strombus*, and *Vasum* can be described as:

$$\delta^{13}\text{C}_{\text{Conus}} = \delta^{13}\text{C}_\text{b} + 0.8\% (\pm 0.2) \quad (6)$$

$$\delta^{13}\text{C}_{\text{Strombus}} = \delta^{13}\text{C}_\text{b} - 0.9\% \quad (7)$$

$$\delta^{13}\text{C}_{\text{Vasum}} = \delta^{13}\text{C}_\text{b} + 1.2\% (\pm 0.1) \quad (8)$$

Interestingly, *Conus* and *Vasum* are both predatory carnivores (Todd, 2001) and have similar  $\delta^{13}\text{C}_{\text{ar}} - \delta^{13}\text{C}_\text{b}$  offsets, whereas *Strombus* are herbivore-detritivores (Aranda et al., 2003) and have a lower  $\delta^{13}\text{C}_{\text{ar}} - \delta^{13}\text{C}_\text{b}$  offset. This may be related to mobility differences between species. For instance, the greater metabolic  $\text{CO}_2$  availability in shell growth in *Strombus* may reflect continual grazing in search of macroalgae as well as leaping locomotion (Miller, 1974), requiring a relatively more active metabolism (Berg, 1975). *Conus*, on the other hand, move very slowly, slowly feed only at night, and remain immobile during digestion of their prey (Kohn, 1959, 1968).

#### 4.4. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ correlations: vestiges of seasonal upwelling and freshening?

Oxygen isotopic profiles in mollusk shells can provide exquisite seasonal temperature records with minimal influence of vital effects (in contrast, for instance, to corals) and can be combined with carbon isotopes to provide unequivocal evidence for upwelling and/or freshening. For all but sample VC04-5, our data show a strong positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ( $R^2 = 0.45$ – $0.46$ ; Table 1), implying dominant influence by freshening with no evidence of upwelling. However,

careful examination of the data reveal two trends, a positive correlation (freshening) for mid to low  $\delta^{18}\text{O}$  values, and a negative correlation (upwelling) for mid to high  $\delta^{18}\text{O}$  values (Fig. 7). The only exception is sample VC04–6, which does not show a significant correlation for upwelling. The inflection point of the two trends should represent “baseline” conditions in which upwelling and freshening are absent. This hypothesis can be tested by averaging the  $\delta^{18}\text{O}$  values for the samples with the three highest  $\delta^{13}\text{C}$  values and determining whether they yield expected temperatures at full salinity. For sample VC04–5,  $-6$ ,  $-7$ , and  $-8$ , these  $\delta^{18}\text{O}$  values are  $-2.12$ ,  $-1.96$ ,  $-2.03$ , and  $-2.05\text{‰}$  respectively. The average of these values ( $-2.04\text{‰}$ ), when combined with fortnightly  $\delta^{18}\text{O}$  ( $+0.09\text{‰}$ ) for water with the highest

fortnightly salinity (34.25), yields an isotopic temperature of  $29.0\text{ °C}$ , matching almost exactly the average temperature ( $28.5\text{ °C}$ ) for sea surface temperatures in non-upwelling periods in the Gulf of Panama (Tao et al., 2013). Nearshore *Conus* shells therefore record upwelling, freshening, and baseline conditions in their isotopic compositions.

With increased depth ( $>10\text{ m}$ ) the dual isotope trends of upwelling and freshening in *Conus* shells from the Gulf of Panama disappear. Of five shells analyzed by Tao et al. (2013), only one (301,474 from 15 m depth) shows the dual trends. None of the Pacific bivalves analyzed by Bemis and Geary (1996), nor the Pacific *Strombus* analyzed by Geary et al. (1992), show this trend. This convolution of the record likely reflects vital effects, microbial respiration in the sediments, and the loss of the strong freshwater signal with increasing depth and water density. While the complexity of the *Conus*  $\delta^{13}\text{C}$  record for deeper specimens is discouraging, the success with beach-collected samples is encouraging as *Conus* shells have long been pursued by shell collectors. Thus, museum specimens provide the potential for focused high-resolution studies of historical climate change and upwelling. In the fossil record, only *Conus* associated with clear sedimentological evidence of very shallow conditions should be used to interpret dual trends of upwelling and freshening.

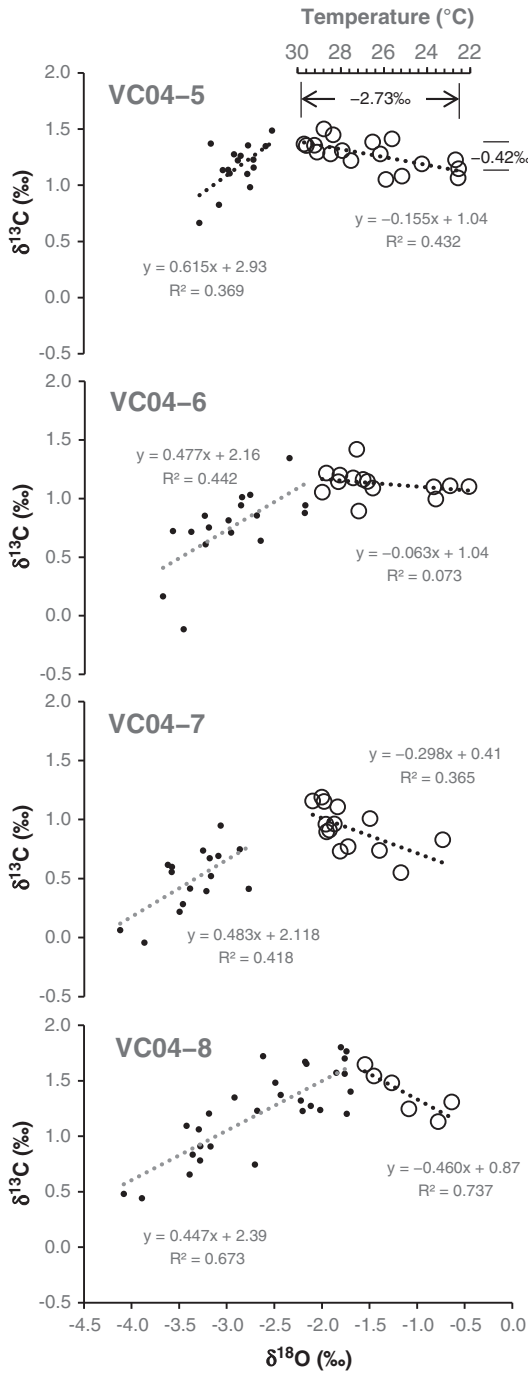
Recently, Sadler et al. (2012) reexamined the effect of temperature on carbon isotope fractionation of aragonite first reported by Grossman and Ku (1986). Grossman and Ku reported higher  $\delta^{13}\text{C}$  values in micromollusks and the aragonitic foraminifera *Hoeglundina elegans* with decreasing temperature (enrichments factor  $\epsilon^{13}_{\text{mollusk-DIC}} [\text{‰}] = 2.66 - 0.131 T [^{\circ}\text{C}]$ ). This empirical equation yields negative aragonite  $\delta^{13}\text{C}$  values for  $29\text{ °C}$  temperatures, inconsistent with the data seen here. Furthermore, the relation should result in a positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  with a slope of  $+0.57$ , opposite that observed for the upwelling, temperature-dependent segment of the  $\delta^{18}\text{O}$  record. Finally, shell  $\delta^{13}\text{C}$  values do not show an increase with depth and decreasing temperature for the Pacific coast of Panama (Tao et al., 2013), further evidence for no significant temperature effect. Nevertheless, the carbonate chemistry and carbon isotope fractionation associated with ambient and body fluids during  $\text{CaCO}_3$  precipitation is complex and we cannot rule out a temperature effect in carbon isotope fractionation in biogenic aragonite, but this effect does not appear to be significant in *Conus* shells.

**5. Conclusions**

Oxygen and carbon isotopic compositions of water and DIC in the Gulf of Panama during the March 2011 to August 2012 sampling period follow seasonal trends with low values during the rainy season and high values during the dry season. Seawater  $\delta^{18}\text{O}$  correlates positively with salinity, reflecting mixing of fresh and marine waters. Dissolved inorganic carbon  $\delta^{13}\text{C}$  and salinity correlate positively only for rainy season samples, reflecting mixing of terrestrial and marine carbon. Dry season samples correlate negatively in response to upwelling of  $^{13}\text{C}$ -depleted DIC at depth.

Shell  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values from four live-collected *Conus* specimens reflect these seasonal patterns in seawater isotopic composition, with  $\delta^{18}\text{O}$  also influenced by cooling associated with seasonal upwelling. Comparison of measured and predicted  $\delta^{18}\text{O}$  values suggest that shells record about 85% of the seasonal variability, presumably due to limited sample resolution, time-averaging of samples, and reduced effect of upwelling closer to the shore. Shell and DIC  $\delta^{13}\text{C}$  values correlate positively, evidence for the fidelity of shells as archives for marine DIC  $\delta^{13}\text{C}$  despite the fact that *Conus* shells incorporate  $12 \pm 2\%$  metabolic carbon based on expected equilibrium and mass balance calculations.

The seasonal contrast on Panama's Pacific coast is recorded in dual trends in *Conus*'  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values, with positive  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  correlations during rainy season growth and negative correlations during dry-season growth. These dual trends are not typically seen in shells collected from subsurface waters, probably because of the lack of a



**Fig. 7.**  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  for *Conus* shells from Veracruz Beach, Gulf of Panama. Note the negative  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  correlation for high  $\delta^{18}\text{O}$  values (upwelling) and positive correlation for low  $\delta^{18}\text{O}$  values.



strong freshening signal. Nevertheless, fossil, archeological, historical and modern beach-collected shells can be used to produce very focused, high-resolution records of historical climate and upwelling.

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