

Chapter 3 Constraints on Late Miocene Shallow Marine Seasonality for the Central Caribbean Using Oxygen Isotope and Sr/Ca Ratios in a Fossil Coral

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3.1 Introduction

Isolation of the Pacific and Caribbean basins by closure of the Central American Seaway (CAS) in the Miocene and Pliocene produced changes in the secular physical and chemical properties of Caribbean surface waters, one possible result of which was an increase in extinction and speciation of marine biota on both sides of the Isthmus of Panama (Jackson et al., 1996; Collins and Coates, 1999). Closure of the CAS was a gradual process spanning approximately 13–2 Ma, but Caribbean environmental conditions changed significantly once water depths reached <100 m by 4.6 million years ago (Keigwin, 1978; Coates et al., 1992, 1996, 2003; Haug and Tiedemann, 1998; Lear et al., 2003; Gussone et al., 2004). Average Caribbean surface water temperatures increased as movement of cool Pacific waters was restricted through the CAS and Caribbean waters became restricted to their own basin (Romine, 1982). Water clarity and calcium carbonate saturation may have also increased (Vermeij and Petuch, 1986), and high Caribbean evaporation rates,

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coupled with westward transport of moisture-laden air to the Pacific, increased salinity in the Caribbean (Romine, 1982).

Changes in the amount of rainfall also may have been affected by closure of the CAS. Gussone et al. (2004) attributed shifts in the $\delta^{18}\text{O}$, Mg/Ca, and $\delta^{44}\text{Ca}$ values of Caribbean planktonic foraminifera between 4.6–4.2 million years ago to shoaling in the CAS and possibly to concomitant shifts in the position of the Intertropical Convergence-Zone (ITCZ). The latter would have changed the intensity of meteoric precipitation, and thus Caribbean sea surface salinities and sea surface $\delta^{18}\text{O}$ values. Latitudinal shifts in the ITCZ have also been proposed for 4.4 million years ago (Billups et al., 1999). Such changes would have implications for ocean salinity in the southern and central Caribbean at both decadal and seasonal scales given the influence of ITCZ position over rainfall in the Orinoco River basin (Hellweger and Gordon, 2002; Watanabe et al., 2002; Estevez et al., 2003).

We lack a clear understanding of how shallow-Caribbean environments changed in response to closure of the CAS. This is particularly true for changes at the seasonal scale, a time frame that plays an important role in determining the composition of shallow marine communities (McClanahan et al., 2001; Swart et al., 2001; Ateberhan et al., 2006). For example, Teranes et al. (1996) investigated temporal changes in the seasonal ranges of venerid bivalve $\delta^{18}\text{O}$ values from both sides of the Isthmus of Panama through final closure of the CAS. Their study suggests greater seasonal temperature variability in the Caribbean in the late Miocene relative to the modern. Isotopic analysis of a 3 million-year-old coral from Florida by Roulier and Quinn (1995) supports significantly decreased seasonal temperature swings in the middle Pliocene Caribbean. Temperature reconstructions in both studies, however, were limited by the coupled influence of water temperature and salinity on oxygen isotopic ratios.

Here we present a 21-year-long, high-resolution stable isotope and trace element record of a late Miocene (~5 million-year-old) coral from the Dominican Republic (Fig. 3.1) that records shallow marine paleoenvironmental conditions prior to final closure of the CAS. This coral serves as one snapshot for the late Miocene central Caribbean that, when integrated with other records, may allow a better understanding of the role played by environmental variables in forcing Neogene faunal turnover in the Caribbean.

3.2 Geological and Environmental Setting

An area with a rich fossil fauna that has been the focus of studies aimed at better understanding the timing, rate, and mode of marine faunal speciation associated with closure of the CAS is the Cibao Valley in the northern Dominican Republic (Fig. 3.1) (Cheetham, 1986, 1987; Nehm and Geary, 1994; Nehm, 2001; Johnson and Perez, 2006). During the late Miocene and early Pliocene, the Cibao Valley was part of a tectonically active graben that was generally subsiding with time (Saunders et al., 1986). One Miocene/Pliocene unit of interest in the Cibao Valley is the

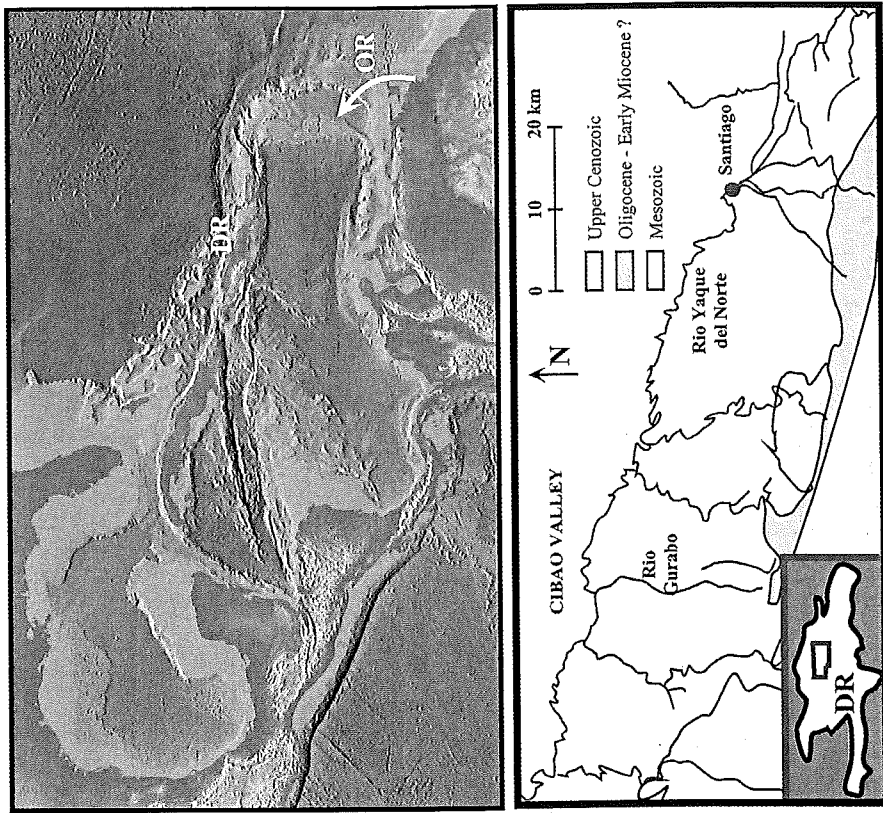


Fig. 3.1 Top: Map of the Circum-Caribbean region. DR = Dominican Republic; OR = Orinoco River discharge. Bottom: coarse geologic map of Cibao Valley

Gurabo Formation, a >400 m thick package of gently dipping, weakly indurated, coral-rich sediments. Gurabo Formation corals grew at depths of <30 m (Goreau and Wells, 1967; Graus and Macintyre, 1989) and were transported down slope as slump deposits and rapidly buried in densely-packed, fine-grained siliclastics and clayey calcareous sediments (Evans, 1986; Saunders et al., 1986) (Fig. 3.2). Based on the excellent preservation of some of these corals, it appears that this low permeability matrix severely limited flow of marine and groundwater through the Gurabo Formation. Today, the Gurabo Formation is exposed across the Cibao Valley in a network of streams including the Rio Gurabo.



Fig. 3.2 Photograph of a coral (not the *G. hilli* discussed here) after excavation from the hillside at NMB location #15855. Clay-rich nature of the Gurabo Formation matrix at this interval is evident in the streaks left by the rock hammer

3.3 Sampling and Analytical Methods

3.3.1 Field Collection and Sample Screening Procedures

An intact coral head of *Goniopora hilli* was excavated from the Gurabo Formation on the bank of the Rio Gurabo at NMB locality 15855 (Saunders et al., 1986), located approximately 275 m in the section, about 115 m above the Cercado-Gurabo Formation contact and ~305 m below the contact with the overlying Mao Formation (Fig. 3.2). The coral was slabbed using a water-cooled trim saw and inspected macroscopically, in thin section, and with scanning electron microscopy (SEM) for signs of meteoric cements (Quinn and Taylor, 2006) and dissolution or recrystallization of the coral skeleton. SEM images obtained at the University of New Mexico Department of Earth and Planetary Sciences reveal extensive primary porosity and preservation of septal ornamentation (Fig. 3.3). A second round of SEM images was obtained at the University of Iowa Department of Geosciences on samples that had been leached by 3% acetic acid for 4 minutes in order to clarify coral microstructure. Visible in these images are fibrous aragonite crystals of the coral skeleton and clusters of aragonite crystals radiating from delicate calcification centers, structures that are readily altered by meteoric diagenesis and demonstrate the excellent preservation of this sample (Reuter et al., 2005) (Fig. 3.3).

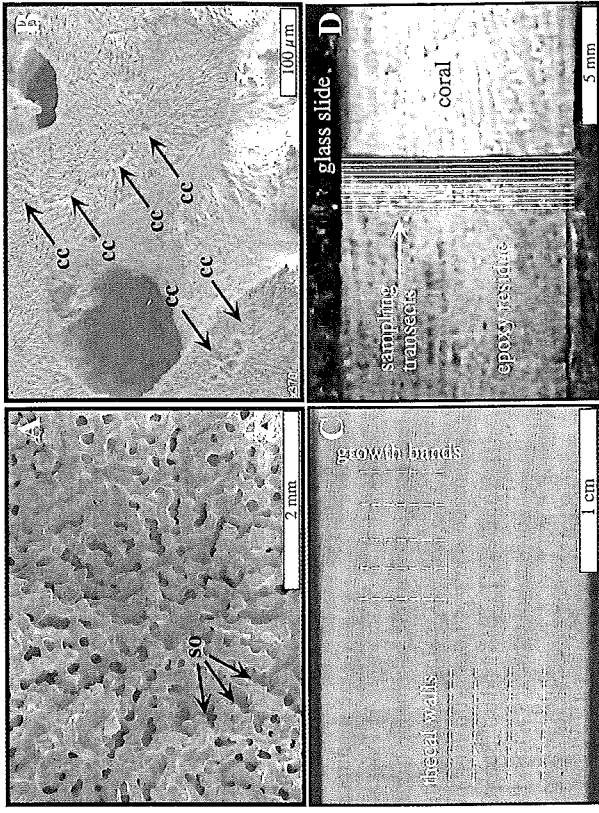


Fig. 3.3 (A) SEM image of unetched *G. hilli* with view perpendicular to maximum growth direction. Note high primary porosity and septal ornaments (so). (B) SEM image of etched *G. hilli* showing fibrous aragonite crystalline structure and preservation of calcification centers (cc). (C) X-radiograph of *G. hilli* exhibiting weakly defined thecal walls and annual growth bands. (D) Downward-looking view of corallite during microsampling at 39,700 μm. White lines denote positions of previous micromilling transects

Next, powdered subsamples were analyzed by X-ray diffraction (XRD) at Cornell College using a Scintag X-ray powder diffractometer with a DMS2000 diffraction management system and a copper target with a graphite monochromator. The scans were run at 40 kV and 30 mA from 25–35° 2θ at a scan rate of 6°/minute, a technique capable of identifying calcite at abundances >1%. No calcite peak was detected in any of the scans from this *G. hilli* sample suggesting a coral composed of 99 + % aragonite. And finally, X-radiographs of 7 mm-thick coral slabs were taken at the University of Iowa College of Dentistry using an accelerating voltage of 60 kV and 25 mA in order to define growth banding. Although faint, both corallite walls and growth bands are visible in X-ray images (Fig. 3.3).

A slab of *G. hilli* was cut from its coral head parallel to the principal growth direction of the corallites using a water-cooled saw, and the slab was then ultrasonicated in distilled water to remove detritus, oven dried at 30°C, and vacuum-impregnated with UV-activated epoxy. No chemical pretreatment technique such as H₂O₂ or NaOH was used to remove organic contaminants (see below). As corallites in *G. hilli* grow curvilinearly, the slab was visually inspected and the individual corallite that remained consistently parallel to the surface of the slab was isolated

using a thin-sectioning saw. The resulting ~5 cm-long section of corallite was then epoxied to a glass slide and polished to thickness of ~1 mm (Fig. 3.3).

3.3.2 Stable Isotope Ratios

Stable isotope analyses were performed at the University of Michigan Department of Geological Sciences using either a Finnigan MAT Kiel I preparation device coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer, or in a Finnigan MAT Kiel IV preparation device coupled to the inlet of a MAT 253 mass spectrometer. Precision and accuracy of data were monitored through daily analysis of a variety of powdered carbonate standards. At least six standards were reacted and analyzed daily, bracketing the sample suite at the beginning, middle, and end of the day's run. Measured precision was maintained at better than 0.1‰ (1 σ) for both carbon and oxygen isotope compositions with isotopic ratios reported relative to the Vienna Pee Dee Belemnite (VPDB) standard. Sample powders for stable isotope analysis were micromilled in parallel traverses across the entire corallite using a Merchanteq micromill, with the first 120 samples incorporating 75 μm of growth and the subsequent 250 samples incorporating 150 μm of growth (Fig. 3.3). Powder was collected at the end of each pass and transferred to stainless steel vials. Given the age and burial conditions of Gurabo Formation corals, we deemed it necessary to ensure that organic contamination was minimized prior to isotopic analysis. Chemical pretreatment such as with H_2O_2 or NaOH may yield unpredictable shifts in coral aragonite $\delta^{18}\text{O}$ values (Grotto et al., 2005). Roasting has also been tied to isotopic shifts in aragonite (Gaffey et al., 1991), as well. Experimental evidence suggests, however, that roasting *in vacuo* at 200°C for 1 hour does not cause the transformations of aragonite to calcite that lead to significant isotopic fractionation (Dauphin et al., 2006) but is effective in driving off volatile organic compounds. In order to assess the impact of roasting on our samples, the first 15 samples milled from the coral (distances 75–1,125 μm) were split, with one half undergoing roasting prior to isotopic analysis and the other half not. The results, displayed in Fig. 3.4, suggest a systematic shift in carbon isotopic values with all 15 carbon isotopic ratios becoming an average of 0.20‰ \pm 0.15‰ higher after roasting. In contrast, only 10 of the oxygen isotopic ratios increased after roasting, while 5 decreased, with an average offset of +0.05‰ \pm 0.10‰, less than the analytical uncertainty. As the shape and range in both the roasted and unroasted carbon and oxygen isotopic ratios remain largely consistent, and as seasonal ranges were the primary focus of this study, the remainder of the samples were roasted prior to analysis.

An additional obstacle to high-resolution geochemical analysis of corals is determining the sampling density (number of samples per year of growth) necessary to adequately capture the full seasonal temperature range. Previous studies of coral $\delta^{18}\text{O}$ seasonality have suggested minimum sampling densities of 50 (Leder et al., 1996), 40 (Watanabe et al., 2002), 14 (Leder et al., 1991), 8 (Klein et al., 1992; Ren

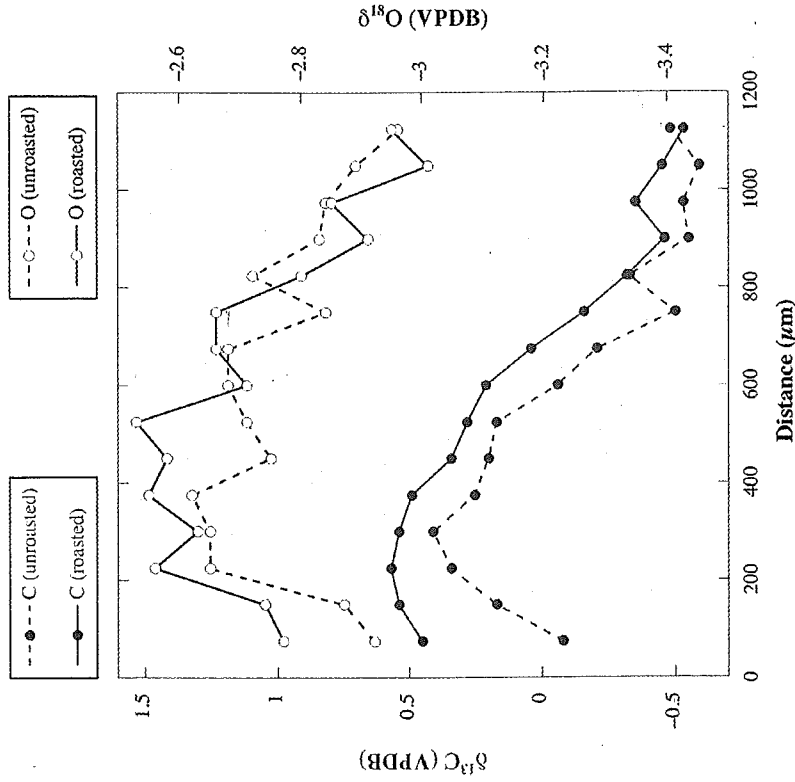


Fig. 3.4 Comparison of carbon and oxygen isotopic ratios in roasted and unroasted coral samples. Note that while $\delta^{13}\text{C}$ values are consistently elevated after roasting and the $\delta^{18}\text{O}$ values exhibit a more non-uniform response, the overall trends remain parallel

et al., 2002), and 6 samples per year of growth (Quinn et al., 1996). Measurement of growth banding and distances between peaks in *G. hilli* isotope profiles yields average-annual growth rates of ~2mm/year. Thus, the 150 μm -deep traverses used here equates to a sampling density of >12 samples per year. Mathematically manipulating these *G. hilli* data demonstrated no signal attenuation at this sampling density relative to the 75 μm -deep traverses (24 samples/year) used for the first 120 samples.

Variations in the stable isotopic composition across the coral skeleton have been identified which can also lead to an artificially reduced seasonal signal. Leder et al. (1996) found reduced seasonal signals in $\delta^{18}\text{O}$ values across endothecal (dissepiments and columella) portions relative to thecal samples that they attributed to calcification of skeletal structures at different times throughout the year, and to time-averaging effects. Watanabe et al. (2002) found significant, but not consistent, differences between oxygen isotopic samples isolated solely from thecal

walls as compared to the entire corallite. In order to test the importance of sampling position in *G. hilli*, we compared (1) traverses milled across the entire corallite at depths of 200 μm and full depth ($\sim 1,000 \mu\text{m}$) across the entire corallite and (2) points drilled to full depth ($\sim 1,000 \mu\text{m}$) but restricted to the (poorly-defined) corallite wall. The results demonstrate significant variability in both carbon and oxygen isotopic ratios with position in the *G. hilli* coral skeleton (Fig. 3.5), but the oxygen isotopic trends defined by these traverses remained similar, and thus the remaining samples were analyzed by transects across the entire corallite.

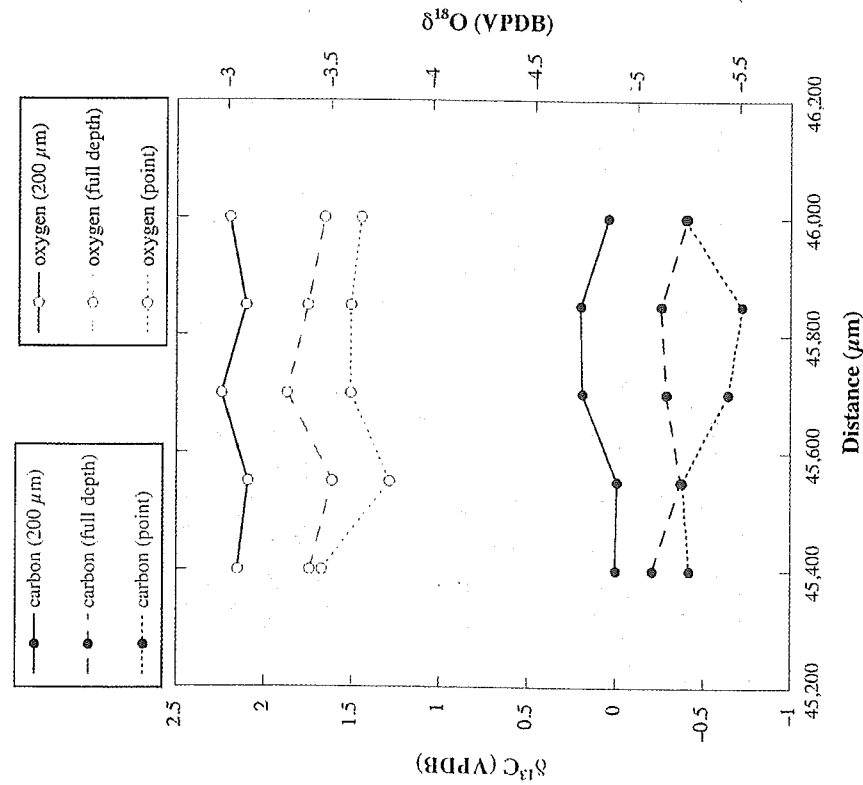


Fig. 3.5 Comparison of carbon and oxygen isotopic ratios with position in the corallite. Note the similarity in oxygen isotopic trends, despite the >0.5% offset between samples of different depth

3.3.3 Strontium/Calcium Ratios

Splits from alternate stable isotope samples were analyzed at the Keck Elemental Geochemistry Laboratory in the Department of Geological Sciences University of Michigan using a Finnigan MAT Element inductively coupled plasma-high resolution mass spectrometer (ICP-MS) and the method of Rosenthal et al. (1999); analytical precision averages 7‰ (1 σ). Although the first three growth years were analyzed, problems with instrument calibration resulted in the offset of measured Sr/Ca ratios from those of adjacent samples, and thus we chose not to include them in this data set. In addition, insufficient powder was available for Sr/Ca analyses of the last ~ 2 growth years, resulting in a Sr/Ca record that is truncated relative to the stable isotope record.

3.4 Constraining Shallow Marine Conditions

When plotted versus distance along the corallite growth axis, carbon and oxygen isotopic ratios define clear and quasi-regular sinusoids (Fig. 3.6). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of coral aragonite are easily altered by replacement of the skeleton by

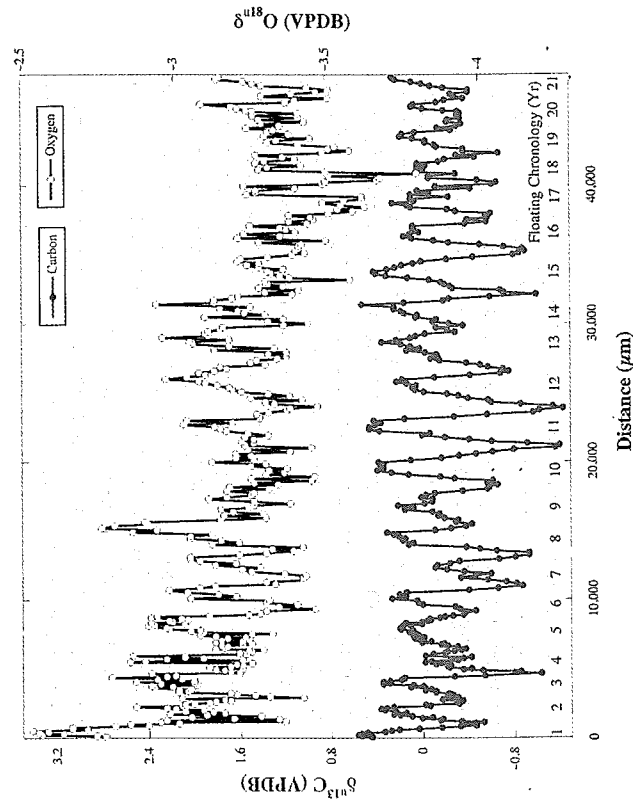


Fig. 3.6 Carbon and oxygen isotopic profiles from *G. hilli*. Floating chronology refers to individual growth years as defined by sinusoids in stable isotopic ratios

secondary calcite or infilling of pore space by marine or meteoric cements. Oxygen isotopic ratios are more likely to be diverted from their original values by diagenetic alteration than carbon isotopic ratios (Key et al., 2005), and this may explain the more regular sinusoids defined by the latter. But carbon isotopic compositions can also be shifted significantly by interaction with ^{12}C -enriched groundwaters reflecting a terrestrial vegetation fingerprint (Hurley and Lohmann, 1989). The well-behaved sinusoids in $\delta^{13}\text{C}$ values, coupled with limited visual evidence for diagenetic alteration, suggest that this sample of *G. hilli* preserves its primary isotopic signals, if not pristinely, then at least with high fidelity.

Oxygen isotopic ratios of coral aragonite reflect several parameters, but the primary controls are the temperature and oxygen isotopic composition of the ambient seawater (Emiliani et al., 1978; Fairbanks and Dodge, 1979; McConnaughey, 1989). Corrège (2006) calculated an average relationship of $0.18\text{‰} - 0.22\text{‰}/^\circ\text{C}$ from published oxygen isotopic studies of corals. Seasonal ranges in $\delta^{18}\text{O}$ values of the Gurabo *G. hilli* average $0.4\text{‰} \pm 0.1\text{‰}$ (1 σ) (Fig. 3.6), a value that if attributed solely to water temperature, corresponds to an average seasonal range of $\sim 2^\circ\text{C}$, nearly identical to modern values from Haiti (Shutz et al., 1985). However, seasonal or long-term changes in ocean water $\delta^{18}\text{O}$ values and salinity, due to evaporation, meteoric precipitation (direct or via riverine discharge), or upwelling, can mask the temperature signals in coral $\delta^{18}\text{O}$ values (Swart et al., 2001; Watanabe et al., 2002).

While both the temperature and the oxygen isotopic composition of ambient seawater control the $\delta^{18}\text{O}$ value of coral aragonite, Sr/Ca ratios in corals have been demonstrated to reflect only water temperature (Beck et al., 1992; Albert and McCulloch, 1997; Gagan et al., 1998). Exceptions that may result in a breakdown of the Sr/Ca-water temperature relationship include corals growing in exceptionally cool waters ($<18^\circ\text{C}$) where inorganic fractionation and/or coral metabolisms are reduced (Shen et al., 1996), in areas of significant upwelling with deep waters of unusual Sr/Ca ratio (De Villiers et al., 1994), or in symbiont-bearing forms (Cohen et al., 2002). However, the Sr/Ca paleothermometer has been demonstrated to record water temperature accurately in many typical marine settings (Schrag and Linsley, 2002), and thus combining oxygen isotope (reflecting temperature + salinity) and Sr/Ca ratios (reflecting temperature) from the same samples allows the parsing of changes in both water temperature and salinity (Ren et al., 2002).

In order to perform this calculation, we obtained Sr/Ca ratios from splits of alternate (odd-numbered) sample powders. Sr/Ca ratios from sinusoids coincident with stable isotope ratios (Fig. 3.7), with the seasonal range in Sr/Ca ratios averaging 0.3 ± 0.1 mmol/mol. Converting these values to a seasonal temperature range requires knowing the exact Sr/Ca – temperature calibration for *G. hilli*. However the only published Sr/Ca calibration for *Goniopora* was constructed using samples from the South China Sea (Yu et al., 2004) (*Goniopora* are extinct in the Caribbean). The relationship defined by Yu et al. (2004) is:

$$\text{SST}(^\circ\text{C}) = -32.8 (\pm 3.5) \times \text{Sr/Ca}_{(\text{mmol/mol})} + 315 (\pm 31) \quad (r = -0.999; n = 48) \quad (1)$$

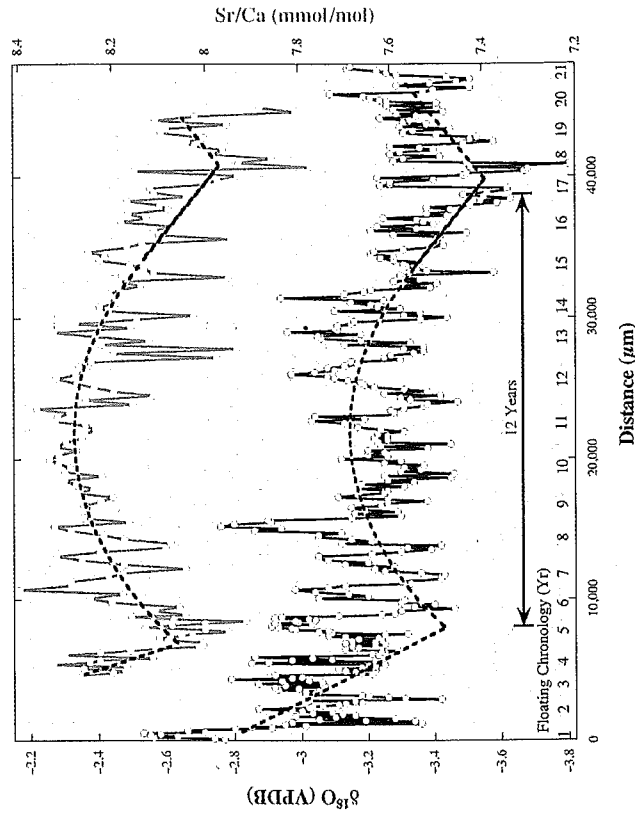


Fig. 3.7 Comparison of oxygen isotopic and Sr/Ca ratios. Sr/Ca analyses were conducted on splits of alternate powders, thus the relatively high sample density for oxygen isotopic analyses. Sr/Ca ratios for growth years 1–2 and 20–21 are not reported owing to analytical errors and insufficient sample powder, respectively. Note the suggested ~ 12 -year “cycle” in both records (dashed line) –

Using this relationship, the 0.3 mmol/mol average seasonal range in Sr/Ca ratios in the *G. hilli* coral translates to a $\sim 9^\circ\text{C}$ range in water temperature and an average annual water temperature of 14°C . But Sr/Ca – temperature calibrations have been shown to vary significantly based on factors including species. The Sr/Ca – temperature relationships for *Porites* and various other genera (*Pocillopora*, *Montipora*, *Favona*, *Diploria*, *Montastraea*, *Diploastrea*, and *Goniopora*) range from -0.03 to -0.09 mmol/mol/ $^\circ\text{C}$ and -0.03 to -0.08 mmol/mol/ $^\circ\text{C}$, respectively. Applying the maximum Sr/Ca – temperature relationship from *Porites* (-0.09 mmol/mol/ $^\circ\text{C}$) to *G. hilli*, on the other hand, corresponds to only $\sim 3^\circ\text{C}$ seasonal temperature range. Complicating matters further is the fact that marine Sr/Ca ratios have changed through the Cenozoic, which would affect Sr/Ca – temperature calibrations (Tripathi et al., 2001; Steuber, 2002). Thus, applying Recent *Goniopora* Sr/Ca – temperature calibrations to a Miocene *G. hilli* introduces significant uncertainty, and temperature and salinity reconstructions must be viewed with caution.

However, keeping in mind these caveats, and assuming that the slope of the Sr/Ca – temperature calibration is correct, we can attempt to reconstruct late Miocene

salinity and water temperature from *G. hilli* $\delta^{18}\text{O}$ and Sr/Ca ratios. The 7°C discrepancy between the oxygen isotope- (2°C) and Sr/Ca-based (9°C) seasonal temperature ranges can be accounted for by a $\sim 1.4\text{‰}$ ($7^\circ\text{C} \times -0.2\text{‰}/^\circ\text{C}$) suppression of the seasonal range in ocean water $\delta^{18}\text{O}$ values. For example, a winter influx of isotopically light, low salinity water would decrease ocean $\delta^{18}\text{O}$ values and offset the increase in coral $\delta^{18}\text{O}$ values due to the drop in water temperature. Alternatively, evaporative enrichment of ^{18}O in surface waters during the summer would offset the decrease in coral $\delta^{18}\text{O}$ values due to higher temperatures. Muting of the range in coral $\delta^{18}\text{O}$ values due to salinity changes has been observed in the western Pacific for corals dating to the Recent and the middle Holocene (Gagan et al., 1998), and significant long-term salinity changes in ambient ocean surface water were documented for the Little Ice Age by Hendy et al. (2002).

How might this have occurred in the Miocene Caribbean? Studies linking the covariance of ocean water $\delta^{18}\text{O}$ values and salinity in the modern Atlantic along eastern North America reveal changes in $\delta^{18}\text{O}$ values of 0.2‰ – 0.6‰ per part per thousand (ppt) salinity (Fairbanks, 1982; Swart et al., 1996, 2001), with the lowest value documented from the Caribbean Antilles, the geographically closest location included in the study. Using the Antilles value of 0.2‰ $\delta^{18}\text{O}$ /ppt salinity, this shift in oxygen isotopic composition translates to a 7 ppt decrease in the seasonal range of ocean water salinity. Discharge from the Orinoco and Amazon rivers routinely forms plumes of low salinity waters (>2 ppt below the regional average) that travel more than 2,000 km from their sources and toward the central and eastern Caribbean (Hu et al., 2004), but discharge from these rivers would have to be increased significantly to sufficiently suppress ocean salinities in the central Caribbean. Alternatively, upwelling of isotopically distinct bottom waters could have played a role in shifting surface ocean $\delta^{18}\text{O}$ values, but the amount and seasonality of late Miocene upwelling and surface flow in the region currently occupied by the Dominican Republic is poorly constrained (Collins, 1996). Barium, with its distinct depth profile in most ocean basins, is a commonly used proxy for upwelling, and future coupling of Ba, Sr/Ca and $\delta^{18}\text{O}$ analyses might help to constrain the magnitude and seasonality of upwelling in the central Caribbean during the late Miocene.

Longer-term trends in temperature/salinity are also suggested by multi-annual $\delta^{18}\text{O}$ and Sr/Ca trends. The *G. hilli* record is insufficient to allow a statistical analysis, but the minima in both oxygen isotope and Sr/Ca ratios suggest a ~ 12 -year cycle (Fig. 3.7). Greer and Swart (2006) report 18–20-year cycles in modern precipitation near the Dominican Republic (Haiti) and in cycles of similar scale preserved by oxygen isotopic anomalies in middle Holocene corals from the Dominican Republic. Both cycles are tied to shifts in the position of the ITCZ (Greer and Swart, 2006). In addition, these authors also suggest a 12–13-year temperature cycle based on Haitian temperature data, but the punctuated nature of their record precludes statistical analysis. The construction of a considerably longer *G. hilli* isotopic record, currently underway, will provide a clearer understanding of the nature of decadal-scale climate cycles.

3.5 Conclusions

Stable isotopic ratios from a well-preserved *Goniopora hilli* suggest that the seasonal range in shallow marine temperature during one 21-year span in the late Miocene was approximately 2°C . Considerably larger seasonal temperature ranges suggested by Sr/Ca ratios appear to reflect a misfit between a Miocene *G. hilli* and Recent *Goniopora* sp. The well-defined sinusoids in both Sr/Ca and carbon and oxygen isotopic ratios argue against diagenetic alteration having significantly overprinted the original isotopic signals, and thus the remaining and as yet unanalyzed portions of this coral may help to more clearly define late Miocene shallow marine seasonality in the central Caribbean.

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Chapter 4 Assessing the Effects of Taphonomic Processes on Palaeobiological Patterns using Turbinid Gastropod Shells and Opercula

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4.1 Introduction

For nearly 30 years the Dominican Republic Neogene has served as a productive research system for exploring a broad array of palaeobiological topics, including speciation (e.g., Cheetham, 1986, 1987; Nehm and Geary, 1994; Nehm, 2005), intraspecific morphological variation (e.g., Anderson, 1994, 1996; Foster, 1986; Nehm, 2001), palaeoecological reconstruction (e.g., Vokes, 1989; Costa et al., 2001), and faunal

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