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The Relationship Between the Ratio of Strontium to Calcium and Sea-Surface Temperature in a Modern *Porites astreoides* Coral: Implications for Using *P. astreoides* as a Paleoclimate Archive

By Tess E. Busch, Jennifer A. Flannery, Julie N. Richey, and Anastasios Stathakopoulos

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Contents

Figures

Tables

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The Relationship Between the Ratio of Strontium to Calcium and Sea-Surface Temperature in a Modern *Porites astreoides* Coral: Implications for Using *P. astreoides* as a Paleoclimate Archive

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Abstract

An inverse relationship has been demonstrated between water temperature and the ratio of strontium to calcium (Sr/Ca) in coral aragonite for a number of Pacific species of the genus *Porites*. This empirically determined relationship has been used to reconstruct past sea-surface temperature (SST) from modern and Holocene age coral archives. A study was conducted to investigate this relationship for *Porites astreoides* to determine the potential for using these corals as a paleotemperature archive in the Caribbean and western tropical Atlantic Ocean. Skeletal aragonite from a *P. astreoides* colony growing offshore of the southeast coast of Florida was subsampled with a mean temporal resolution of 14 samples per year and analyzed for Sr/Ca. The resulting Sr/Ca time series yielded well-defined annual cycles that correspond to annual growth bands in the coral. Sr/Ca was regressed against a monthly SST record from C-MAN buoy station FWYF1 (located at Fowey Rocks, Florida), resulting in the following Sr/Ca-SST relationship: Sr/Ca = –0.040*SST + 10.128 (R = –0.77). A 10-year time series of Sr/Ca-derived SST yields annual cycles with a 10–12 degree Celsius seasonal amplitude, consistent with available local instrumental records. We conclude that Sr/Ca in *Porites astreoides* from the Caribbean/Atlantic region has high potential for developing subannually resolved modern and recent Holocene SST records.

Introduction

Corals as Climate Recorders

As the global climate system responds to anthropogenic forcing, the need to better understand baseline regional climate variability becomes increasingly important. Instrumental observations of sea-surface temperature (SST) are spatially and temporally limited, and therefore proxy reconstructions are needed to extend the observational record back in time. Massive reef-building corals are ideal archives for subannual to centennial-scale climate reconstructions because of their natural abundance in shallow-water tropical regions, their ability to create continuous skeletal chronologies marked by annual couplets of high-and-low density bands, and the ability of a single colony to grow for centuries (Lough, 2010). Hermatypic corals (including species of the genus *Porites,* as well as several others) have provided high-resolution geochemical records of climatic variability throughout the recent Holocene epoch (0–10,000 years before present [BP]) (cf. Corrège, 2006; Sadler and others, 2014).

The ratio of strontium to calcium (Sr/Ca) incorporated within a coral skeleton can be used to reconstruct SST records on the basis of the thermodynamic relationship between the SST of seawater and the incorporation of the strontium ion into the calcium carbonate ($CaCO_3$) skeleton. Colder temperatures increase the Sr to Ca ratio as more Sr^{2+} from the surrounding seawater replaces the Ca^{2+} in the aragonite $CaCO_3$ skeleton (Smith and others, 1979).

Genus *Porites*

Massive *Porites* species are the most commonly used corals for paleoclimate reconstruction studies in the Indo-Pacific region. These *Porites* species are slow growing, long-lived, and have been the subject of numerous paleoclimate reconstructions (i.e., Gagan and others, 2000; DeLong and others, 2007). *Porites* species have been shown to produce highly reproducible Sr/Ca records, displaying strong seasonal cycles (Allison and Finch, 2004; DeLong and others, 2007; Wei and others, 2007).

No long-lived massive *Porites* species grow in the Caribbean/Atlantic region. *Porites astreoides,* a smaller, short-lived species, is abundant in the Caribbean and surrounding Atlantic waters; however, no effort has been made to reconstruct a SST record from this species, using either Sr/Ca or oxygen isotopes. Although many stony corals are on the decline in the Caribbean/Atlantic region, *P. astreoides* is becoming ever more abundant in reef communities (Green and others, 2008) and thus may provide a valuable paleoclimate archive if it can be established as a reliable temperature recorder.

The collection of cores of Holocene reef framework, which comprises an assortment of fossil coral species, is becoming an effective means of extracting Holocene SST reconstructions (Sadler and others, 2014). In order to get a complete Holocene paleoclimate record, geochemical signals for all dominant reef-building coral species need to be calibrated using modern instrumental SST data, including *P. astreoides,* which are widespread spatially throughout the fossil record.

Purpose and Scope

The purpose of this report is to analyze the Sr/Ca ratios in *P. astreoides* from the southeast coast of Florida (Fort Lauderdale). A preliminary study was conducted to assess the fidelity of Sr/Ca-based SST reconstructions from *P. astreoides* to determine the potential of using these corals as a paleoclimate archive. The objectives of the study were to (1) examine the annual growth rates of this species (previously determined as 3.67 ± 0.65 millimeters per year [mm yr^{-1}], Elizalde-Rendon and others, 2010), (2) determine whether annual Sr/Ca cycles were present and, if so, whether they can be related to local SST, and (3) compare the SST calibration from *P. astreoides* to other published calibrations of coral Sr/Ca from both Pacific *Porites spp.* and other coral species from the Caribbean/Atlantic region.

Methods

The U.S. Geological Survey (USGS) Coastal and Marine Science Center in St. Petersburg, Fla., acquired a *Porites astreoides* specimen that was collected in March 2006 and had been growing in less than 8 meters of water near the Port Everglades Channel off the coast of Fort Lauderdale.

The coral was slabbed into five, 4-mm-thick pieces using a wet table saw with a diamond blade. All slabs were cleaned using a Branson Sonifer 450 device and were x-rayed at the USGS St. Petersburg Coastal and Marine Science Center (SPCMSC) using an Ecotron x-radiograph system. The age model for the *P. astreoides* specimen was determined by counting annual density bands on the coral x-ray back from 2006 (the year the specimen was collected).

The coral slab was microsampled using a continuous microsampling program on a computer-driven triaxial micromill. Two parallel paths (P1 and P2) were drilled along the growth axis to confirm reproducibility of the geochemical signal. Samples were drilled using a 0.7-mm-diameter drill bit, 1.5 mm sampling depth, and an advance interval of 0.35 mm, which generated approximately 14 samples per year. A divot was drilled 2.25 mm into the coral every 12 samples to provide reference points on the x-ray image.

An aliquot of the resulting sample of coral powder was weighed (between 88–237 micrograms) and dissolved in a specific volume of 2 percent trace-metal grade nitric acid (HNO_3) to obtain a target calcium concentration of 20 parts per million (ppm) for elemental analysis. Sr/Ca determinations were made on a PerkinElmer 7300 dual view inductively coupled plasma optical emission spectrometer (ICP-OES) at the USGS SPCMSC. The raw data were corrected to determine Sr/Ca by using the drift correction method described by Schrag (1999) and an internal gravimetric standard (IGS). The average corrected IGS precision for Sr/Ca was 0.008 millimoles per mole (mmol mol^{-1}) (1σ, n=70). A second standard of homogenized powder from a *Porites lutea* (PL) coral specimen was analyzed for Sr/Ca to test for any potential matrix effects in the coral skeleton. The PL standard had an average corrected precision of 0.013 mmol mol^{-1} (1σ, n=100).

A local SST record spanning 1996–2006 was obtained from National Data Buoy Center (NDBC) station FWYF1 at Fowey Rocks, offshore of south Miami, Fla. (fig. 1). The annual SSTs at Fowey Rocks range from 21 degrees Celsius (ºC) in the winter months to ~31 ºC during the summer months (NOAA, 2015). The conversion of raw Sr/Ca values of paths P1 and P2 from the depth domain to the time domain was performed using AnalySeries 2.0.4.2 software (Paillard and others, 1996). This was achieved by matching summer Sr/Ca minima to SST maxima for each annual cycle and adding additional tie points to match winter, spring, autumn, and points in between for maximum alignment. Calibration of Sr/Ca to SST was determined using reduced major axis regression. Annual linear extension rates in the coral were determined by measuring the distance (in millimeters) between annual Sr/Ca seasonal cycles.

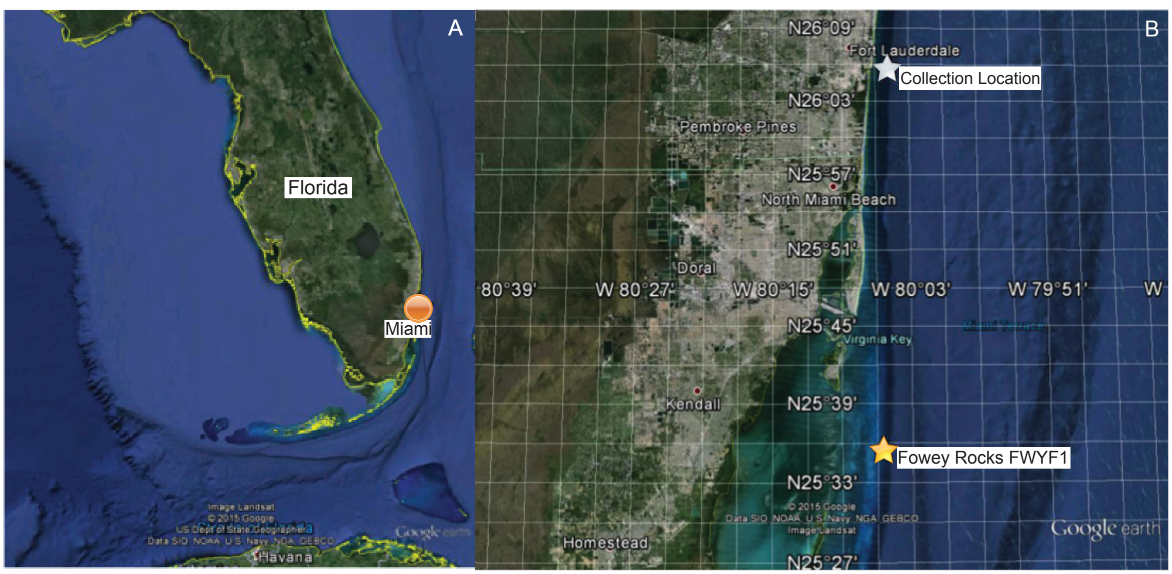

Figure 1. (A) Map of south Florida showing the location of Miami (orange dot). (B) Greater Miami area map showing the *P. astreoides* collection location on the near-shore reef ridge offshore of Fort Lauderdale, near the Port Everglades Channel (silver star) and the location of the C-MAN buoy station FWYF1 at Fowey Rocks, offshore of south Miami (yellow star). Maps provided by Google Earth (Data Source: SIO, NOAA, US Navy, NGA, GEBCO; Image: Landsat) accessed on January 12, 2015.

Results and Discussion

Linear Extension Rates

The average annual linear extension rate of the *Porites astreoides* specimen was ~5 mm yr^{-1} over the sampling interval (1996–2006). Individual years varied between 3.9 and 8.1 mm yr^{-1}, slightly higher than the results of Elizalde-Rendon and others (2010) (3.67 ± 0.65 mm yr^{-1}). These results are consistent with linear extension rates published for Pacific *Porites* spp. (6.3 mm yr^{-1}, *Porites lutea*, Chen and others, 2013), but are lower than other published rates (10 mm yr^{-1}, *Porites lutea,* DeLong and others, 2013; 8−15 mm yr^{-1}, multiple *Porites* species, Alibert and McCulloch, 1997; 11−16 mm yr^{-1}, *Porites lutea*, Wei and others, 2000). The *P. astreoides* sample used in this study displayed a slight increasing trend in extension rates with decreasing Sr/Ca (increasing SST, $R^2 = 0.194$, insignificant at the 95 percent confidence interval), whereas the opposite trend has been observed in other *Porites* spp. (Grove and others, 2013; Tanzil and others, 2013).

Sr/Ca Data

Both paths sampled on the *Porites astreoides* slab show distinct Sr/Ca cycles, which are interpreted as annual SST cycles (fig. 2). The annual Sr/Ca cycles are well-defined between 2002 and 2005. The top 4 mm of the coral were excluded from the Sr/Ca data because that growth represents a period

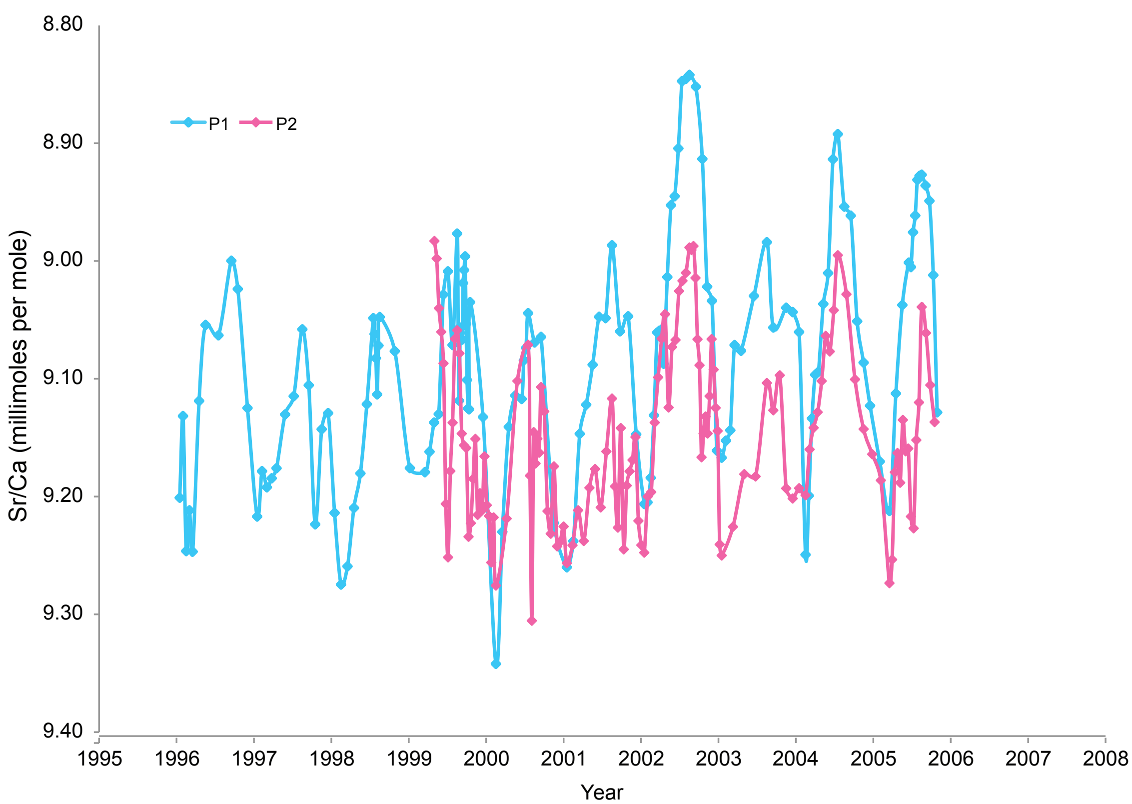

Figure 2. Sr/Ca values are plotted in the time domain on the x-axis. Sr/Ca values are plotted with sea-surface temperature values in reverse on the y-axis so that warmer temperatures are up. Two paths were drilled in the *P. astreoides* sample and analyzed for Sr/Ca: Path 1 (P1, blue curve) and Path 2 (P2, pink curve). Only P1 was used for further analysis because the time domain for P1 is longer than for P2.

of time during which the coral was relocated from its original oceanic location to an experimental aquarium. The oldest portion of the coral specimen lacks pronounced annual Sr/Ca cycles. This could be the result of alteration of the skeleton by bioeroders or diagenesis, or ontogenetic effects on the juvenile portion of the skeleton. The Sr/Ca cycles were overlain on annual density bands visible on the x-ray (fig. 3) to verify the age-depth relationship. Path 2 displayed a reduced seasonal Sr/Ca cycle compared to Path 1, with colder biased summer Sr/Ca values. Additional study is needed on *P. astreoides* to understand heterogeneity in Sr/Ca within the coral skeleton.

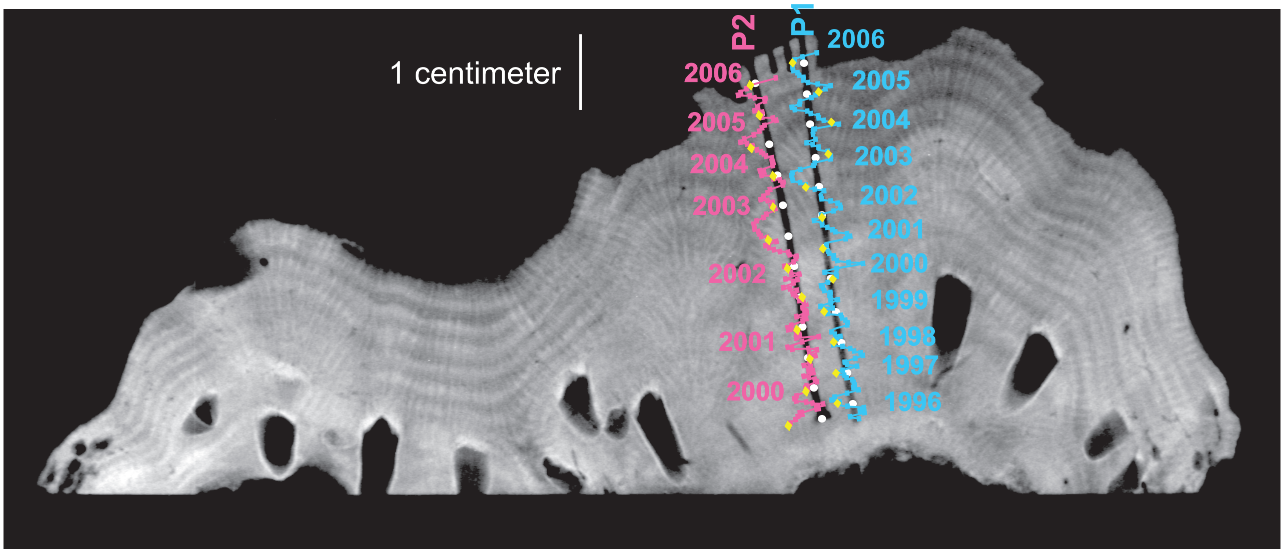

Figure 3. X-radiograph of the *P. astreoides* specimen sampled. Sr/Ca values of Path 1 (P1, blue) and Path 2 (P2, pink) are overlaid onto the x-radiograph in time and depth space. The yellow dots represent Sr/Ca samples associated with visible divots (white circles) on the coral x-radiograph. Chronology was established by counting annual density bands backward from 2006 (the year the coral was collected).

Calibration With SST

Sr/Ca for 2002–2005 was calibrated with monthly SST data from C-MAN buoy station FWYF1 at Fowey Rocks, located ~65 kilometers from the *P. astreoides* colony. The relationship between SST and Sr/Ca in the *P. astreoides* colony (fig. 4) was

$$Sr/Ca = -0.040(\pm 0.004)*SST + 10.128(\pm 0.958)$$

This equation was applied to the raw Sr/Ca time series from the *P. astreoides* to derive temperature estimates for 1996–2006 (fig. 5). Path 1 was used to represent the Sr/Ca-SST data because of the longer temporal coverage of this path compared to that of Path 2.

The resulting Sr/Ca-SST record contains well-defined seasonal cycles that range from ~21 °C to ~33 °C, which is comparable to the observed annual temperature range of 21–33 °C for the region (NOAA, 2015). Sr/Ca-based temperatures are slightly warmer than the monthly C-MAN buoy SST data from FWYF1, likely due to uncertainties resulting from a short calibration interval (5 years) and the fact that the buoy location is several (65) kilometers from the coral collection site. Sr/Ca-SST was resampled to monthly resolution by assigning a 12-month even time-step using AnalySeries 2.0.4.2 (Paillard and others, 1996). Mean annual SSTs were calculated by averaging mean monthly data for January through December of each year.

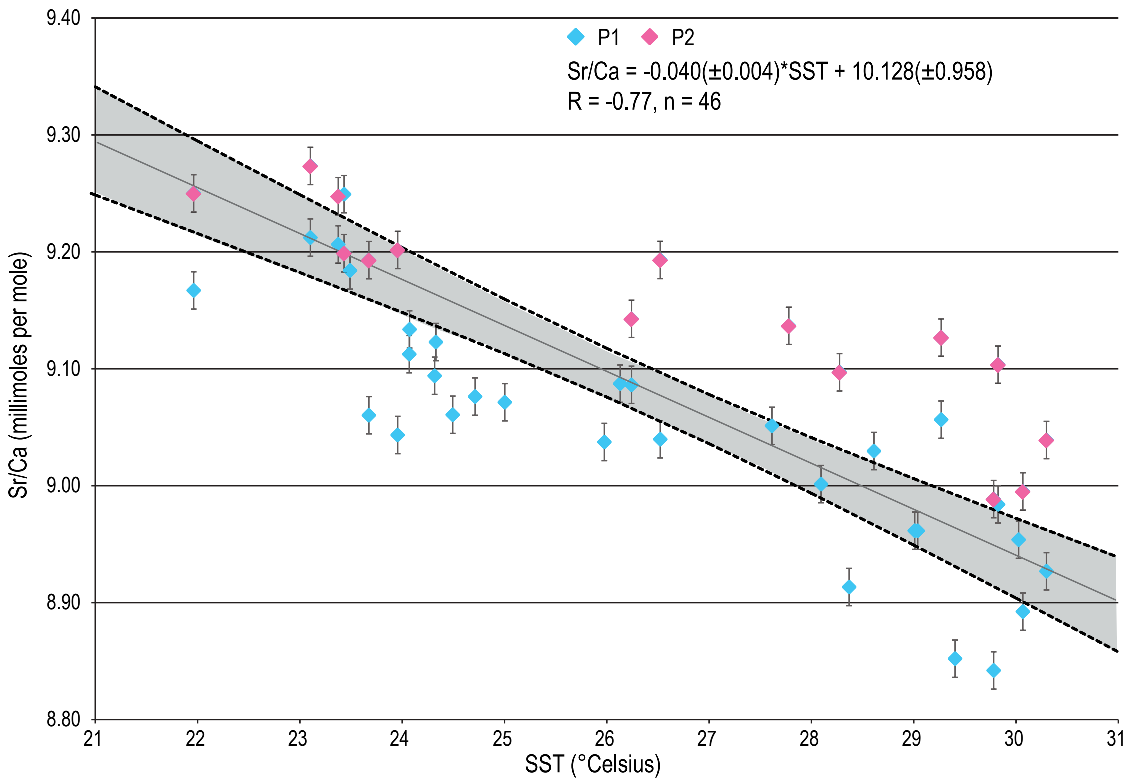

Figure 4. Sr/Ca-SST regression using reduced major axis of monthly Sr/Ca values from both Path 1 (blue diamonds) and Path 2 (pink diamonds) and monthly C-MAN buoy station FWYF1 SST data (n = 46). Only data for 2002–05 were used in the calibration. The shaded region indicates standard error of the regression at the 95 percent confidence interval. Error bars are standard error of the mean. The regression produced the equation Sr/Ca = –0.040(±0.004)*SST + 10.128(±0.958).

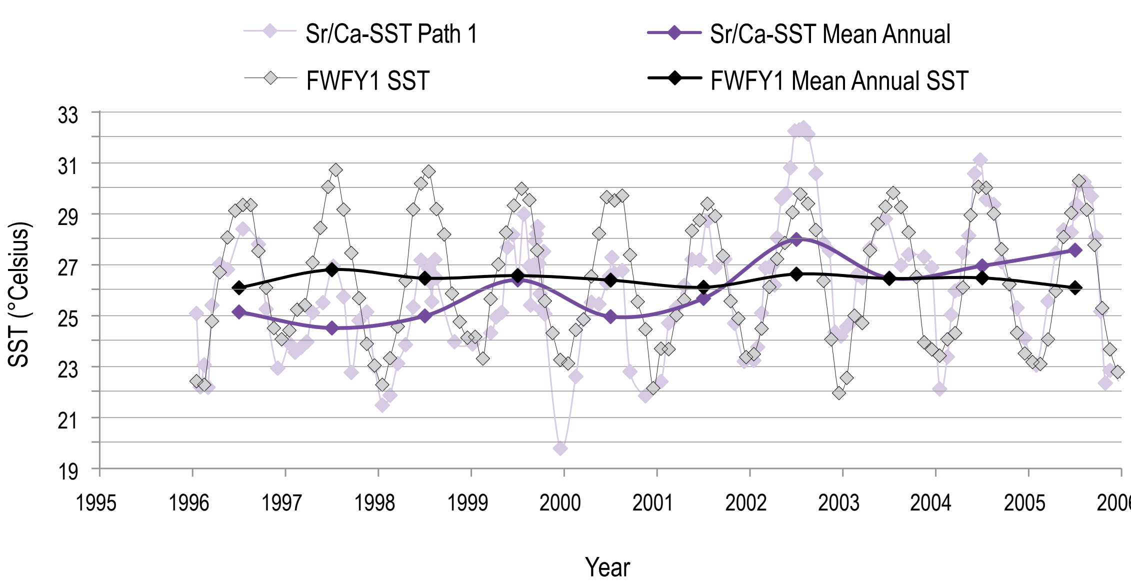

Figure 5. Sr/Ca data from Path 1 converted to coral-derived SST values (light purple curve) from the computed regression equation (Sr/Ca –0.040*SST +10.128). Monthly SST data from C-MAN buoy station FWYF1 are plotted in gray. Mean annual Sr/Ca-SST data are plotted in dark purple, along with the mean annual SST data from C-MAN buoy station FWYF1 (black curve).

Finally, the slope of the *P. astreoides* calibration equation generated in this study was compared to the equations previously published for Pacific *Porites* spp. and other coral species found along the Florida coast (fig. 6). The *P. astreoides* equation in this report has a similar slope to the equations generated using *Porites lutea* from the Pacific Ocean (cf. Corrège, 2006; DeLong and others, 2007). Other studies from the Pacific region using *Porites lobata* have generated calibration equations with steeper slopes than that found in the current study (0.061, Wu and others, 2014). Published Sr/Ca-SST equations using coral specimens from the Dry Tortugas National Park (west coast of Florida) also have similar slopes (*Siderastrea siderea*, DeLong and others, 2011; *Orbicella* [formerly *Montastraea,* Budd and others, 2012] *faveolata*, Flannery and Poore, 2013). Additional calibration equations are available using *O. faveolata* from Biscayne National Park (Swart and others, 2002) and Looe Key Reef (Smith and others, 2006), and those studies also show comparable slopes to the one generated in the current study. We conclude that *P. astreoides* holds great potential as a recorder of paleotemperature and should be utilized in studies on modern and fossil specimens from the Caribbean/Atlantic region.

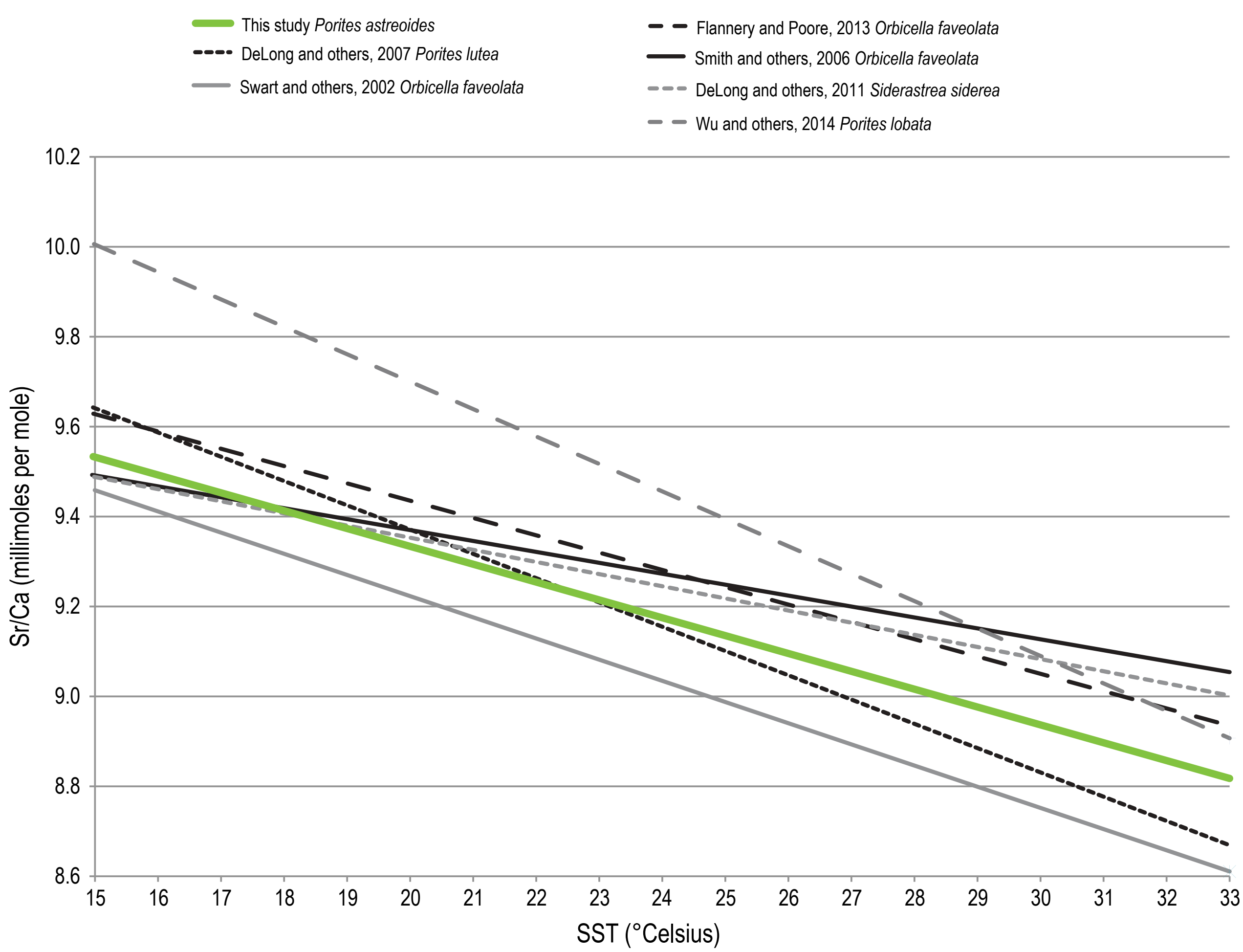

Figure 6. The slope of the regression line generated in the current study (green line) is similar to those generated by DeLong and others (2007) for a *Porites lutea* from the Pacific Ocean and other available equations from the Caribbean/Atlantic region on various coral species (Swart and others, 2002; Smith and others, 2006; DeLong and others, 2011; Flannery and Poore, 2013). The slope generated in the current study, however, is lower than that generated by Wu and others (2014) on a *Porites lobata* coral from the Pacific and other slopes compiled by Corrège (2006; not shown).

Table 1. Summary of published calibration equations of various Caribbean/Atlantic coral species and representative members of the genus *Porites* (slopes and y-intercepts reported). For more Sr/Ca-SST calibration equations for the genus *Porites*, see Corrège (2006).
[$mmol\ mol^{-1}$, millimoles per mole; $mmol\ mol^{-1}\ °C^{-1}$, millimoles per mole per degrees Celsius]

SST Dataset	slope m ($mmol\ mol^{-1}\ °C^{-1}$)	y-intercept b ($mmol\ mol^{-1}$)	R (goodness of fit)	Number of regressors	Species
This study	–0.040	10.128	–0.77	46	*Porites astreoides*
Wu and others (2014)	–0.061	10.92	–0.62	146	*Porites lobata*
DeLong and others (2007)	–0.054	10.451	–0.94	392	*Porites lutea*
Swart and others (2002)	–0.0471	10.165	–0.88	12	*Orbicella faveolata*
Smith and others (2006)	–0.0284	9.962	–0.95	494	*Orbicella faveolata*
Flannery and Poore (2013)	–0.0392	10.2053	–0.98	20	*Orbicella faveolata*
DeLong and others (2011)	–0.042	10.070	–0.97	115	*Siderastrea siderea*

Conclusions

We demonstrate for the first time that *Porites astreoides* from the western Atlantic region exhibits well-defined annual cycles in Sr/Ca along its growth axis. When calibrated with local monthly SST data, Sr/Ca from *P. astreoides* shows a significant negative linear relationship with temperature, with a similar slope to the Sr/Ca-SST relationships of Pacific *Porites* species and Atlantic *Orbicella* and *Siderastrea* species. Its mean annual linear extension rate of ~5 mm yr^{-1} is within the range of linear extension rates observed in other members of the genus *Porites*. On the basis of this linear extension rate and the presence of distinct seasonal cycles in Sr/Ca, *P. astreoides* has good potential as an archive of subannual resolution paleotemperature records and could be used to further examine both modern and recent Holocene specimens from the Caribbean and western tropical Atlantic.

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