



A high-resolution calibration of Sr/Ca thermometry using the Caribbean coral *Montastraea annularis*

P. K. Swart

Division of Marine Geology and Geophysics, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149, USA (pswart@rsmas.miami.edu)

H. Elderfield and M. J. Greaves

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK (he101@esc.cam.ac.uk; mg109@esc.cam.ac.uk)

[1] A relationship has been established between the Sr/Ca ratio in the skeleton of the scleractinian coral *Montastraea annularis* and sea surface water temperature in south Florida. In order to obtain this correlation, specimens of *Montastraea annularis* were transplanted to a site at a local reef where every two to three months throughout a 2-year period the corals were stained with Alizarin-red S and where water temperature, which annually ranges between $\sim 20^{\circ}$ and 30°C , was continually monitored. At the end of the experimental period the coral skeleton was sampled at a rate of ~ 50 samples per year, each sample corresponding to only around $20\ \mu\text{g}$ of calcium carbonate. For the 2.5-year period, the Sr/Ca ratio exhibited excellent correlation in the first year ($R^2 = 0.83$; Sr/Ca (mmol/mol) = $10.11 - 0.0452 \times \text{SST} (^{\circ}\text{C})$), but a rather poorer correlation in the second year ($R^2 = 0.68$; Sr/Ca (mmol/mol) = $10.09 - 0.0406 \times \text{SST} (^{\circ}\text{C})$). Averaging the data into monthly values for year 1, we determined a relationship of (Sr/Ca (mmol/mol) = $10.165 - 0.0471 \times \text{SST} (^{\circ}\text{C})$). On the basis of the excellent correlation between temperature and Sr/Ca, we feel that this relationship is the most accurate. Discrepancies in the second year are suggested to arise from slight sampling errors relative to the stain lines.

Components: 5181 words, 4 figures, 1 table.

Keywords: Strontium; coral; calcium; temperature.

Index Terms: 4825 Oceanography: Biological and Chemical: Geochemistry; 4875 Oceanography: Biological and Chemical: Trace elements; 1694 Global Change: Instruments and techniques.

Received 15 January 2002; **Revised** 22 May 2002; **Accepted** 31 May 2002; **Published** 30 November 2002.

Swart, P. K., H. Elderfield, and M. J. Greaves, A high-resolution calibration of Sr/Ca thermometry using the Caribbean coral *Montastraea annularis*, *Geochem. Geophys. Geosyst.*, 3(11), 8402, doi:10.1029/2002GC000306, 2002.

Theme: Biogenic Calcium Carbonate

Guest Editor: Peggy Delaney

1. Introduction

[2] The Sr/Ca ratio of coral skeletons has been shown to exhibit an inverse relationship with water

temperature [Weber, 1973; Goreau, 1977; Houck *et al.*, 1977; Smith *et al.*, 1979]. However, only the advent of determination of the Sr/Ca ratio to a precision better than 0.1% [Beck *et al.*, 1992] has

Table 1. Summary of Previous Relationships Between Temperature and Sr/Ca Ratios in the Form $Sr/Ca = a + b \times T^{\circ}C^a$

Study	Species	<i>a</i>	<i>b</i>	Number	<i>R</i>
This study (1989)	<i>Montastraea annularis</i>	10.165	-0.471	12	-0.88
Averaged to monthly values					
This study (1989–1991)	<i>Montastraea annularis</i>	9.994	-0.0377	98	-0.94
This study (1989)	<i>Montastraea annularis</i>	10.11	-0.0440	~60	-0.91
This study (1990)	<i>Montastraea annularis</i>	10.11	-0.0406	~27	-0.82
Weber [1973]		10.84	-0.0800	NA	
Smith <i>et al.</i> [1979]		11.01	-0.0710	NA	
Beck <i>et al.</i> [1992] and Beck [1994]		10.479	-0.0624	10	
de Villiers <i>et al.</i> [1994]	<i>Porites lobata</i>	10.956	-0.0795	11	-0.97
	<i>Pocillopora eydoiouxi</i>	11.004	-0.0763	14	-0.96
	<i>Pavona clavus</i>	10.646	-0.0675	4	-0.83
de Villiers <i>et al.</i> [1995]	<i>Pavona clavus</i> (6 mm/yr)	10.25	-0.0417	5	-0.89
	<i>Pavona clavus</i> (12 mm/yr)	10.11	-0.0388	9	-0.88
	<i>Pavona clavus</i> (14 mm/yr)	9.92	-0.0331	12	-0.73
	<i>Porites lobata</i>	10.52	-0.0569	14	-0.97
	<i>Porites lobata</i>	10.96	-0.0795	12	-0.99
	<i>Porites lobata</i>	11.36	-0.0904	12	-0.95
Mitsuguchi <i>et al.</i> [1996]	<i>Porites lutea</i>	10.5	-0.0608	13	-0.85
Shen <i>et al.</i> [1996]	<i>Porites lobata</i>	10.307	-0.0505	10–12	-0.95
	<i>Porites lutea</i>	10.350	-0.0528	10–12	-0.98
Alibert and McCulloch [1997]	<i>Porites mayeri</i>	10.485	-0.0615	14	-0.98
	<i>Porites lutea</i>	10.17	-0.0507	10	-0.93
	<i>Porites lutea</i>	10.425	-0.0604	8	-0.96
	<i>Porites lobata</i>	10.56	-0.0629	8	-0.94
	<i>Porites lobata</i>	10.21	-0.0505	12	-0.96
Gagan <i>et al.</i> [1998]	<i>Porites lutea</i>	10.78	-0.0660	25	-0.80
	<i>Porites lutea</i>	10.73	-0.0639	25	-0.98
	<i>Porites lutea</i>	10.68	-0.0616	25	-0.99
Kinsman and Holland [1969]	Inorganic aragonite	10.66	-0.0390	NA	

^aThe number of samples refers to the number of samples taken per calendar year. Regression values are those quoted in the original paper.

allowed precise documentation of paleotemperatures in coral skeletons. Despite several further studies, there is no single accepted Sr/Ca and temperature relationship (Table 1) with the result that the precision of paleotemperature estimates are much worse than the precision of Sr/Ca measurements. The differences, between the various calibrations, have been attributed to growth rate and calcification rate effects [e.g., de Villiers *et al.*, 1995]. Recent calibration studies [Shen *et al.*, 1996; Alibert and McCulloch, 1997], while acknowledging the outstanding problems, have successfully rationalized much literature data and offer a more optimistic view of Sr/Ca paleothermometry than shown by de Villiers *et al.* [1995]. However, not only do problems exist which have led us to make the high-resolution calibration described in this paper, but there have been no calibration between temperature and Sr/Ca on coral species from the Atlantic, all previous studies involving corals have been carried out on species

from the Pacific [de Villiers *et al.*, 1994, 1995; Beck *et al.*, 1992; McCulloch *et al.*, 1994; Shen *et al.*, 1996; Alibert and McCulloch, 1997].

[3] Calibration of the Sr/Ca ratio with temperature has been previously achieved by correlating Sr/Ca and $\delta^{18}O$ coral records or relating samples to density banding or periods of maximum and minimum temperature, the correlation in the latter case being achieved by relating samples with maximum Sr/Ca ratio to period of lowest temperature and vice versa. Shen *et al.* [1996] have made perhaps the most detailed calibration study to date, taking into account previously identified uncertainties and using a direct comparison of coral chemistry and measured water temperature (Table 1).

[4] In this study, we make use of specimens of the Caribbean species *Montastraea annularis* which had been grown in the field under well characterized conditions and which were previously used for

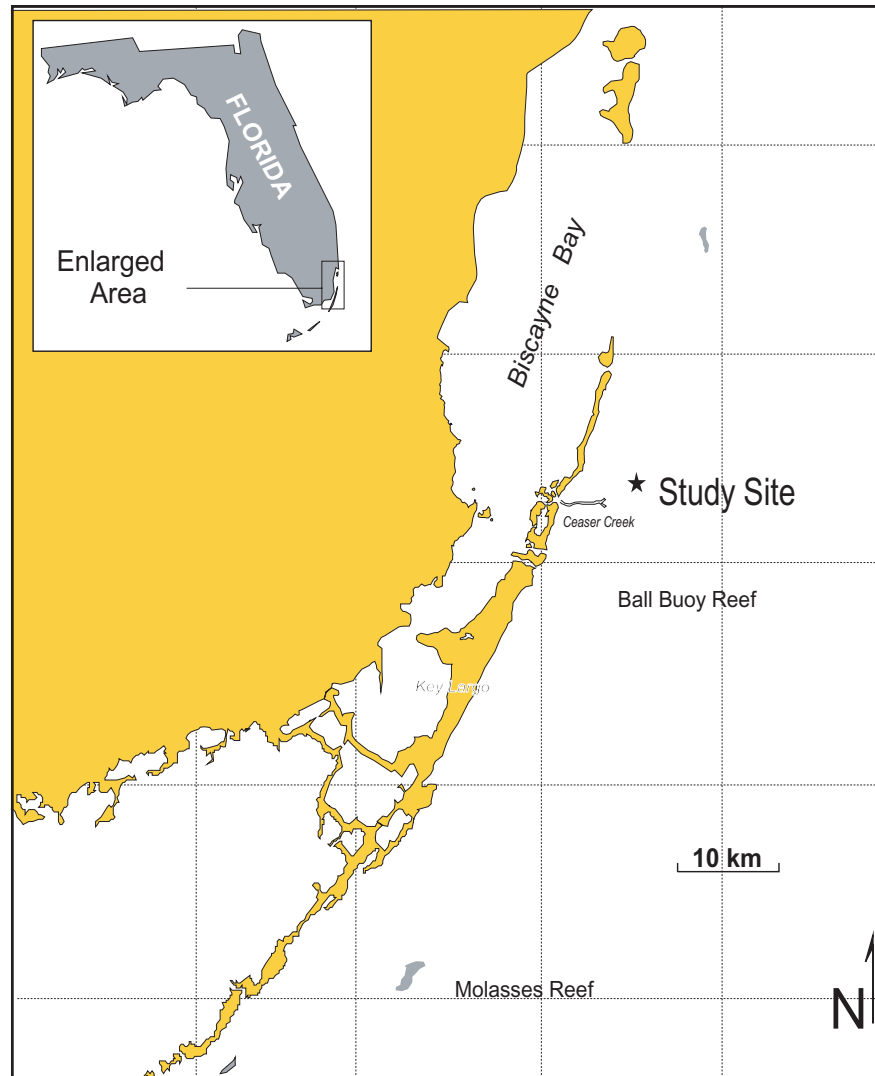


Figure 1. Location of experiment. Also shown are locations of sites (solid circles) from which temperature data were measured (see text for details).

a calibration study on oxygen and carbon isotopic compositions [Leder *et al.*, 1996; Swart *et al.*, 1996a]. The relatively well-characterized conditions under which these corals grew enable us to make a very high-resolution correlation of the Sr/Ca ratio of the coral and SST.

2. Methods

2.1. Study Site

[5] The study site was a small patch reef “Alina’s Reef,” within Biscayne National Park, Florida at

25°23.42N, 80°10.29W, ~6.5 km southeast of Elliot Key and between Hawk Channel and the linear bank reefs further offshore (Figure 1). In the spring of 1988 a Plexiglas platform measuring 1.5 × 1.5 m was placed at 5.5 m depth in the sea grass adjacent to Alina’s Reef. Twelve small colonies of *M. annularis*, each ~10–15 cm height by 8–10 cm diameter, were collected from the adjacent reef and cemented in growth position to the platform. The corals were arranged on the platform such that individual field incubation chambers could be fitted over each nodule and sealed to the platform during the experimental procedure (see Swart *et al.*

[1996a] for further details of the experimental procedure). The corals were allowed to acclimatize for 18 months before commencement of the growth experiment. Every two to three months, after physiological measurements were made, the corals were stained with Alizarin-red S. At the conclusion of the experiment, the corals were removed from the platform and returned to the laboratory. Growth rate and density data reported from these corals [Leder *et al.*, 1996; Swart *et al.*, 1996a] revealed them to have growth and calcification rates comparable to other corals from the same reefs [Hudson *et al.*, 1994] and seemingly unaffected by the trauma of transplantation. The tissues of the corals were removed for analysis [Swart *et al.*, 1996a], and the skeletons were subjected to X-radiography and sampled for their stable oxygen and carbon isotopic composition [Leder *et al.*, 1996; Swart *et al.*, 1996a]. One specimen, BNP-4, was analyzed for its Sr/Ca ratio.

2.2. Temperature

[6] A Hydrolab Datasonde I temperature monitoring device, which was installed by Biscayne National Park (BNP) during the spring of 1990 within a few m of and at the same depth as the research platform at Alina's Reef, provided a continuous record of in situ temperature readings (one-hour intervals). A second Hydrolab was situated on a patch reef 7 km south of Alina's Reef (Ball Buoy). Data from this site were used to fill in gaps (days to weeks) that occurred in the record from Alina's Reef. For the period prior to the deployment of the Hydrolabs, temperature records were obtained from a C-man monitoring station located at Molasses Reef, ~50 km southwest of the BNP site. This station, maintained by the Florida Institute of Oceanography, provided SST data extending back in time prior to August 1988. During the periods when temperature records for these three stations overlapped, the correlation coefficients between the hydrolab at Alina's reef and Ball Buoy and between Ball Buoy and Molasses were 0.98 and 0.99, respectively. As a result of this high degree of correlation, we felt justified in using all three data sets for correlation to the Sr/Ca ratio of the coral skeletons. The temperature assigned to

each sample taken from the coral skeleton consists of the average temperature for all days between the adjacent samples.

2.3. Salinity

[7] As this study was not initiated originally to determine the temperature dependence of the Sr/Ca ratio in coral skeletons, we did not collect water samples for Sr and Ca analyses. However, salinity was periodically measured in conjunction with the oxygen isotopic composition of the water. These data reveal only small changes in the salinity throughout the experimental period [see Leder *et al.*, 1996].

2.4. Sampling

[8] An important component of the study reported in this paper is the ability to extract and analyze fine increments of skeletal growth from the coral to provide a high-resolution record of seasonal variations in skeletal chemistry. This topic was extensively discussed relative to the corals investigated in this study [Leder *et al.*, 1996]. Sections for Sr/Ca analyses were cut to bisect an individual corallite parallel to the major growth axis and were 1–6 mm thick. The coral was drilled along the thecal wall (0.5–1 mm) of an individual corallite (~5 mm), where previous studies [Leder *et al.*, 1996] indicated that the best chronology could be obtained. Microsamples for Sr/Ca were extracted from the skeleton using a low speed milling technique with 0.5 mm diameter diamond drill bits and a micro-drill whose speed was manually regulated using a rheostat. This method is essentially identical to that described by Leder *et al.* [1996] with the exception that the movement of the sample was controlled by a computerized *x-y-z* stage. Each increment in this study advances the drill 170 μm , and the depth of sampling was always 0.34 mm. As the drill advanced along the theca, the positions of the stain lines were noted for later correlation to time. The stain lines acted as a guide to skeletal growth and provided time control [Leder *et al.*, 1996]. Dates were assigned to each of the sample positions by interpolating between the known, fixed stain dates. A sample was considered to fall on the date of

staining when it was taken from the peak of the stain line (representing the prevailing growing edge of one costa). In addition a comparison was made between this method and the method of assigning the maximum and minimum temperatures to minimum and maximum values of the Sr/C ratio.

2.5. Analysis

[9] Sample powders, stored dry in acid washed glass vials, were dissolved in 0.5 mL of 0.5M HCl acid, and the solutions immediately transferred to acid cleaned polypropylene microcentrifuge tubes. The Sr/Ca ratios were determined by isotope dilution after mixing with a ^{42}Ca - ^{44}Ca - ^{84}Sr spike, evaporating to dryness and loading directly onto a single Ta filament prior to analysis using a VG Sector 54 7-collector mass spectrometer. The ^{42}Ca - ^{44}Ca - ^{84}Sr spike solution was calibrated against a mixed Ca-Sr solution diluted gravimetrically from standards prepared from CaCO_3 and SrCO_3 (Johnson Matthey, puratronic). The average precision of the measured Sr/Ca ratios, standard error of the mean calculated by propagating the errors of the isotope ratio measurements, was $\pm 0.03\%$ (2s). Replicate analyses of a laboratory coral standard gave $\text{Sr/Ca} = 9.468 \pm 0.015$ mmol/mol (2 s.d., $n = 16$). For comparison to stable oxygen isotopic data we used the isotopic record previously published [Leder *et al.*, 1996].

3. Results and Discussion

3.1. Results

[10] The Sr/Ca ratio of the drilled corals varied seasonally between 8.624 and 9.085 mmol/mol and covaried with temperature and the oxygen isotopic composition of the coral (Figures 2a and 2b). Comparison of the Sr/Ca ratio with the $\delta^{18}\text{O}$ for the coral skeletons showed a positive correlation of the form:

$$\text{Sr/Ca} = 9.722(\pm 0.036) + 0.20(\pm 0.010)(\delta^{18}\text{O}). \quad (1)$$

In this and following equations, one standard error of the slope and intercept are given in brackets. The Sr/Ca data for the entire sampling period are compared with the temperature record in Figure 3.

When the entire data set are considered together, a least squares fit gives a linear relationship between Sr/Ca and SST of the form (Figure 4)

$$\text{Sr/Ca} = 9.994(\pm 0.042) - 0.0377(\pm 0.0029) \cdot [\text{SST}(n = 95; r^2 = 0.62)]. \quad (2)$$

In this equation and all subsequent equations, Sr/Ca is in mmol/mol and SST in $^{\circ}\text{C}$. When the records for different years are considered, we see that the values of intercept and slope of the Sr/Ca-SST relationships decrease from 1989 to 1990 (Table 1):

$$\begin{aligned} &1989 \\ \text{Sr/Ca} &= 10.110(\pm 0.042) - 0.0449(\pm 0.0028) \\ &\cdot [\text{SST}(n = 60; r^2 = 0.83)] \end{aligned} \quad (3)$$

$$\begin{aligned} &1990 \\ \text{Sr/Ca} &= 10.089(\pm 0.039) - 0.0406(\pm 0.0027) \\ &\cdot [\text{SST}(n = 27; r^2 = 0.68)]. \end{aligned} \quad (4)$$

3.2. Chronological Effects

[11] Despite the fact that we employed a sampling resolution significantly greater than that used in previous studies which have attempted to correlate temperature to the Sr/Ca ratio in coral skeletons [de Villiers *et al.*, 1994, 1995; Beck *et al.*, 1992; Gagan *et al.*, 1998; McCulloch *et al.*, 1994; Mitsuguchi *et al.*, 1996], there is considerable scatter in our data, and the equation describing the Sr/Ca-SST correlation differs significantly from much of the literature data. From a comparison of Sr/Ca and SST data over the sampling period (Figure 3), it appears that the data from 1990 appears anomalous in that these data show an offset between the two records. We suspect that the anomalous correlation for 1990 has arisen from errors in the chronology obtained from the stain lines. This problem arises because the coral is a three-dimensional structure and the position of the stain lines may change with depth beneath the surface of the coral. Hence although it may appear that a sample is drilled from a particular time increment in the skeleton, by drilling into the sample material from different time periods may be sampled.

[12] In most other calibrations of the Sr/Ca and $\delta^{18}\text{O}$ values of coral skeletons with temperature

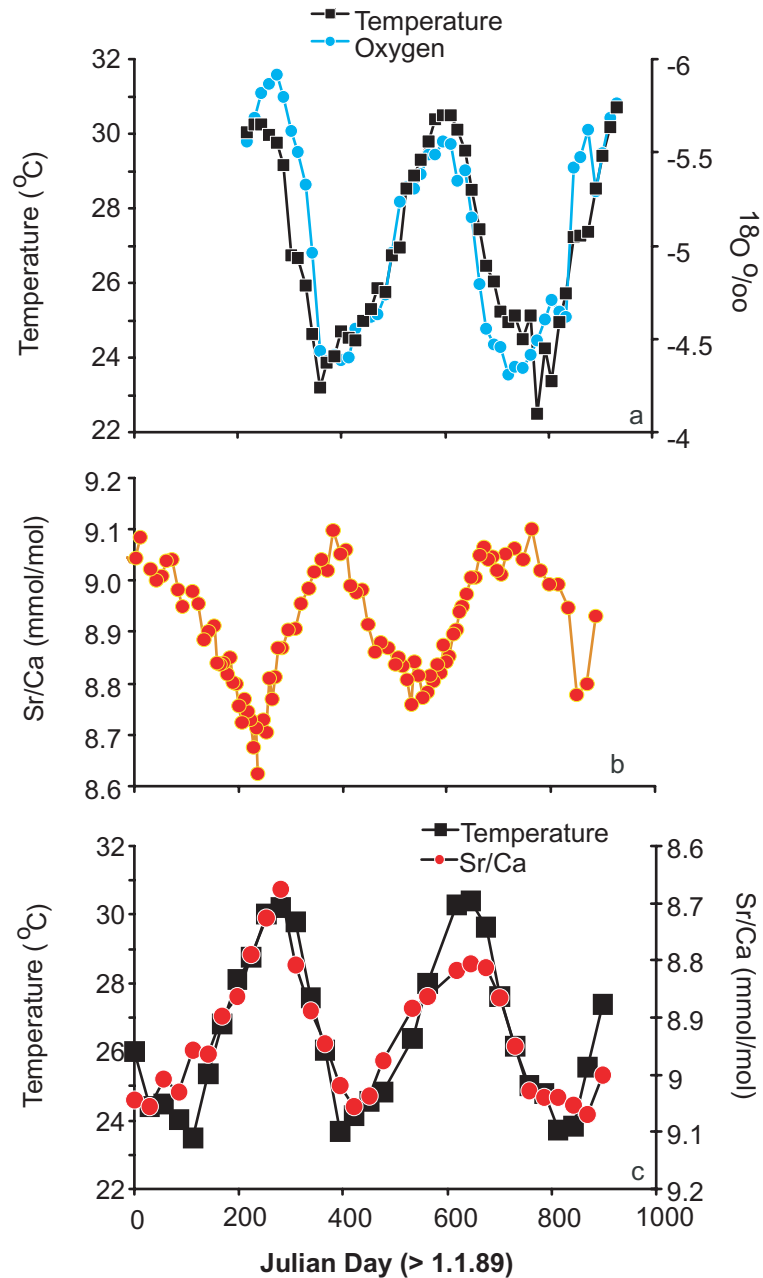


Figure 2. (a) The Sr/Ca of the coral skeleton versus Julian day since 1.1.89. (b) SST and $\delta^{18}\text{O}$ from the same coral (the $\delta^{18}\text{O}$ has been corrected for the isotopic composition of the water) versus Julian day since 1.1.89 for monthly averaged data. (c) Data from Figure 2a averaged to monthly values and plotted against mean monthly temperatures.

[Wellington *et al.*, 1996; Beck *et al.*, 1992], the correlation between the temperature record and skeletal $\delta^{18}\text{O}$ or the Sr/Ca ratio was not obtained through the use of stain lines, but rather through using the temperature record itself and matching the minima in the $\delta^{18}\text{O}$ or the Sr/Ca ratio with maximum temperatures. In such calibrations this procedure was carried out over a number of years

and provides essentially an annual two-point calibration. This method makes a prior assumption of the correlation between the dependent and independent variable and does not allow for other complications such as variation in water chemistry, growth rate effects, physiological effects, and sampling problems which may influence the relationship between Sr/Ca, $\delta^{18}\text{O}$, and temperature. A

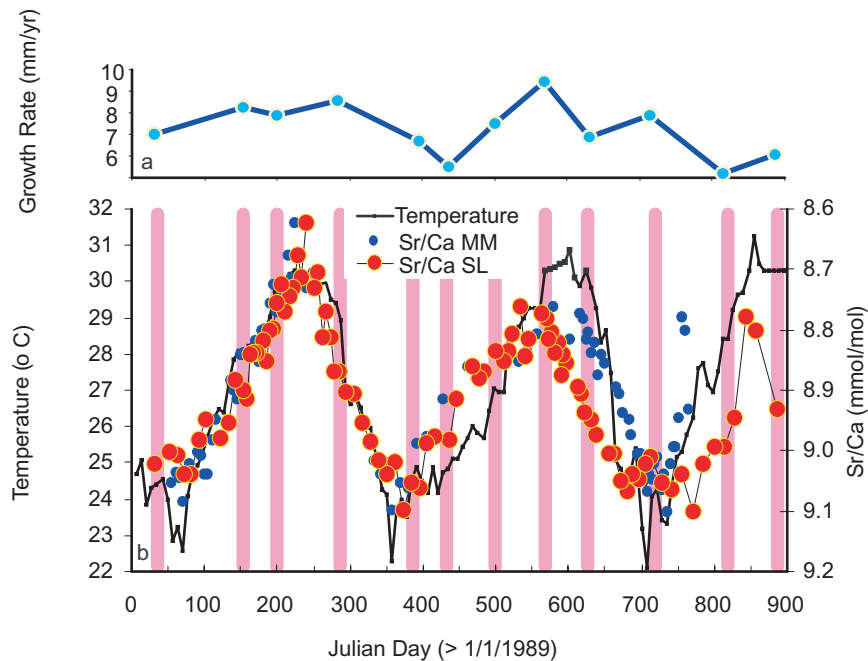


Figure 3. (a) Growth rate of coral utilized in this study as determined from stain lines. (b) Sr/Ca and SST versus Julian day. Vertical dashed lines represent the position of the stain lines. Large circles represent the chronology of the Sr/Ca data calculated using the stain lines, while small circles represent chronology calculated by matching maximum Sr/Ca ratios with minimum temperatures.

second approach [Alibert and McCulloch, 1997] matched perturbations in the Sr/Ca ratio to similar perturbations in the temperature record and assumed that they were related. Using this technique, up to 14 correlation points were obtained within one year (Table 1). Another approach matches the annual pattern of high density bands, which are generally known to form during a

specific time of the year, and then places the dependant variable within the time framework. This technique still assumes a linear growth between the growth bands and also suffers from the problem that density bands do not always form during the exact same time period within each year. This present study utilizes the approach of staining the coral skeleton in the field with Alizarin-red S at

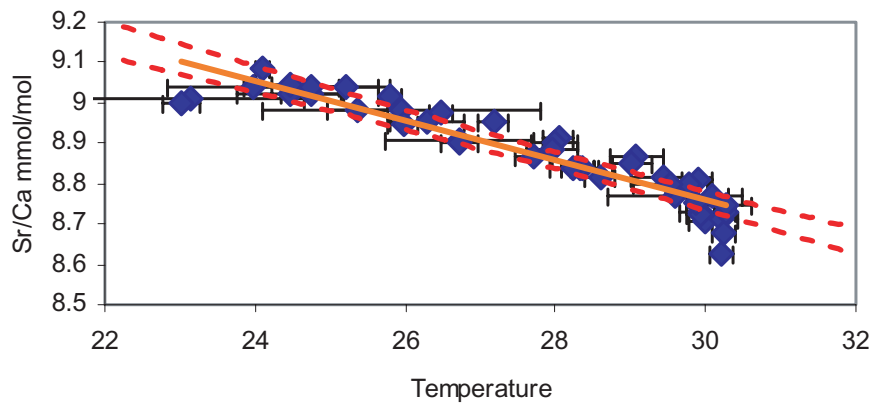


Figure 4. Correlation of Sr/Ca versus. SST. The error bars for the Sr/Ca ratio represent ± 0.02 mmol/mol, the error determined for the Sr/Ca analyses. The error bars for the temperature represent the total range of temperatures experienced by the coral during the time it formed the skeleton analyzed for Sr/Ca. The dotted lines represent the range in uncertainty at the 95% confidence limits of the calibration line using the range of temperature represented by each analyses.

approximately quarterly intervals and then extrapolating time between the sampled intervals. This technique therefore represents a more precise method of obtaining the intraannual chronology. However, even with this method it is difficult to precisely correlate the material drilled from the skeleton with instrumental temperature records because of problems relating the three-dimensional nature of the coral skeleton to a two-dimensional stain line. Hence, it is possible to drill into material that was formed at a different time compared to the skeleton at the surface. This problem is particularly manifest during periods of rapid temperature change. Therefore the simplest explanation for the discrepancy between Sr/Ca ratio and temperature evident in the second half of the 1990 record (Figure 3) is that a period of summer growth of ~ 100 days was not adequately sampled. We do not think that the chronology based on the stain lines was compressed during this time period as the growth rate did not appear to be depressed between the stain lines which bordered the period during which the Sr/Ca ratio did not appear to correlate with the water temperature (Figure 3).

3.3. Sampling Resolution

[13] Although there have been several studies which have reported high-resolution geochemical proxy data from coral skeletons, most calibration studies, which have attempted to calibrate the temperature dependence of the Sr/Ca ratio in coral skeletons, have used a sampling resolution far coarser than employed in this study (See Table 1). The number of samples used in our study represents essentially a weekly resolution and compares with approximate monthly or lower resolution from most of the previous studies. In order to consider the fact that the material extracted from the skeleton may not accurately represent the material deposited during the time period presented by the stain lines, we have plotted the Sr/Ca values with their associated error against the temperature and the standard deviation of the temperature during the period represented by the sample (Figure 4).

[14] In order to compare our data to the relationships measured by previous researchers, we have used a

rectangular interpolation method to convert our data to monthly values and recalculated the relationship between Sr/Ca and temperature (Figure 2c). This exercise provides a relationship closer to those reported in the literature. For example in 1989, the relationship changes to $Sr/Ca = 10.165 - 0.0471 \times SST$ from that listed in equation (3). In choosing an appropriate sampling resolution, it is important to realize that even though a sample may represent a certain fraction of the linear growth rate and therefore may equate to a given time period, such calculations do not take into consideration variation in growth rate through the year as well as complications in the architecture of the coral skeleton. Hence even a monthly sampling resolution takes material which represents a period greater than one month and material from time periods which are not adjacent to the target month. This problem can be exasperated during periods when the temperature changes rapidly over a period of weeks. Previous calibration studies have examined the temperature dependence of the Sr/Ca ratio in coral skeletons over a relatively restricted range in temperatures (5° to $6^{\circ}C$) [Alibert and McCulloch, 1997; de Villiers et al., 1994; Shen et al., 1996]. In contrast the range of temperatures based on daily mean temperatures in this study was $10^{\circ}C$, while mean monthly temperatures varied by as much as $8^{\circ}C$. The restricted range of temperatures investigated previously, although providing a more uniform benign environment for growth, did not allow investigation of temperature extremes, which may have adversely affected growth rate possibly causing kinetic effects or problems with sampling resolution.

3.4. Possible Changes in the Sr/Ca of Seawater

[15] The role of changing Sr/Ca in seawater has been investigated by several workers and generally found to be small at most locations [de Villiers et al., 1994]. These workers concluded that the potential influence of seawater Sr/Ca variations may be larger in areas of upwelling where relatively Sr rich waters might influence the surface communities. Upwelling along the Florida Keys is a well-known phenomenon, occurring periodically in the summer and is associated with slightly lower temperatures and increases in the concentrations of

nitrate and phosphate [Lee *et al.*, 1994]. There have been no investigations of changes in the Sr/Ca ratios of these waters, but they are likely to have elevated Sr/Ca ratios similar to those described by de Villiers *et al.* [1994]. Hence these waters may be responsible for the ~ 0.1 anomaly in the Sr/Ca ratio during the summer months. Further variations in the seawater Sr/Ca ratio may arise as a result of the influence of the input of freshwater, which can have both lower or higher Sr/Ca ratios than seawater depending upon the nature of local carbonate terrain. The reefs in this study are known to be influenced by freshwater input from the Florida Everglades through Biscayne Bay [Swart *et al.*, 1996b]. These waters have a relatively high and uniform concentration of calcium (2.1 mM), but a wide range of Sr concentrations (0.025 to 0.4 mM) [Sonntag, 1987]. The wide range of Sr concentrations arise from the recrystallization of the Pleistocene aged Miami limestone, which is a mixture of low-Mg calcite and aragonite. Depending on the precise Sr/Ca ratio and absolute concentration of Sr and Ca in the groundwaters influencing the reefs, one can expect changes in salinity of the order actually observed (34 to 36) to significantly influence the Sr/Ca ratio of the reefal waters in this region. Changes in the Sr/Ca ratios of waters in the area have been documented to take place with moderate changes in salinity [Dwyer and Cronin, 2001]. In the case of this study the waters exhibited a pronounced decrease in their $\delta^{18}\text{O}$ values between 1989 and 1990 of $\sim 0.5\text{‰}$ [Leder *et al.*, 1996]. On the basis of known correlations between salinity and $\delta^{18}\text{O}$ for this area, such a change could have been responsible for a decrease in the Sr/Ca ratio measured in the skeletons during this time period.

3.5. Influence of Growth Rate on the Sr/Ca Ratio

[16] Although the Sr/Ca ratio in aragonite have been shown to be independent of precipitation rate over 1.5 orders of magnitude in inorganically precipitated aragonite [Mucci *et al.*, 1989], the influence of growth rate on the Sr/Ca ratio of coral skeletons has been postulated by Weber

[1973] and de Villiers *et al.* [1995]. Other workers have discounted growth rates as being important in controlling the skeletal Sr/Ca ratio [Alibert and McCulloch, 1997]. de Villiers *et al.* [1995] compared specimens of the same species with growth rates of between 4 and 8 mm/yr and showed changes in the relationship between Sr/Ca and temperature. However, their conclusions may have arisen as a result of inadequate sampling within a given time period. We suggest this possibility because the gradient of the correlation between temperature and oxygen isotopic composition reported by de Villiers *et al.* [1995] is significantly less than the well-established relationship between temperature and oxygen [Weber, 1973; Leder *et al.*, 1996]. The growth rate in our study varied by approximately a factor of 2 [Leder *et al.*, 1996; Swart *et al.*, 1996a, 1996b] and shows no apparent correlation with the Sr/Ca ratio in the coral skeleton, the highest growth rates being in the summer with lower rates during the winter. Within these ranges of growth rates it is possible that higher frequency variation occurred, particularly during the periods of high and low temperatures when growth rates were probably lower than normal. The primary effect of growth rate reduction in these periods, rather than a kinetic effect on the Sr/Ca ratio itself, would be to reduce the ability to sample these periods of low growth and their consequent extremes in Sr/Ca ratios. This would be manifested as a relationship between Sr/Ca and SST with a reduced slope.

3.6. What is the Reason for the Range in Calibration Constants?

[17] Our values are lower than all literature data with the exception of two calibrations by Alibert and McCulloch [1997] and that of Shen *et al.* [1996], which are within error identical to ours, and three correlations of *Pavona clavus* based on sparse sampling [de Villiers *et al.*, 1995]. Shen *et al.* [1996] have been able to rationalize some of the differences between reported calibrations by making corrections for local differences in the Sr/Ca ratio of seawater. As shown above this may be more important than previously believed. How-

ever, differences still remain. One obvious practical difficulty is that, even with our sampling method, it is difficult to precisely correlate the material drilled from the skeleton with instrumental temperature records.

4. Conclusions

[18] Although the relationship between the Sr/Ca ratio in the skeleton of *Montastraea annularis* and SST is similar to that reported for other corals, the slope of the relationship is less than that previously reported except for two recent studies by Shen *et al.* [1996] and Alibert and McCulloch [1997]. Although this phenomenon is normally a result of an inadequate number of samples being taken in a year, this cannot be the case in this study as our sample rate was greater than 50 samples/year. We believe that the differences between our correlation for Sr/Ca and temperature and previous correlations for other species from the Pacific may relate to problems of sampling the complex skeleton of this species together with the wide range of temperatures at this particular locality.

Acknowledgments

[19] The authors would like to thank Jim Leder and Alina Szmant for field and technical assistance. Amel Saied, and Ann Williams are thanked for their help with analyses. This work was supported by NSF grants OCE-8900005 and OCE-9217993 (PKS) and by the U.K. Natural Environmental Research Council (HE). Improvement of this manuscript benefited from comments by three anonymous reviewers.

References

- Alibert, C., and M. McCulloch, Strontium/calcium ratios in modern *Porites* corals from the Great Barrier Reef as a proxy for sea surface temperature: Calibration of the thermometer and monitoring of ENSO, *Paleoceanography*, *12*, 345–363, 1997.
- Beck, J. W., E. Edwards, F. Ito, J. Taylor, F. Recy, P. Rougerie, and H. C. Joannot, Sea surface temperature from coral skeletal strontium/calcium ratios, *Science*, *257*, 644–647, 1992.
- Beck, J. W., Sea-surface temperature from coral skeletal strontium calcium ratios (Vol. 257, pg 644, 1992), *Science*, *264*, 891, 1994.
- de Villiers, S. D., G. T. Shen, and B. K. Nelson, The Sr/Ca temperature relationship in coralline aragonite: Influence of variability in (Sr/Ca) seawater and skeletal growth parameters, *Geochim. Cosmochim. Acta*, *58*, 197–208, 1994.
- de Villiers, S. D., B. K. Nelson, and A. R. Chivas, Biological controls on coral Sr/Ca and $\delta^{18}\text{O}$ reconstructions of sea surface temperatures, *Science*, *269*, 1247–1249, 1995.
- Dwyer, G. S., and T. M. Cronin, Ostracode shell chemistry as a paleosalinity proxy in Florida Bay, *Bull. Am. Paleontology*, *361*, 249–276, 2001.
- Gagan, M. K., L. K. Ayliffe, D. Hopley, J. A. Cali, E. Mortimer, J. Chappell, M. T. McCulloch, and M. J. Head, Temperature and surface-ocean water balance of the Mid-Holocene tropical Western Pacific, *Science*, *279*, 1014–1018, 1998.
- Goreau, T., Seasonal Variations of Trace Metals and Stable Isotopes in Coral skeleton: Physical and Environmental Controls, paper presented at Third International Coral Reef Symposium, Rosenstiel School of Mar. and Atmos. Sci., Univ. of Miami, Miami, 1977.
- Houck, J. E., R. W. Buddemeier, S. V. Smith, and P. L. Jokiel, The response of coral growth rate and skeletal strontium content to light intensity and water temperature, paper presented at Third International Coral Reef Symposium, Rosenstiel School of Mar. and Atmos. Sci., Univ. of Miami, Miami, 1977.
- Hudson, J. H., K. J. Hanson, R. B. Halley, and J. L. Kindinger, Environmental implications of growth rate changes in *Montastraea annularis* Biscayne National Park, Florida, *Bull. Mar. Sci.*, *54*, 647–669, 1994.
- Kinsman, D. J., and H. D. Holland, The co-precipitation of cations-IV the co-precipitation of Sr^{2+} with aragonite between 16–96°C, *Geochim. Cosmochim. Acta*, *33*, 1–17, 1969.
- Leder, J. J., P. K. Swart, A. Szmant, and R. Dodge, The origin of variations in the isotopic record of scleractinian corals, I, Oxygen, *Geochim. Cosmochim. Acta*, *60*, 2857–2870, 1996.
- Lee, T., M. Clarke, E. Williams, A. Szmant, and T. Berger, Evolution of the Tortugas gyre and its influence on recruitment in the Florida Keys, *Bull. Mar. Sci.*, *54*, 621–646, 1994.
- McCulloch, M., M. Gagan, G. Mortimer, A. Chivas, and P. Isdale, A high resolution Sr/Ca and $\delta^{18}\text{O}$ coral record from the Great Barrier Reef, Australia, and the 1982–1983 El Nino, *Geochim. Cosmochim. Acta*, *58*, 2747–2754, 1994.
- Mitsuguchi, T., E. Matsumoto, O. Abe, T. Uchida, and P. J. Isdale, Mg/Ca thermometry in coral skeletons, *Science*, *274*, 961–963, 1996.
- Mucci, A., R. Canuel, and S. Zhong, The solubility of calcite and aragonite in sulfate-free seawater and the seeded growth kinetics and composition of precipitates at 25°C, *Chem. Geol.*, *74*, 309–320, 1989.
- Shen, C., T. Lee, C. Chen, C. Wang, C. Dai, and A. Li, The calibration of D[Sr/Ca] versus sea surface temperature relationship for *Porites* coral, *Geochem. Cosmochim. Acta*, *60*, 3849–3858, 1996.
- Smith, S., R. Buddemeier, R. Redale, and J. Houck, Strontium-calcium thermometry in coral skeletons, *Science*, *204*, 404–406, 1979.
- Sonntag, W., Chemical Characteristics of water in the super-



- official aquifer system, Dade County Florida, *Water Resour. Invest. Rep. 87-4080*, U.S. Geol. Surv., Reston, Va., 1987.
- Swart, P. K., R. E. Dodge, and H. D. Hudson, A 240-year stable oxygen and carbon isotopic record in a coral from South Florida: Implications for the prediction of precipitation in South Florida, *Palaios*, *11*, 362–375, 1996a.
- Swart, P. K., J. J. Leder, A. Szmant, and R. E. Dodge, The origin of variations in the isotopic record of Scleractinian corals, II, Carbons, *Geochim. Cosmo. Acta*, *60*, 2871–2886, 1996b.
- Weber, J. N., Incorporation of strontium into reef coral skeletal carbonate, *Geochim. Cosmochim. Acta*, *37*, 2173–2190, 1973.
- Wellington, G. M., R. B. Dunbar, and G. Merlen, Calibration of stable oxygen isotope signatures in Galapagos corals, *Paleoceanography*, *11*, 467–480, 1996.