



Interpreting sea surface temperature from strontium/calcium ratios in *Montastrea* corals: Link with growth rate and implications for proxy reconstructions

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[1] We analyzed strontium/calcium ratios (Sr/Ca) in four colonies of the Atlantic coral genus *Montastrea* with growth rates ranging from 2.3 to 12.6 mm a⁻¹. Derived Sr/Ca–sea surface temperature (SST) calibrations exhibit significant differences among the four colonies that cannot be explained by variations in SST or seawater Sr/Ca. For a single coral Sr/Ca ratio of 8.8 mmol mol⁻¹, the four calibrations predict SSTs ranging from 24.0° to 30.9°C. We find that differences in the Sr/Ca–SST relationships are correlated systematically with the average annual extension rate (ext) of each colony such that Sr/Ca (mmol mol⁻¹) = 11.82 (±0.13) – 0.058 (±0.004) × ext (mm a⁻¹) – 0.092 (±0.005) × SST (°C). This observation is consistent with previous reports of a link between coral Sr/Ca and growth rate. Verification of our growth-dependent Sr/Ca–SST calibration using a coral excluded from the calibration reconstructs the mean and seasonal amplitude of the actual recorded SST to within 0.3°C. Applying a traditional, nongrowth-dependent Sr/Ca–SST calibration derived from a modern *Montastrea* to the Sr/Ca ratios of a conspecific coral that grew during the early Little Ice Age (LIA) (400 years B.P.) suggests that Caribbean SSTs were >5°C cooler than today. Conversely, application of our growth-dependent Sr/Ca–SST calibration to Sr/Ca ratios derived from the LIA coral indicates that SSTs during the 5-year period analyzed were within error (±1.4°C) of modern values.

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1. Introduction

[2] Several distinct, although not necessarily global, climatic events during the last 1000 years, such as the Little Ice Age (LIA, ~500–100 years B.P.), suggest that recent anthropogenically forced climate change is superimposed upon natural centennial-scale climate variability [Jones and Mann, 2004; National Research Council, 2006]. Separating the impact of anthropogenic activity on climate from the natural background variability requires accurate reconstructions of the nature and magnitude of past climate variability. While geochemical proxy records from biogenic carbonates have provided valuable information about the behavior of the climate system over this time period [e.g., Hendy et al., 2002; Cronin et al., 2003; Black et al., 2004; Lund and Curry, 2006], inconsistent results in some regions have prevented a robust characterization of natural climatic changes. For example, proxy reconstructions suggest that sea surface temperatures (SSTs) in the Caribbean region during the LIA were <1° to >3°C cooler than today, and some data sets suggest that the surface ocean was fresher

while others indicate more saline conditions than modern [Winter et al., 2000; Watanabe et al., 2001; Nyberg et al., 2002; Lund and Curry, 2006]. There are several possible reasons for such discrepant results including seasonally biased SST estimates derived from foraminifera [Thunell and Reynolds, 1984; Mohiuddin et al., 2004], smoothing due to bioturbation, chronological uncertainties associated with large errors on radiocarbon dates, and uncertainties associated with the calibration and interpretation of geochemical proxies.

[3] Massive, long-lived corals are unique archives of ocean climate that may circumvent some of the uncertainties of other reconstructions. Dense and rapidly extending coral skeletons can be sampled at subseasonal resolution with absolute age control because of annual density bands. Long-lived corals can provide continuous proxy records over multiple centuries [e.g., Hendy et al., 2002] that are not prone to bioturbation, and young fossil coral can be U/Th dated to within ±5 years [Cobb et al., 2003]. Nevertheless, interpreting coral geochemistry in terms of climatic parameters is not always straightforward [Lough, 2004]. For example, Sr/Ca–SST calibrations derived to date from single colonies of the Atlantic coral *Montastrea*, a predominant genus in both modern and fossil reefs [Weil and Knowlton, 1994; Hubbard et al., 2005] show significant, yet unexplained differences [Swart et al., 2002; Smith et al., 2006]. This implies that paleo-SST estimates derived using these calibrations depend heavily on which calibration is applied. For example, applying

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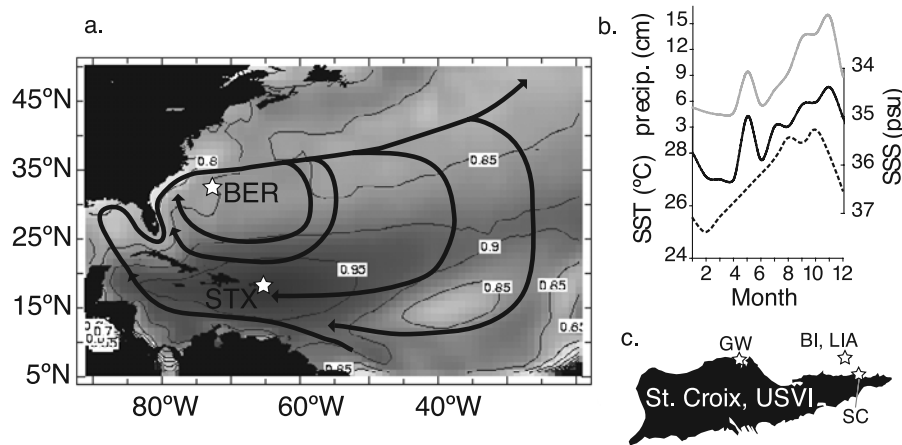


Figure 1. (a) Correlation of IGOSS sea surface temperature (SST) at St. Croix (STX) with the greater tropical and subtropical North Atlantic. Contours are correlation coefficient (r) values. Black arrows indicate general oceanic circulation. STX and Bermuda (BER) are coral collection sites. (b) Climatological St. Croix precipitation, SST, and sea surface salinity (SSS) [Department of Conservation and Cultural Affairs, 1986]. (c) Local STX map showing collection sites for modern (GW, SC, and BI) and Little Ice Age fossil (LIA) corals.

existing *Montastrea* Sr/Ca–SST calibrations [Swart *et al.*, 2002; Smith *et al.*, 2006] to a coral with a typical skeletal Sr/Ca ratio of $8.8 \text{ mmol mol}^{-1}$ predicts paleo-SSTs ranging from 29.0° to 40.9°C .

[4] In this study we measured Sr/Ca in four *Montastrea* colonies that had mean annual extension rates ranging from 2.3 to 12.6 mm a^{-1} . Oxygen isotopic ratios ($\delta^{18}\text{O}_c$) also were measured in the three fastest growing corals. The derived Sr/Ca calibrations exhibited systematic offsets that were correlated with differences in the annual average skeletal extension rate of each colony. No growth rate effect was evident in $\delta^{18}\text{O}_c$. We derived a growth rate–dependent Sr/Ca–SST calibration using three corals, and independently verified its accuracy using the fourth coral. We also applied our growth rate–dependent calibration to a fossil *Montastrea* that grew in the early LIA (400 years B.P.), and compared our result with that predicted using a traditional, nongrowth-dependent Sr/Ca–SST calibration.

2. Study Site

[5] St. Croix, U.S. Virgin Islands ($17^\circ 45'\text{N}$, $64^\circ 45'\text{W}$) lies in the eastern Caribbean Sea and is bathed by water of predominantly North Atlantic subtropical gyre origin [Hernandez-Guerra and Joyce, 2000]. SST is highly correlated with SST throughout the broader tropical Atlantic (Figure 1a) suggesting that our study site is well situated to capture regional SST variability. The seasonal amplitude of SST at St Croix is $\sim 4^\circ\text{C}$ with an annual minimum in February and an annual maximum in September (Figure 1b). The influence of freshwater river discharge is small, and the regional hydrologic budget is controlled largely by precipitation [Yoo and Carton, 1990]. Precipitation varies seasonally in association with annual insolation-driven meridional migrations of the Intertropical

Convergence Zone (ITCZ), a band of increased precipitation at the confluence of interhemispheric easterly trade winds.

3. Methods

3.1. Coral Collection and Sampling

[6] Live *Montastrea faveolata* corals were collected from three sites on St. Croix (GW, SC and BI) (Figure 1c). An additional specimen, a slow growing *Montastrea franksi* colony collected on Bermuda's (BER) south shore reef [Cohen and Thorrold, 2007], was also included in this study. GW and SC corals were collected from $\sim 1 \text{ m}$ of water, while BI and BER samples were recovered from water depths of 10 and 13 m, respectively. In addition to the live modern corals, we also analyzed a *Montastrea faveolata* specimen that grew during the early LIA. A $\sim 10\text{-cm}$ -long piece was retrieved from a drill core taken in 6 m of water along the southeastern submerged Holocene reef of Buck Island, St. Croix [Hubbard *et al.*, 2005]. The drill core specimen was AMS radiocarbon dated to have a calibrated age of 400 years B.P. (conventional $^{14}\text{C} = 750 \pm 60$ years, 2σ range 490–270 years B.P.) [Hubbard *et al.*, 2005; Hughen *et al.*, 2004; M. Stuvier, P. J. Reimer, and R. W. Reimer, CALIB radiocarbon calibration, execute version 5.0.2, <http://calib.qub.ac.uk/calib/>, 2005].

[7] All corals were slabbed parallel to the axis of maximum growth using a water-cooled tile saw, and briefly ultrasonicated in deionized water. A 7-mm-wide slab was removed from the center of each colony and x-rayed to obtain information about coral growth rates and to establish a chronology from the annual density bands. X-radiographs were taken at the local hospital in Falmouth, MA, using settings of 55 kV and 1.6 mAs, a focal distance of 1 m and exposure time of 0.16 s. The LIA specimen was assessed for

diagenetic alteration using x-ray diffraction [Hubbard *et al.*, 2005] and examination of skeletal ultrastructure in petrographic thin sections.

[8] A Merchantek micromill was used to remove powdered subsamples from the St. Croix corals. Because *Montastrea* corals exhibit variability in $\delta^{18}\text{O}_c$ and Sr/Ca ratios among different skeletal elements [Leder *et al.*, 1996; Smith *et al.*, 2006], we removed subsamples from the exothecal wall only. Our sampling tracks were continuous, $\sim 300\ \mu\text{m}$ deep, $\sim 100\ \mu\text{m}$ wide, and advanced in $\sim 400\ \mu\text{m}$ increments along the coral growth axis. $\sim 100\ \mu\text{g}$ of powder was split into aliquots of $\sim 30\ \mu\text{g}$ for $\delta^{18}\text{O}_c$ and $\sim 70\ \mu\text{g}$ for Sr/Ca analyses. The $\delta^{18}\text{O}_c$ was determined using a Finnigan MAT 252 mass spectrometer with an analytical error of $\pm 0.07\text{‰}$ [Ostermann and Curry, 2000]. Sr/Ca ratios were analyzed using a ThermoFinnigan Element II inductively coupled plasma mass spectrometer (ICP-MS) following the method of Rosenthal *et al.* [1999]. Precision for Sr/Ca is $\pm 0.02\ \text{mmol mol}^{-1}$ based on replicate standard analyses ($n = 73$).

[9] To avoid significant dampening of the annual Sr/Ca cycle in the slow growing coral, Sr/Ca ratios from the BER *Montastrea franksi* were measured by a Cameca 3f ion microprobe as described by Cohen *et al.* [2004] and Gaetani and Cohen [2006]. BER data were generated at $50\ \mu\text{m}$ intervals that are equivalent to a temporal resolution of ~ 10 days. Seasonally resolved $\delta^{18}\text{O}_c$ measurements were not generated for the slow growing BER, and no $\delta^{18}\text{O}_c$ data are reported for this coral.

3.2. Water Collection and Sampling

[10] Monthly surface water samples ($\sim 1\ \text{m}$ depth) were collected at GW, SC and BI sites from January to May 2006 ($n = 12$). High-density polyethylene vials (60 mL volume) were triple rinsed with seawater, filled to overflowing, sealed with parafilm and shipped to the Woods Hole Oceanographic Institution for analysis. Sr/Ca ratios of seawater samples were measured using a ThermoFinnigan Element II high sector field ICP-MS following the protocol of Gaetani and Cohen [2006].

3.3. Instrumental SST Records

[11] Local St. Croix SST data were provided from three sources. First, we installed Onset HOBO data loggers at BI, GW and SC to measure bihourly water temperature at the depth of coral collection. Loggers recorded SST from 7 May 2006 to 7 February 2007, with a precision of $\pm 0.2^\circ\text{C}$. Second, the National Park Service provided bihourly water temperature data for Buck Island, St. Croix from 1 January 1992 to 23 January 2007. A Ryan TempMentor 1.0 at a depth of 10 m collected these data. Third, the National Oceanographic and Atmospheric Administration's (NOAA) monitoring station at Salt River, St. Croix (http://www.coral.noaa.gov/crw/real_data.shtml), adjacent to the GW site, supplied hourly SST data from 1 January 2005 to 4 May 2006. In addition, we used the Integrated Global Ocean Services System (IGOSS) satellite-derived SST ($1^\circ \times 1^\circ$ grid box) to obtain weekly

Table 1. Summary of Coral Geochemical Data and Reconstructed SST^a

Sample	Age (years B.P.)	Years (A.D.)	Growth Rate (mm a ⁻¹)	Sr/Ca (Mean/Amplitude) (mmol mol ⁻¹)	$\delta^{18}\text{O}$ (Mean/Amplitude) (‰)	Seawater Sr/Ca (mmol mol ⁻¹)	Growth-Dependent SST (Mean/Amplitude) (°C)	ΔIGOSS (°C)	Nongrowth-Dependent SST (Mean/Amplitude) (°C)	ΔIGOSS (°C)
BI	Modern	2002–2006	12.6	8.50/0.26	-4.7/0.9	8.46 ± 0.01	28.0/2.6	0.14/-0.72	27.9/3.3	0.02/0.06
GW	Modern	1995–2000	10.1	8.73/0.34	-4.7/1	8.48 ± 0.02	27.3/3.4	-0.14/0.57	25.5/5.0	-2.52/1.97
SC	Modern	1997–2000	8.0	8.84/0.28	-4.7/0.7	8.53 ± 0.02	27.4/3.0	-0.27/-0.29	23.5/3.7	-4.19/0.67
BER	Modern	1998–2001	2.3	9.46/0.78	–	–	24.3/8.6	0.15/0.24	15.3/10.6	-8.92/10.62
LJA	400 ± 60	5 years	5.2	8.88/0.35	-3.5/1.1	–	28.4/3.5	–	22.6/4.3	–

^aMean values amplitudes are calculated from annual maxima and minima following equations (1) and (2). ΔIGOSS is IGOSST SST subtracted from coral-based SST reconstructions.

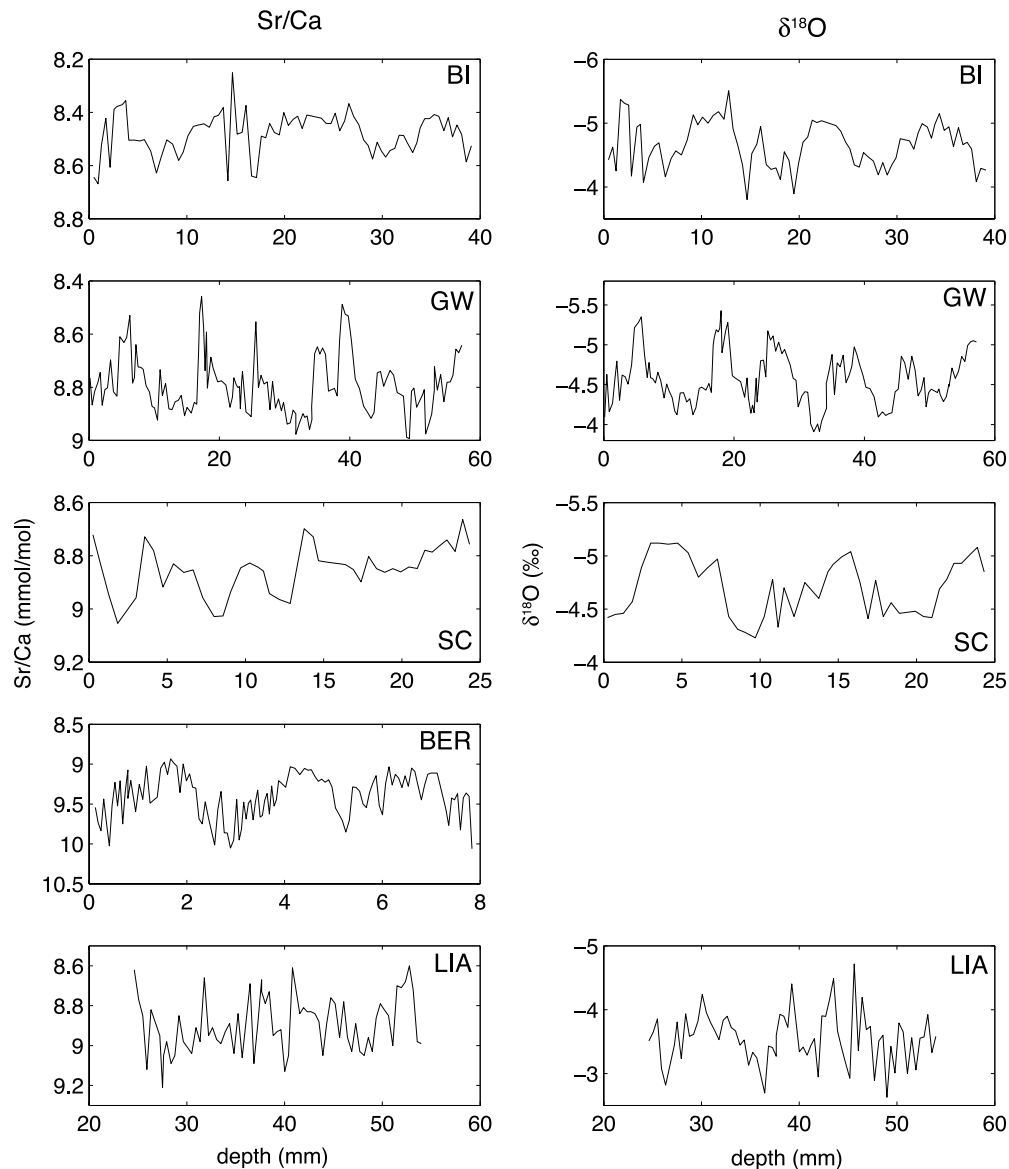


Figure 2. (left) Sr/Ca and (right) $\delta^{18}\text{O}$ data versus sampling depth in *Montastrea* from modern STX (BI, GW, SC), modern Bermuda (BER) and a Little Ice Age fossil (LIA). A slow extension rate prevented high-resolution $\delta^{18}\text{O}$ measurements of BER.

regional SST at both St. Croix and Bermuda [Reynolds and Smith, 1994] from 1 January 1983 to 7 February 2007.

4. Results

4.1. Instrumental SST Records

[12] In situ SST records from the three St. Croix sites were highly correlated ($r^2 = 0.91\text{--}0.96$) and consistent between 7 May 2006 and 7 February 2007. Maximum and minimum SSTs were within 0.25°C at all sites. Peak SC SST was $\sim 0.25^\circ\text{C}$ warmer than the average high, while minimum GW SST was $\sim 0.25^\circ\text{C}$ cooler than the average low. IGOSS SSTs were $\sim 0.1^\circ\text{C}$ cooler than our logged in

situ SSTs in the summer, and $\sim 0.1^\circ\text{C}$ warmer in winter. Since intersite SST differences were negligible, and since logged SSTs were consistent with IGOSS satellite data, we constructed Sr/Ca–SST calibrations at each site using the weekly resolved IGOSS data.

4.2. Seawater Sr/Ca Ratios

[13] Seawater Sr/Ca at each site had typical ocean values [deVilliers, 1999], but exhibited small intersite differences. The Sr/Ca ratios of GW and BI seawater were within error: 8.46 ± 0.01 (1σ) and 8.48 ± 0.02 mmol mol^{-1} , respectively (Table 1). Site SC had a seawater Sr/Ca value of 8.53 ± 0.02 mmol mol^{-1} .

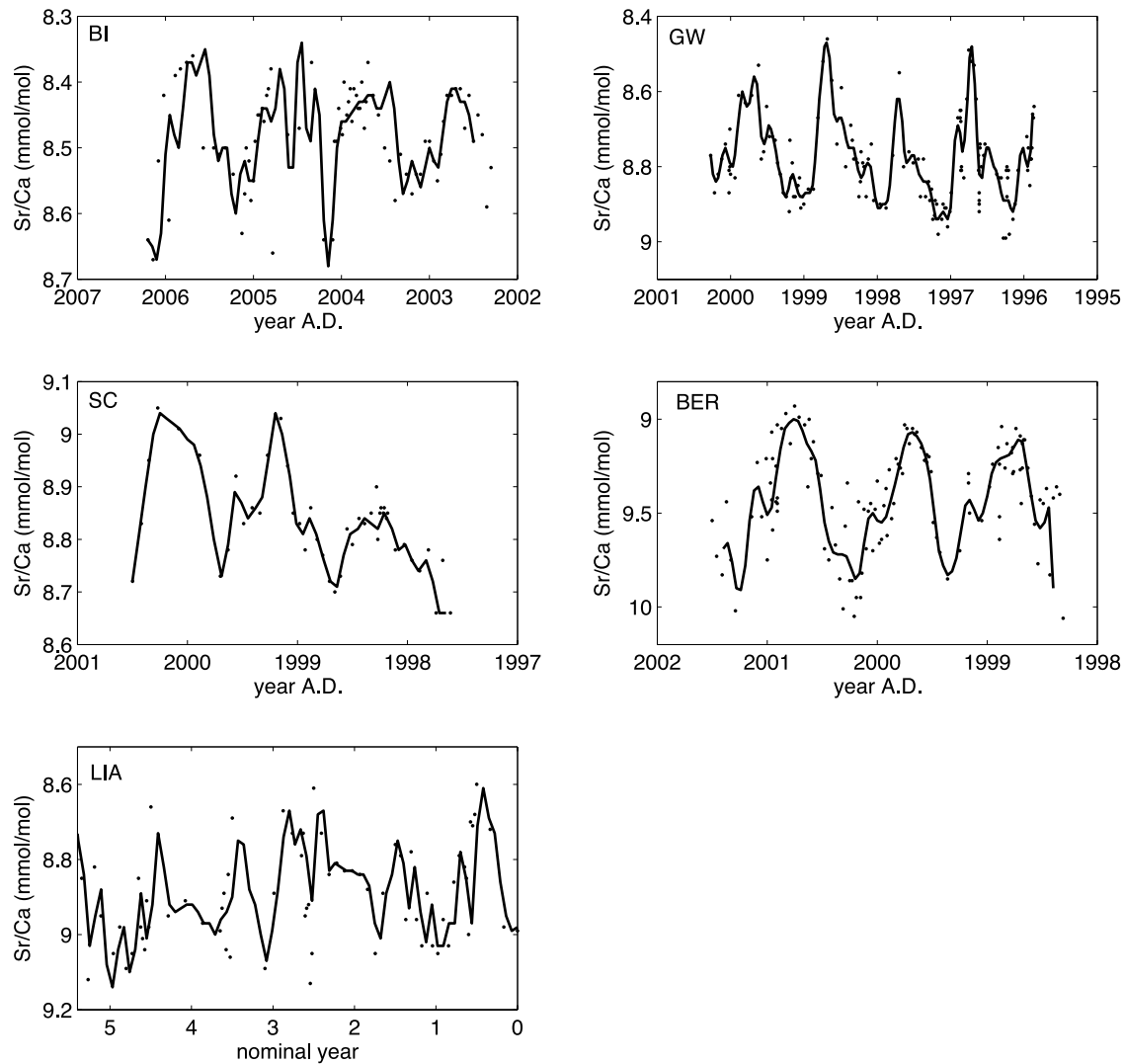


Figure 3. Unfiltered (points) and low-pass filtered (line) Sr/Ca versus age for *Montastrea* from three modern STX sites (BI, GW, and SC), Bermuda (BER), and a Little Ice Age fossil (LIA). Our age model fixes Sr/Ca maxima and minima to SST minima and maxima.

4.3. Modern Coral Extension Rate, Sr/Ca, and $\delta^{18}\text{O}_c$

[14] The mean annual extension rate of each colony was determined by measuring the distance between annual high-density bands in the x-radiographs. These measurements were independently cross-checked against the mean distance between $\delta^{18}\text{O}_c$ maxima and minima in BI, GW and SC. While variability within a colony was small (± 4 –7% RSD), mean annual extension rates ranged from 2.3 to 12.6 mm a^{-1} between the colonies studied (Table 1).

[15] Annual cycles were detected in coral Sr/Ca and $\delta^{18}\text{O}_c$ ratios at all sites (Figures 2 and 3). Geochemical data were assigned ages by tying Sr/Ca maxima and minima to SST minima and maxima, and linearly interpolating between tie points. The shape of the annual Sr/Ca cycles in modern corals differed from that of annual SST cycles because of intra-annual variability in skeletal extension rate. Our uniform sampling distance along the thecal wall means periods of faster extension were sampled more frequently. To avoid

biasing data toward periods of higher extension rates, we compared data from each colony using the maximum and minimum values of each annual cycle rather than the entire annual data set.

[16] Annual Sr/Ca cycles were low-pass filtered to remove high-frequency variability with a periodicity of less than 60 days, such as that associated with tidal cycles [Cohen and Sohn, 2004]. To maintain consistency, the same Butterworth filter was applied to IGOSS SST and $\delta^{18}\text{O}_c$ data (Figure 3). The average of the three highest and three lowest values in each annual cycle was used to represent the annual maximum and minimum $\delta^{18}\text{O}_c$, and Sr/Ca ratio for each colony, as well as the relevant IGOSS SST. Mean Sr/Ca and $\delta^{18}\text{O}_c$ were then calculated as follows:

$$(\Sigma \text{max} + \Sigma \text{min}) / (n_{\text{max}} + n_{\text{min}}) \quad (1)$$

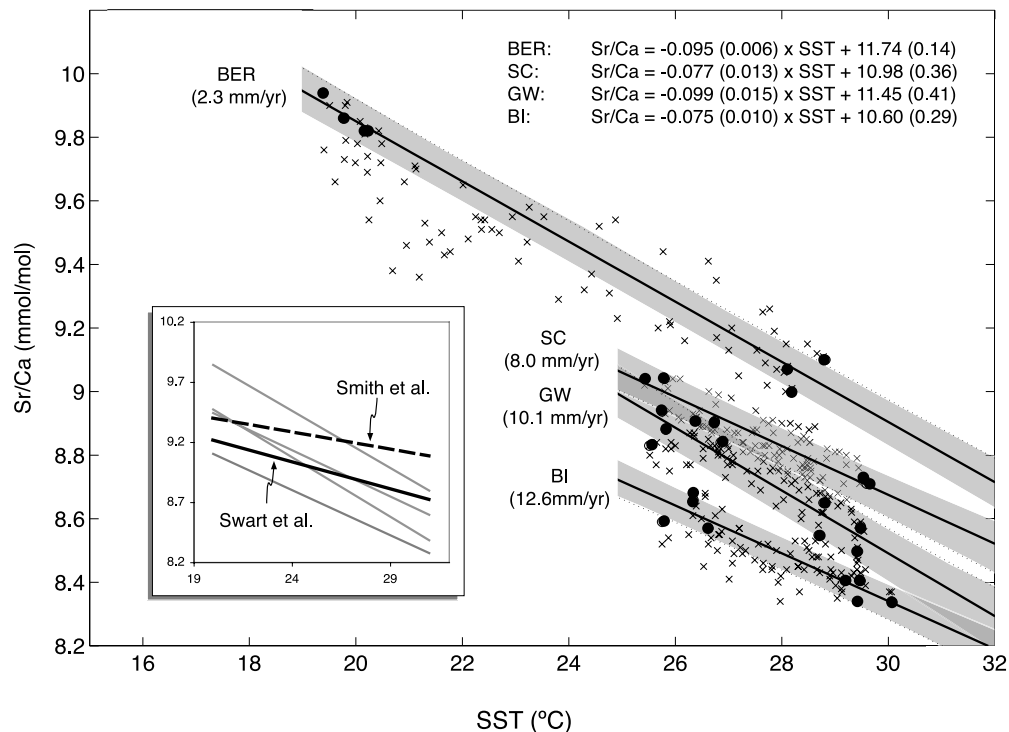


Figure 4. Sr/Ca–SST regressions from maxima and minima of filtered BI, GW, SC, and BER data (circles). All filtered data (crosses) are shown for comparison. Regressions exhibit systematic offsets toward higher Sr/Ca with slower mean annual extension rates. Shaded regions indicate standard error of reconstructed SST at the 95% confidence interval. (inset) Sr/Ca–SST regressions from this study (gray lines) differ from *Montastrea* Sr/Ca–SST calibrations of Swart *et al.* [2002] (black line) and Smith *et al.* [2006] (dashed line). See section 5.1.

The amplitude of Sr/Ca and $\delta^{18}\text{O}_c$ annual cycles was calculated as follows:

$$(\Sigma \max / n_{\max}) - (\Sigma \min / n_{\min}) \quad (2)$$

In both equations (1) and (2) max and min are the values of each coral's maxima and minima, and n_{\max} and n_{\min} are counts of the number of maxima and minima for a given coral.

[17] Mean Sr/Ca ratios exhibited an inverse correlation with mean annual extension rates. The mean Sr/Ca ratio of BI, growing at 12.6 mm a^{-1} , was $8.50 \text{ mmol mol}^{-1}$, while the mean Sr/Ca ratio of BER, growing at 2.3 mm a^{-1} , was $9.46 \text{ mmol mol}^{-1}$ (Table 1). No relationship was found between extension rates and coral $\delta^{18}\text{O}_c$ in the St Croix corals over their growth rate range of 8.0 – 12.6 mm a^{-1} .

4.4. Sr/Ca–SST Calibration

[18] Sr/Ca–SST calibrations were generated for each of the four corals by linearly regressing Sr/Ca maxima and minima against IGOSS SST minima and maxima (Figure 4). We did not adjust coralline Sr/Ca ratios for the slight differences in seawater Sr/Ca between sites. Regression slopes were subparallel, but y intercepts were systematically offset from one another over the range of typical coral Sr/Ca ratios and Caribbean SSTs. These offsets were equivalent to a SST difference of over 6°C at a Sr/Ca value of 8.8 mmol

mol^{-1} . Similar offsets were evident in unfiltered Sr/Ca–SST calibrations indicating the observed offsets were not an artifact of filtering.

[19] We used multiple linear regression to describe SST in terms of both Sr/Ca and mean annual extension rate. Data from three of the four corals analyzed (BI, GW and BER) were used to construct the regression. The best fit using this approach was:

$$\begin{aligned} \text{Sr/Ca}(\text{mmol mol}^{-1}) = & 11.82(\pm 0.13) - 0.058(\pm 0.004) \\ & \times \text{ext} - 0.092(\pm 0.005) \\ & \times \text{SST}(\text{°C}) \end{aligned} \quad (3)$$

where ext is the mean annual extension rate in mm a^{-1} . The error estimate on SST calculated from equation (3) is $\pm 1.4^\circ\text{C}$ at the 95% confidence interval using typical error propagation methods [Bevington, 1969].

[20] We used data from the fourth coral (SC) to assess the accuracy of our growth-dependent calibration. The mean and amplitude of SSTs derived from SC Sr/Ca ratios using equation (3) were both within 0.3°C of observed IGOSS values. SST maxima derived from SC were 0.4°C cooler than IGOSS, while minima were cooler by 0.1°C . These differences were all well within the $\pm 1.4^\circ\text{C}$ error for SSTs reconstructed from equation (3).

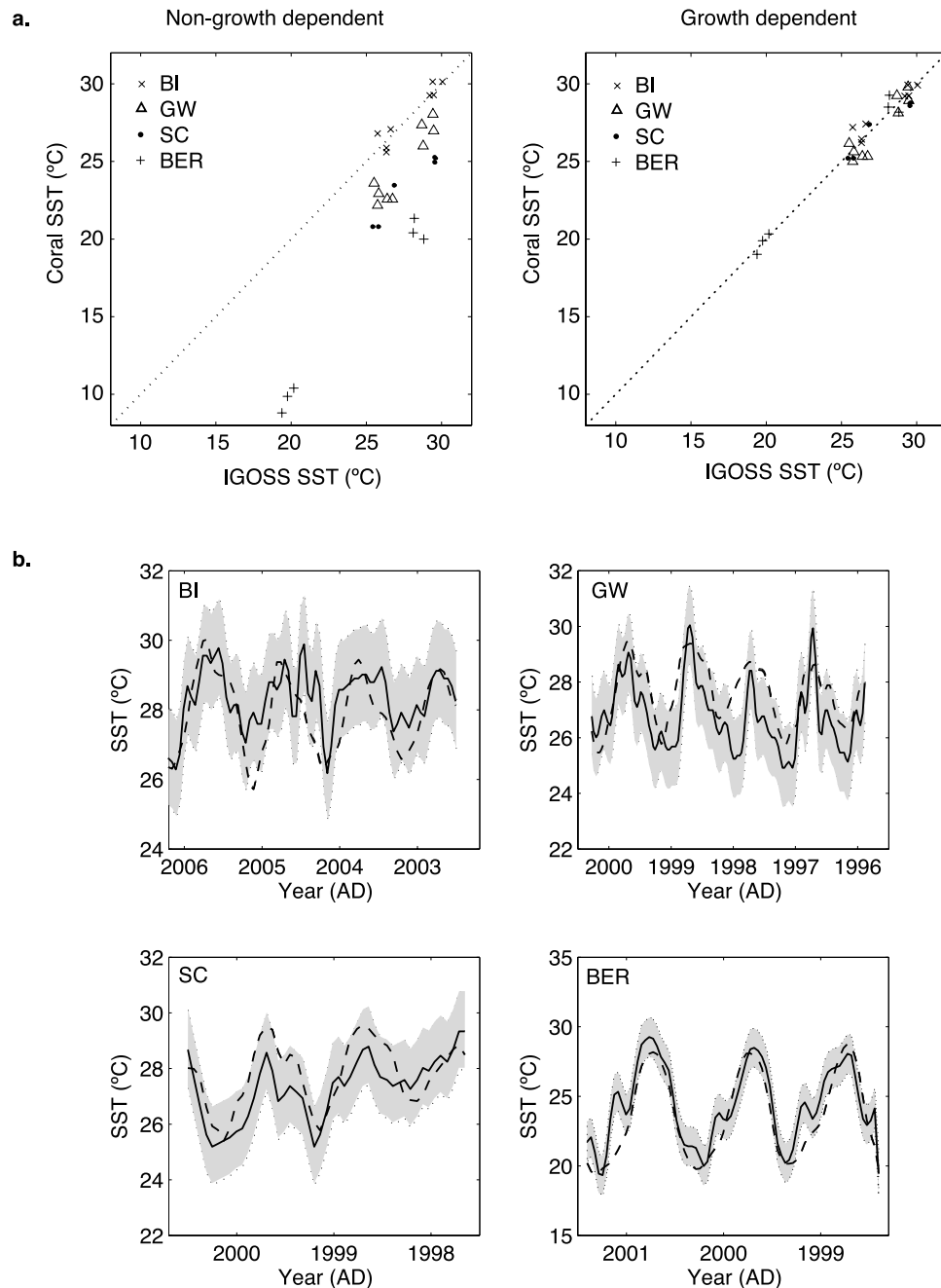


Figure 5. (a) Coral-derived SST versus IGOSS SST for growth-dependent and nongrowth-dependent calibrations. (left) Nongrowth-dependent SST estimates apply the BI calibration to annual Sr/Ca maxima and minima from BI (crosses), GW (triangles), SC (points), and BER (plus signs). (right) Growth-dependent SST estimates apply equation (3) to the same Sr/Ca maxima and minima data. Growth-dependent SSTs fall significantly closer to the 1:1 line than nongrowth-dependent SSTs, which can underestimate SST by over 9°C at slow growth rates. (b) Comparison of coral-derived SST from equation (3) (solid line) with IGOSS SST (dashed line) over the period of coral growth. Shaded areas indicate the standard error of reconstructed SST at the 95% confidence interval.

[21] Application of equation (3) to the Sr/Ca maxima and minima of all four corals accurately captured IGOSS SST maxima and minima using a single equation (Figure 5). The difference between coral-derived mean SST and IGOSS mean SST ranged from -0.14° to 0.15°C for the three

corals used in the calibration, and was -0.27°C for the verification coral. SST time series, derived by applying equation (3) to all Sr/Ca data for each coral, were also in good agreement with IGOSS SST (Figure 5b). A calibration constructed from BI, SC and BER yielded a similarly

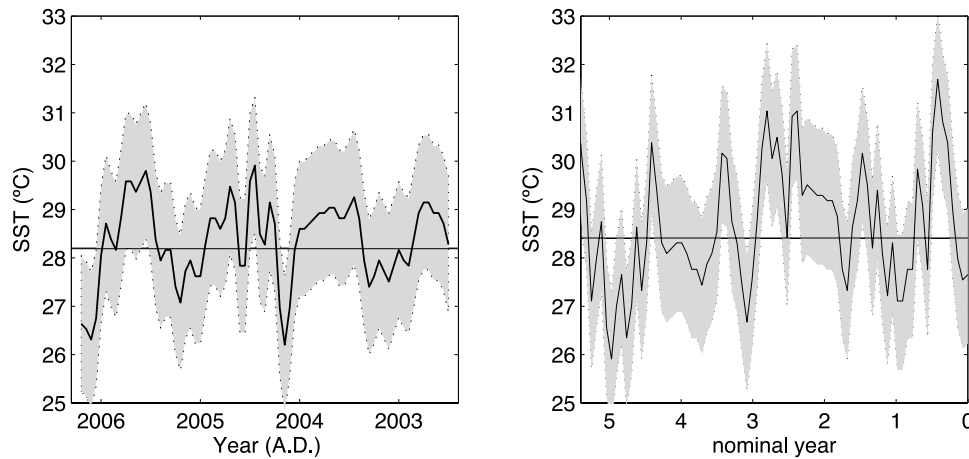


Figure 6. Coral-derived SST for BI (2003–2006 A.D.) and LIA (400 years B.P.) estimated from equation (3). BI is the modern site closest to the LIA drill core and is used to represent modern conditions. Shaded areas indicate the standard error of reconstructed SST at the 95% confidence interval.

good verification of GW. Including BI and BER in the calibration was required to accurately reconstruct SST in all four corals.

[22] We also derived SST from the Sr/Ca maxima and minima of each coral using a conventional nongrowth-dependent calibration based on the Sr/Ca–SST relationship derived from the BI coral. Excluding extension rate resulted in SST estimates as much as 9.0°C cooler than the observed IGOSS SST (Figure 5a). SC SST maxima derived from the nongrowth-dependent calibration were on average 4.0°C cooler than observed SST, while minima were on average 4.4°C cooler.

4.5. Little Ice Age

[23] The mean annual extension rate of the LIA *Montastrea* was 5.2 mm a⁻¹, based on x-radiograph gray scale analysis. The specimen exhibited no evidence of diagenetic alteration. Visual inspection of petrographic thin sections using transmitted light microscopy indicated that the LIA coral's centers of calcification were intact and that skeletal pore spaces were free of secondary aragonite.

[24] Mean SST derived from the LIA coral Sr/Ca ratios using our growth-dependent calibration was 28.4°C, with a seasonal amplitude of 3.5°C (Figure 6 and Table 1). In contrast, application of the conventional nongrowth-dependent Sr/Ca–SST calibration to LIA Sr/Ca yielded a mean SST of 22.6°C with a seasonal amplitude of 4.3°C. The modern coral BI was collected adjacent to the LIA drill site, and we used BI-derived SSTs to compare LIA reconstructions with the modern. Mean LIA SST derived from the growth-dependent calibration was within error of SST derived from the modern BI coral (28.0°C) using the same calibration. Conversely, mean LIA SST calculated using the nongrowth-dependent Sr/Ca–SST calibration was 5.3°C cooler than the modern BI coral.

5. Discussion

5.1. Sources of Sr/Ca Offsets

[25] The differences we observe between Sr/Ca–SST regressions derived for different *Montastrea* colonies indicate that *Montastrea* Sr/Ca ratios are not solely a function of SST. The observed offsets cannot be explained by local

Table 2. Proportion of Seasonal Coral Sr/Ca Variability Explained by Intersite SST and Seawater Sr/Ca Variations^a

Sample	$\Delta\text{Coral Sr/Ca}_{\text{min}}$ (mmol mol ⁻¹)	ΔSST (°C)	$\Delta\text{Sr/Ca}_{\text{SST}}$ (mmol mol ⁻¹)	$\Delta\text{Sr/Ca}_{\text{sw}}$ (mmol mol ⁻¹)	Total (mmol mol ⁻¹)	$\Delta\text{Coral Sr/Ca}_{\text{min}}$ (%)
<i>Summer</i>						
GW	0.14	0	0	0.02	0.02	14.3
SC	0.32	0.25	-0.02	0.07	0.05	14.7
<i>Winter</i>						
GW	0.24	-0.25	0.02	0.02	0.04	17.9
SC	0.33	0	0	0.07	0.07	21.2

^aDeltas (Δ) represent the difference in each parameter relative to that parameter at BI. Summer values compare mean minimum coral Sr/Ca with maximum SST measured by in situ SST loggers at each site. Winter values compare mean maximum coral Sr/Ca with minimum SST. Seawater Sr/Ca was not measured through a full annual cycle, and the same intersite differences ($\Delta\text{Sr/Ca}_{\text{sw}}$) are used in summer and winter. The difference in coral Sr/Ca expected from intersite SST differences ($\Delta\text{Sr/Ca}_{\text{SST}}$) assumes a sensitivity of -0.09 mmol mol⁻¹ °C⁻¹. $\Delta\text{Sr/Ca}_{\text{sw}}$ and $\Delta\text{Sr/Ca}_{\text{SST}}$ were added to estimate the total coral Sr/Ca variability expected from intersite SST and seawater Sr/Ca variations. Total values were ~14–21% of the intersite Sr/Ca variations observed in corals ($\Delta\text{Coral Sr/Ca}$).

intersite variations in SST or seawater Sr/Ca. Assuming a Sr/Ca–SST sensitivity of $-0.09 \text{ mmol mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$, the differences in SST and seawater Sr/Ca ratios we measured between sites can account for no more than 22% of the observed variability in coral Sr/Ca among BI, GW and SC (Table 2).

[26] Two recent *Montastrea spp.* Sr/Ca–SST calibrations [Swart *et al.*, 2002; Smith *et al.*, 2006] have less negative slopes than those suggested by our data that may be caused by undersampling during part of an annual cycle (Figure 4). Separately applying Swart *et al.*'s [2002] summer and winter Sr/Ca values to our equation (3) calculates a summer SST that is within error of observed IGOSS summer SST (29.6°C), while the reconstructed winter value underestimates IGOSS winter SST (23.3°C) outside of error. This may indicate peak winter Sr/Ca was not captured in that calibration despite a high sampling rate. Furthermore, Smith *et al.* [2006] sampled considerably deeper ($\sim 1 \text{ mm}$) into coral skeletons to produce up to $400 \mu\text{g}$ of carbonate powder. This approach may sample multiple skeletal elements, not just the thecal wall, a possibility that is consistent with their diminished $\delta^{18}\text{O}_c$ -SST sensitivity (-0.08 to $-0.12\text{‰ }^{\circ}\text{C}^{-1}$) compared to previous studies (-0.17 to $-0.24\text{‰ }^{\circ}\text{C}^{-1}$).

[27] Instead, differences among Sr/Ca–SST calibrations derived from different *Montastrea* colonies may be caused by processes associated with biogenic mineralization referred to as “vital effects.” Other studies have reported an inverse correlation between coral growth rate and Sr/Ca ratios [deVilliers *et al.*, 1995; Cardinal *et al.*, 2001; Goodkin *et al.*, 2005], but this relationship is not straightforward and is not apparent in all species. The Sr/Ca ratios of abiogenic aragonites precipitated experimentally from seawater show a positive correlation with crystal growth rate [Gabitov *et al.*, 2006], which is opposite from what we observe in *Montastrea*. This suggests crystal extension rate per se is not the mechanism linking coral Sr/Ca ratios with skeletal extension rate. Rather, we propose that the inverse relationship between Sr/Ca and growth rate in *Montastrea* is consistent with the Rayleigh fractionation model for coral biomineralization, in which compositional variability is driven in large part by variations in the mass fraction of aragonite precipitated by the coral from a batch of calcifying fluid [Gaetani and Cohen, 2006; Cohen *et al.*, 2006]. In the case of Sr/Ca, the more aragonite precipitated from a batch of fluid, the lower the Sr/Ca ratio of the coral aragonite will be because the partition coefficient for Sr^{2+} between fluid and aragonite is greater than that for Ca^{2+} [Gaetani and Cohen, 2006]. Interpreted within this framework, the correlation between Sr/Ca and growth rate in *Montastrea* suggests a correlation between the mass fraction aragonite precipitated (“precipitation efficiency”) and average annual skeletal extension rate. Intra-annual variations in “precipitation efficiency” may cause higher-frequency Sr/Ca variations, but we cannot assess these impacts without improved knowledge of growth rate variability within a year. While there is clearly a link between skeletal composition and skeletal growth rate in the *Montastrea* analyzed in this study, such a link has not been observed in many *Porites*

spp. corals where intercolony differences in Sr/Ca ratios have been observed [e.g., Felis *et al.*, 2004].

[28] Nevertheless, in the case of *Montastrea*, incorporating growth rate significantly improves the predictive capabilities of our calibration and allows us to apply a single equation to corals from several sites. SST estimates derived from application of the growth-dependent calibration to the modern corals are far more accurate than those derived from application of a nongrowth-dependent calibration (Figure 5). The implication of our results for interpreting Sr/Ca ratios of fossil corals in terms of SST is seen in our estimate of LIA SSTs derived using a nongrowth-dependent calibration. A cooling of 5.3°C relative to today exceeds most estimates of tropical SST cooling during the Last Glacial Maximum [Pflaumann *et al.*, 2003; Schmidt *et al.*, 2006] and would likely have caused significant changes in coral reef fauna that are not evident in the St. Croix drill cores [Hubbard *et al.*, 2005]. Further, a depression of mean annual SST below the 24°C isotherm would limit the growth of most *Montastrea* species [Carricart-Ganivet, 2004].

5.2. Comparison of LIA Paleoclimate Records

[29] While our short LIA record cannot be considered representative of the spatial and temporal variability of the entire 500-year long LIA period, our results are generally consistent with geochemical evidence from foraminifera that indicate slight ($<1^{\circ}\text{C}$) SST cooling in the Florida Straits at ~ 500 years B.P. [Lund and Curry, 2006]. Our results are inconsistent however, with LIA cooling estimates of >2 – 3°C from Caribbean corals, foraminiferal assemblages and sclerosponge geochemistry [Winter *et al.*, 2000; Watanabe *et al.*, 2001; Nyberg *et al.*, 2002; Haase-Schramm *et al.*, 2003, 2005]. Winter *et al.* [2000] interpreted coral $\delta^{18}\text{O}_c$ as a SST proxy although it is a function of both SST and $\delta^{18}\text{O}_{\text{sw}}$, and the 3°C LIA cooling estimate may reflect a small or negligible cooling accompanied by a large $\delta^{18}\text{O}_{\text{sw}}$ anomaly. If the $\delta^{18}\text{O}_c$ measured in our St. Croix corals is interpreted solely in terms of temperature (using equation (2) of Watanabe *et al.* [2001]), we calculate a similarly large LIA cooling of $\sim 5^{\circ}\text{C}$. Rather than measuring Sr/Ca, Watanabe *et al.* [2001] analyzed coral Mg/Ca ratios to estimate LIA SSTs. However, recent studies show that physiological processes, rather than temperature, exert the dominant influence on coral Mg/Ca ratios [Meibom *et al.*, 2006; Gaetani and Cohen, 2006; Reynaud *et al.*, 2007].

[30] In addition, a component of the apparent discrepancies between our LIA coral SST estimates and previous estimates based on coral and foraminifera may reflect natural variability. LIA Caribbean climate likely varied on multidecadal timescales [Vellinga and Wu, 2004; Haase-Schramm *et al.*, 2005], and foraminiferal Mg/Ca suggests relatively warm SSTs in the Caribbean from 400 to 500 years B.P. [Black *et al.*, 2007]. Though subject to large radiocarbon dating errors, even the 2σ age range for our LIA coral suggests it grew during a warmer LIA interval prior to the greatest cooling near 1700 A.D. [Jones and Mann, 2004; Black *et al.*, 2007], which may explain why we do not detect a large LIA SST change during this time.

[31] Assuming that LIA SSTs were not significantly cooler, the observed higher coral $\delta^{18}\text{O}_c$ is best explained

by higher $\delta^{18}\text{O}_{\text{sw}}$. This hint of a saltier Caribbean is consistent with evidence from a variety of other archives suggesting increased LIA aridity throughout the region because of a southerly migration of the ITCZ [Haug et al., 2001; Hodell et al., 2005; Lund and Curry, 2006]. The position of the ITCZ is sensitive to small ($\sim 0.5^\circ\text{C}$) perturbations of the Atlantic cross-equatorial SST gradient [Chiang et al., 2002], suggesting that small variations in LIA SST do not preclude significant changes in the hydrologic cycle.

6. Conclusions

[32] 1. Sr/Ca ratios of *Montastrea* corals in this study are a function of both SST and mean annual colony extension rate.

[33] 2. The inverse relationship observed between growth rate and coral Sr/Ca is consistent with a biomineralization mechanism in which coral Sr/Ca is governed in large part by the mass fraction of aragonite precipitated and Rayleigh fractionation.

[34] 3. A Sr/Ca–SST calibration that incorporates coral growth rate significantly improves correlations between coral Sr/Ca ratios and instrumental SST.

[35] 4. Applying a conventional nongrowth-dependent Sr/Ca–SST calibration estimates modern SSTs that are up to 9.0°C cooler than observed, and calculates SSTs in a 5-year

LIA (400 years B.P.) window that are more than 5.0°C cooler than today.

[36] 5. Application of the growth-dependent calibration yields SSTs during this 5-year LIA period that are within $\pm 1.4^\circ\text{C}$ of modern, i.e., our calibration error.

[37] 6. Higher Caribbean coral $\delta^{18}\text{O}_{\text{c}}$ during this 5-year LIA window suggests an increase in $\delta^{18}\text{O}_{\text{sw}}$ that is consistent with previous evidence of more arid conditions and may be explained by a southerly shift in mean ITCZ position.

[38] 7. Applying the approach presented here to existing and future *Montastrea* spp. across a wide range of annual linear extension rates may allow a single, robust calibration.

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References

- Bevington, P. R. (1969), Propagation of error, in *Data Reduction and Error Analysis for the Physical Sciences*, chap. 4, pp. 56–65, McGraw Hill, New York.
- Black, D. E., R. C. Thunell, A. Kaplan, L. C. Peterson, and E. J. Tappa (2004), A 2000-year record of Caribbean and tropical North Atlantic hydrographic variability, *Paleoceanography*, *19*, PA2022, doi:10.1029/2003PA000982.
- Black, D. E., R. C. Abahazi, R. C. Thunell, A. Kaplan, E. J. Tappa, and L. C. Peterson (2007), An 8-century tropical Atlantic SST record from the Cariaco Basin: Baseline variability, twentieth-century warming, and Atlantic hurricane frequency, *Paleoceanography*, *22*, PA4204, doi:10.1029/2007PA001427.
- Cardinal, D., B. Hamelin, E. Bard, and J. Pätzold (2001), Sr/Ca, U/Ca and $\delta^{18}\text{O}$ records in recent massive corals from Bermuda: Relationships with sea surface temperature, *Chem. Geol.*, *176*, 213–233, doi:10.1016/S0009-2541(00)00396-X.
- Carricart-Ganivet, J. P. (2004), Sea surface temperature and the growth of the west Atlantic reef-building coral *Montastrea annularis*, *J. Exp. Mar. Biol. Ecol.*, *302*, 249–260, doi:10.1016/j.jembe.2003.10.015.
- Chiang, J. C. H., Y. Kushnir, and A. Giannini (2002), Deconstructing Atlantic Intertropical Convergence Zone variability: Influence of the local cross-equatorial sea surface temperature gradient and remote forcing from the eastern equatorial Pacific, *J. Geophys. Res.*, *107*(D1), 4004, doi:10.1029/2000JD000307.
- Cobb, K. M., C. D. Charles, H. Cheng, M. Kastner, and R. L. Edwards (2003), U-Th dating living and young fossil corals from the central tropical Pacific, *Earth Planet. Sci. Lett.*, *210*, 91–103, doi:10.1016/S0012-821X(03)00138-9.
- Cohen, A. L., and R. A. Sohn (2004), Tidal modulation of Sr/Ca ratios in a Pacific reef coral, *Geophys. Res. Lett.*, *31*, L16310, doi:10.1029/2004GL020660.
- Cohen, A. L., and S. R. Thorrold (2007), Recovery of temperature records from slow-growing corals by fine scale sampling of skeletons, *Geophys. Res. Lett.*, *34*, L17706, doi:10.1029/2007GL030967.
- Cohen, A. L., S. R. Smith, M. S. McCartney, and J. van Etten (2004), How brain corals record climate: An integration of skeletal structure, growth and chemistry of *Diploria labyrinthiformis* from Bermuda, *Mar. Ecol. Prog. Ser.*, *271*, 147–158, doi:10.3354/meps271147.
- Cohen, A. L., G. A. Gaetani, T. Lundaly, B. H. Corliss, and R. Y. George (2006), Compositional variability in a cold-water scleractinian *Lophelia pertusa*: New insights into “vital effects,” *Geochem. Geophys. Geosyst.*, *7*, Q12004, doi:10.1029/2006GC001354.
- Cronin, T. M., G. S. Dwyer, T. Kamiya, S. Schwede, and D. A. Willard (2003), Medieval Warm Period, Little Ice Age and 20th century temperature variability from Chesapeake Bay, *Global Planet. Change*, *36*, 17–29, doi:10.1016/S0921-8181(02)00161-3.
- Department of Conservation and Cultural Affairs (1986), Marine water quality measurements in Chenay Bay, 1975–1986, report, Charlotte Amalie, St. Thomas, Virgin Islands.
- deVilliers, S. B. (1999), Seawater strontium and Sr/Ca variability in the Atlantic and Pacific Oceans, *Earth Planet. Sci. Lett.*, *171*, 623–634, doi:10.1016/S0012-821X(99)00174-0.
- deVilliers, S., B. K. Nelson, and A. R. Chivas (1995), Biological controls on coral Sr/Ca and $\delta^{18}\text{O}$ reconstructions of sea surface temperatures, *Science*, *269*, 1247–1249, doi:10.1126/science.269.5228.1247.
- Felis, T., G. Lohmann, H. Kuhnert, S. J. Lorenz, D. S. Cholz, J. Patzold, S. A. Al-Rousan, and S. M. Al-Moghrabi (2004), Increased seasonality in Middle East temperatures during the last interglacial period, *Nature*, *429*, 164–168, doi:10.1038/nature02546.
- Gabitov, R. I., A. L. Cohen, G. A. Gaetani, M. Holcomb, and E. B. Watson (2006), The impact of crystal growth rate on element ratios in aragonite: An experimental approach to understanding vital effects, *Geochim. Cosmochim. Acta*, *70*(18), A187–A220, doi:10.1016/j.gca.2006.06.377.
- Gaetani, G. A., and A. L. Cohen (2006), Element partitioning during precipitation of aragonite from seawater: A framework for understanding paleoproxies, *Geochim. Cosmochim. Acta*, *70*, 4617–4634, doi:10.1016/j.gca.2006.07.008.
- Goodkin, N. F., K. A. Huguen, A. L. Cohen, and S. R. Smith (2005), Record of Little Ice Age sea surface temperatures at Bermuda using a growth-dependent calibration of coral Sr/Ca, *Paleoceanography*, *20*, PA4016, doi:10.1029/2005PA001140.
- Haase-Schramm, A., F. Böhm, A. Eisenhauer, W.-C. Dullo, M. M. Joachimski, B. Hansen, and J. Reitner (2003), Sr/Ca ratios and oxygen isotopes from sclerosponges: Temperature history of the Caribbean mixed layer and thermocline during the Little Ice Age, *Paleoceanography*, *18*(3), 1073, doi:10.1029/2002PA000830.
- Haase-Schramm, A., F. Böhm, A. Eisenhauer, D. Garbe-Schonberg, W. C. Dullo, and J. Reitner (2005), Annual to interannual temperature variability in the Caribbean during the Maunder sunspot minimum, *Paleoceanography*, *20*, PA4015, doi:10.1029/2005PA001137.
- Haug, G. H., K. A. Huguen, D. M. Sigman, L. C. Peterson, and U. Rohl (2001), Southward mi-

- gration of the intertropical convergence zone through the Holocene, *Science*, *293*, 1304–1308, doi:10.1126/science.1059725.
- Hendy, E. J., M. K. Gagan, C. A. Alibert, M. T. McCulloch, J. M. Lough, and P. J. Isdale (2002), Abrupt decrease in tropical Pacific Sea surface salinity at end of Little Ice Age, *Science*, *295*, 1511–1514, doi:10.1126/science.1067693.
- Hernandez-Guerra, A., and T. M. Joyce (2000), Water masses and circulation in the surface layers of the Caribbean at 66°W, *Geophys. Res. Lett.*, *27*, 3497–3500, doi:10.1029/1999GL011230.
- Hodell, D. A., M. Brenner, J. H. Curtis, R. Medina-Gonzalez, E. I. C. Can, A. Albarnaz-Pat, and T. P. Guilderson (2005), Climate change on the Yucatan Peninsula during the Little Ice Age, *Quat. Res.*, *63*, 109–121, doi:10.1016/j.yqres.2004.11.004.
- Hubbard, D. K., H. Zankl, I. Van Heerden, and I. P. Gill (2005), Holocene reef development along the northeastern St. Croix shelf, Buck Island, Virgin Islands, U.S., *J. Sediment. Res.*, *75*, 97–113, doi:10.2110/jsr.2005.009.
- Hughen, K. A., et al. (2004), Marine radiocarbon age calibration, 26–0 ka BP, *Radiocarbon*, *46*, 1059–1086.
- Jones, P. D., and M. E. Mann (2004), Climate over past millennia, *Rev. Geophys.*, *42*, RG2002, doi:10.1029/2003RG000143.
- Leder, J. J., P. K. Swart, A. M. Szmant, and R. E. Dodge (1996), The origin of variations in the isotopic record of scleractinian corals. 1. Oxygen, *Geochim. Cosmochim. Acta*, *60*, 2857–2870, doi:10.1016/0016-7037(96)00118-4.
- Lough, J. M. (2004), A strategy to improve the contribution of coral data to high-resolution paleoclimatology, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *204*, 115–143.
- Lund, D. C., and W. Curry (2006), Florida Current surface temperature and salinity variability during the last millennium, *Paleoceanography*, *21*, PA2009, doi:10.1029/2005PA001218.
- Meibom, A., et al. (2006), Vital effects in coral skeletal composition display strict three-dimensional control, *Geophys. Res. Lett.*, *33*, L11608, doi:10.1029/2006GL025968.
- Mohiuddin, M. M., A. Nishimura, Y. Tanaka, and A. Shimamoto (2004), Seasonality of biogenic particle and planktonic foraminifera fluxes: Response to hydrographic variability in the Kuroshio Extension, northwestern Pacific Ocean, *Deep Sea Res., Part I*, *51*, 1659–1683.
- National Research Council (2006), *Surface Temperature Reconstructions for the Last 2,000 Years*, 196 pp., Natl. Acad. Press, Washington, D.C.
- Nyberg, J., B. A. Malmgren, A. Kuijpers, and A. Winter (2002), A centennial-scale variability of tropical North Atlantic surface hydrography during the late Holocene, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *183*, 25–41, doi:10.1016/S0031-0182(01)00446-1.
- Ostermann, D. R., and W. B. Curry (2000), Calibration of stable isotopic data: An enriched $\delta^{18}\text{O}$ standard used for source gas mixing detection and correction, *Paleoceanography*, *15*, 353–360, doi:10.1029/1999PA000411.
- Pflaumann, U., et al. (2003), Glacial North Atlantic: Sea-surface conditions reconstructed by GLAMAP 2000, *Paleoceanography*, *18*(3), 1065, doi:10.1029/2002PA000774.
- Reynaud, S., C. Ferrier-Pages, A. Meibom, S. Mostefaoui, R. Mortlock, R. Fairbanks, and D. Allemand (2007), Light and temperature effects on Sr/Ca and Mg/Ca ratios in the scleractinian coral *Acropora* sp., *Geochim. Cosmochim. Acta*, *71*, 354–362, doi:10.1016/j.gca.2006.09.009.
- Reynolds, R. W., and T. M. Smith (1994), Improved global sea surface temperature analyses using optimum interpolation, *J. Clim.*, *7*, 929–948, doi:10.1175/1520-0442(1994)007<0929:IGSSTA>2.0.CO;2.
- Rosenthal, Y., M. P. Field, and R. M. Sherrell (1999), Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry, *Anal. Chem.*, *71*, 3248–3253, doi:10.1021/ac981410x.
- Schmidt, M. W., M. J. Vautravers, and H. J. Spero (2006), Western Caribbean sea surface temperatures during the late Quaternary, *Geochim. Geophys. Geosyst.*, *7*, Q02P10, doi:10.1029/2005GC000957.
- Smith, J. M., T. M. Quinn, K. P. Helmle, and R. B. Halley (2006), Reproducibility of geochemical and climatic signals in the Atlantic coral *Montastraea faveolata*, *Paleoceanography*, *21*, PA1010, doi:10.1029/2005PA001187.
- Swart, P. K., H. Elderfield, and M. J. Greaves (2002), A high-resolution calibration of Sr/Ca thermometry using the Caribbean coral *Montastraea annularis*, *Geochim. Geophys. Geosyst.*, *3*(11), 8402, doi:10.1029/2002GC000306.
- Thunell, R. C., and L. A. Reynolds (1984), Sedimentation of planktonic foraminifera: Seasonal changes in species flux in the Panama Basin, *Micropaleontology*, *30*, 243–262, doi:10.2307/1485688.
- Vellinga, M., and P. L. Wu (2004), Low-latitude freshwater influence on centennial variability of the Atlantic thermohaline circulation, *J. Clim.*, *17*, 4498–4511, doi:10.1175/3219.1.
- Watanabe, T., A. Winter, and T. Oba (2001), Seasonal changes in sea surface temperature and salinity during the Little Ice Age in the Caribbean Sea deduced from Mg/Ca and $^{18}\text{O}/^{16}\text{O}$ ratios in corals, *Mar. Geol.*, *173*, 21–35, doi:10.1016/S0025-3227(00)00166-3.
- Weil, E., and N. Knowlton (1994), A multi-character analysis of the Caribbean coral *Montastraea annularis* (Ellis and Solander, 1786) and its two sibling species, *M. faveolata* (Ellis and Solander, 1786) and *M. franksi* (Gregory, 1895), *Bull. Mar. Sci.*, *55*, 151–175.
- Winter, A., H. Ishioroshi, T. Watanabe, T. Oba, and J. Christy (2000), Caribbean sea surface temperatures: Two-to-three degrees cooler than present during the Little Ice Age, *Geophys. Res. Lett.*, *27*, 3365–3368, doi:10.1029/2000GL011426.
- Yoo, J.-M., and J. A. Carton (1990), Annual and interannual variation of the freshwater budget in the tropical Atlantic Ocean and the Caribbean Sea, *J. Phys. Oceanogr.*, *20*, 831–845, doi:10.1175/1520-0485(1990)020<0831:AAI-VOT>2.0.CO;2.

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