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Reproducibility of geochemical and climatic signals in the Atlantic coral *Montastraea faveolata*

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[1] Monthly resolved, 41-year-long stable isotopic and elemental ratio time series were generated from two separate heads of *Montastraea faveolata* from Looe Key, Florida, to assess the fidelity of using geochemical variations in *Montastraea*, the dominant reef-building coral of the Atlantic, to reconstruct sea surface environmental conditions at this site. The stable isotope time series of the two corals replicate well; mean values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are indistinguishable between cores (compare 0.70‰ versus 0.68‰ for $\delta^{13}\text{C}$ and -3.90‰ versus -3.94‰ for $\delta^{18}\text{O}$). Mean values from the Sr/Ca time series differ by 0.037 mmol/mol, which is outside of analytical error and indicates that nonenvironmental factors are influencing the coral Sr/Ca records at Looe Key. We have generated significant $\delta^{18}\text{O}$ –sea surface temperature (SST) ($R = -0.84$) and Sr/Ca–SST ($R = -0.86$) calibration equations at Looe Key; however, these equations are different from previously published equations for *Montastraea*. Variations in growth parameters or kinetic effects are not sufficient to explain either the observed differences in the mean offset between Sr/Ca time series or the disagreement between previous calibrations and our calculated $\delta^{18}\text{O}$ –SST and Sr/Ca–SST relationships. Calibration differences are most likely due to variations in seawater chemistry in the continentally influenced waters at Looe Key. Additional geochemical replication studies of *Montastraea* are needed and should include multiple coral heads from open ocean localities complemented whenever possible by seawater chemistry determinations.

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1. Introduction

[2] Measurements of sea surface temperature (SST) and sea surface salinity (SSS) in the tropical oceans are spatially and temporally limited, which hinders understanding of tropical ocean-atmosphere dynamics on subcentennial time-scales. Increasing our understanding of tropical climate prior to the instrumental period requires the use of proxy indicators of tropical surface ocean variability. The geochemistry of coral skeletons is one such climate proxy, which also has the added benefit of having subannual resolution. Stable isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and elemental ratio variations (Sr/Ca, Mg/Ca) are the most widely used coral-based climate proxies.

[3] The $\delta^{18}\text{O}$ of the coral skeleton varies in response to changes in both temperature and seawater $\delta^{18}\text{O}_w$ (δ_w). The δ_w , in turn, has been shown to vary linearly with patterns of salinity although the slope of that relationship varies as a function of location [Fairbanks *et al.*, 1992]. Coral skeletal $\delta^{18}\text{O}$ records alone have proven an effective tool in tracking SST [e.g., Fairbanks and Dodge, 1979], δ_w [e.g., Cole *et*

al., 1993; Linsley *et al.*, 1994; Le Bec *et al.*, 2000], and combined variations in SST and δ_w [Gagan *et al.*, 2000].

[4] Coral Sr/Ca thermometry has been increasingly used as an independent means to estimate SST. Some workers have used paired measurements of coral Sr/Ca and $\delta^{18}\text{O}$ to estimate δ_w , and thus salinity over a variety of time periods [McCulloch *et al.*, 1994; Gagan *et al.*, 1998; Cardinal *et al.*, 2001; Correge *et al.*, 2004; Kilbourne *et al.*, 2004]. Sr/Ca ratios of biogenic aragonite are controlled by both a temperature-dependent distribution coefficient and the Sr/Ca ratio of the fluid from which it is precipitated (Sr/Ca_w) [Kinsman and Holland, 1969; Smith *et al.*, 1979]. As a result of the long residence times of strontium and calcium in the global ocean (6 and 0.7×10^6 years, respectively, for Sr and Ca [Pilson, 1998]), seawater is often assumed to have an invariant Sr/Ca_w ratio over the time periods of most coral-based climate reconstructions. Recent work by several investigators has questioned this assumption. de Villiers *et al.* [1994] found small variations in Sr/Ca_w in the Galapagos Islands associated with upwelled waters from depth. These Sr/Ca_w variations translate into temperature variations $\leq 0.2^\circ\text{C}$. Direct measurements of Pacific Sr/Ca_w indicate a difference of ~ 0.03 mmol/mol ($\sim 0.5^\circ\text{C}$) between water at the surface and ~ 100 m [de Villiers *et al.*, 1994; Alibert *et al.*, 2003]. Time series measurements of Sr/Ca_w taken from the shallow waters of southern Taiwan indicate a range of 0.033 mmol/mol over the course of one year [Shen *et al.*, 1996]. More recent data from the Indian Ocean adjacent to Western Australia show large variations in surface Sr/Ca values ranging from 8.6 to 9.2 mmol/mol [de Deckker,

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2004]. Seawater Sr concentrations also respond to the sequestering of Sr in the celestite (SrSO_4) skeleton of acantharian populations [Bernstein *et al.*, 1992]. These marine pelagic protists are globally distributed in surface oligotrophic waters and may also impact Sr/Ca values measured in corals [Brass, 1980; de Deckker, 2004]. Indeed, recent studies have suggested that seawater Sr variations greatly exceed those of seawater Ca variations, and this variation is thought to be a major factor responsible for disparities in Sr/Ca thermometers in *Porites* [Sun *et al.*, 2005]. Thus, despite the long ocean residence times of Sr and Ca, several studies have begun to address the potential impact of both the spatial and temporal variability of Sr/Ca_w in open and coastal oceans.

[5] Coral Sr/Ca may also be influenced by variations in coral growth, specifically extension and calcification rates. de Villiers *et al.* [1994] concluded that slower (faster) extension rates were associated with higher (lower) *Pavona* Sr/Ca ratios creating an offset between two different sampling transects on the same coral with different extension rates (6 versus 12 mm/yr). However, other studies have shown no relationship between *Porites* Sr/Ca and skeletal extension rate over a much larger range of extension rates (8–24 mm/yr) [Shen *et al.*, 1996; Alibert and McCulloch, 1997; Gagan *et al.*, 1998]. Moreover, Alibert and McCulloch [1997] demonstrated that coral Sr/Ca is also independent of calcification rate by showing the similarity of Sr/Ca time series in two separate specimens with contrasting growth parameters. Alibert and McCulloch [1997] also emphasized the importance of sampling the major growth axis as opposed to a marginal region between adjacent fans of corallites to minimize any growth-related effect on Sr/Ca. There have been few studies on Sr/Ca variations in *Montastraea*, but in one such study Swart *et al.* [2002] indicated an impact on coral Sr/Ca by both sampling density and the difficulties of sampling a complex skeleton; however, they concluded that there is a robust and highly significant relationship between Sr/Ca and SST in *Montastraea*.

[6] Coral-based climate reconstructions of climate variability in the Atlantic in general, and in the Caribbean specifically, have lagged behind that of the Pacific and Indian Oceans largely because of the community's focus on interannual to centennial-scale climate variability in the other tropical ocean basins. *Montastraea* has proven to be a very utilitarian coral and previous workers have used these corals to develop records of ocean circulation [Druffel, 1983; Druffel and Suess, 1983], upwelling [Reuer *et al.*, 2003; Guilderson *et al.*, 2005], and temperature and insolation [Fairbanks and Dodge, 1979; Gischler and Oschmann, 2005]. Also, application of a paired geochemical approach (Mg/Ca, $\delta^{18}\text{O}$) has been employed over short time windows to assess changes in temperature and salinity in the Caribbean during the Little Ice Age [Watanabe *et al.*, 2001b]. In spite of previous work, a better understanding of continuous interannual to centennial-scale climate variability in the tropical Atlantic is needed, and it is logical that the dominant reef-building coral of the Atlantic, *Montastraea*, will play a significant role in any coral-based climate reconstruction of this region.

[7] Previous studies have investigated geochemical reproducibility in *Porites* over decadal timescales [Guilderson and Schrag, 1999; Linsley *et al.*, 1999; Stephans *et al.*, 2004], whereas in *Montastraea* it has only been addressed over a period of a few years [Leder *et al.*, 1996; Swart *et al.*, 1996c; Watanabe *et al.*, 2002]. The next logical and necessary step is to assess the reproducibility of geochemical signals of climate variability in *Montastraea* on decadal timescales. In this study we use geochemical time series generated from two *M. faveolata* coral heads drilled at Looe Key, Florida, to assess how well these two records replicate, and we evaluate whether the geochemical variations in these records reflect environmental variability at this site.

2. Methods

2.1. Setting

[8] Looe Key, Florida (Figure 1), is a part of the Florida Keys National Marine Sanctuary and is located in the central portion of the Florida Keys (24°33.4'N, 81°24.75'W). Bihourly measurements of SST were made at Looe Key Reef from 1990 to 1995 and from 1997 to 1999 (H. Hudson, unpublished data, 1999). These highly resolved, but short, in situ SST time series were augmented with 1° × 1° gridded SST data from the HadISST1 database [Rayner *et al.*, 2003] extracted at 24°N, 81°W. In situ data were resampled to monthly resolution and compared with the gridded data, which revealed that the gridded SST product sometimes underestimates winter SST by up to 2°C (Figure 2a). We created a composite SST time series by adjusting the gridded data set based upon its linear relationship with in situ SST (Figure 2b) from 1961 to 2002, excluding the 7 years of in situ SST. Mean annual SST for 1961–2002 is 26.6°C (±0.2°C, σ_t). Average maximum SST values (30.0°C) occur in August and average minimum SST values (23.1°C) occur in February. These monthly SST extremes (summer SST–winter SST) produce an average annual cycle of 6.9°C at Looe Key. As an additional check on our augmentation of the gridded data set, we compare our temperature time series with independent measurements of temperature collected as part of the SERC-FIU Water Quality Monitoring Network taken near quarterly at the reef site from 1995 to 2003 (Figure 2b) and find that the two data sets agree well.

[9] Precipitation patterns over south Florida resemble those typical of subtropical systems with the largest amount of rainfall received in the warm summer months (July–September) and the least in the winter. Determinations of salinity are also available directly from Looe Key reef on a near quarterly basis collected at the same time as the independent temperature measurements. Data from this site indicate a range of salinity >2 psu from 1995 to 2003 (Figure 2c). A more complete, although spatially averaged (~175 nm², centered on Looe Key), time series over the same time interval indicates a general in-phase relationship between SSS and SST with maximum values in salinity coinciding with maximum SST; however, the phasing of SSS and SST is somewhat variable with a few seasons (i.e., summer 1998 and winter 2001) completely out of phase. Low-salinity events were recorded in March 1996, August

Figure 1. Location map of Looe Key, Florida, United States. Looe Key resides on the seaward (south) side of the Florida Keys and within the Florida Keys National Marine Sanctuary. The study areas of both *Surge and Lohmann* [2002] and *Leder et al.* [1996] are marked by dashed circles.

1998, and December 1999. In each of these months, precipitation in southern Florida was below normal, suggesting the freshwater source is continental rather than coming from direct precipitation at the site. The three highest salinity measurements in the record (June 1997, May 1999, and June 2001) all occur in the spring when latent heat flux and evaporation rates are the highest [Virmani and Weisberg, 2003]. Despite the short record length, there appears to be an annual component to SSS variability in addition to variation independent of the annual cycle of SST.

2.2. Coral Sampling

[10] Two cores of *Montastraea faveolata* (LK1, LK23) were collected in August 2002 in 4 m of water at the seaward side of Looe Key reef from within a 300 m radius of each other. *Montastraea faveolata* has been previously termed *Montastraea annularis*, but recently has been separated into three sibling species [Knowlton et al., 1992] with *M. faveolata* being described as the large massive form that is usually utilized for paleoclimate work. Both LK1 and LK23 cores are 3 cm in diameter and 40 and 31.5 cm long, respectively. Each core was slabbed into three portions: two outer pieces and a center flat slab with a thickness of ~5 mm. X-radiographs were made from each flat slab and show clear annual banding (Figure 3). Microsampling for geochemical analysis was performed using a computer-controlled triaxial drill. The center flat portion of LK1 was unavailable for geochemical and additional densitometry analysis; therefore we performed microsampling of LK1

along the inward facing (flat) outer portion of the core. The top portion of LK1 chipped off during initial sampling so a parallel segment (~1.5 years) was drilled and the data from this segment were spliced into the time series. Powder from each sample was collected along the major axis of growth on the exothecal wall at 0.5 mm increments using a 1 mm diameter drill bit which penetrated each slab to a depth of 1 mm. This sampling yields an average sampling rate of ~14 samples/year. Horizontally sampled portions of the slab were performed in the same manner with a 0.5 mm forward step. High-resolution data from LK23 (40 samples/year) were likewise collected with a 0.5 mm diameter drill bit with a reduced forward movement of the drill (~0.2 mm step). A more detailed discussion of sampling effects is found in section 4.2.1.

2.3. Densitometry

[11] Coral slab LK23 was X-radiographed for densitometry after geochemical samples were collected. Coral slabs and wedges were placed on Kodak Industrex AA440 Ready-pack film and exposed at 70 KvP and 15 ma for 7.0 s with a source to object distance (SOD) of 1 m. A sheet of aluminum was X-radiographed at the same settings to remove influences of the inverse square law and heel effects. Films were developed manually based on manufacturer's specifications. Film negatives were digitized using a medical film single-line scanner.

[12] Relative optic density of the X-radiograph was calibrated to skeletal bulk density of the coral slab using the CoralXDS+program (see K. P. Helmle et al., CoralXDS-The

Figure 2. (a) Time series comparison of in situ (solid) and gridded (dashed) sea surface temperature (SST) data (HadISST1.1 [Rayner *et al.*, 2003]) over their common period of overlap. Summer maximum temperatures are well matched in the records; however, the gridded SST product tends to underestimate the SST minima. Discrepancies in the winter SST can be as large as 2°C. The equation relating these two variables ($\text{HadISST} = 0.83(\text{in situ}) + 4.95$, $R = 0.98$ and $N = 103$) was used to adjust the gridded SST time series, which extends back to 1870, to create an augmented SST record (HadISST*) that more accurately reflects local, reef site SST. (b) Comparison between temperatures derived from the augmented in situ gridded data set (HadISST*, dashed line) and independent daily measurements taken approximately quarterly at Looe Key reef (solid line, open circles). (c) Spatially averaged ($\sim 175 \text{ nm}^2$) approximately quarterly salinity measurements taken about Looe Key reef from 1995 to 2004.

Coral X-radiograph Densitometry System, Nova Southeastern University, National Coral Reef Institute, posted 4 September 2002, available at <http://www.nova.edu/ocean/coralxds/index.html>). Densitometry transects were collected adjacent to, but not overlapping, the drilling trough already present on the slab. Annual bands were delimited based on the zero point of the second derivative (inflection point) between density maxima and minima from a smoothed cubic spline curve of the density data. Density data (g/cm^3) were averaged for annual periods using the inflection points of each high-density band as the delimiter. Annual linear extension data (cm) were the distances from the inflection points at the end (top) of each high-density band. Calcification data (g/cm^2) were calculated as the product of annual linear extension and annual density data.

[13] Direct densitometry measurements of LK1 were unobtainable because the microdrilled portion of the core had been embedded with epoxy to a metal frame; however, an X-radiograph taken of the original center slab was digitized and used for gray scale luminance measurements (0–255) which provides accurate linear extension data, but cannot be used for collecting density or calcification data because of the lack of a known wedge standard and background X-radiograph.

2.4. Geochemical Analysis

[14] The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses were performed by reacting $\sim 30\text{--}80 \mu\text{g}$ of coral powder with phosphoric acid at 70°C in a Kiel III autosampling device connected to a ThermoFinnigan Delta PlusXL mass spectrometer. Replicate analyses of NBS-19 ($n = 274$) run alongside the coral samples indicate an instrumental precision of 0.02‰ and 0.06‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. All values are reported in standard delta notation relative to the VPDB isotopic standard using the conventional notation.

[15] Elemental analyses of Sr/Ca and Mg/Ca were performed using a Perkin-Elmer 4300 DV ICP-OES. Sample preparation involved diluting $\sim 75\text{--}300 \mu\text{g}$ of coral powder in variable volumes of 2% trace metal grade HNO_3 to achieve a target solution concentration of $\sim 20 \text{ ppm Ca}$. Internal gravimetric references were run between every sample to correct for machine drift following the methods of Schrag [1999]. Precision of our internal gravimetric standard (1σ) was 0.009 mmol/mol for Sr/Ca and 0.013 mmol/mol for Mg/Ca ($n = 256$). The accuracy of this standard's Sr/Ca value has been externally verified by mass spectrometric analysis at the University of Minnesota Isotope Laboratory. As an additional measure of precision, homogenized powder of *Porites lutea* was included in each

Figure 3. Positive X-radiograph images of slabs from coral cores (left) LK1 and (right) LK23. Distinct density banding is evident in both slabs and is in a near-perpendicular orientation with respect to the axis of the core. Select years are noted in each slab for comparison. Drill paths for each core are indicated by solid vertical lines on each coral slab.

run. These values indicate a precision (1σ) of 0.016 mmol/mol for Sr/Ca and 0.044 mmol/mol for Mg/Ca ($n = 363$).

2.5. Data Analysis

[16] Geochemical variations versus depth were translated to a time axis by pairing maximum (minimum) Sr/Ca values with minimum (maximum) SST using the Analyseries software [Paillard *et al.*, 1996]. The resultant time series were interpolated to monthly values for comparison with the instrumental SST time series. This age model was verified at an annual scale by comparison with the timing of the annual density-banding pattern. Despite good time-depth control at an annual scale, subannual timing cannot be verified by use of densitometry methods. We estimate an average time assignment error at any one point within a particular year to be ~ 2 months. No evidence was present to indicate any type of physical or chemical hiatus over the length of both cores.

[17] Correlation values are reported as Pearson Product Moment correlation coefficients and are significant at the 95% confidence interval or greater. Climatology calculations are commensurate with the time period of coral growth, 1961–2002. Statistical significance of the calculation of means (i.e., error estimates) is a function of the number of degrees of freedom which is dependent upon the number of independent observations. Given the serial order correlation that exists in a time series because of the annual cycle, the calculated number of degrees of freedom was determined by use of a runs test [see Davis, 2002].

3. Results

3.1. Coral Skeletal Geochemistry

[18] Well-defined annual cycles are characteristic of the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Sr/Ca time series (Figure 4 and Table 1). The Mg/Ca time series (not shown) exhibits an irregular pattern which is presumably due to either the varying presence of organic material and inorganic detritus [Watanabe *et al.*, 2001a] or small contributions of brucite ($\text{Mg}(\text{OH})_2$) [Buster and Holmes, 2006] and will not be discussed.

[19] The climatology of the $\delta^{13}\text{C}$ record indicates peak values occur every year in June or August (LK1 and LK23, respectively) with the most negative values occurring in December. Mean $\delta^{13}\text{C}$ values are $0.70\text{‰} \pm 0.06$ (σ_x) and $0.68\text{‰} \pm 0.05$ (σ_x) for LK1 and LK23. The overall difference in mean values between LK1 and LK23 over the 41 years of record is the same as analytical error (0.02‰ , Figure 4) and is small when compared with the results of previous studies (0.82‰ [Watanabe *et al.*, 2002] and 0.17‰ [Swart *et al.*, 1996c]). However, when taken as the absolute value of differences between each monthly value in the two time series, the average difference becomes 0.46‰ . The difference drops to 0.24‰ after removing variability occurring at less than 2 years. A significant long-term trend toward more negative $\delta^{13}\text{C}$ values is present in both time series and is $-0.02\text{‰}/\text{year}$.

[20] Mean $\delta^{18}\text{O}$ values of LK1 and LK23 during 1961–2002 differ by 0.04‰ (LK1, $-3.90\text{‰} \pm 0.02$ (σ_x); LK23, $-3.94\text{‰} \pm 0.03$ (σ_x)) and are not significantly different (t test, $p > 0.99$). There is a $0.21 \pm 0.01\text{‰}$ (σ_x) difference in

Figure 4. Time series (1961–2002) of (a) adjusted SST, (b) coral Sr/Ca, (c) coral $\delta^{18}\text{O}$, (d) coral $\delta^{13}\text{C}$, and (e) annual extension rate. Data from coral core LK1 (shaded lines, triangles) and LK23 data (dashed lines, diamonds) are shown in Figures 4b–4e. Annual extension rates are measured from the preceding summer (i.e., 1978 is summer of 1977 to summer 1978). Mean values of each geochemical variable for each core are to the right of each geochemical time series. Error bars on mean values are $\pm 1\sigma$. Standard errors of each mean value are reported in the text.

absolute value between each monthly value in the two time series; this value drops almost in half to $0.11 \pm 0.01\%$ (σ_x) at periods greater than 2 years. The difference in monthly $\delta^{18}\text{O}$ values reaches a maximum around 1976. This difference is explained in part by the larger amplitude of LK23 compared with LK1 from 1970 to 1978 (Figure 4). This may be explained by the larger growth rates exhibited

by LK23 over LK1 during this time interval, which implies that periods of higher extension rate are yielding better resolution of the annual cycle. The climatological annual cycle in $\delta^{18}\text{O}$ is characterized by average amplitudes of 0.55‰ (LK1) and 0.60‰ (LK23) with the most negative $\delta^{18}\text{O}$ values occurring in August and the most positive values in February, which corresponds with the warmest

Table 1. Summary of Geochemical Data for Corals LK1 and LK23 for 1961–2002^a

	Mean Plus/Minus Standard Error			Amplitudes		
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Sr/Ca	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Sr/Ca
LK 1	-0.70 ± 0.06	-3.90 ± 0.02	9.193 ± 0.007	1.3	0.55	0.191
LK 23	-0.68 ± 0.05	-3.94 ± 0.03	9.230 ± 0.004	1.1	0.65	0.194
Average	-0.69 ± 0.05	-3.92 ± 0.02	9.211 ± 0.006	1.2	0.60	0.192
Mean Monthly Difference	0.46 ± 0.03	0.21 ± 0.02	0.068 ± 0.005	0.22	0.09	0.004

^aMean monthly difference between the cores (LK1–LK23) is calculated as the average of the absolute value of monthly differences. Amplitudes are calculated as the difference between the maximum and minimum climatological values. Isotope values are reported in ‰ VPDB and Sr/Ca is reported in mmol/mol.

and coolest months of the year. The coincidence of minimum and maximum values in $\delta^{18}\text{O}$ and SST was not forced in the creation of the age model for each of these time series.

[21] Mean Sr/Ca values for the two cores from 1961 to 2002 are 9.193 ± 0.007 (σ_x) and 9.230 ± 0.007 (σ_x) mmol/mol and the 0.037 mmol/mol difference in means is significant ($p > 0.95$). Amplitudes of the seasonal cycle based on the climatological cycle are comparable between the two coral Sr/Ca records at ~ 0.19 mmol/mol. The absolute value of difference between each monthly value in the two time series is 0.068 ± 0.004 (σ_x) mmol/mol and after removing variability occurring at < 2 years the value drops to 0.055 ± 0.005 (σ_x) mol/mol. The variances of each time series are statistically equivalent (F test, $p > 0.95$) suggesting that both records are capturing the same variability despite difference in the means taken over the entire time interval of study.

3.2. Geochemical Relationships With SST

[22] The regression relationship developed for the two-core averaged (i.e., stacked) monthly time series of $\delta^{18}\text{O}$ -SST and Sr/Ca-SST over the 41 years of monthly variation are as follows:

$$\delta^{18}\text{O} = -0.101(\pm 0.005) * \text{SST} - 1.24(\pm 0.13),$$

$$[n = 494, R = -0.84] \quad (1)$$

$$\text{Sr/Ca} = -0.0282(\pm 0.002) * \text{SST} + 9.962(\pm 0.035),$$

$$[n = 494, R = -0.86] \quad (2)$$

Individual regression equations for both $\delta^{18}\text{O}$ and Sr/Ca on SST are summarized in Tables 2 and 3. Generating the regression using just the maximum and minimum values each year yields a slope within error bars (2σ) for $\delta^{18}\text{O}$ -SST (-0.091 ± 0.01 , $n = 83$, $R = -0.93$) and a slightly more negative slope for Sr/Ca-SST (-0.0298 ± 0.004 , $n = 83$, $R = -0.95$). While the relationships with SST are not significantly different between LK1, LK23, or in the averaged data, they are significantly different from the equations of both *Leder et al.* [1996] and *Swart et al.* [2002] (Table 2). In fact, application of the Sr/Ca-SST relationship of *Swart et al.* [2002] to the Looe Key data yields a mean SST that is $> 6^\circ\text{C}$ less than observed SST and merits closer inspection of this result. Regression equations of both $\delta^{18}\text{O}$ and Sr/Ca with the ~ 7 years of in situ SST reveal statistically equivalent relationships to the regression equations generated using gridded, composite SST. The difference in mean $\delta^{18}\text{O}$ values between cores translates to a difference in SST of $\sim 0.4^\circ\text{C}$ using the stacked $\delta^{18}\text{O}$ -SST equation and is within our analytical error. However, the overall difference in the mean Sr/Ca values between the two cores equates to 1.3°C using the stacked Sr/Ca-SST equation. From a mean annual (August–July) perspective (Figure 5), there are episodes of general agreement, yet neither LK1 nor LK23 are precise recorders of temperature over the entire time

Table 2. Regression Relationships for $\delta^{18}\text{O}$ -SST and Sr/Ca-SST From 1961 to 2002^a

	RMA		OLS		R	SE_m	SE_b
	m	b	m	b			
	$\delta^{18}\text{O}$ -SST						
LK 1	-0.108	-1.02	-0.079	-1.79	-0.73	± 0.007	± 0.18
LK23	-0.119	-0.76	-0.090	-1.56	-0.75	± 0.008	± 0.19
Stack	-0.101	-1.24	-0.085	-1.67	-0.84	± 0.005	± 0.13
Stack, max/min	-0.091	-1.52	-0.084	-1.69	-0.93	± 0.004	± 0.10
<i>Leder et al.</i> [1996]			-0.22	1.18		± 0.02	± 0.10
	Sr/Ca -SST						
LK 1	-0.0324	10.054	-0.0233	9.812	-0.72	± 0.002	± 0.054
LK23	-0.0321	10.083	-0.0252	9.900	-0.79	± 0.002	± 0.048
Stack	-0.0282	9.962	-0.0243	9.856	-0.86	± 0.002	± 0.035
Stack, max/min	-0.0298	10.000	-0.0284	9.962	-0.95	± 0.002	± 0.054
<i>Swart et al.</i> [2002]			-0.0471	10.165	-0.88		

^aErrors are in 1σ ; $n = 494$ for all Looe Key equations except the maximum/minimum (max/min) regression is $n = 83$. Reduced major axis (RMA) and ordinary least squares (OLS) equations are provided for comparison along with literature values. SE denotes standard error. Equations are in the form ($\delta_c - \delta_w$) = $m\text{SST} + b$ and $\text{Sr/Ca} = m\text{SST} + b$.

Table 3. Pearson Product Moment Correlation Coefficients^a

	LK1			LK23			SST
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Sr/Ca	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Sr/Ca	
LK1 $\delta^{13}\text{C}$		0.09	0.08	0.31	-0.14	-0.02	0.12
LK1 $\delta^{18}\text{O}$	-0.30		0.35	0.22	0.09	0.20	-0.28
LK1 Sr/Ca	-0.25	0.67		0.02	0.09	-0.04	-0.15
LK23 $\delta^{13}\text{C}$	0.59	-0.19	-0.21		0.05	0.32	-0.04
LK23 $\delta^{18}\text{O}$	-0.45	0.57	0.56	-0.28		0.51	-0.22
LK23 Sr/Ca	0.35	0.63	0.53	-0.14	0.78		-0.31
SST	0.49	-0.73	-0.72	0.38	-0.75	-0.79	

^aBold values indicate $p \geq 0.99$. Italicized (nonitalicized) values are correlation coefficients between anomalies (original monthly time series).

interval. The greatest monthly offset between the two Sr/Ca records occurs around 1965 and equates to $\sim 7^\circ\text{C}$ (Figure 4) and is clearly not indicative of actual SST conditions experienced in situ on the reef.

[23] Direct regression of $\delta^{18}\text{O}$ onto SST does not take into account variations in δ_w which can either contribute to or subtract from estimates of SST. Application of the equation of Leder *et al.* [1996] to the Looe Key data requires a substitution of 0.8‰ for δ_w to obtain the correct mean value of instrumental SST. Additional variation in δ_w must occur to account for the difference in variance between $\delta^{18}\text{O}$ -SST and instrumental SST time series. The range in salinity from the quarterly measurements taken at the reef site 1995–2004 (2.1 psu) equates to a range in δ_w of $\sim 0.6\text{‰}$ – 0.8‰ using a salinity- δ_w relationship from southern Florida Bay [Swart *et al.*, 1999].

[24] We investigate the potential causes for the $\delta^{18}\text{O}$ -SST and Sr/Ca-SST differences between our work and previous calibrations as well as some of the larger geochemical excursions in the time series in sections 4.2 and 4.3.

3.3. Water Chemistry and the Relationship Between Coral $\delta^{18}\text{O}$ and Sr/Ca

[25] The monthly $\delta^{18}\text{O}$ and Sr/Ca time series covary in cores LK1 and LK23 ($R = 0.67$ and 0.78 , respectively). This is also true of the averaged time series and produces the relationship:

$$\begin{aligned} \text{Sr/Ca (mmol/mol)} = & 0.28(\pm 0.02) * \delta^{18}\text{O (‰ VPDB)} \\ & + 10.31(\pm 0.05), [n = 494, R = 0.85] \end{aligned} \quad (3)$$

The relationship between $\delta^{18}\text{O}$ and Sr/Ca, ‰ when cast in terms of anomalies from the annual cycle, accounts for over 30% ($R = 0.55$, $p \geq 0.99$) of the variance between the two records and is compelling considering that SST accounts for $< 11\%$ of the variance ($R = -0.33$, -0.34 , $p \geq 0.99$, Sr/Ca and $\delta^{18}\text{O}$, respectively; Figure 6). This observation requires an explanation that can simultaneously affect both $\delta^{18}\text{O}$ and Sr/Ca.

[26] Variations in water chemistry independent of temperature have been shown to affect coralline Sr/Ca [de Villiers *et al.*, 1994, 1995; Shen *et al.*, 1996] and $\delta^{18}\text{O}$ [Linsley *et al.*, 1999; Le Bec *et al.*, 2000]. We investigate this possibility by isolating the covariation between Sr/Ca and $\delta^{18}\text{O}$

Figure 5. Mean annual (August–July) values of SST: (top) Sr/Ca and (bottom) $\delta^{18}\text{O}$ for LK1 (dashed line) and LK23 (shaded line) compared with SST (solid line). Mean annual SST is scaled to the stacked mean annual relationship between both LK1 and LK23.

Figure 6. Time series of anomalies in (a) SST, (b) stacked coral Sr/Ca, and (c) stacked coral $\delta^{18}\text{O}$. Anomalies were calculated as differences from the monthly climatological means calculated for the 1961–2002 interval (right). The solid line in Figures 6a–6c is the monthly record filtered with a 25-point convolution-type filter with a half-amplitude response at 24 months to remove higher-frequency variability. Note the stronger relationship between Sr/Ca and $\delta^{18}\text{O}$ anomalies despite a weaker relationship with SSTA.

by removing the contribution of SST. For coral $\delta^{18}\text{O}$ this was accomplished by calculating δ_w using the relationships of Leder *et al.* [1996] (equation (4)):

$$\delta_{\text{water}} = \frac{(SST - 5.33)}{4.519} + \delta_{\text{coral}} \quad (4)$$

The general thermodynamic relationship describing the distribution of trace elements between solid ($\text{Sr}/\text{Ca}_{\text{aragonite}}$) and liquid (Sr/Ca_w) phases has been described by Kinsman and Holland [1969] is expressed by the distribution coefficient $K(T^\circ\text{C})$ (equation (5)). Smith *et al.* [1979] later refined the relationship between $K(T)$ and temperature specifically for coral, as opposed to inorganic aragonite, and produced equation (6).

$$K(T) = \frac{\text{Sr}/\text{Ca}_{\text{aragonite}}}{\text{Sr}/\text{Ca}_w} \quad (5)$$

$$K(T) = 1.30 - 0.0094 * T \quad (6)$$

A simple rearrangement and substitution allows us to solve for a variable Sr/Ca of the water:

$$\text{Sr}/\text{Ca}_{\text{water}} = \frac{\text{Sr}/\text{Ca}_{\text{coral}}}{1.30 - 0.0094 * T} \quad (7)$$

Using equations (4) and (7) we calculate mean seawater Sr/Ca and $\delta^{18}\text{O}$ to be 8.775 ± 0.013 mmol/mol and 0.79 ± 0.03 ‰, respectively, over the 41 years of the coral time series (Figure 7a). The calculated parameters of δ_w and Sr/Ca_w are positively related by the relationship

$$\text{Sr}/\text{Ca}_w (\text{mmol/mol}) = 0.39 * \delta_w (\text{‰ SMOW}) + 8.47, \quad [n = 494, r^2 = 0.89] \quad (8)$$

Synchronous changes in δ_w and Sr/Ca_w over the annual cycle imply a common forcing ($R = 0.94$, $p > 0.999$). Closer inspection of the anomalies from the annual cycle also show a strong degree of covariance ($R = 0.64$, $p > 0.999$; Figures 7b and 7c).

Figure 7. Calculated values of seawater (a) $\delta^{18}\text{O}$ (δ_w , solid line) and Sr/Ca (Sr/Ca_w , dashed line) and (b) $\delta^{18}\text{O}$ and (c) Sr/Ca anomalies based on the stacked coral record. Sr/Ca_w is calculated using the combined relationships of Kinsman and Holland [1969] and Smith *et al.* [1979]: $\text{Sr}/\text{Ca}_w = \text{Sr}/\text{Ca}_{\text{coral}} / (1.30 - 0.0094(\text{SST}))$. Seawater $\delta^{18}\text{O}$ is calculated by solving for δ_w using the equation of Leder *et al.* [1996]. Average annual cycles of predicted (d) Sr/Ca_w and (e) δ_w calculated from the coral record and instrumental SST for the time period 1961–2002. The timing of the curves is such that they impart a signal opposite to that imposed by temperature.

[27] Interestingly, the annual cycle of both Sr/Ca_w and δ_w moves out of phase from the annual temperature cycle (Figures 7d and 7e). In effect, this acts to suppress the annual cycle of both coral Sr/Ca and $\delta^{18}\text{O}$ (i.e., more positive Sr/Ca_w values in the summer will cause more apparent negative temperatures) and is consistent with the observations of Halley *et al.* [1994]. Thus application of our calibration equations to corals in an environment where the relationship between the timing of temperature and water chemistry is not as strong or absent entirely will act to inflate the amplitude of the annual cycle. The subtractive effect of δ_w on coral $\delta^{18}\text{O}$ in an environment where SST and salinity are in phase simply prevents the generation of the full annual cycle in temperature when measurements of δ_w are absent.

[28] Age model construction, which fixes maximum (minimum) Sr/Ca with minimum (maximum) SST, assumes that $\Delta\text{SST} \gg \Delta\text{Sr}/\text{Ca}_w$. However, if this is not true, or if water chemistry variations change the apparent timing of the

Sr/Ca peak, then our SST assessment will be biased. Therefore we have also developed an independent age model for LK23 that makes no a priori assumptions about the relationship between Sr/Ca and SST. Annual high-density bands in *Montastraea* are generally formed during the summer months, although the exact timing of such banding can vary between July and September in the Florida Keys [Hudson *et al.*, 1976; Leder *et al.*, 1991]. Our alternate age model assumes that high-density skeletal bands form in August, the month of warmest SST. Calibration results of both Sr/Ca and $\delta^{18}\text{O}$ with SST from this density-based age model are consistent (within error) with the slopes obtained from using Sr/Ca-SST age model.

4. Discussion

4.1. Intercoral Geochemical Comparisons

[29] The LK1 and LK23 $\delta^{13}\text{C}$ time series are largely in agreement with one another at both an annual and decadal

scale. The $\delta^{13}\text{C}$ records of both corals exhibit a long-term decreasing trend on the order of $-0.02\text{‰}/\text{year}$ which is close to the estimated change ($-0.026\text{‰}/\text{year}$) in the $\delta^{13}\text{C}$ of dissolved organic carbon (DIC) because of the Suess effect in the Atlantic from 1950 to 1993 [Kortzinger *et al.*, 2003]. Long-term changes in the DIC pool of this area have also been recorded by other corals in this region [Swart *et al.*, 1996a, 1996b], but without direct water measurements of DIC for comparison it remains only a casual correlation to attribute this solely to the Suess effect and ignore the effects of potential land use changes [Halley *et al.*, 1994].

[30] The overall mean $\delta^{18}\text{O}$ of LK1 and LK23 differs by 0.04‰ , which is within our analytical error, and is significantly less than the range of other worker's multidecadal estimates in *Porites* corals collected at the same reef ($\sim 0.15\text{--}0.4\text{‰}$) in the central and western tropical Pacific [Guilderson and Schrag, 1999; Linsley *et al.*, 1999; Cobb *et al.*, 2003; Stephans *et al.*, 2004]. Our results are also consistent with the shorter-term studies on *Montastraea* in Puerto Rico and Biscayne Bay, Florida, that have reported differences of 0.08‰ [Watanabe *et al.*, 2002] and 0.22‰ [Leder *et al.*, 1996]. Guilderson and Schrag [1999] suggest such offsets are due to the time-varying kinetic equilibrium of the coral and concluded that decadal-scale or secular trends reflect environmental change rather than a variation in isotopic disequilibria due to variable calcification rates.

[31] The Sr/Ca records of LK1 and LK23 contain the same amount of variance, but have different means. There are intervals of good agreement between the corals and other intervals of substantial difference. The difference in overall mean Sr/Ca value between the cores is exacerbated by the divergence of the records before 1968 and especially in the 1965–1967 portion of LK23. Closer inspection of this time period reveals the least dense band in LK23 formed in 1966 and may be linked to absence of a fully developed geochemical summer in this year. An alternative explanation of the pre-1968 offset in means could possibly be related to the unavoidable consequence of two-dimensional sampling of a coral that exhibits three-dimensional growth. Variations of the thecal wall into and out of the plane of the slab may impart some bias in the results; however, it is unlikely given the reproducibility of the record outside of this time interval. Whatever the reason is, given the close proximity of these two corals, it seems logical that some process beyond environmental forcing is responsible for this unexpected result. The larger difference in Sr/Ca relative to $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ suggests that differences in Sr/Ca between corals may be somewhat reflective of the individual nature of some corals. The ultimate explanation for the deviation in the Sr/Ca records at this time period must not only account for the difference in Sr/Ca, but must also consider the notable consistency between corals in both the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records during this same time interval.

4.2. Growth Impacts on Coral Geochemistry

[32] The impact of growth-related processes on coral $\delta^{18}\text{O}$ and, more recently, coral Sr/Ca has been studied, but no consensus has been reached. Observations of invariant coral $\delta^{18}\text{O}$ or Sr/Ca with extension rate [Shen *et al.*, 1996; Alibert and McCulloch, 1997; Gagan *et al.*, 1998; Marshall and

McCulloch, 2002; Mitsuguchi *et al.*, 2003; Allison and Finch, 2004] contrast with observations of variable $\delta^{18}\text{O}$ and/or Sr/Ca with extension rate [Land *et al.*, 1975; McConnaughey, 1989b; de Villiers *et al.*, 1995; Cohen *et al.*, 2001; Goodkin *et al.*, 2005]. We explore two proposed mechanisms that may explain these reports as they pertain to this study.

4.2.1. Sampling Considerations and Growth Effects

[33] The resolution at which a coral skeleton is sampled for geochemical analysis has an effect on the amplitude of the annual cycle that is recovered [Leder *et al.*, 1996; Quinn *et al.*, 1996; Swart *et al.*, 1996c; Crowley *et al.*, 1999; Watanabe *et al.*, 2002]. The reason for this can be twofold: The combination of vertical extension and calcification can change the amount of material deposited to the skeleton throughout the year. On the basis of the results of both Mendes [2004] and Leder *et al.* [1996] we infer the amount of material deposited to the skeleton to be greater over a shorter distance in the summer than in other times of the year, which in turn agrees with the timing of the high-density bands [Highsmith, 1979]. The geochemical implication of this growth regime is a time-averaging effect resulting from the increased amount of material laid down over shorter distances in the core. This implies a potential sampling bias against the slower extending times of the year (high-density portions), with *Montastraea* extending slowest in the summer [Swart *et al.*, 1996c; Mendes, 2004]. Hence variations in the amplitude of the geochemical signal may arise because of a relative oversampling of nonsummer months and undersampling of summer months. Leder *et al.* [1996] recommend sampling the coral skeleton on the order of 50–55 times per year to capture the full range of seawater temperatures (i.e., both maximum and minimum temperatures experienced on the reef at a quasi-weekly resolution) using coral $\delta^{18}\text{O}$ in regions that exhibit a large seasonal range of seawater temperatures ($\sim 9^\circ\text{C}$; Florida Keys). Data from both Leder *et al.* [1996] and Watanabe *et al.* [2002] document a disproportionate reduction in estimated SST amplitude with decreasing sampling resolution (i.e., a proportionally larger reduction in amplitude with coarser sampling density). This disproportionate reduction in amplitude has been shown to change the slope in the $\delta^{18}\text{O}$ -SST relationship between monthly and annual calibrations [Crowley *et al.*, 1999].

[34] Recovery of the full temperature range may not even be possible in some environments. Halley *et al.* [1994] sampled a *Montastraea annularis* from the Florida Keys at 70 samples per year and were still unsuccessful in recovering the expected amplitude in $\delta^{18}\text{O}$ based upon the observed temperature range. They concluded that isotopically heavy values of $\delta^{18}\text{O}$ imported from Florida Bay subtract from the temperature signal. In such an environment it should be expected that regression of temperature against $\delta^{18}\text{O}$ would yield different slopes. We have also collected data taken from LK23 at a resolution of 40 samples per year (Figure 8). Owing to the small amount of coral powder generated with this higher sampling resolution, it was not possible to make paired determinations, but rather elemental and isotopic values were obtained from different sampling paths chosen to overlap the same time period. Average amplitudes from

Figure 8. Comparison of drilling ~40 samples per year (diamonds) with sampling 14 samples per year (triangles) on (a) Sr/Ca, (b) $\delta^{18}\text{O}$, and (c) $\delta^{13}\text{C}$.

the samples obtained at 14 samples per year are 78%, 75% and 60% of the amplitudes of the 40 samples per year transects for Sr/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively, and are much noisier in character. Regression of the high-resolution data, resampled to monthly values, against SST yields similarly low slope coefficients compared to previously published slopes (-0.0355 ± 0.003 , Sr/Ca; -0.122 ± 0.013 , $\delta^{18}\text{O}$). These results are in line with the conclusions of Halley *et al.* [1994] in that increased sampling resolution does not yield geochemical amplitudes expected based on temperature alone for reefs adjacent to the influence of Florida Bay.

[35] Continuous sampling at a constant depth increment down core leads to a variable sampling rate through the core because of the changing extension rate of the coral. This equates to sampling resolutions ranging from 10–22 samples/year in this study. Leder *et al.* [1996] sampled their *Montastraea annularis* coral at roughly weekly resolution (50–55 samples/year of growth) in an effort to avoid the nonlinear extension effects discussed earlier. We investigate the difference between our calibration equations and those of Leder *et al.* [1996] and Swart *et al.* [2002] as a function of sampling density by looking at the three warmest month

calibrations (summer; July–September; presumed slowest extending portion of the year) and contrasting them with the three coldest month's calibrations (winter; January–March). Winter was selected to minimize any potential overlap due to age model errors. The slopes of winter- and summer-based calibrations from the averaged records for both $\delta^{18}\text{O}$ and Sr/Ca are significantly different from each other ($p > 0.95$) with winter calibrations having slopes that are more similar to the slope of the $\delta^{18}\text{O}$ -SST relationship determined via weekly sampling over the annual growth increment. This suggests a seasonal bias against slower growing times of the year. Notwithstanding the effects of sampling, if high rates of calcification are coupled with sufficiently slow extension rates then even high-resolution (weekly) sampling of the coral skeleton may not be sufficient to capture the potential full amplitude of the geochemical signal.

[36] An additional factor that should be considered in sampling *Montastraea* is the horizontal variability that exists between different skeletal elements. We generated Sr/Ca values across the width of the LK23 slab to assess the variability that may be introduced because of the inclusion of other skeletal elements that, while in the same horizontal plane of the coral relative to the density band, may have

Figure 9. Horizontal variations in Sr/Ca across several corallites in LK23. Black horizontal lines indicate drill paths. Shaded bars indicate position of high-density bands. Sr/Ca values from the 41-year climatology place the timing of the horizontal transects as September (top) and February (bottom), and this is in general agreement in terms of distance away from high-density bands. Drilling deviations away from the exothecal wall can result in the incorporation of nonideal skeletal elements. These skeletal elements, when taken from a horizontal perspective, are not deposited to the skeleton at the same time during the year or are deposited at a different rate than the exothecal wall.

been deposited at a different time than the exothecal wall. Two transects were sampled (Figure 9), and geochemical values based on the 41-year climatology of the vertically sampled transect place their timing at approximately February and September of 1986. Values obtained during the vertical sampling are commensurate with values generated from other exothecal walls on the horizontal transect. Variation between corallite elements is large ($1\sigma = 0.07$ mmol/mol) and equates to over 2°C , highlighting the need for special care when generating long time series. The inclusion of some of the other skeletal elements is undesirable, yet may be an unavoidable reality when generating long time series because of the meandering growth of the corallite through the plane of the slab.

4.2.2. Kinetic Effects

[37] Genera-specific differences in mean $\delta^{18}\text{O}$ and Sr/Ca have been observed in a multitude of taxa based upon differences in vital effects [Weber and Woodhead, 1970] and average extension rates [Weber, 1973], respectively. Growth-related impacts on *Pavona* coral $\delta^{18}\text{O}$ and Sr/Ca have been reported [McConnaughey, 1989b; de Villiers et al., 1995]. One of the main conclusions drawn by McConnaughey [1989b] is that the fastest growing portions of the skeleton must be sampled because the degree of isotopic variation is too variable in the slower growing

portions. Despite these observations in *Pavona*, the reports of kinetic effects in *Porites* that are sampled along the major axis of growth are more ambiguous for Sr/Ca. Conflicting results of ion microprobe analyses of Sr/Ca in *Porites* suggest that either growth rate effects depress mean annual Sr/Ca [Cohen and Hart, 2004], or that there is no effect [Allison and Finch, 2004]. Felis et al. [2003] measured pronounced $\delta^{18}\text{O}$ enrichment in *Porites* at extension rates less than 6 mm/yr when examining the maximum axis of growth in a range of different colonies with growth rates of 2–15 mm/yr; however, in the work of Gagan et al. [1998] two corals each growing at 12 and 22 mm/yr at the same location showed no discernable difference in $\delta^{18}\text{O}$ or Sr/Ca. From these two studies it appears that linear extension rates may have an influence on coral $\delta^{18}\text{O}$ and Sr/Ca at the slowest of extension rates, the overall character of the geochemical signal is constant above some threshold level in *Porites*, and coral geochemical signals recorded in the slowest of extending years in any coral genus and should be viewed with caution.

[38] We explore and attempt to identify the potential impact of skeletal growth parameters upon Sr/Ca and $\delta^{18}\text{O}$ in *Montastraea* recognizing that the body of literature relating geochemical values to extension rates, irrespective of calcification, in *Montastraea* is grossly limited compared to that of *Porites*. Comparisons of Sr/Ca-SST and $\delta^{18}\text{O}$ -SST with skeletal growth parameters yields the highest significant correlations with density ($R = 0.35$, $R = 0.25$, $p > 0.99$, respectively) which agrees with the relationship between the timing of high- and low-density band formation with water temperature [Weber et al., 1975]. Over the 41 years of data, a small, yet significant correlation exists on an interannual basis between SST residuals and both calcification and extension (Figure 10). However, at the most, the influence of either calcification or extension can explain less than 10% of the residual SST values and on a monthly basis, the correlation coefficients become trivial. We extend our analysis by comparing the differences between our five fastest and slowest growing years for both corals. Variations in extension rate exhibited by these corals have no appreciable impact on mean $\delta^{18}\text{O}$ or Sr/Ca, amplitude of the annual cycle, or contribute to deviations from calculated SST. In a careful study, Mendes [2004] measured intra-annual extension rates at a monthly scale in a Jamaican *Montastraea*. The slowest extending periods were observed to occur in September with variable extension rates occurring other times during the year. The fastest extending period of time actually occurs the month preceding (August) the slow extending portion. Given this information, it seems unlikely that the pattern in the mean annual cycle of calculated water parameters (Figures 7d and 7e) can be produced by variable intra-annual skeletal extension rates.

[39] Kinetic effects in coral time series have largely been associated with deviations in extension rates; however, aside from growth rate parameters, kinetic effects have also been documented by a functional linkage between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ positively trending toward equilibrium values [McConnaughey, 1989a, 1989b]. This relationship has been utilized by some authors to correct portions of their records where kinetic impacts are clearly evident

Figure 10. Variations in residual SST based on the respective calibration equations for LK1 (dashed line) and LK23 (solid line) for coral (a) Sr/Ca and (b) $\delta^{18}\text{O}$. Residuals are compared with LK23 growth parameters of (c) calcification, (d) extension, and (e) density. Extension rates for Figure 10 are derived by the Sr/Ca-time-depth relationship. All time series have been filtered to remove variability occurring at less than 2 years by use of a 25-point convolution-type filter with a half-amplitude response at 24 months. Correlation values are given for LK23 between each individual growth parameter and both (left) Sr/Ca-SST residual and (right) $\delta^{18}\text{O}$ -SST residual. Residuals are calculated as the difference between instrumental SST and estimates of SST based on $\delta^{18}\text{O}$ or Sr/Ca. Italicized values are at $p > 0.95$. LK1 growth parameters are not included as the core was unsuitable for densitometry analysis. Growth parameters for LK23 are insufficient to explain the variance in the geochemical records that remains after accounting for SST.

[Guilderson and Schrag, 1999]. The negative relationship between coral $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in both Looe Key corals (slopes: -0.14 ± 0.02 , LK1; -0.12 ± 0.02 , LK23) would imply that if kinetic effects are evident in these data, then the environmental impacts must exceed those of kinetic impacts (Figure 11). The impact of variable calcification rates on the Looe Key Sr/Ca and $\delta^{18}\text{O}$ records are modest to insignificant (Figure 10) and at the most can explain only $\sim 10\%$ of the signal. Therefore, while it is tempting to attribute the synchronous changes in δ_w and Sr/Ca_w, or $\delta^{18}\text{O}$ and Sr/Ca to a kinetic mechanism, we are unable to arrive at this conclusion because of the lack of any mathematical consistency both over the 41 years of record and between cores. We therefore conclude that the range of both extension and calcification rates exhibited by these Looe Key corals are not sufficient to appreciably alter the geochemical signal and changes in the

residual SST values must be explained by a mechanism other than growth parameters.

4.3. Hydrographic Considerations

[40] Variations in water properties in the Florida Keys have been tied to upwelling along the Florida Keys, tidal mixing of the waters of Florida Bay with the Straits of Florida, groundwater input, and long-term transport of water from the Gulf of Mexico to the Atlantic [Lee *et al.*, 1994; Smith, 1994; Porter *et al.*, 1999; Lee and Smith, 2002; Reich *et al.*, 2002; Smith, 2002]. The isotopic composition of rainfall in south Florida is variable and ranges from 0 to -8‰ versus SMOW [Swart *et al.*, 1989], and a 2-year quasi-weekly time series of measurements of Gulf Stream waters have a mean value of 1.1‰ versus SMOW with an average range of 0.5‰ [Leder *et al.*,

Figure 11. Scatterplot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for both LK1 (diamonds, solid line) and LK23 (triangles, dashed line). The negative relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in both corals is opposite to that observed in species where kinetic effects have a large impact on the geochemical signal. Equilibrium values (shaded gray box) are calculated using the temperature range at the reef site and mean δ_{w} and DIC $\delta^{13}\text{C}$ values from Leder *et al.* [1996] and Swart *et al.* [1996c].

1996]. The contribution of waters from the semienclosed basin of Florida Bay has been documented by satellite imagery to affect the Florida Keys [Roberts *et al.*, 1982] and may affect Looe Key seasonally [Porter *et al.*, 1999]. Low transport rates and large amounts of evaporation (i.e., increased latent heat flux) in the spring and summer [Lee and Smith, 2002; Virmani and Weisberg, 2003] can result in Florida Bay waters having $\delta^{18}\text{O}$ values as high as +3.36‰ versus VSMOW [Swart and Price, 2002]. An additional complication in interpreting these records over multiple seasons is that the salinity- δ_{w} relationship in Florida Bay is not a straightforward mixing between isotopically light fresh water and heavier marine water (see discussion given by Swart *et al.* [1996b]), but is complex and can result in isotopically heavy fresh waters mixing with relatively light marine waters. In two previous coral studies in the Florida Keys, both Halley *et al.* [1994] and Leder *et al.* [1991] suggest that isotopically enriched Florida Bay waters could potentially affect summer $\delta^{18}\text{O}$ water values in the reef tract resulting in a reduced $\delta^{18}\text{O}$ -SST amplitude, although the coral $\delta^{18}\text{O}$ -SST calibration equation of Leder *et al.* [1996] was derived over a time period where small changes in the water $\delta^{18}\text{O}$ were noted. Looe Key is more susceptible to the influence of Florida Bay waters than the more northern Florida Keys locations of the Leder *et al.* [1991, 1996] studies lending credence to this possibility and is consistent with our calibration results.

[41] Measurements of seawater Sr/Ca are not available at Looe Key; however, other studies in the greater Florida area report seawater Sr/Ca values of 8.78 mmol/mol [Swarzenski *et al.*, 2001] and 8.4 mmol/mol [Surge and Lohmann,

2002]. Highly elevated ratios of Sr/Ca, between 13.5 to 14.7 mmol/mol, have been reported for submarine groundwaters discharging from the Floridian limestone aquifer system [Swarzenski *et al.*, 2001]. The potential impact of these type of submarine discharged waters has not been assessed at Looe Key, but could potentially change the character of deeper waters (>25 m) that are known to upwell at this site [Lee *et al.*, 1994; Szman and Forrester, 1996]. Additionally, groundwater is input to Florida Bay via tidal pumping [Corbett *et al.*, 1999] and, depending upon the level of interaction with waters from the deeper aquifer, can yield larger Sr/Ca ratios than would be expected from open-ocean water. Conversely, Sr/Ca ratios of fresh waters measured in three estuaries in SW Florida have greatly reduced values and show variations in Sr/Ca with salinity, ranging from <2–~8 mol/mol along the freshwater-to-saltwater gradient [Surge and Lohmann, 2002]. Hence, unlike open-ocean settings, large changes in water chemistry prove to be problematic for coral-climate reconstructions in this continentally influenced zone. The delivery and, hence, relative impact, of each of these sources confounds the isolation of temperature in coral Sr/Ca records at Looe Key.

[42] The various sources of water to Looe Key can be depicted in a mixing diagram by plotting Sr/Ca_w versus δ_{w} (Figure 12). The end-members have large ranges in both Sr/Ca_w and δ_{w} , and there is a general trend ranging from estuarine values to groundwater values with the calculated coral values falling in the middle. Synchronous changes in the timing of the data in Figures 7d and 7e coincide with the annual cycle of precipitation, and are suggestive of a climatologically persistent link between water chemistry on the reef and rainfall. Despite this observation, on short timescales, physical processes such as spatial precipitation patterns, tidal pumping, riverine outflow, and wind-driven circulation act to “muddy the waters” by inducing variable lag times for delivery to the reef. However, when taken from a longer climatological perspective there is stronger evidence for regional interpretation of the most persistent patterns.

[43] An additional independent line of geochemical evidence that supports the conclusion that changes in water chemistry are influencing the coral geochemical record comes from the work of Purdy *et al.* [1989], who document amplified concentrations of ^{90}Sr and depleted concentrations of $^{234,240}\text{Pu}$ in annual bands of *Montastraea annularis* in the Florida Keys when contrasted with an open ocean site (Bermuda). Since ^{90}Sr has no natural source and is only produced as a product of nuclear weapons testing, the only mechanism that could concentrate large quantities of ^{90}Sr beyond levels expected from direct fallout alone must come from coastal run-off sources. Moreover, a coastal run-off explanation is further substantiated by depleted concentrations of $^{234,240}\text{Pu}$ during the same period of coral growth, which is consistent with scavenging by particles in coastal waters.

5. Conclusions

[44] We compared monthly resolved geochemical variations of Sr/Ca, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ in two separate heads of

Figure 12. Mixing diagram comparing literature Sr/Ca_w and δ_w values and coral-based seawater values calculated from equations (4) and (7). Florida Bay Sr/Ca_w values are assumed to be a mean value between estuary and ocean values. Literature values are derived from *Surge and Lohmann* [2002], *Swart and Price* [2002], *Swarczewski et al.* [2001], *Leder et al.* [1996], and *Böhlke et al.* [1999]. Coral-derived values of Sr/Ca_w and δ_w are indicated by the shaded box and overlap typical ocean values.

Montastraea faveolata from Looe Key Reef, Florida, over a 41-year interval to assess how well two corals from the same reef record sea surface environmental conditions. The stable isotope time series replicate well between the two coral heads as is evidenced by their indistinguishable mean values. In contrast, the mean Sr/Ca values of the two corals

differ significantly and indicate that nonenvironmental factors are influencing the coral Sr/Ca records at Looe Key.

[45] Synchronous anomalies in coral Sr/Ca and $\delta^{18}\text{O}$ are independent of changes in SST. Direct regression of $\delta^{18}\text{O}$ and Sr/Ca onto SST yields equations that are significantly different from previously published equations for *Montastraea*. Variations in growth parameters or kinetic impacts are not sufficient to explain this difference in calibrations, which is most likely due to variations in water chemistry not accounted for in the regression analysis. Similar to the $\delta^{18}\text{O}$ - δ_w -SST relationship, we have isolated Sr/Ca variations in water chemistry over the length of the instrumental record by solving a modified $\text{Sr}/\text{Ca}_{\text{coral}}\text{-Sr}/\text{Ca}_w\text{-SST}$ relationship which includes an additional variable to account for the water parameters. Our results highlight the confounding impact of variable water chemistry on the use of paired Sr/Ca and $\delta^{18}\text{O}$ in *Montastraea* paleothermometry at this site.

[46] Future work on Atlantic *Montastraea* should include the generation of additional geochemical records, multiple decades in length, complemented whenever possible by seawater chemistry determinations so that a more complete assessment of the climate utility of *Montastraea* can be made. Also, additional studies of replication involving more specimens will allow for greater confidence in interpretation of paleoclimate records derived from *Montastraea* corals.

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