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Assessing coral Sr/Ca–SST calibration techniques using the species *Diploria strigosa*

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ABSTRACT

The coral species *Diploria strigosa* is a promising archive for paleoclimate reconstruction in the tropical Atlantic, but limited work has been accomplished thus far to quantify the relationship between strontium to calcium ratios and sea surface temperatures in this species. In this study, we collected three modern *D. strigosa* coral colonies from Anegada, British Virgin Islands to refine the use of this species as a paleoclimate archive. Three regression techniques including ordinary least squares, reduced major axis, and weighted least squares were used to assess how assumptions implicit in these regression methods influence the calibration. Our analysis demonstrated that regression slopes were strongly impacted by the assumptions about data uncertainty. We recommend using the unbiased weighted least squares regression technique for calibrating the Sr/Ca paleothermometer, especially when precise local sea surface temperature data are unavailable. Combining our Sr/Ca data with previously published data from this species results in a multi-site, multi-colony temperature sensitivity of $-0.046(\pm < 0.001)$ mmol/mol/°C for mean-centered monthly data, $-0.059(\pm 0.001)$ mmol/mol/°C for monthly anomalies, and $-0.063(\pm 0.004)$ for annual anomalies. We suggest these relationships are the best available characterization of the temperature dependence of Sr/Ca in *D. strigosa*, and can be utilized in future paleoclimate reconstructions.

1. Introduction

A few key genera of reef-building corals are used in most paleoclimate studies to reconstruct tropical sea surface temperature (SST) (Corrège, 2006; DeLong et al., 2007; Saenger et al., 2008). *Porites* is the genus most often used in the Pacific (e.g., Corrège, 2006; Gagan et al., 2012; McGregor and Gagan, 2003; Shen et al., 1996), whereas the *Montastraea annularis* species complex (now formally assigned to the genus *Orbicella* (Budd et al., 2012)) is commonly used in the Atlantic (e.g., Kilbourne et al., 2008; Saenger et al., 2008; Smith et al., 2006; Swart et al., 2002; Watanabe et al., 2001, 2002).

The genus *Diploria* is another abundant massive coral genus commonly found growing on Atlantic reefs but it has been used much less extensively for paleoclimate research. Initial work on the genus *Diploria* primarily focused on slow growing specimens of the species *Diploria labyrinthiformis* from Bermuda (Cohen and Thorrold, 2007; Cohen et al., 2004; Draschba et al., 2000; Goodkin et al., 2005, 2007; Kuhnert et al., 2002). The corals used in these studies had annual growth rates in the 2–5 mm range and many researchers noted a significant impact of coral growth rates on geochemistry in these slow-growing specimens (Cardinal et al., 2001; Cohen et al., 2004; Goodkin et al., 2005, 2007). Cohen and Thorrold (2007) recommended extremely fine sampling of this species to minimize the impact of biosmoothing (Gagan et al., 2012) and time-transgressive sampling on climate reconstructions. Alternatively, Goodkin et al. (2007) suggested a growth-corrected calibration based on three different corals. The goal of their study was to provide a universal calibration that could be applied generally to *D. labyrinthiformis*, both modern and fossil specimens.

Research on the species *Diploria strigosa* is not as well developed as for *D. labyrinthiformis*. Hetzinger et al. (2006) published a 41-year Sr/Ca-SST calibration for a fast growing *D. strigosa* from Guadaloupe, and suggested that *D. strigosa* was a promising archive of Atlantic SST information. They pointed out that faster growth rates in their coral specimen led to less time integration of the sub-samples than with the slower-growing specimens of *D. labyrinthiformis* examined to date (see Sadler et al., 2014 and their Fig. 4 for an excellent explanation of the relevant skeletal geometry). Three subsequent studies utilized Hetzinger's calibration, citing it as the best available calibration for this species (Giry et al., 2010, 2012; Hetzinger et al., 2010). Giry et al. (2010) investigated the sub-millimeter scale Sr/Ca heterogeneity in a specimen of *D. strigosa*. Their results supported the conclusion by Hetzinger et al. (2006) that time integration of drilled samples is much less in these faster-growing specimens than in the slow-

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growing *D. labyrinthiformis*. Additionally, Giry et al. (2010) suggested that micro-milling the thecal wall with a fine (0.6 mm) drill bit was the best method for extracting a climate signal from this species to avoid skeletal elements with strong non-climatic Sr/Ca signals.

In this study we further refine the use of this species for paleoclimate reconstructions. Hetzinger et al. (2006) defined the Sr/Ca–temperature slope in *D. strigosa* using a single coral colony, but as Goodkin et al. (2007) pointed out, multi-colony calibrations are inherently more accurate for paleoclimate reconstructions than those that use individual coral specimens selected from a population. In this study, we explore calibration slopes from multiple modern corals and combine them to provide a more robust Sr/Ca-SST calibration for this species. We utilize new data from multiple specimens of *D. strigosa* which grew offshore from Anegada, British Virgin Islands, in the northern Caribbean, and combine it with existing data from specimens which grew offshore from Guadeloupe (Hetzinger et al., 2006) and Bonaire (Giry et al., 2012), to create a regionally applicable calibration slope.

Most prior calibration studies used the Ordinary Least Squares (OLS) regression technique, which has been shown to have limitations derived from implicit assumptions about measurement errors (Solow and Huppert, 2004). In this study, we explore the use of OLS and compare it to other methods that have been recommended as alternates, such as reduced major axis (RMA) regression (Quinn and Sampson, 2002; Nurhati et al., 2009) and weighted least squares (WLS) (DeLong et al., 2007, 2011, 2014; Thirumalai et al., 2011). We compare multiple calibration techniques with the same data to assess how assumptions implicit in different regression methods influence the resulting calibration slopes and we provide our best estimate of the Sr/Ca–temperature sensitivity for this coral species.

2. Data and methods

2.1. Sampling

The coral samples used in this study were collected as hand samples in March 2013 from the beach berm at Soldier Point, Anegada (Fig. 1). Beach berm deposits of coral boulders are common on high-energy coastlines in reef-growing areas and they provide a near unlimited supply of short (decades-long) coral records from a variety of time periods. We collected pristine-looking coral boulders with the goal of creating a replicated 20th century calibration without any damage to living coral colonies, minimizing the ecological impact of our paleoclimate research.

Approximately 5 cm diameter cores were drilled from each of the three coral boulders in the field. The cores were designated 13AN17, 13AN18, 13AN19 and were cut along the growth direction into approximately 5 mm thick slabs using a tile saw dedicated to cutting coral cores. Each slab was individually immersed in a clean plastic container with deionized water and ultrasonicated for 30 min. Following a rinse in deionized water, the samples were air-dried and stored covered with clean Kimwipes®.

Coral slabs were drilled using a computer-controlled micromilling system, equipped with a 0.5-mm diameter carbide steel dental drill bit. Before drilling the coral slabs, annual extension rates were estimated by measuring the distance between ten density band couplets. The targeted sampling resolution was 12 samples per year. Sub-samples of skeletal powder were extracted carefully at a constant sampling depth of 0.5 mm per sub-sample along the center of the thecal wall, to obtain the best chronology and environmental signal possible (Giry et al., 2010). Thin-section billets were cut adjacent to the micro-sampling paths in each core. No evidence of secondary aragonite or calcite were found in the thin sections.

2.2. Coral Sr/Ca

Sr/Ca ratios in the coral aragonite were measured using a Perkin Elmer Optima 8300 Inductively Coupled Plasma Optimal Emission Spectrometer (ICP-OES) at the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory campus. We weighed 150 ± 50 μg coral powder from each sample and dissolved it in different volumes (2–4 mL) of 2% trace-metal grade nitric acid to bring the concentration of calcium to ~20 ppm. Calibration standards with known calcium and strontium concentrations were used to convert instrumental signal intensity to sample concentration. Reference standards were measured before and after each sample to calculate an instrumental drift correction to be applied to the data, as per Schrag (1999). The calcium and strontium concentrations of the reference standards were similar to the samples, with values of ~20 ppm and 400 ppb, respectively. An in-house laboratory coral standard prepared from an *Orbicella faveolata* coral dissolved in 2% trace-metal grade nitric acid to similar calcium concentration as the samples provided an independent check of analytical precision and accuracy. The Sr/Ca ratios of these two standards were cross calibrated with ICP-OES instruments at the University of Texas at Austin Analytical Laboratory for Paleoclimate Studies and the US Geological Survey in St. Petersburg, Florida. Long-term analytical precision for the reference standard solution is 0.12%

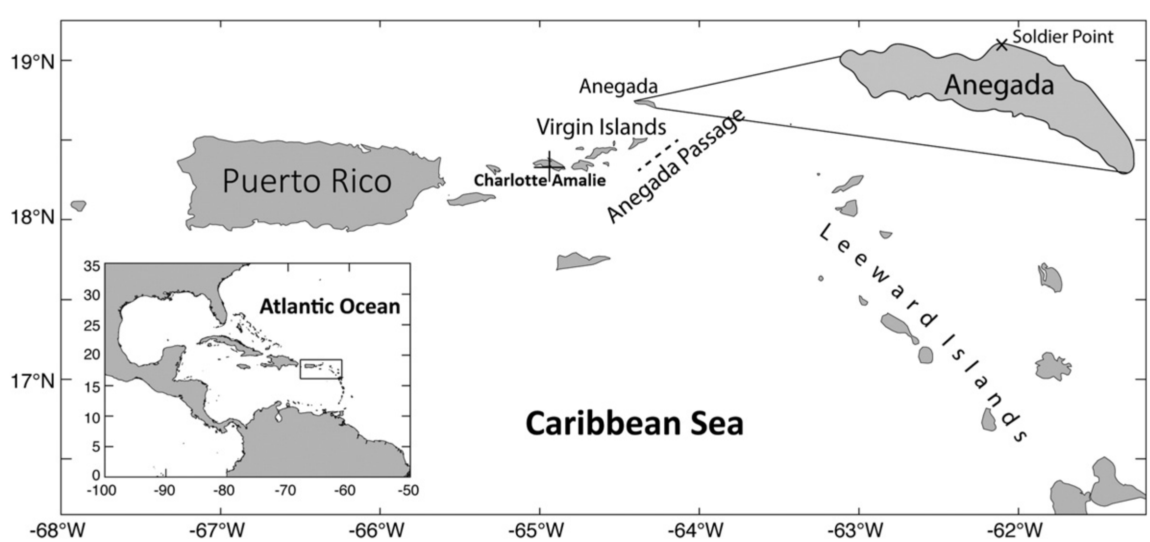

Fig. 1. Samples for this study were obtained from a beach berm deposit at Soldier Point on the north side of Anegada, British Virgin Islands. This carbonate island lies on the border between the Caribbean Sea and the tropical North Atlantic. Buoy-based SST data discussed in the paper came from Charlotte Amalie harbor on St. Thomas in the U.S. Virgin Islands.