High-resolution Sr/Ca records in sclerosponges calibrated to temperature in situ

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Abstract

Ratios of strontium to calcium have been analyzed by laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) in a skeletal section of the scleropore Ceratoporella nicholsoni. The growth period, representative of 3 yr, was stained in the skeleton with a fluorochrome (calcine). Temperatures were recorded at 2 h intervals within the shallow, cryptic reef enclosure that the scleropore inhabited on the northern coast of Jamaica, allowing the formulation of a direct empirical relationship between Sr/Ca and temperature. To verify this calibration, Sr/Ca ratios of two sclerosponges of the same species from depths of 67 m and 136 m in Exuma Sound, Bahamas, were analyzed by LA-ICP-MS and compared to the temperatures from these depths over a decade prior to collection. The result is an independently verified, high-resolution empirical calibration for the temperature sensitivity of Sr/Ca ratios in the aragonite skeletons of sclerosponges from Jamaica and the Bahamas. The calibration is a first for C. nicholsoni and indicates that sclerosponges are more sensitive temperature recorders than zooxanthellate corals. It represents an important step in establishing skeletal geochemistry of sclerosponges as a proxy of temperature in the upper 250 m of the ocean.

Keywords: paleoceanography, scleropore, Ceratoporella nicholsoni, Sr/Ca ratios, ocean temperature, calibration.

Introduction

Issues of the oceans’ roles in global climate change have increased the demand for records of the oceans’ heat content over the past millennium. Unfortunately, high-resolution geochemical proxies in the aragonite skeletons of scleractinian corals, including the concentration of minor elements such as strontium, are limited to near-surface waters and to the past 200–300 yr. Sclerosponges can potentially extend pre-instrumental ocean temperature and salinity records beyond the past millennium and below the thermocline in tropical and subtropical waters, because of their greater depth range (0–250 m) and longer life span (500–1000 yr) (Lang et al., 1975; Swart et al., 1998a, 1998b).

The massive scleropore Ceratoporella nicholsoni lives in cryptic environments at depths as great as 250 m throughout the Caribbean Sea, inhabiting deep areas under overhangs and shallower enclosures and cavities formed nearer the reef crest. In such environments, they have been found in many parts of the Bahamas (Lee Stocking Island [Swart et al., 1998a], Acklins Island [Lazareth et al., 2000], Tongue of the Ocean [Swart et al., 2002b]) as well as in Belize (Swart et al., 1998b), Turks and Caicos (Verheyden et al., 2002), and Jamaica. In both Jamaica and Acklins Island, C. nicholsoni have been found in crevices shallow enough to be accessible to scuba (20–30 m). C. nicholsoni secretes a dense aragonite skeleton at rates of ~200 μm/yr (Benavides and Druffel, 1986; Willenz, 1988; Willenz and Hartman, 1985, 1999). Thus, specimens of only 20 cm diameter can potentially possess ages in the vicinity of 1000 yr.

As with zooxanthellate corals, interest in sclerosponges as paleoclimate proxies is focused on their dense fibrous aragonite skeletons. C. nicholsoni is the most massive of the Caribbean sclerosponges, and its skeleton contains regularly spaced concentric bands. Radiometric dating suggests that these bands are not annual in nature (Benavides and Druffel, 1986; Swart et al., 2002b); however, their presence indicates the potential of sclerosponges as proxies because the dense skeleton is deposited in an organized chronological manner. It has been established that the δ18O values of scleropore skeletons are close to being in equilibrium with seawater (Boehm et al., 2000; Druffel and Benavides, 1986) and that sclerosponges faithfully record the decrease in atmospheric δ13C values due to industrialization—the δ13C Suess effect (Boehm et al., 2002, 1996; Swart et al., 1998a, 1998b, 2002b; Lazareth et al., 2000; Moore et al., 2000). Scleropore δ13C records, for example, have been used to measure the change in δ13C (DIC—dissolved inorganic carbon) associated with CO2 increases in the atmosphere related to industrialization (Boehm et al., 1996, 2002; Druffel and Benavides, 1986).

Compared to the number of stable isotope studies, there have been fewer reports of minor element contents in the skeletons of sclerosponges. By using the δ13C Suess effect to produce an age model, Lazareth et al. (2000) showed that C. nicholsoni recorded changes in the Pb content of the atmosphere-ocean system due to the proliferation of automobiles during the early twentieth century. In addition, the works of Lazareth et al. (2000) and Swart et al. (2002b) have shown that minor and trace element ratios can be analyzed at very high spatial resolution with laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) owing to the density of the aragonite skeletons of C. nicholsoni. Differences in trace element concentrations between sclerosponges and zooxanthellate corals were reported by Swart et al. (1998b), who showed that sclerosponges generally incorporate ~2000 ppm more strontium into their aragonite skeletons. Little information, however, is available on the relationship between Sr/Ca and temperature for any scleropore species. Such information is necessary to differentiate between salinity and temperature signatures preserved in δ18O records of sclerosponges.

To further advance the use of sclerosponges as paleoclimate proxies, this paper reports the direct calibration of high-resolution scleropore Sr/Ca ratios to indicate temperature records from Discovery Bay, Jamaica. This calibration is independently verified by using two individuals of C. nicholsoni from depths of 67 m and 136 m in the Bahamas. The calibration between temperature and Sr/Ca ratios represents a significant step in establishing sclerosponges as recorders of temperature and salinity of the upper 200 m of tropical oceans.

Methods

Sample Collection—Jamaica and Bahamas

In May 2002, a fragment of a specimen of C. nicholsoni was collected from a submarine crevice (25 m depth) at Pear Tree Bottom, off the northern coast of Jamaica, east of Discovery Bay (Fig. 1). This specimen was stained in August 1999 with calcine, a fluorochrome (Willenz and Hartman, 1985), to provide a skeletal marker for the calibration of Sr/Ca in C. nicholsoni. The other specimen was collected from the Bahamas, in Exuma Sound, in a fracture of a reef (Fig. 1).
coinciding with the beginning of our temperature record. The incubation procedure did not interrupt the growth of the sclerosponge and the sclerosponge appeared healthy up to one week after staining.

For verification, two specimens of the same species were selected from a collection accumulated at the University of Miami in 1992 during submersible explorations of the steep slope of Bahamas Bank, off the coast of Lee Stocking Island in Exuma Sound (Fig. 1). These samples of *C. nicholsoni* were selected because they represent a wide depth range (67 to 136 m) over which there is significant difference in temperature.

**Temperature Records**

Temperature records in Jamaica were taken every 2 h by using Stow-Away Digital TidBit temperature loggers attached to the base of the stained sclerosponge. Temperature loggers were changed periodically and checked against several other temperature-recording devices for accuracy. In the Bahamas, temperature records were kept between 1982 and 1992 by the Caribbean Marine Research Laboratory on Lee Stocking Island. The records were from 32 m, 105 m, 145 m, and 215 m.

**Analysis by LA-ICP-MS**

High-resolution LA-ICP-MS data were obtained by using a Finnigan MAT Element magnetic sector field ICP-MS with a New Wave 213 nm LA system for the Jamaican specimen and a Thermo Finnigan Element2 ICP-MS with a 266 nm New Wave LA system for the Bahamas specimens. The sclerosponges were slabbred to a thickness of ~1 mm and mounted on petrographic slides. Sections were scrubbed with a nylon brush in Milli-Q water (Millipore Water Systems), subjected to sonification for 5 min in Milli-Q water, and then triple rinsed with ultrapure 1% HNO₃ and Milli-Q water sequentially. Laser sampling of the Jamaican sclerosponge was conducted along lines that were 1.4 mm in length, 20 μm apart, and ran parallel to the concentric bands of the sclerosponge skeleton. The spot size of the laser was 20 μm, with a repetition rate of 10 Hz and a scan speed of 5 μm·s⁻¹ along the lines during sample acquisition. We therefore generated ~10 samples per year, assuming an average growth rate of 200 μm. Spatial resolution was higher in the Bahamas sclerosponges with sample lines that were 10 μm apart and using a 10 μm spot size. All other laser settings were identical to the Jamaican samples. A helium gas stream was used to transport the vaporized material of each laser sample to the ICP-MS. The carrier gas was mixed with a wet aerosol (1% w/w HNO₃) from a self-aspirating PFA nebulizer (20 μL·min⁻¹) in a dual-inlet quartz spray chamber. An aragonite reference material from fish otoliths was used as a standard and measured at intervals throughout the analyses (Yoshinaga et al., 2000). Analyses of this reference material (n = 153) run during assays of the Bahamas sclerosponges provided a mean Sr/Ca ratio of 2.878 ± 0.008 mmol·mol⁻¹ (1σ), after correcting for mass bias using an internal laboratory standard. Replicate measurements of an internal laboratory standard run at intervals (n = 11) throughout the Jamaican sclerosponge analyses gave a value of 2.24 ± 0.042 mmol·mol⁻¹ (1σ).

**RESULTS**

**Temperature Records**

Water temperatures in Jamaica at the calibration site (25 m) ranged between 25 and 30 °C (Fig. 2A). As expected, the temperature range was greater in the Bahamas (Fig. 2B), 19 °C at 215 m to 30 °C in near-surface waters, because of the inclusion of deeper waters in the record. Seasonal minima and maxima in the Bahamas show a higher degree of lag time as well as diminishing amplitudes with depth (Fig. 2B).

**Growth Rate**

The distance between the calcine stain band and the surface of the skeleton in the Jamaican sclerosponge was measured by the techniques outlined in Willenz and Hartman (1985, 1999). Measurements along 60 individual calicles indicated a growth rate of 181 μm·yr⁻¹ (n = 60, σ = 15.23 μm·yr⁻¹). This growth rate approaches the lower limits of the variable growth rates observed in sclerosponges (Benavides and Druffel, 1986; Swart et al., 2002b; Willenz and Hartman, 1999).

**Sr/Ca Ratios**

Ratios of Sr/Ca in the Jamaican sclerosponge ranged between 9.45 and 9.90 mmol·mol⁻¹; seasonal maxima and minima were well represented in the time series (Fig. 3A). Ratios of Sr/Ca in the Bahamas were consistently higher than those in Jamaica, averaging 9.88 mmol·mol⁻¹ at 67 m and 10.09 mmol·mol⁻¹ at 136 m (Fig. 3B).

**Age Model**

Although application of an average growth rate of 181 μm·yr⁻¹ to the Sr/Ca ratios sampled at 20 μm intervals produced a significant linear relationship with the temperature record (r² = 0.58), a simplified constant growth rate was not ideal because seasonal extremes in both records did not match exactly. The calcine stain line was our only age control, thus we assumed that Sr/Ca maxima correlated with temperature minima between the stain line and the surface in order to maximize accuracy of calibration. Testing this assumption by calculating growth rates between annual cycles, we observed a range in growth rate between 140 and 350 μm·yr⁻¹, with a time-weighted average of 197 μm·yr⁻¹. This result is within the 95% confidence interval of the growth rate of 181 μm·yr⁻¹ determined strictly from the calcine stain bands. Such a detailed age model was not constructed for the Bahamian sclerosponges because lack of prior staining of the skeletons prevented the establishment of a primary age control.

**Calibration**

A direct calibration of the Jamaican sample (equation 1, r² = 0.67) was produced from correlation of the Sr/Ca record to the tem-
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Figure 2. A: Detailed temperature records were taken in situ from cave in Jamaica heavily populated by sclerosponges. Digitally recorded temperatures were taken every 2 h, but only daily averages are shown (black line). This detailed temperature record was interpolated to the number of Sr/Ca measurements between each seasonal extreme in Sr/Ca record (black triangles) to facilitate comparison between two records (Fig. 3). Interpolation did not affect seasonal amplitude of record. B: Semicontinuous temperature records from four different depths off of slope of Lee Stocking Island, Bahamas, were used for independent verification of Jamaica calibration. Average annual temperature for each sclerosponge was obtained by interpolating linearly between average temperatures of decade-long records above and below each sclerosponge. Temperature records were kept by Caribbean Marine Research Center on Lee Stocking Island.

Figure 3. A: By using calcein staining (represented by dark vertical bar) as control and Sr/Ca cyclicity as detailed age model, high-resolution laser-ablation inductively coupled plasma–mass spectrometry measurements of Sr/Ca ratios were compared to interpolated temperature record. Error bars on calibration points from Jamaican calibration (hollow circles) represent analytical error of replicates of standard reference material (1H9268/H115490.042 mmol·mol−1H115461). Seasonal extremes are apparent in both temperature and Sr/Ca records. B: Use of linear-regression model (heavy black line, Cerato- porella [C.] nicholsoni verified) through calibration points (solid diamonds with error bars) as well as Bahamas verification points (hollow triangles with error bars) yields calibration presented in equation 2. Larger error bars on Bahamas verification points represent larger error assumed in averaging decade of data, including seasonal extremes. Comparison of this study’s verified direct calibration with calibration using inorganic aragonite (dashed line, Kinsman and Holland, 1969) and average results for zooxanthellate corals (hollow squares with dashed line) shows that sclerosponge Sr/Ca ratios possess more sensitivity to temperature changes. Line shown for coral calibrations is average of slopes and intercepts taken from Swart et al. (2002a), but not calibration in itself.

\[
\text{Sr/Ca} = 12.75 \pm 2.19 - 0.111 \pm 0.055 T, \quad (1)
\]

where the Sr/Ca ratio is in mmol·mol⁻¹ and \(T\) is temperature (in °C).

We independently verified equation 1 by using sclerosponges collected from different depths (67 and 136 m) at Lee Stocking Island in the Bahamas. To calculate the average Sr/Ca ratios correlating to the decade-long temperature record, we assumed a growth rate of 200 μm·yr⁻¹ for both sclerosponges and averaged the high-resolution Sr/Ca data from the top 2 mm of the sclerosponge. Because the average Sr/Ca values were compiled from such a volume of data, changing the assumed growth rate within published limits (Swart et al., 2002b) did not significantly affect the average Sr/Ca ratios from each sponge. We calculated an average temperature over a decade of records from temperature loggers maintained at different depths (30, 105, 145, and 215 m) by the Caribbean Marine Research Laboratory on Lee Stocking Island and interpolated from between the two depths constraining the depth of each sclerosponge. This verification technique yielded two data points to compare with the direct calibration performed in situ in Jamaica. The result (shown in Fig. 3B, \(r^2 = 0.78\)) is described by

\[
\text{Sr/Ca} = 12.50 \pm 1.25 - 0.102 \pm 0.034 T. \quad (2)
\]

The two verification points extend the Jamaican calibration down to 23 °C.

**DISCUSSION**

The incorporation of Sr/Ca ratios from the Bahamas into an empirical equation from Jamaica is based on the assumption that strontium concentrations are conservative throughout the Caribbean. Although this assumption was controversial after earlier investigations into oceanic strontium content (Brass, 1974), improvements in analytical techniques have shown that oceanic Sr/Ca values vary as a function of geography and depth (deVilliers, 1999), but these variations are not as large as the original geochemical ocean sections study (GEOSECS).
hinted (Brass, 1974). Only Jamaica has a potentially significant source of fluvial inputs of strontium; however, no data are currently available to evaluate how that fact may affect the assumption of Sr/Ca conservation between Jamaica and the Bahamas. In the northern Atlantic Ocean, the increase in Sr/Ca with depth is smaller than in other areas (−0.05 mmol·mol⁻¹ through the top 250 m in the North Atlantic as opposed to 0.08 mmol·mol⁻¹ in the southwest Pacific and South Atlantic [devilliers, 1999]). This relatively small increase with depth cannot account for the difference in Sr/Ca values (0.21 mmol·mol⁻¹) through the Bahamas depth transect used to verify the Jamaican calibration.

The issue of temperature sensitivity of sclerosponge Sr/Ca ratios is important because of the large depth range inhabited by sclerosponges. Even in tropical oceans, sclerosponges must be able to record seasonal temperature amplitudes of the magnitude of only 2.5 °C if they are to be used below the mixed layer as recorders of ambient temperature. The range of Sr/Ca ratios in both the Jamaican and Bahamian sclerosponges was higher than the ranges typically observed in zooxanthellate corals (beck et al., 1992; Marshall and McCulloch, 2002; Smith et al., 1979). Coupled with the smaller temperature range typical of deep, cryptic sclerosponge habitats, temperature sensitivity of Sr/Ca ratios in sclerosponges would be expected to be higher than in zooxanthellate corals. Zooxanthellate corals express a range of slopes between 0.03 mmol·(mol·K)⁻¹ and 0.09 mmol·(mol·K)⁻¹ for the Sr/Ca vs. temperature relationship (Swart et al., 2002a); the average value is 0.059 mmol·(mol·K)⁻¹ (σ = 0.01). Compared to the slope of equation 2, coral Sr/Ca ratios show approximately half the sensitivity to temperature change as sclerosponges, although some species of coral can approach the sensitivity of sclerosponges.

In addition, Sr/Ca ratios in sclerosponges are nearly three times more sensitive to temperature change than Sr/Ca ratios in inorganic aragonite (fig. 3B) (Kinsman and Holland, 1969). The observation that the inorganic aragonite line is between both biogenic aragonite lines suggests significant differences in calculation mechanisms between sclerosponges and zooxanthellate corals, an interpretation that is supported by comparing the overall concentrations of other minor elements in sclerosponges to those of corals. Concentrations of boron, magnesium, and barium are lower in sclerosponges, whereas concentrations of strontium and uranium are significantly higher in sclerosponges (Swart et al., 1998b). Such differences in minor element concentration between sclerosponges and corals may be expected, because these organisms are physiologically very different due to the presence of an algal symbiont in zooxanthellate corals.

**CONCLUSIONS**

We have shown that it is possible, by using LA-ICP-MS techniques, to obtain samples at a sufficient resolution to calibrate the temperature dependence of Sr/Ca ratios in the slow-growing sclerosponge C. nicholsoni over a period of 3 yr. Over a small time period, constant-growth-rate assumptions do not provide as accurate an age model as one determined by using the cyclicity of Sr/Ca ratios, which is assumed to be annual. The resulting calibration of Sr/Ca ratios to temperature represents a key step in using sclerosponges as recorders of the heat content of the ocean, both above and below the thermocline.

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