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Recovery of temperature records from slow-growing corals by fine scale sampling of skeletons

Anne L. Cohen[1] and Simon R. Thorrold[1]

[1]   We used laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) to analyze Sr/Ca ratios in 5 colonies of the Atlantic corals, *Diploria labyrinthiformis* and *Montastrea franski*, each growing less than 5 mm yr^{-1}. By targeting the centers of septa we avoided thickening deposits to achieve an analytical sampling resolution of 5-10 days. The sensitivity of Sr/Ca to temperature (-0.096 mmol/mol/°C) is ~3 times higher than previously reported for these species and equivalent to that exhibited by fast-growing *Porites* corals from the Indo-Pacific. The Sr/Ca-sea surface temperature (SST) calibrations derived from these corals were not statistically different and were independent of colony growth rate over the period studied. Data from 4 *D. labyrinthiformis* colonies were pooled to produce a single Sr/Ca-SST calibration with a calculated standard error on the predicted ocean temperature of ±0.51°C. Applying our calibration to Sr/Ca analyses of *D. labyrinthiformis* skeleton deposited in the late 18th century indicated that average annual sea surface temperatures around Bermuda were ~1°C cooler than today. **Citation:** 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.

1.   Introduction

[2]   The skeletons of long-lived corals have considerable potential to provide information about past ocean conditions. However, one major limitation on the application of coral-based geochemical proxies in paleoceanographic reconstructions is the observation that conspecifics experiencing the same environmental conditions may yield different calibration equations. These differences are not insignificant. For instance, three recent studies of the Bermudan brain coral *Diploria* predict ocean temperatures ranging from 23°C through 30°C from a coral Sr/Ca value of 9 mmol mol^{-1} [*Cardinal et al.*, 2001; *Kuhnert et al.*, 2005; *Goodkin et al.*, 2005; H. Kuhnert, personal communication, 2005]. This variability limits the applicability of individual Sr/Ca-temperature calibrations to the coral from which it was initially derived, and makes it very difficult to extract accurate temperatures from fossil corals for which a sample-specific calibration cannot be established.

[3]   Two processes with the potential to induce variability amongst coral proxy calibrations in the absence of environmental variability are physiological processes or "vital effects", and skeletal growth processes. Numerous studies have cited "vital effects" to explain intra- and inter-specific variability in skeletal chemistry but the potential effect of skeletal growth mechanisms has been little studied. In all corals, skeletal growth involves an initial extension (upward growth) of skeletal elements and their subsequent thickening (outward growth) (Figure 1) [*Barnes et al.*, 1995]. Extension is driven primarily by accretion of centers of calcification (COCs) that form a semi-continuous narrow band down the middle of skeletal elements, parallel to the upward growth axis of the skeleton. Thickening occurs as aragonite fibers grow outward from the COCs, more-or-less perpendicular to the upward growth axis (Figure 1b). Thickening continues for as long as the skeletal elements are in contact with tissue [*Barnes and Lough*, 1993], which may be several months to a year. Techniques that employ a drill or microtome to subsample the skeleton for chemical analysis (hereafter referred to as "bulk sampling") include material from both the initial extension and all or part of the thickening deposit. Thus bulk samples inherently combine skeleton accreted over a period of time into a single subsample. *Barnes et al.* [1995] predicted that inclusion of thickening deposits in skeletal subsamples would lead to dampening and distortion of the true annual cycle. Further, *Cohen et al.* [2004] suggested that variations in the seasonality of thickening within and among coral colonies may bias the integrated signal toward the season when most thickening occurs.

[4]   We used laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) to analyze Sr/Ca ratios along the centers of septa in the septothecal walls of two Atlantic corals, *Diploria labyrinthiformis* and *Montastrea franksi*. Previous Sr/Ca-temperature calibrations for *Diploria* and *Montastrea* were derived using traditional "bulk" sampling techniques to remove skeletal subsamples. Our sampling strategy targeted the initial extension deposits only, avoiding thickening deposits to achieve an analytical sampling resolution of 5–10 days.

2.   Materials and Methods

[5]   Three *D. labyrinthiformis* colonies were collected on April 15th, 1999 from 13 m depth ~1 km offshore of John Smith Bay (JSB), on the south-east terrace of Bermuda (32°10′N, 64°30′W). On June 1st, 2000, September 24th, 2000 and January 24th, 2001, one *D. labyrinthiformis* and one *M. franski* colony were stained live with sodium alizarin sulphonate and harvested on June 1st, 2001 [*Cohen et al.*, 2004]. A subsample of skeleton, ~5 mm wide by ~20 mm long, was cut from the tip of a slab removed from the center of each colony [*Cohen et al.*, 2004], epoxy-mounted in a 25.4 mm diameter Al ring and polished with a

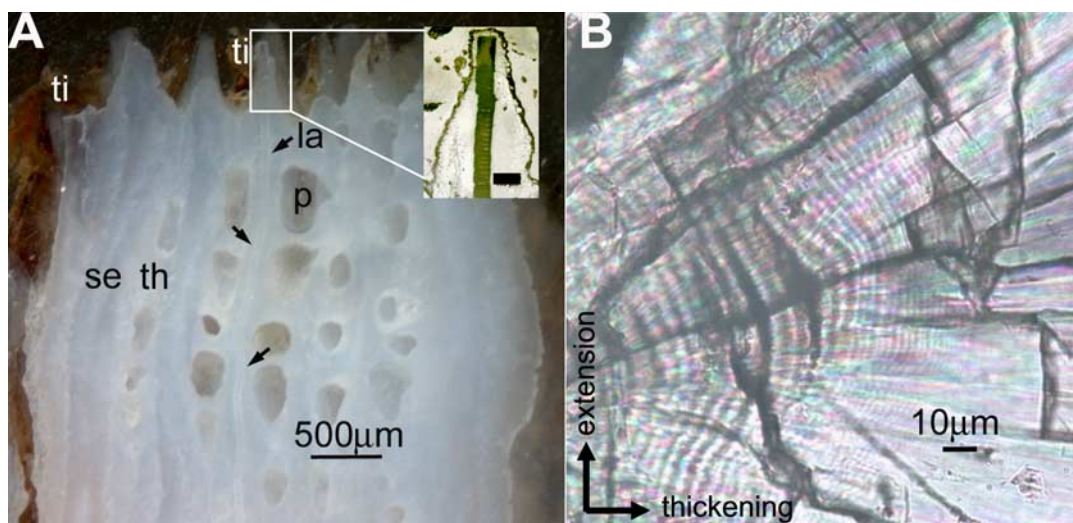[1]Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

Figure 1. (a) Sectioned, polished tip of the septothecate wall of *D. labyrinthiformis*. Arrows indicate laser line (la) down the center of a septum (se). Ti = tissue; th = theca; p = pore spaces. The inset shows the tip of the lasered septum, magnified to demonstrate the position of the laser line. Scale Bar = 100 μm. (b) Petrographic thin-section of crystal bundles emerging from COCs (not visible) in the septum of *D. labyrinthiformis*. Daily growth bands [*Risk and Pearce*, 1992] are dark lines in the crystal bunds that indicate the duration of skeletal thickening process and the rate of crystal growth.

0.3-μm alumina suspension. Tissue was not removed. We assayed Sr/Ca ratios using LA ICP-MS. A 213nm Nd:YAG laser (nominal beam diameter of 10 μm) coupled to a single collector sector field ICP-MS assayed Sr/Ca ratios from a 50 μm × 50 μm raster at the centers of septa (Figure 1, inset). Internal precision (n = 72) of Sr/Ca ratios from laser samples averaged 0.45% (±1 standard error). A dissolved aragonite standard, certified for Ca and Sr [*Sturgeon et al.*, 2005], was measured every 5 samples to account for variations in elemental mass bias [*Swart et al.*, 2002]. External precision (relative standard deviation) of Sr/Ca measurements on a dissolved aragonite lab standard was 0.28% (n = 241). Centers of septa were identified by the COCs which appear on the polished skeletal surface as a continuous vertical opaque line <10 μm wide. Data were not collected from regions where the opaque line of centers was not visible. At the centers of septa, where bundles of crystals are just emerging from the COCs, fine daily growth bands [*Risk and Pearce*, 1992] in the crystal bundles indicate that outward crystal growth rates in all the colonies are ~10-μm day^{-1} (Figure 1b). Using the upward extension rates of each colony (Table 1) and an outward crystal growth rate of 10-μm day^{-1}, we calculated the analytical

sampling resolution of our raster to be 5 days for corals extending upward by 10-μm day^{-1} (4 mm year^{-1}) and 10 days for corals extending upward by 5-μm day^{-1} (2 mm year^{-1}).

[6] Mean monthly water temperatures from 1992 to 2001, recorded between 0 and 20m depth at Hydrostation S, 15 nautical miles southeast of Bermuda, were used to calibrate the Sr/Ca thermometer (http://www.bbsr.edu/cintoo/hydrostation/hydrostation.html). We applied a 4-pole, zero-phase Butterworth low pass digital filter with corner period of 35 days to all Sr/Ca and temperature data to remove high-frequency oscillations with periods of ≤1 month [*Oppenheim and Swart*, 1989; *Cohen and Sohn*, 2004]. The standard error (*s.e.*) on SSTs predicted from coral Sr/Ca was calculated using the following statistic:

$$s.e. = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{n-2}} \cdot \sqrt{1 + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{\sum (x_i - \bar{x})^2}}$$

where y_i is the measured temperature for a given Sr/Ca ratio, $\hat{y}_i$ is the temperature predicted from the Sr/Ca-SST regression, x_0 is the Sr/Ca ratio for which the uncertainty is being

Table 1. Data for Corals Analyzed in This Study[a]

Coral ID	Extension Rate, mm yr^{-1}	Number of Annual Cycles	Regression Equation[b]
BERS1	3.8	2 (1999–2000)	T(°C) = −10.15 (±0.52)*Sr/Ca + 115.79 (±4.72)
BERMF001	2.6	4 (1997–2000)	T(°C) = −9.48 (±0.47)*Sr/Ca + 109.22 (±4.29)
BER002	3.4	4 (1995–1999)	T(°C) = −10.22 (±0.80)*Sr/Ca + 115.32 (±7.23)
BER003	4.6	3.5 (1995–1999)	T(°C) = −10.99 (±0.52)*Sr/Ca + 122.22 (±4.6)
BER004	2.1	7 (1992–1999)	T(°C) = −9.70 (±0.55)*Sr/Ca + 111.12 (±4.97)
Diploria pooled		9 (1992–2000)	T(°C) = −10.08 (±0.38)*Sr/Ca + 114.53(±3.14)

[a]BERS1 and BER002-BER004 are *D. labyrinthiformis*; BERMF001 is *M. franski*. Growth rates are estimated from the peak winter-to-peak winter distance between successive annual Sr/Ca cycles. The 95% confidence interval for the slope and intercept of the Sr/Ca-SST regression equations are in parenthesis.

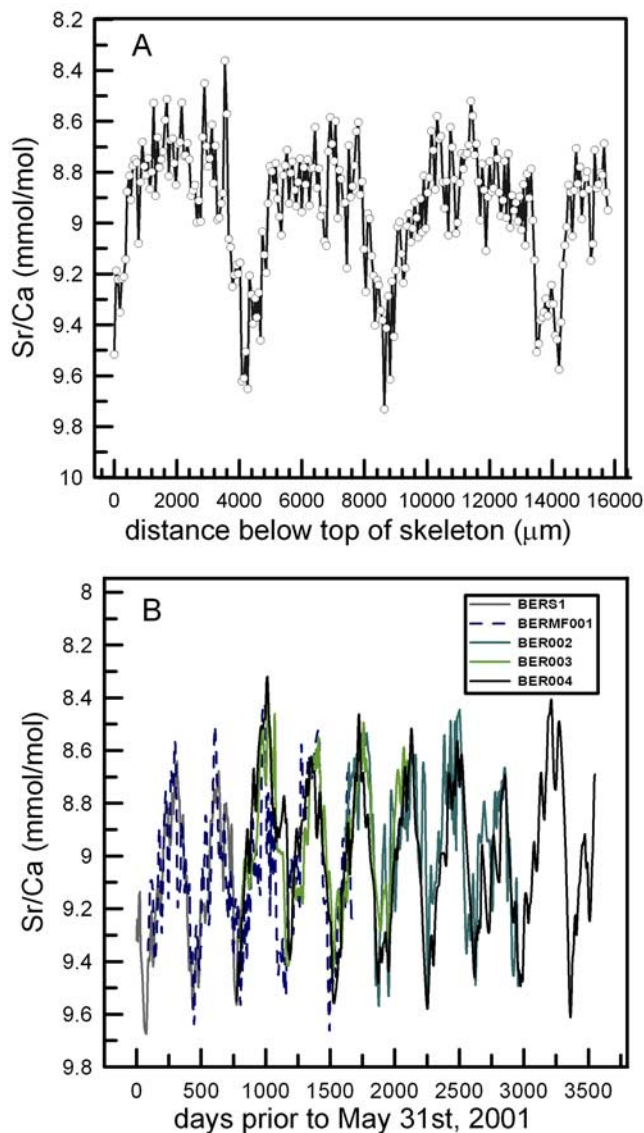[b]Sr/Ca ratios are in mmol mol^{-1}.

Figure 2. (a) Unfiltered Sr/Ca ratios measured in a *D. labyrinthiformis* sample (BER003) plotted against distance from the tip of the skeleton. (b) 35-day filtered Sr/Ca profiles from all 5 corals plotted against estimated time in days from the date the final colonies were harvested.

calculated, $\bar{x}$ is the mean Sr/Ca ratio (measured), x_i is the Sr/Ca ratio for a given temperature and $\bar{x}$ is the mean Sr/Ca ratio of the time series [e.g., *Chatterjee et al.*, 2000].

[7] Finally, we measured Sr/Ca ratios at the base of a large *D. labyrinthiformis* colony collected at JSB in May 2000. This colony was not included in our calibration study. Annual band counts on x-radiographs indicate a colony age of 225 years [*Goodkin et al.*, 2005] and we targeted growth bands spanning ∼1775–1780 AD.

3. Results

[8] Annual Sr/Ca cycles in *D. labyrinthiformis* and *M. franksi* generated by LA ICP-MS display a non-sinusoidal waveform characterized by extended summers and short winters (Figure 2a). This pattern contrasts with the temper-

ature record and indicates strong seasonality in skeletal extension. Chronologies were assigned by assuming high (low) Sr/Ca ratios corresponded with low (high) SSTs. The plateau in Sr/Ca minima was assumed to represent the warmest 3 months of the annual SST cycle (JAS). Similarly, distinct peaks in wintertime Sr/Ca ratios (Figure 2a) were assumed to represent the coolest 3 months of the year (JFM).

[9] Superimposed upon the annual Sr/Ca cycles are high-frequency oscillations characteristic of coral Sr/Ca data generated by fine-scale sampling [*Cohen and Sohn*, 2004] (Figure 2a). Once chronologies were assigned, we used the low pass filter to remove high-frequency oscillations from the Sr/Ca data. This enabled us to compare the annual Sr/Ca cycles amongst the corals studied and their relationship to the annual cycle in water temperature (Figure 2b).

[10] The filtered Sr/Ca ratios were binned into 30-day intervals. Following *Cardinal et al.* [2001], we derived the Sr/Ca-SST calibrations by comparing monthly-averaged maxima and minima in each annual Sr/Ca cycle, with monthly-averaged minima and maxima in each annual SST cycle. Differences amongst the slope and intercept values of the *Diploria* calibration equations are statistically insignificant at the 95% confidence level (Table 1). The average monthly *D. labyrinthiformis* data were pooled, yielding a single 9-year long Sr/Ca time series (Figure 3a). Cross-spectral methods using multi-taper techniques yield a (squared) coherency estimate of 0.95 for the pooled Sr/Ca data and the SST record at the annual period.

[11] Sr/Ca profiles generated using Sr/Ca-SST calibrations from bulk sample analyses capture about 25–50% of the amplitude of the annual Sr/Ca cycle revealed by the laser analyses (Figure 3b). Annual Sr/Ca cycles in bulk samples milled from the thecal wall of *D labyrinthiformis* are dampened and skewed toward the wintertime, whereas those milled from the ambulacrum are dampened and skewed toward the summertime (Figure 3b).

[12] A single *D. labyrinthiformis* Sr/Ca-SST calibration equation was derived from the pooled Sr/Ca data using the mean maximum and minimum Sr/Ca ratios in each annual cycle. In addition, we used monthly averaged Sr/Ca ratios measured about the January and June Alizarin stain lines of the stained coral (BERS1) to provide mid-year data (Figure 4a):

$$T(°C) = -10.08(\pm0.38) * Sr/Ca(\text{mmol mol}^{-1}) + 114.53(\pm3.14)$$

[13] The mean *s.e.* on predicted SSTs is ±0.51°C for Sr/Ca ratios between 8 mmol mol^{-1} and 10 mmol mol^{-1}. We applied this calibration to Sr/Ca ratios generated from the base of the large *D. labyrinthiformis* colony. The 5 annual Sr/Ca cycles, spanning ∼1775–1780 AD, display the typical waveform of extended summers and short winters that we found in the analyses of contemporary skeleton. A 35-day low pass filter was applied to the raw data which were then binned into 30-day averages. The derived average monthly SSTs are plotted against Station S monthly climatology from 1954–2000 AD (Figure 4b). Our data indicate that average maximum SSTs (26.4 ± 0.9°C) over the 5-year period were 1.2°C cooler around 1775 AD than the average
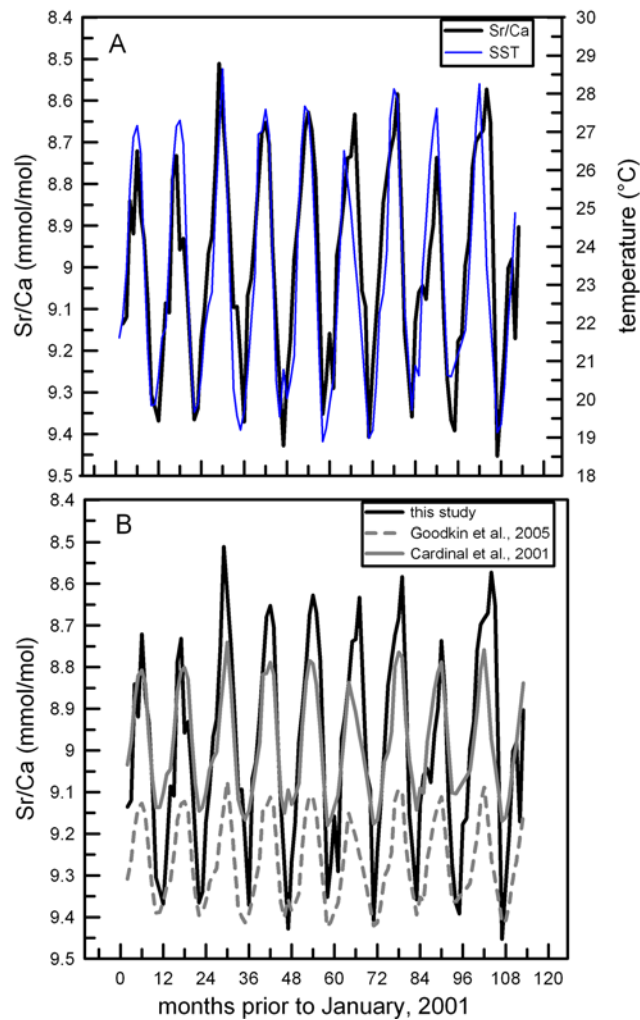
Figure 3. (a) Pooled 30-day averaged Sr/Ca ratios from all *Diploria* colonies (this study, solid black line) scaled to monthly averaged Station S SSTs (blue line). (b) Sr/Ca ratios as in Figure 3a (solid black line) shown with Sr/Ca profiles predicted from independently derived Sr/Ca-SST calibrations for *Diploria* using bulk sampling techniques. Grey solid line reconstructed using the calibration for BDA135-223 of *Cardinal et al.* [2001]; broken lines reconstructed using the monthly calibration of *Goodkin et al.* [2005].

maximum since 1954 AD. Similarly, wintertime SSTs around 1775 AD (17.62 ± 0.5°C) were 1.7°C cooler than the average minimum since 1954 AD. The average annual SST for the 5-year period was 22°C, ~1°C cooler than the average annual SST recorded at Hydrostation S from 1954–1997 (23.05°C).

4. Discussion

[14] *Diploria* and *Montastrea* are septothecate corals that build corallite walls of thickened septa. Formation of septa occurs by initial deposition of COCs and subsequent growth of bundles of needle-shaped crystals that radiate outward at an angle of ~70-90 degrees (Figure 1). Outward growth of crystal bundles continues from the edges of septa until
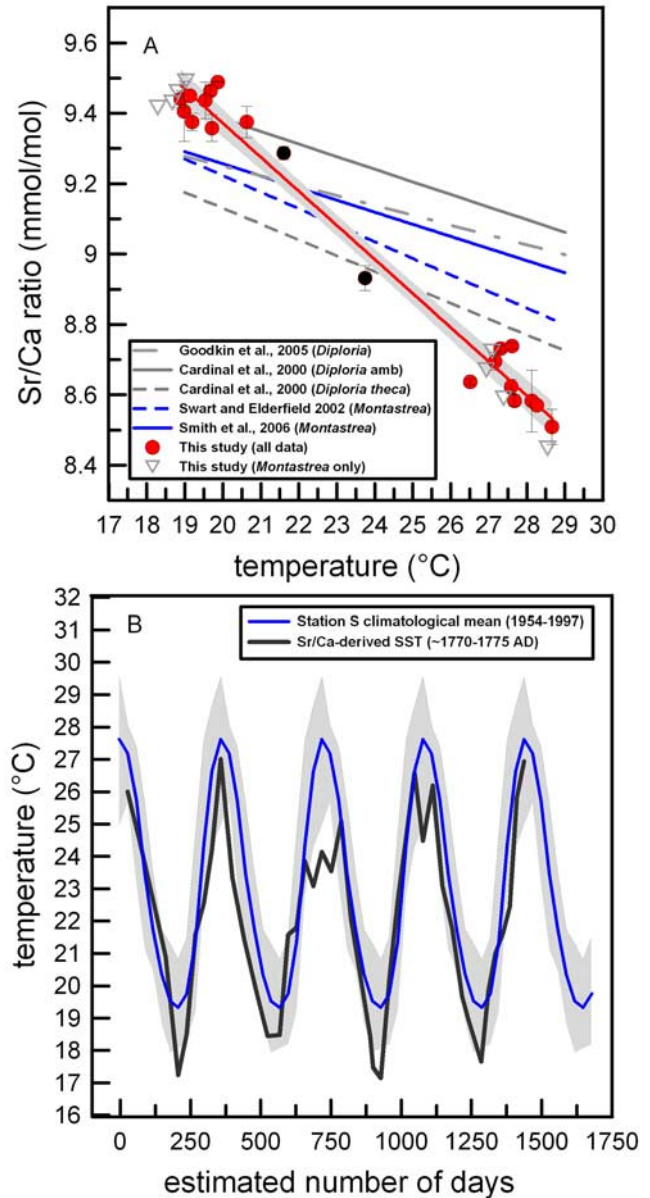

Figure 4. (a) Sr/Ca-SST regression equations derived from 30-day averaged *Diploria* (red circles) and *Montastrea* (black triangles) (this study), shown with Sr/Ca-SST calibrations derived for both genera using bulk sampling techniques. Black circles are Sr/Ca data at the January and June stain lines in BERS1. The shaded area denotes the 95% confidence interval for the *Diploria* data. Solid blue line represents calibration from *Smith et al.* [2006]. (b) A five-year window on Bermuda SSTs ~225 years ago derived from Sr/Ca ratios of a massive long-lived *Diploria* (black solid line) using the Sr/Ca-SST relationship derived in Figure 4A. Blue solid line is averaged monthly SSTs recorded at Station S between 1954 AD and 2001 AD. The shaded region represents the maximum and minimum SSTs recorded at Hydrostation S since the start of instrumental recordings there.

crystals from adjacent septa meet to form the theca. In *D. labyrinthiformis*, fine daily growth bands in the crystal bundles are evident in petrographic thin-section (Figure 1b). Spacing between adjacent bands decreases along the length of the needles from 10-μm near the calcification centers to <0.5-μm at their distal tips. The numbers of bands and their spacing indicates that the full width of the septotheca (~1 mm) may be achieved over a period of at least 200 days [*Cohen et al.*, 2004]. Consequently, when septothecae are sampled with a 1 mm diameter drill bit, skeleton removed can represent as much as 6 months growth, independent of the vertical resolution achieved.

[15] By targeting the centers of skeletal elements of *D. labyrinthiformis* and *M. franski*, we avoided these thickening deposits. Our results indicate that the sensitivity of Sr/Ca to temperature for these species (0.096 mmol mol^{-1}/°C) is ~3 times higher than previously reported based on bulk analyses (Figure 4a) and equivalent to that of fast-growing Pacific *Porites* (-0.1 mmol mol^{-1}/°C) analyzed by microbeam techniques [*Cohen and Sohn*, 2004]. Clearly, bulk sampling significantly dampens the amplitude of the annual Sr/Ca cycle.

[16] The absence of statistically significant differences amongst Sr/Ca-SST relationships derived for the different *Diploria* colonies contrasts with previous findings based on bulk sampling (Figure 4a) [e.g., *Cardinal et al.*, 2001; *Goodkin et al.*, 2007]. We propose two reasons for this. First, by targeting the centers of septa, laser sampling effectively eliminates the bias introduced by the seasonality and duration of the skeletal thickening process. The result is an increase in the amplitude of the annual Sr/Ca cycles and representation of both summer and wintertime variability. Conversely, annual Sr/Ca cycles generated by bulk sampling are considerably dampened and skewed toward the season of maximum extension (summer on the ambulacrum) or thickening (winter on the theca). Therefore, small differences in skeletal growth processes amongst skeletal elements in the same corallite and between colonies may contribute significantly to the spread of Sr/Ca-SST calibrations. Secondly, our analyses targeted the centers of septa where crystal growth rates are consistent. By excluding the variable, slower-growing outer regions of the septa, our sampling minimized differences amongst colonies that may be linked to different growth rates.

[17] Due to the spread of Sr/Ca-temperature calibrations amongst different corals, paleotemperature reconstructions traditionally require calibration of individual coral colonies. Usually, a Sr/Ca-SST relationship is established for the period of instrumental data, and the same calibration applied to older parts of the same coral. A single calibration is rarely transferable across different colonies, different species or different regions, limiting our confidence in temperature derivations from fossil corals for which a specific calibration cannot be established. Our approach minimized artifacts associated with bulk sampling and found no significant differences amongst Sr/Ca-SST calibrations of the *Diploria* corals. This enabled us to apply the calibration derived from live corals to Sr/Ca ratios measured in skeleton accreted ~225 years ago.

[18] Our result indicates that the average annual SSTs around Bermuda were ~1°C (±0.51) cooler than the average between 1954 and 1997. This estimate is within error of

δ^{18}O-SSTs derived from foraminifera on the Bermuda Rise ~230 years ago [*Keigwin*, 1996] and in agreement with Kaplan extended MOH5SSTAs in the mid-19th century for a 5 × 5° grid square centered on 62.5°W 32.5°N [*Kaplan et al.*, 1998]. It is also within error of the growth-corrected Sr/Ca-based SSTs derived by *Goodkin et al.* [2005] for the same section of coral using bulk sampling techniques. Without applying a correction for changes in coral growth rate, bulk samples from the base of the coral yielded average annual SSTs of ~24°C, i.e., ~1°C warmer than the modern. [*Goodkin et al.*, 2005] The absence of a relationship between coral growth rate and Sr/Ca in the laser-sampled data, and the absence of significant differences in Sr/Ca-SST relationships amongst the coral colonies, suggests that selectively targeting the centers of skeletal elements minimized skeletal growth effects evident in the bulk sampled data.

5. Conclusions

[19] Our results do not exclude physiological "vital effects" as an important component of the compositional variability in coral skeletons. Even in our laser-sampled data, processes associated with Raleigh fractionation account for up to 75% of the amplitude of the annual Sr/Ca cycle [*Gaetani and Cohen*, 2006]. Nevertheless, there is clearly a relationship between temperature and the processes driving Raleigh fractionation in these corals, and that relationship sets the Sr/Ca-temperature dependence. Our data show that thickening deposits of variable age and growth rate are additional sources of variability in Sr/Ca ratios amongst different coral colonies, that could distort the temperature-dependent signal in bulk sampled data. Therefore, selective sampling of the centers of septa and exclusion of thickening deposits could significantly improve the fidelity and reproducibility of coral proxy records.

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A. L. Cohen and S. R. Thorrold, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. (acohen@whoi.edu)