Growth and composition of high-Mg calcite in the skeleton of a Bermudian gorgonian (*Plexaurella dichotoma*): Potential for paleothermometry

Zoë A. Bond  
*School of Ocean and Earth Science, National Oceanography Centre, Southampton, European Way, Southampton SO14 3ZH, UK (zab@noc.soton.ac.uk)*  
*Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA*

Anne L. Cohen  
*Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA*

Struan R. Smith  
*Bermuda Biological Station for Research, Ferry Reach, St. Georges, GE01, Bermuda*  
*Now at Department of Biology, Georgia State University, Atlanta, Georgia 30303, USA.*

William J. Jenkins  
*Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA*

[1] We used a secondary ion mass spectrometry (SIMS) ion microprobe to analyze magnesium-to-calcium (Mg/Ca) and strontium-to-calcium (Sr/Ca) ratios of high-Mg calcite loculi within the skeleton of a shallow water gorgonian, *Plexaurella dichotoma*, from Bermuda. A cross section of the gorgonian skeleton reveals loculi embedded within proteinaceous gorgonin arranged in concentric rings about the axial core. Viewed in cross section, the loculi are fan-shaped, 10–140 μm in diameter, and composed of bundles of needle-shaped crystals that appear to radiate out from a calcification center. Discrete sample spots, each 20 μm diameter, were sputtered from successive loculi along a sample track 3 mm long. Over this distance, 25 bands of high-low density gorgonin couplets were encountered, estimated to represent the period 1963 to 1988. Mg/Ca ratios show an overall, positive correlation with annual sea surface temperatures (SSTs) that is strongest in the autumn months (October–December). High-resolution analyses along the growth axes of individual loculi reveal low variability and no trend, consistent with our interpretation of seasonal growth of these calcite inclusions. The sensitivity of Mg/Ca to interannual changes in average autumn temperatures is 0.47 mmol/mol per °C. Conversely, interannual variability in calcite Sr/Ca does not follow the interannual variability in SST and may be influenced primarily by growth rate.
1. Introduction

Much of what we know about the history of Earth’s climate system is derived from the chemical composition of biogenic skeletons preserved in the geologic record. The isotopic and elemental composition of scleractinian corals, including massive reef corals and deep-sea species, have proven to be useful tools for paleoceanographic reconstruction, providing information about the surface and deep oceans on timescales of decades to millennia [e.g., Dunbar and Cole, 1999]. The banded skeletons of gorgonian corals (Cnidaria: Octocorallia) are also potentially valuable archives of past climate. Gorgonians inhabit the world’s oceans from the equator to the poles, from the shallows to great depths. Unlike the scleractinia, gorgonian coral skeletons are formed of a proteinaceous material gorgonin within which the mineralized components, usually calcite, are embedded in a locular form [e.g., Lewis et al., 1992] (Figure 1). The mixture of organic and inorganic materials within the gorgonian skeleton provides a unique opportunity to develop novel tracers of ocean circulation. Nevertheless, the utility of gorgonian corals as paleoceanographic archives has been less well explored than that of the scleractinia. The limited number of investigations of the composition of calcified regions in the gorgonian skeleton, including sclerites, indicate that the elemental chemistry, especially the Mg/Ca content of gorgonian calcite may be a valuable proxy for ocean temperature [Chave, 1954; Weinbauer and Velimirov, 1995; Weinbauer et al., 2000; Heikoop et al., 2002; Thresher et al., 2004].

Compared with reef corals, the minute dimensions of the gorgonian skeleton prohibit the use of conventional bulk sampling techniques to produce highly resolved proxy time series. In this paper we report results of SIMS ion microprobe analyses of Mg/Ca and Sr/Ca ratios in high-Mg calcite deposits “loculi” accreted by a shallow water Bermudian gorgonian Plexaurella dichotoma. This species is common on Bermuda and throughout the Caribbean from ~3 to 45 m depth [Sterrer, 1986; Humann and DeLoach, 2002] and was chosen for this study because the axial skeleton is heavily mineralized (~20% dry weight) [Lewis et al., 1992]. While the diameter of the skeleton is typically 1 cm or less, the micro scale sampling capabilities of the ion microprobe enabled us to construct...
a 25 year long proxy time series across 3 mm of skeleton. In addition, we were able to assess the chemical homogeneity within individual loculi.

2. Sample Collection, Preparation, and Analyses

A live colony of *Plexaurella dichotoma* (Figure 1) was collected at 6 m depth from Bailey’s Bay Flats (32°21′73″N, 064°44′84″W), an inner lagoon reef site on the north shore of the Bermuda platform, on 27 September 2001 (Figure 2a). The base of the colony, 1.5 cm in diameter was dried and the coenenchyme removed to reveal the axial skeleton (Figure 1e). Sclerites, the shape, ornamentation and size of which are species specific, were isolated from the coenenchymal tissue (Figure 1b) and were used to confirm our initial species identification based on overall colony morphology. The axial skeleton was sectioned across its width into slabs 0.5 cm thick. Sections selected for growth band counts and micro structural examination were set in epoxy resin, vacuum impregnated, sectioned further using a Buehler thin sectioning system, ground and highly polished to a thickness of 110 μm. A growth band is defined here as one high- and low-density couplet of organic gorgonin, including the embedded calcitic loculi (Figure 3). Growth band widths ranged from 60–240 μm, with an average width of 120 μm. Growth bands were counted under 20X magnification in both transmitted and reflected light. Due to the difficulty in resolving individual bands in certain regions of the skeleton, a minimum of eight radial transects were counted across each section. On the basis of the variability in the number of bands distinguished in repeat counts of a single section, we estimate the error as ±4 bands per section. Assuming the bands are annual accretions [Grigg, 1974; Druffel et al., 1995; Andrews et al., 2002; Risk et al., 2002; Marschal et al., 2004], this translates to an error estimate on our age model of ±4 years.

One section was selected for SIMS ion microprobe analysis on the basis of the clarity of banding...
and the continuity of calcite loculi across a radial transect. Thirty-eight bands were counted across a radius of approximately 5 mm, indicating a colony age of 38 ± 4 years. The section was epoxy-mounted in a 100 mm round aluminum ring and polished with 1 mm alumina followed by 0.2 mm colloidal silica. Sr/Ca and Mg/Ca ratios were measured using the Cameca IMS 3f ion microprobe. A 3 nA O⁷/C0⁷ primary ion beam was used to sputter select areas of successive calcite loculi in situ along a transect starting at the central core of the sectioned skeleton to the outer bands. Due to the low abundance of loculi in the outermost layers of the skeleton, we focused our analyses on the period 1963–1988. We also made several, high-resolution measurements within the larger loculi, starting at the base near the calcification center and following a straight path toward the center of the outer edge. Sample spots were 10–20 μm in diameter and approximately 5 μm deep. A single spot was occupied for 3 minutes while measuring secondary ion intensities for ²⁴Mg, ⁴²Ca and ⁸⁸Sr. Contributions from molecular ions including ⁴⁴Ca-dimer were suppressed using a 50–110 eV energy window, which reduces molecular interferences to <0.1%. Cleanliness of the utilized mass spectrum has been demonstrated for Mg, Ca and Sr by measurement of isotope ratios [Hart and Cohen, 1996]. Ion microprobe ratios were converted to molar ratios using a standard curve based on two calcite standards (OKA C2 and Blue calcite 0875) for which Mg/Ca and Sr/Ca ratios have been independently established [Hart and Cohen, 1996; Cohen et al., 2001]. Internal measurement precision for both 24/42 and 88/42 was 0.4% (2σ).

### 3. Results

#### 3.1. Structure and Growth of Loculi

Calcification of the *Plexaurella dichotoma* skeleton is concentrated in specific regions of the colony. Heaviest calcification was observed at the center of the colony base, and in the branches (Figure 3). The loculi grow both radially (i.e., thickening) and longitudinally (i.e., lengthening) resulting in rod-shaped structures 10–20 μm in diameter and approximately 5 μm deep. A single spot was occupied for 3 minutes while measuring secondary ion intensities for ²⁴Mg, ⁴²Ca and ⁸⁸Sr. Contributions from molecular ions including ⁴⁴Ca-dimer were suppressed using a 50–110 eV energy window, which reduces molecular interferences to <0.1%. Cleanliness of the utilized mass spectrum has been demonstrated for Mg, Ca and Sr by measurement of isotope ratios [Hart and Cohen, 1996]. Ion microprobe ratios were converted to molar ratios using a standard curve based on two calcite standards (OKA C2 and Blue calcite 0875) for which Mg/Ca and Sr/Ca ratios have been independently established [Hart and Cohen, 1996; Cohen et al., 2001]. Internal measurement precision for both 24/42 and 88/42 was 0.4% (2σ).

**Figure 3.** (a) Polished thin section of *Plexaurella dichotoma* basal cross section showing the distribution of calcite loculi (white) and the banding patterns of gorgonin (brown) (scale bar 1 mm). (b) Illustration of how bands were deciphered. A growth band contains one high- and low-density gorgonin couplet plus any embedded calcite loculi. (c) A younger portion (branch section) of the colony with concentric banding and greater calcification (arrow indicates the central core, scale bar 1 mm).

**Figure 4.** Calcite loculi of *Plexaurella dichotoma* viewed in reflected light (scale bar 100 μm). (a) Fan-shaped loculi (white) embedded in bands of gorgonin (black) viewed in cross section. Needle-shaped crystals of high-Mg calcite emerge from a common nucleation point at the base of the loculus, fanning out as they extend to form a crescent shape. Discrete loculi may continue to grow laterally and sometimes fuse with adjacent loculi. (b) Longitudinal view of loculi showing variation in width due to gorgonin fibers (gf) restricting growth (cracks developed along loculi during sample preparation).
Lewis et al. [1992] for other Plexaurella species. In cross section, the ultrastructural composition of the loculi is visible as radiating arrays of fine needle-shaped crystals that appear to emerge from a common center. Bands of gorgonin seem to constrain the outward growth of these needle crystals. Fine bands, approximately 2 μm wide are visible within the loculi of *P. dichotoma*. They are oriented perpendicular to the growth axis, similar to those described by Lewis et al. [1992] in *Plexaurella nutans*, *P. grisea* and *P. fusifera*.

3.2. Time Series

Mg/Ca ratios of the loculi of *P. dichotoma* range from 144.09 mmol/mol to 341.15 mmol/mol and Sr/Ca ratios range from 1.99 mmol/mol to 3.53 mmol/mol. Mg/Ca and Sr/Ca time series constructed along the radial transect were compared against SSTs recorded at Hydrostation S for the period 1963–1988. Mg/Ca and Sr/Ca ratios collected from loculi within each discrete growth band were averaged and normalized, and the correlation with SST determined with positive/negative time lags. Interannual variability in Mg/Ca correlates positively with interannual SST variability; the highest correlation ($r^2 = 0.32$) between annually averaged SSTs and Mg/Ca obtained with a 3 year lag. The best correlation between Sr/Ca and SST was inverse ($r^2 = 0.35$) obtained with an 8 year time lag. Although a time lag of 3 years for the Mg/Ca data could be explained due to band count error (band counts and hence associated years are only accurate to ±4 years) the time lag of 8 years for Sr/Ca cannot and so these results are clearly inconclusive. We next explored the correlations amongst seasonal SSTs and skeletal chemistry, hypothesizing that the bulk of a loculus is accreted over a shorter time frame than one year. Highest correlations were obtained for the autumn season (October–December). Mg/Ca correlates positively with autumn SST: $r^2 = 0.45$ with zero lag ($P < 0.10$, df = 17) (Figure 5a). The sensitivity of *P. dichotoma* Mg/Ca to changes in interannual SST (autumn) is calculated from this correlation as Mg/Ca = (46.75*SST) – 879.24. Sr/Ca correlates inversely with autumn SST for the first half of the time series: $r^2 = 0.43$ with zero lag ($P < 0.10$, df = 17), but fails to capture the SST variability after about 1976 (Figure 5b).

3.3. Variability Within Loculi

To assess within loculus skeletal chemistry variability, seven loculi (100–140 μm width) were analyzed for Mg/Ca and Sr/Ca at high-resolution along the axis of maximum growth, i.e., along a straight path from the calcification center to the edge of the loculus (Figure 6a). The Mg/Ca and Sr/Ca mean values and standard deviations were calculated for each within loculus transect and each growth band. Within loculus variation is compared to the yearly variation in Figures 6b and 6c. For the within loculus data, with two exceptions, (1983 for Mg/Ca and 1979 for Sr/Ca), low variability observed along the major growth axis supports our hypothesis that the bulk of a loculus may be accreted over a short time frame (autumn). Larger variation is observed within the annual growth bands of 1975, 1978, and 1982. The data contributing to this large variability come from sample spots located at the lateral ends of the loculi, offset from the major growth axis. This observation suggests that subsequent lateral growth (widening) of the loculi may occur at different times of the year.

4. Discussion

The mineralized components of the *P. dichotoma* skeleton are discrete crescent-shaped rods of high-Mg calcite (i.e., >5% Mg [Chave, 1954]) composed of radiating bundles of needle crystals. The spherulitic morphology of the calcite crystals in *P. dichotoma* are rarely observed in inorganic calcites [Tracy et al., 1998] but have been described in other calcitic biominerals including scleractinian corals and avian eggshells [e.g., Lowenstam and Weiner, 1989]. Spherulitic morphologies in general are considered indicative of rapid crystal growth rates [e.g., Bryan and Hill, 1941; Lofgren, 1974; Lowenstam and Weiner, 1989].

Loculi are most abundant at the center of the base and in the branches of the gorgonian skeleton. Calcification provides strength to the thinnest, weakest portions of the colony and it is in these areas of the skeleton that lateral fusing of loculi is observed. The crescent shape of the loculi may be an indication of constraints imposed by the organic gorgonin on biomineral growth. Undulations in the gorgonin, perhaps associated with longitudinal channels containing gastrodermal canals at the axis surface [Marschal et al., 2004], mold the growing loculi into small crescents that may fuse laterally with adjacent loculi to form semicontinuous bands of calcite. This fusion indicates that the loculi, although constrained by gorgonin at their outer edge, may continue to thicken at their lateral...
margins. The lateral fusion of adjacent crescents toward the center of the skeleton implies that lateral growth of the calcite needles could continue for several months after their initial accretion, a phenomenon also observed in the aragonitic needles of coral sclerodermites [Barnes and Lough, 1993; Cohen et al., 2004].

The Mg/Ca ratios reported here for _P. dichotoma_ agree well with those reported by Chave [1954] for the sclerites of a Bermudian _Plexaurella_ species (205 mmol/mol). Whereas both are significantly higher than those reported by Weinbauer et al. [2000] for the high-Mg calcite skeleton of the red coral, _Corallium rubrum_. The positive correlation between Mg/Ca and SST that we observed for _P. dichotoma_ calcite is in agreement with that observed for a range of biogenic calcite skeletons, including gorgonians [Chave, 1954; Weinbauer and Velimirov, 1995; Weinbauer et al., 2000; Thresher et al., 2004], as well as data obtained from laboratory grown inorganic calcites [Mucci and Morse, 1983; Huang and Fairchild, 2001]. Despite the positive correlation obtained between Mg/Ca and SST, there are clearly phase offsets in some years. For example, peak SSTs obtained in 1979 and 1983 appear to be captured by peaks in Mg/Ca ratios exactly one year earlier (Figure 5a). This most likely reflects uncertainties in the age model based on band counting and the assumption that

![Figure 5. Mg/Ca and Sr/Ca time series spanning years 1963–1988 plotted against interannual SSTs averaged over the autumn period only. (a) Mg/Ca correlates positively with SST. (b) Sr/Ca correlates inversely with SST for the first half of the time series but fails to capture the interannual SST variability after about 1976.](image-url)
the outermost band was accreted during 2001. As sample collection took place at the end of the warm summer period (27 September 2001) the bulk of the 2001 loculus growth may not yet have occurred. Nevertheless, the magnitude of the offsets is within our estimated age error of 4 years. Future validation of the age model by independent dating techniques (bomb tritium and radiocarbon measurements of the skeletal banding) may strengthen the correlations and at the same time, enable more precise calculations of the Mg/Ca temperature dependence for this species.

[13] In Figure 7, we compare the Mg/Ca-SST relationship obtained in this study for P. dichotoma...
high-Mg calcite with that reported for gorgonian calcite [Weinbauer et al., 2000], gorgonian sclerites [Chave, 1954; Weinbauer and Velimirov, 1995], high-Mg foraminiferal calcite [Toyofuku et al., 2000] and inorganic calcite [Oomori et al., 1987]. The sensitivity of *Plexaurella dichotoma* Mg/Ca to changes in temperature is apparently much higher than has been observed for other biogenic and inorganic calcites and is a full order of magnitude higher than that reported by Weinbauer et al. [2000] for *C. rubrum*. The reasons for these differences are unclear at this point but may be a function of the Mg/Ca content of the skeleton; i.e., the higher the Mg content, the higher the sensitivity of Mg to temperature. The differences amongst Mg/Ca-SST relationships obtained for gorgonian calcites may, in addition, reflect the different calibration techniques used to derive them. For example, the relationship for *Plexaurella dichotoma* in this study was obtained by comparing interannual Mg/Ca variability within a single colony against interannual SST variability over a 25 year time period, whereas other relationships have been established using different colonies collected at different sites or depths [e.g., Weinbauer et al., 2000].

Variability in *Plexaurella dichotoma* Sr/Ca ratios track the interannual SST variability for the first half of the record but fail to do so after 1976, remaining relatively invariant for the remaining 12 years (Figure 5b). This suggests that *Plexaurella dichotoma* Sr/Ca may be controlled by factors other than ocean temperature. Experimental determination of laboratory grown inorganic calcites indicates that growth rate is the main control on Sr/Ca composition [Zhong and Mucci, 1989]. Growth rate effects on Sr incorporation into biogenic calcites have been observed in gorgonian sclerites [Weinbauer and Velimirov, 1995], the axial skeleton of *C. rubrum* [Weinbauer et al., 2000], and coccolithophores [Stoll et al., 2002]. Heikoop et al. [2002] reported a Sr/Ca-SST relationship for deep-sea gorgonians but suggested that growth rate may be a factor influencing Sr incorporation into the skeleton. While these interpretations may reasonably apply to the Sr/Ca content of *Plexaurella dichotoma* high-Mg calcite, the absence of interannual growth rate data for our colony precluded an examination of the association between Sr/Ca content and growth rate. However, this hypothesis should be easily testable by comparing colonies of varying growth rates collected at the same site.

The increased correlation between Mg/Ca and SST for SSTs averaged over the time period October through December and the lack of significant chemical variability within individual loculi, may indicate a preferred timing of calcite growth in this species, which is post-reproductive season for other *Plexauridae* on Bermuda [De Putron, 2002]. It is feasible to suggest that the maximum energy available for growth occurs after the spawning period, July through September. Other carbonate-accreting species on Bermuda, including the massive reef coral *Diploria labyrinthiformis*, exhibit maximum skeletal extension rates from late September through February [Cohen et al., 2004].

Figure 7. Comparison of Mg/Ca–temperature relationships in calcite. The sensitivity of *Plexaurella dichotoma* Mg/Ca to changes in temperature is higher than has been observed for other biogenic and inorganic calcites.
5. Conclusions

[16] The carbonate components “loculi” of the *P. dichotoma* skeleton are discrete, elongate rods up to 5 mm long and 140 μm wide. Measured Mg/Ca and Sr/Ca ratios of loculi indicate high-Mg calcite. Loculi are composed of bundles of needle-shaped crystals that radiate from a common center, a morphology consistent with rapid growth. Assuming growth bands are annual in periodicity, Mg/Ca shows a general correlation with interannual SST (autumn), while Sr/Ca appears to be controlled by factors other than SST, potentially growth rate. The growth morphology of loculi, correlation of Mg/Ca with autumnal SST, low variability within individual loculi and the increased availability of energy in the post-reproductive season, suggest a preferred timing of calcite growth in this species during the autumn months.

[17] Further study of the apparent high sensitivity of *P. dichotoma* Mg/Ca to changes in SST would be valuable. Additional investigations to consider relationships between skeletal growth rate and Sr/Ca would be beneficial to further clarify our calcitic loculi seasonal growth hypothesis, and to expand the potential of gorgonian corals as paleoceanographic archives.

Acknowledgments

[18] The authors are most grateful to Graham Webster and Joanna Pitt (BBSR, Benthic Ecology Research Programme) for assistance with collection of corals at Bermuda; Samantha De Putron (BBSR, Benthic Ecology Research Programme) for providing the in situ temperature data and sharing her expertise on gorgonian reproductive habits; Graham Layne and Nobu Shimizu (WHOI) for assistance with the ion microprobe measurements; John Ford and Bob Jones (SOC) for preparation of petrographic thin sections; and Glenn Gaetani (WHOI) for use of his laboratory facilities. Hydrostation S and BATS temperature data were obtained from BBSR. This study was supported by an Independent Study Award from the Woods Hole Oceanographic Institution 270051.81; NERC grant GR3/12800; a WHOI Ocean Life Institute grant to A.L.C.; and Bermuda Government, in support of the Benthic Ecology Research Programme at BBSR to S.R.S. Support for the WHOI Northeast National Ion Microprobe Facility was provided by NSF EAR-9628749. This manuscript was improved by comments from three anonymous reviewers. This is WHOI contribution 11396 and BBSR contribution 1661 Vol 50.

References


Dunbar, R. B., and J. E. Cole (1999), Annual records of tropical systems (ARTS), PAGES workshop report, Series 99-1, 71 pp., PAGES, Bern, Switzerland.


