



Compositional variability in a cold-water scleractinian, *Lophelia pertusa*: New insights into “vital effects”

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[1] We analyzed Sr/Ca and Mg/Ca ratios in the thecal wall of *Lophelia pertusa*, a cold-water coral, using SIMS ion microprobe techniques. The wall grows by simultaneous upward extension and outward thickening. Compositional variability displays similar trends along the upward and outward growth axes. Sr/Ca and Mg/Ca ratios oscillate systematically and inversely. The sensitivity of *Lophelia* Sr/Ca ratios to the annual temperature cycle ($-0.18 \text{ mmol} \cdot \text{mol}^{-1}/^{\circ}\text{C}$) is twice as strong as that exhibited by tropical reef corals, and four times as strong as the temperature dependence of Sr/Ca ratios of abiogenic aragonites precipitated experimentally from seawater. A comparison of the skeletal composition of *Lophelia* with results from precipitation calculations carried out using experimentally determined partition coefficients suggests that both temperature-dependent element partitioning and seasonal changes in the mass fraction of aragonite precipitated from the calcifying fluid influence the composition of *Lophelia* skeleton. Results from calculations that combine these effects reproduce both the exaggerated amplitude of the Sr/Ca and Mg/Ca oscillations and the inverse relationship between Sr/Ca and Mg/Ca ratios.

Components: 5531 words, 4 figures, 1 table.

Keywords: coral; aragonite; vital effects; Sr/Ca; Mg/Ca; deep-sea.

Index Terms: 0419 Biogeosciences: Biomineralization; 0473 Biogeosciences: Paleoclimatology and paleoceanography (3344, 4900).

Received 1 May 2006; **Revised** 12 September 2006; **Accepted** 5 October 2006; **Published** 15 December 2006.

Cohen, A. L., G. A. Gaetani, T. Lundälv, B. H. Corliss, and R. Y. George (2006), Compositional variability in a cold-water scleractinian, *Lophelia pertusa*: New insights into “vital effects”, *Geochem. Geophys. Geosyst.*, 7, Q12004, doi:10.1029/2006GC001354.

1. Introduction

[2] The Sr/Ca ratios of aragonite precipitated experimentally from seawater, and the aragonite skeletons of tropical hermatypic corals and sclerospores decrease with increasing water temperature [e.g., *Kinsman and Holland*, 1969; *Gaetani and Cohen*, 2006; *Beck et al.*, 1992; *Haase-Schramm et al.*, 2003]. This provides a powerful tool for reconstructing the surface temperatures of the tropical and subtropical paleo-oceans. However, the temperature dependence of Sr/Ca in tropical zooxanthellate (symbiont-bearing) corals is almost three times stronger than it is in abiogenic aragonites, indicating that processes associated with biogenic mineralization influence skeletal composition. Prior studies suggested a link between photosynthesis by coral zooxanthellae, calcification or growth rate, and skeletal chemistry [e.g., *Weber*, 1973; *McConnaughey*, 1989a, 1989b; *de Villiers et al.*, 1995; *Cohen et al.*, 2002]. However, data from stable isotope ratio ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) analyses of cold-water corals suggest that despite the absence of zooxanthellae, their skeletons are precipitated far out of isotopic equilibrium with seawater [e.g., *Mikkelsen et al.*, 1982; *Mortensen and Rapp*, 1998; *Smith et al.*, 2000; *Spiro et al.*, 2000; *Adkins et al.*, 2003]. To date, the elemental composition of cold-water corals remains relatively unexplored (with a few exceptions [e.g., *Hart and Cohen*, 1996; *Montagna et al.*, 2005; *Shirai et al.*, 2005]), so the nature and extent of “vital effects” on elemental ratios has not been extensively studied.

[3] Here we present results from a study of the elemental composition of *Lophelia pertusa*, an azooxanthellate, colonial cold-water coral that is commonly found in North Atlantic waters. We used Sr/Ca and Mg/Ca ratios obtained from SIMS (secondary ion mass spectrometry) analyses of a single *Lophelia pertusa* corallite, to identify factors forcing compositional variability in the skeleton. The corallite, shown in Figure 1a, is the tube-shaped skeleton accreted by an individual coral polyp (animal) during its lifetime. The perimeter of the corallite is defined by the thecal wall (t in Figure 1a), which grows simultaneously upward (extension) and outward (thickening) (indicated by red vertical and horizontal arrows respectively in Figure 1a). In this study, we focused our analyses on the thecal wall, generating two elemental profiles: one following the vertical or upward growth axis (vertical red arrow in Figure 1a) and one

following the horizontal or outward growth axis of the wall (horizontal red arrow in Figure 1a).

2. Skeletal Structure and Analytical Technique

2.1. Sample Preparation

[4] A single corallite from a specimen of the branching coral *Lophelia pertusa*, collected live in June 2003 from 129 m depth on the Tisler Reef, NE Skagerrak ($58^{\circ}59'\text{N}$, $10^{\circ}58'\text{E}$), was sectioned longitudinally to expose the internal skeleton (Figure 1a). The total length of the theca is 19 mm. After sonication to remove debris, keeping tissue intact, the section was dried at 60°C , epoxy-mounted in a 1"-diameter Al ring and final polished with $0.3\ \mu\text{m}$ alumina suspension.

2.2. Skeletal Structure

[5] In reflected light, alternating opaque (white) and translucent bands oriented parallel to the upward growth axis of the corallite were clearly visible (Figures 1a and 1c). *Wainwright* [1964] showed that the opaque zones correspond with nucleation sites where tiny, randomly oriented crystals are seeded. As they grow, these crystals become increasingly oriented along their c axes, forming the translucent zone. Thus outward growth or thickening of the thecal wall occurs through repeated cycles of crystal nucleation and growth.

[6] In this specimen, we identified a main or primary (1°) nucleation zone that was continuous from the base to the tip of the theca. In petrographic thin section, the 1° nucleation zone was evident as a continuous dark column $\sim 10\text{--}20\ \mu\text{m}$ wide, packed with tiny aggregations of nuclei $\sim 10\ \mu\text{m}$ in diameter (Figure 1d). We also identified two secondary (2°) nucleation zones (Figure 1c) that did not reach the tip of the theca and were narrow and discontinuous in thin section.

[7] Banding was also evident across the wall, perpendicular to the upward growth axis. First, in the septa, fine bands were spaced $400\text{--}500\ \mu\text{m}$ apart (Figure 1a). These are identical to the monthly growth bands identified in *Lophelia pertusa* by *Mortensen and Rapp* [1998]. Second, within the theca, opaque zones that mimicked remnant thecal tips were located $\sim 3\ \text{mm}$, $8\ \text{mm}$ and $12\ \text{mm}$ from the base of the theca. These appeared equivalent to the annual growth bands identified by *Mortensen and Rapp* [1998]. On the basis of this banding,

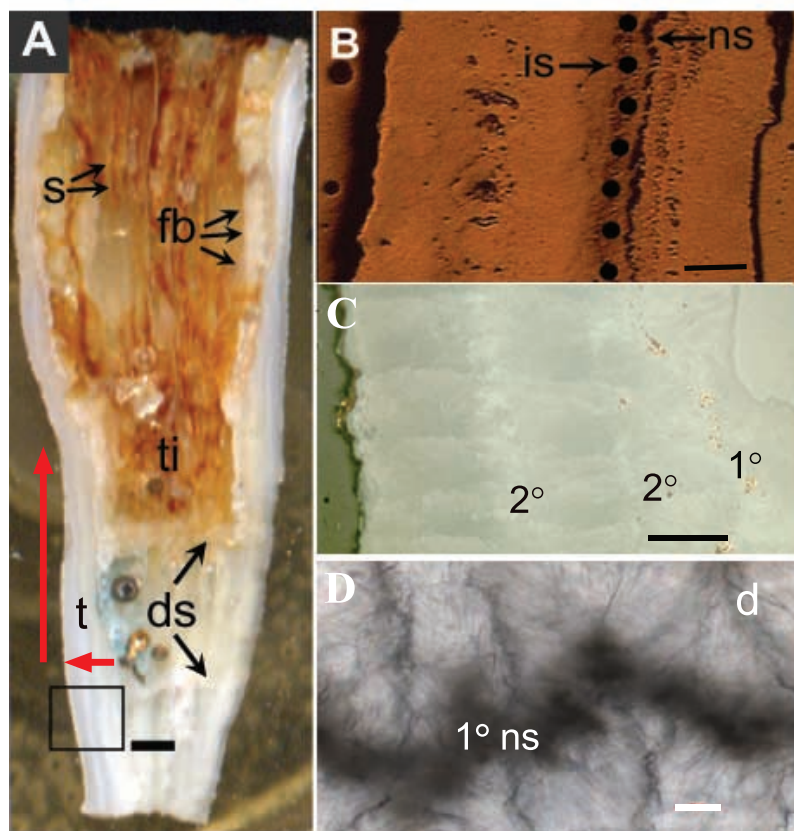


Figure 1. Mesostructural and microstructural features of *Lophelia* corallite viewed in reflected light. In Figure 1a the thecal wall (t) encloses the tissue (ti) that rests on horizontal dissepiments (ds). The thecal wall is bisected by the septa (s), within which fine bands (fb) are recognized. Wall growth occurs simultaneously upward, indicated by the vertical red arrow, and outward, indicated by the horizontal red arrow. The lengths of the red arrows represent 1 year of upward growth and 3 years of outward growth, respectively. Scale bar is 1 mm. In Figure 1b, a polished gold-coated section of the *Lophelia* thecal wall is shown with ion probe sample spots (is) tracking adjacent to the 1° nucleation site (ns) to generate a Sr/Ca profile along the upward growth axis. Scale bar is 100 μm . Figure 1c shows a magnified section of the thecal wall enclosed by box in Figure 1a, illustrating opaque 1° and 2° nucleation zones separated by translucent crystal growth regions. Growth direction is right to left. Scale bar is 100 μm . Figure 1d is a 30- μm -thick doubly polished petrographic thin section of *Lophelia* skeleton showing discrete nuclei clusters of the primary nucleation site (1° ns) and fans of needle crystals radiating out from these sites. Sharp discontinuities (d) are evident where needles from adjacent bundles meet and growth is discontinued. Scale bar is 10 μm .

annual extension rate for this corallite is estimated to be $\sim 5000 \mu\text{m}$.

2.3. SIMS Analyses

[8] To analyze the composition of the theca, we employed analytical conditions identical to those used to analyze the Sr/Ca and Mg/Ca ratios of zooxanthellate reef corals [Hart and Cohen, 1996]. Measurements were made with a Cameca 3f Ion Microprobe employing a 4 nA O^- primary ion beam accelerated at 12.5 keV, and a 20- μm -diameter sample spot. Secondary ion intensities for $^{24}\text{Mg}^+$, $^{88}\text{Sr}^+$ and $^{42}\text{Ca}^+$ were measured using a -80 eV (± 30) energy filter and converted to molar

ratios using a carbonatite standard (OKA) with Mg/Ca and Sr/Ca ratios determined by solution ICP-MS to be 4.47 mmol/mol and 19.3 mmol/mol respectively. Ion probe analyses of unknowns (i.e., coral) are normalized to the standard following each session. Routine instrument precision for ion probe analyses of $^{24}\text{Mg}/^{42}\text{Ca}$ and $^{88}\text{Sr}/^{42}\text{Ca}$ are 1.2% and 0.3% respectively. Replicate analyses of the OKA standard over 6 sessions spanning 13 months are reproducible to within 2.2% ($^{24}\text{Mg}/^{42}\text{Ca}$) and 1.1% ($^{88}\text{Sr}/^{42}\text{Ca}$).

[9] Fourteen approximately equidistant analyses of Sr/Ca and Mg/Ca ratios were made across the wall (indicated by red horizontal arrow in Figure 1a),

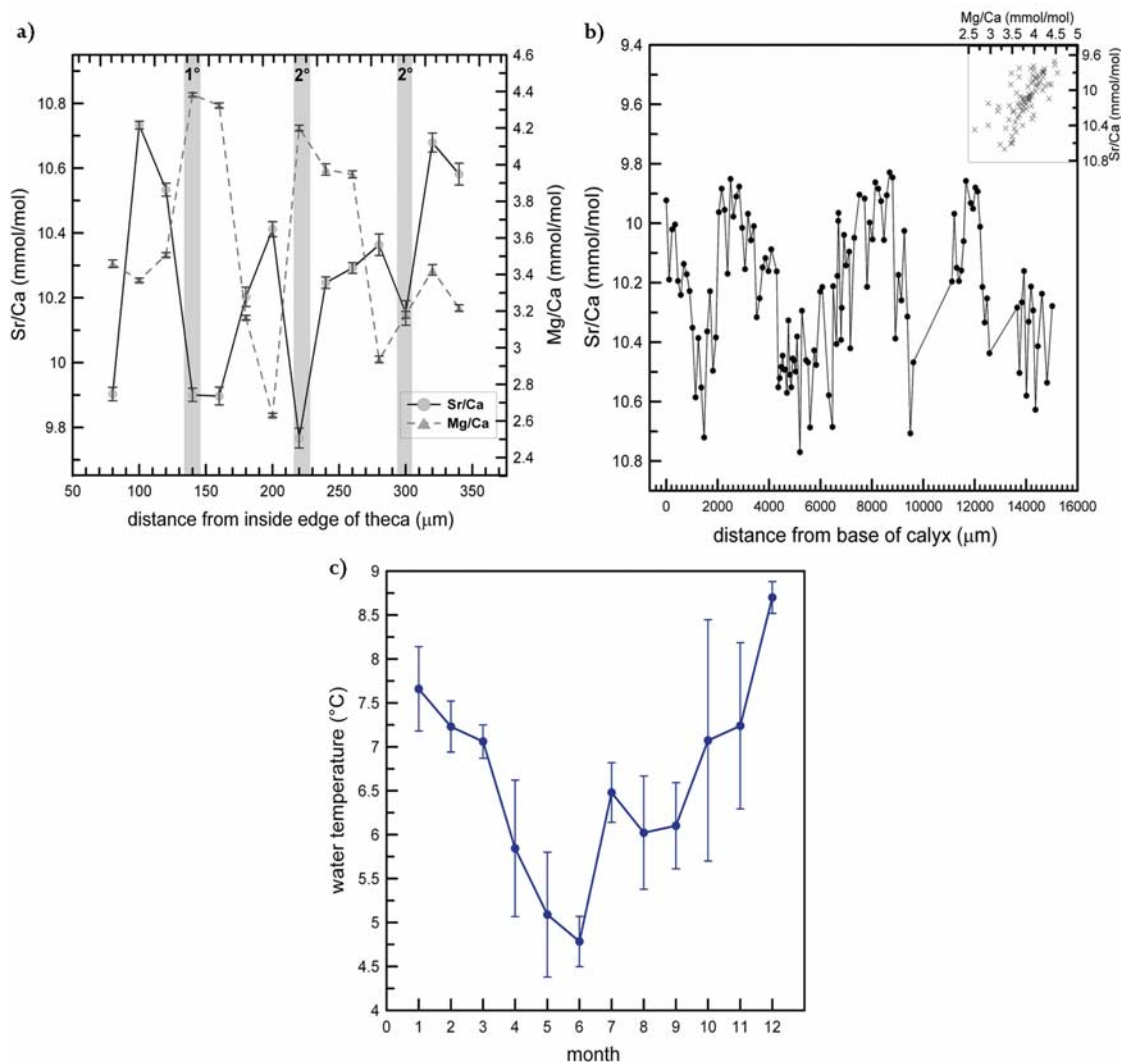


Figure 2. (a) Sr/Ca and Mg/Ca ratios measured across the theca, 6000 μm from the base of the calyx, plotted against distance from the inside edge of the theca. The locations of nucleation sites are indicated by shaded bars. (b) Sr/Ca ratios measured within a single “translucent” growth band along a 15000- μm -long track running parallel to the upward growth axis of the theca (shown in Figure 1b). Inset: Sr/Ca and Mg/Ca ratios measured within this translucent band show inverse correlation. (c) Averaged monthly water temperatures recorded in the NE Skagerrak ($58^{\circ}52'N$ – $59^{\circ}00'N$; $10^{\circ}58'E$ – $11^{\circ}06'E$), at and near the collection site between 1967 and 2005. All data available between 125 m and 135 m depth within this grid box were used to construct an averaged monthly climatology. Error bars show standard deviation about the mean.

6000 μm from its base. These analyses spanned successive nucleation and growth regions. To construct the Sr/Ca time series up the wall (indicated by red vertical arrow in Figure 1a), we focused the ion microprobe analyses on the translucent zone proximal to the primary (1°) nucleation site which provided an easily identifiable track for navigation (Figure 1b). These analyses did not include the nucleation zones. Data were collected at ~ 100 μm intervals over a distance of 15000 μm and Mg/Ca ratios were measured for a subset of these analyses. Within the last 5000 μm , irregularities in the

skeletal structure prevented us from making continuous measurements in that region.

3. Analytical Results

[10] Sr/Ca and Mg/Ca ratios measured across the thecal wall are shown in Figure 2a. The analyses span nucleation and growth regions, and elemental ratios vary significantly and systematically. Sr/Ca ratios vary by $\sim 10\%$, from ~ 9.8 $\text{mmol} \cdot \text{mol}^{-1}$ to ~ 10.8 $\text{mmol} \cdot \text{mol}^{-1}$. Lowest Sr/Ca ratios coincide with opaque (nucleation) bands and tend to

Table 1. Water Temperature Data Used to Assess the Response of Coral Skeletal Composition to Changing Water Temperature Over the Year^a

Month	Average Temperature (125–135 m)	Std Deviation	Number of Days Observed	Years Represented	Data Source
January	7.66 (7.40)	0.48 (0.56)	31 (6)	2005 (1968–1990)	TMBL data logger [Wisshak et al., 2005]
February	7.23 (6.49)	0.29 (0.20)	28 (3)	2005 (1984–1989)	TMBL data logger [Wisshak et al., 2005]
March	7.06 (6.00)	0.19 (0.20)	15 (4)	2005 (1967–1981)	TMBL data logger [Wisshak et al., 2005]
April	5.84	0.78	8	1970–1975	Wisshak et al. [2005]
May	5.09	0.71	8	1984–1985	Wisshak et al. [2005]
June	4.78	0.29	4	1980–1987	Wisshak et al. [2005]
July	6.48	0.34	2	1967	Wisshak et al. [2005]
August	6.02	0.64	14	1971–1989	Wisshak et al. [2005]
September	6.10	0.49	4	1967–1979	Wisshak et al. [2005]
October	7.07	1.37	1	1979	Wisshak et al. [2005]
November	7.24	0.95	5	1987–1990	Wisshak et al. [2005]
December	8.69 (8.10)	0.18 (1.05)	11 (2)	2004 (1983–1985)	TMBL data logger [Wisshak et al., 2005]

^a All data were collected in the NE Skaggerak between 125 and 135 m depth between 1967 and 2005. Two independent data sets were used. In situ temperatures recorded half-hourly at the collection site between December 2004 and March 2005 were provided by Tomas Lundälv, Tjörnö Marine Biological Laboratory. For the remaining months (April through November) we used data from Wisshak et al. [2005], collected by the Swedish Fisheries Board between 1967 and 1990. Averaged monthly temperatures from December through March in the Wisshak et al. [2005] data set are provided in parentheses for comparison with the in situ data.

increase along the length of each fiber bundle, causing Sr/Ca ratios to vary in a zigzag pattern across the wall. Mg/Ca ratios range from ~ 2.6 mmol/mol through ~ 4.4 mmol \cdot mol⁻¹, a variation of 40%. Highest Mg/Ca ratios are found in the opaque bands and tend to decrease along the length of each spherulite, in a manner antithetical to that observed for Sr/Ca. If these oscillations are annual, they imply an average thecal “thickening” rate of ~ 100 μ m \cdot yr⁻¹.

[11] Sr/Ca ratios measured up the wall also range from 9.8 mmol \cdot mol to 10.8 mmol \cdot mol⁻¹ (Figure 2b), and Mg/Ca ratios also show an inverse correlation with Sr/Ca ratios (Figure 2b, inset). 3 full Sr/Ca cycles were resolved over a distance of 15000 μ m. If these are annual, an extension rate of ~ 5000 μ m \cdot yr⁻¹ is implied, 50 times higher than the thickening rate, and consistent with our estimate based on banding.

4. Estimating the Temperature Dependence of *Lophelia* Sr/Ca

[12] To calculate the temperature dependence of the Sr/Ca variability in the *Lophelia* skeleton, we compared the data with instrumental records of temperature available for the NE Skaggerak. In the northern Kosterfjord (59°00'N, 11°06'E) about 10 km from the Tisler Reef site, temperatures were recorded from 1967 through 1990 [Wisshak et al., 2005]. In addition, in situ data loggers deployed on the Tisler Reef at 129 m depth recorded daily temperature fluctuations from 12 December 2003 through 15 March 2004 (T. Lundälv, unpublished data, 2005). Because the in situ record alone does not provide a full annual temperature cycle, these data were supplemented by the Wisshak et al. [2005] data set (Table 1). Monthly averaged temperatures between 125–135 m depth reveal a regular seasonal pattern with highest temperatures obtained in December and lowest temperatures obtained in June (Figure 2c). Over the time period considered, temperatures in the *Lophelia* habitat ranged from an average minimum of 4.8°C (June) through an average maximum of 8.7°C (December).

[13] If the Sr/Ca cycles in the thecal wall are assumed to be annual, then it is clear that the wall extends upward much more rapidly (~ 5000 μ m \cdot yr⁻¹) than it thickens (~ 100 μ m \cdot yr⁻¹). Therefore the sampling resolution achieved up the wall (up to 50 samples per year) is much higher than that achieved across the wall (~ 5 sam-

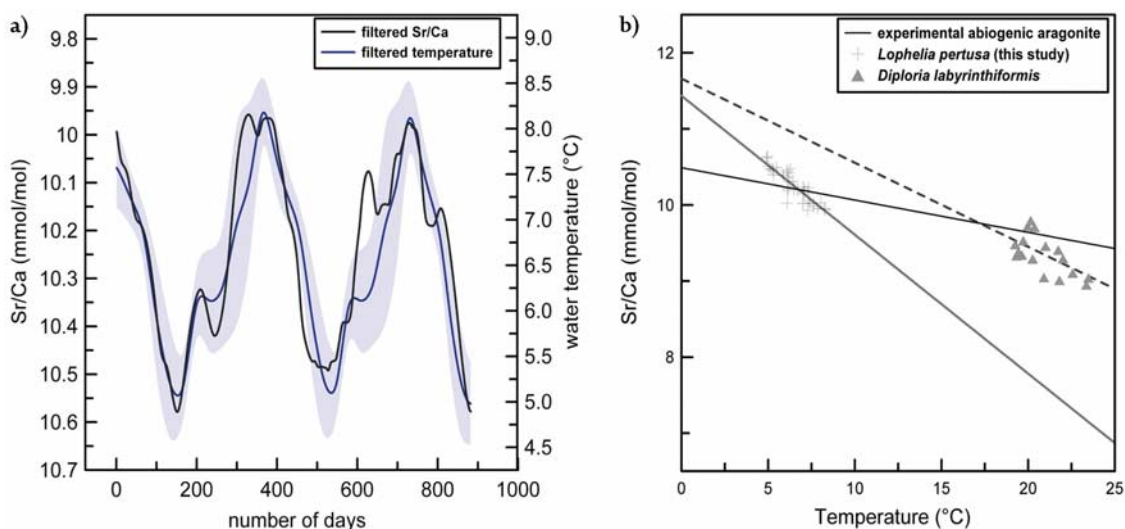


Figure 3. (a) Sr/Ca ratios measured along the thecal wall of *Lophelia pertusa* plotted against recorded monthly water temperatures after a 60-day low-pass filter was applied to each data set. Shaded region indicates the standard deviation on the recorded temperatures. The data sets are aligned along the x axis by assuming that maximum Sr/Ca ratios correspond with minimum water temperatures, and vice versa, as they do in tropical corals. Note that the temperature cycle is duplicated in the second year. (b) Sr/Ca-temperature regression equation derived for *Lophelia* (crosses) using data in Figure 3a, compared with the Sr/Ca-T relationships derived for experimental abiogenic aragonites grown from seawater (solid line) and the tropical zooxanthellate coral *Diploria labyrinthiformis* (triangles) [Gaetani and Cohen, 2006]. Note that the coral regression lines are extrapolated outside of the temperature range over which the data were collected for purposes of comparison.

ples per year). For this reason, we utilized the Sr/Ca data generated up the wall to evaluate the response of Sr/Ca to changes in water temperature. High frequency Sr/Ca oscillations are superimposed upon the low frequency cycles (Figure 2b). We used a 4-pole, zero-phase, low-pass Butterworth digital filter with corner period of 60 days [Cohen and Sohn, 2004] to remove the high-frequency Sr/Ca oscillations and reveal the annual cycles (Figure 3a). The same filter was applied to the temperature data. The annual range of Sr/Ca ratios over the two full years of the filtered data is $9.95\text{--}10.6\text{ mmol} \cdot \text{mol}^{-1}$. The annual range in the filtered temperature data is $5^{\circ}\text{--}8.25^{\circ}\text{C}$ (Figure 3a).

[14] The Sr/Ca record was compared with the temperature data by assuming maximum Sr/Ca corresponds to minimum temperature, and vice versa. We also assumed that the coral accreted skeleton and recorded the water temperature fluctuations throughout the year. With these assumptions in mind, the Sr/Ca-temperature relationship can be described by the following equation: $\text{Sr/Ca} = -0.18 \pm 0.002 (\text{T}^{\circ}\text{C}) + 11.44 \pm 0.011$ ($r^2 = 0.78$). In Figure 3b, the Sr/Ca-T relationship derived for *Lophelia* is compared with that derived for abiogenic aragonite ($\text{Sr/Ca} = -0.038 \pm 0.004 (\text{T}^{\circ}\text{C}) + 10.43 \pm 0.19$; $r^2 = 0.95$) and with

the Sr/Ca-T relationship derived for the tropical zooxanthellate coral, *Diploria labyrinthiformis* ($\text{Sr/Ca} = -0.092 \pm 0.001 (\text{T}^{\circ}\text{C}) + 11.30 \pm -0.03$) [Gaetani and Cohen, 2006], also measured using SIMS. Note that although Sr/Ca ratios of both abiogenic and biogenic aragonites decrease with increasing temperature, the difference in slope of the Sr/Ca-T relationship between the biogenic and abiogenic aragonites indicates the magnitude of the “vital effect” in the coral skeletons, which is greatest in the *Lophelia*.

5. Discussion

[15] Several studies have identified “vital effects” as playing a significant role in forcing Sr/Ca variability in the skeletons of zooxanthellate corals. The most obvious evidence for a “vital effect” is the sensitivity of coral Sr/Ca to changes in water temperature over the annual cycle. Two independent studies of the Sr/Ca exchange between experimentally precipitated abiogenic aragonite and seawater show that the temperature dependence is actually quite small, approximately $-0.039\text{ mmol} \cdot \text{mol}^{-1}/^{\circ}\text{C}$ [Kinsman and Holland, 1969; Gaetani and Cohen, 2006], compared with that exhibited by zooxanthellate corals (-0.08 to $-0.10\text{ mmol} \cdot$

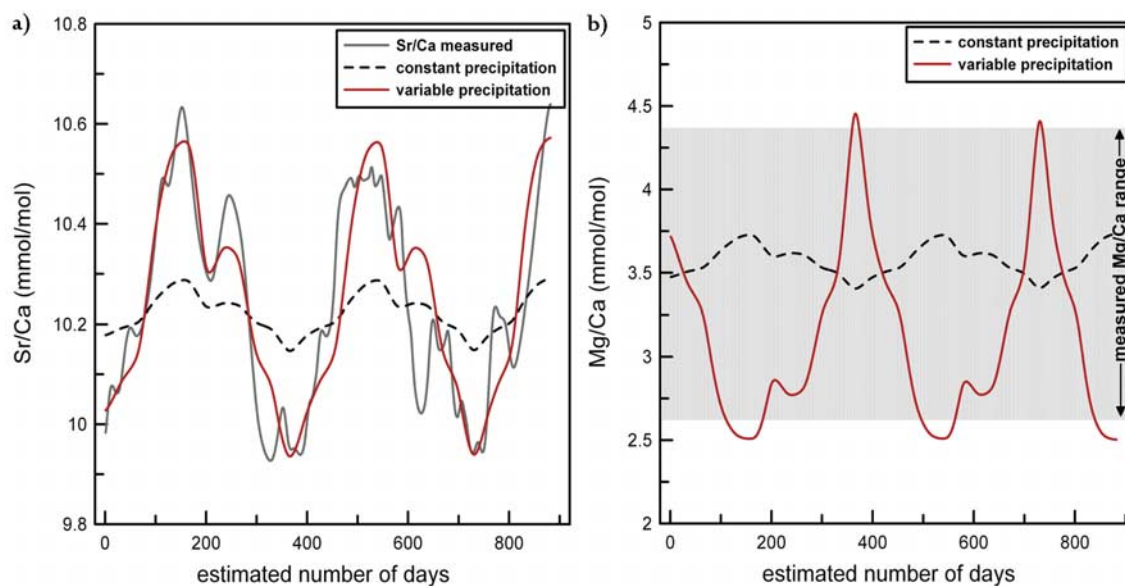


Figure 4. (a) Comparison of Sr/Ca ratios measured along a track parallel to the primary nucleation sites of *Lophelia* (gray line) with results from precipitation calculations carried out assuming that the fraction of aragonite precipitated from a given mass of calcifying fluid is constant (dashed line) or varies as a linear function of temperature through the year (red line). (b) Comparison of Mg/Ca ratios predicted by precipitation calculations carried out assuming that the fraction of aragonite precipitated from a given mass of calcifying fluid is constant (dashed line) or varies as a linear function of temperature through the year (red line). Note that keeping the fraction of aragonite precipitated constant produces a positive correlation between Mg/Ca and Sr/Ca, which is the relationship found in experimental aragonites. Allowing the fraction of aragonite precipitated to vary produces a negative correlation between Mg/Ca and Sr/Ca, which is the relationship found in the *Lophelia* skeleton. The range of Mg/Ca ratios measured in the *Lophelia* is indicated by the shaded region.

mol⁻¹/°C) [de Villiers *et al.*, 1995; Gaetani and Cohen, 2006]. Cohen *et al.* [2002] suggested that the exaggerated temperature dependence exhibited by zooxanthellate corals is linked to enhanced calcification rates driven by zooxanthellate photosynthesis. However, the *Lophelia* data, indicating an even stronger temperature dependence (-0.18 mmol · mol⁻¹/°C), demonstrate that presence of zooxanthellae is not a prerequisite for this “vital effect.”

[16] A second indication of the influence of vital effects on *Lophelia* skeletal chemistry is the inverse correlation between Sr/Ca and Mg/Ca ratios. A recent experimental precipitation study carried out to investigate partitioning of Sr²⁺, Mg²⁺ and Ca²⁺ between aragonite and seawater demonstrated that both Sr/Ca and Mg/Ca ratios in abiogenic aragonite decrease with increasing temperature [Gaetani and Cohen, 2006]. In *Lophelia*, the exaggerated dependence of Sr/Ca on temperature, and the inverse correlation between Sr/Ca and Mg/Ca indicates that the influence of temperature on partitioning is not the primary control on skeletal chemistry.

[17] To further investigate the origin of these vital effects, we carried out precipitation calculations using experimentally determined partition coefficients for Mg²⁺, Ca²⁺ and Sr²⁺ between abiogenic aragonite and seawater [Gaetani and Cohen, 2006]. Details of the calculations are presented in Appendix A. The principal conclusions from these calculations are that there are two mechanisms capable of producing variability in aragonite Sr/Ca and Mg/Ca ratios and they operate simultaneously during the growth of coral skeleton. First, for a specific mass fraction of aragonite precipitated from the calcifying fluid, the Sr/Ca and Mg/Ca ratios in the solid both decrease with increasing temperature due to changes in the aragonite-seawater partition coefficients. This is the direct effect of temperature on Sr and Mg partitioning into aragonite. Conversely, increasing the mass fraction of aragonite precipitated at a given temperature causes the Sr/Ca ratio of the aragonite to decrease, and the Mg/Ca ratio to increase. This is because the partition coefficient for Sr into aragonite is greater than that for Ca, whereas the partition coefficient for Mg is smaller than that for Ca [Gaetani and Cohen, 2006]. Therefore, as the

amount of aragonite precipitated from a given volume of calcifying fluid increases, the Sr/Ca ratio of the calcifying fluid decreases, as does the Sr/Ca ratio of the bulk precipitate. Conversely, the Mg/Ca ratio of the calcifying fluid increases, as does the Mg/Ca ratio of the bulk precipitate.

[18] Results from our calculations demonstrate that the compositional variability of the *Lophelia* skeleton can be explained by a combination of these two effects: (1) direct temperature dependence of element partitioning between aragonite and seawater, and (2) seasonal variation in the mass fraction of aragonite precipitated by the organism from a given mass of calcifying fluid (“precipitation efficiency”). The predicted influence of temperature alone on the Sr/Ca ratios of aragonite precipitated from Tisler Reef seawater (dashed curve) is compared with the Sr/Ca ratios measured in the *Lophelia* skeleton (gray curve) in Figure 4a. Temperature-dependent variations in partitioning account for ~25% of the Sr/Ca variability. These calculations also predict a positive correlation between Mg/Ca and temperature, and between Mg/Ca and Sr/Ca ratios (Figure 4b). These relationships are opposite from those observed in the coral skeleton and reinforce the conclusion that temperature alone cannot account for the compositional variability observed in *Lophelia*.

[19] A second set of calculations were carried out in which both partitioning and mass fraction of aragonite precipitated, were varied through the year to match the amplitude of the measured Sr/Ca cycle. Results from these calculations indicate that, when combined with the temperature dependence of partition coefficients determined from abiogenic aragonite, a monotonic increase in “precipitation efficiency” from 0.10 wt% at 4.9°C to 0.22 wt% at 8.4°C can explain the amplitude of the Sr/Ca cycles measured in *Lophelia*. Note that we consider these absolute values to be rough estimates that can be significantly refined through incorporation of a full Mg/Ca and Ba/Ca time series into the calculations [Gaetani and Cohen, 2006]. What is important is that the calculations indicate a doubling of “precipitation efficiency” over the annual cycle.

[20] We combined this annual variation in “precipitation efficiency” with experimentally determined partition coefficients to forward model the Mg/Ca ratios of aragonite precipitated over the temperature range experienced by the *Lophelia* (Figure 4b). Both the range of Mg/Ca ratios measured in the coral skeleton and the negative correlation between Sr/Ca and Mg/Ca are reproduced

(Figure 4b). This close agreement between the calculation results and the coral skeleton strongly suggests that the compositional variability in the *Lophelia* skeleton is due to a combination of variations in both water temperature and “precipitation efficiency” through the year.

6. Implications for Biomineralization

[21] In the *Lophelia* thecal wall, compositions characteristic of high “precipitation efficiency” (highest Mg/Ca and lowest Sr/Ca ratios), correspond with nucleation. This indicates that the mass fraction of aragonite precipitated is highest during nucleation. In abiogenic systems, the mass fraction of aragonite precipitated from the calcifying fluid is controlled by the saturation state of that fluid [Burton and Walter, 1987]. Thus it appears that large changes in the saturation state of the coral calcifying fluid occur over the seasonal cycle. In the waters inhabited by *Lophelia*, limited temperature variability over the annual cycle indicates that temperature alone is unlikely to drive the doubling of aragonite “precipitation efficiency” that is indicated by our calculations. In tropical reef-building corals, it is thought that elevation of the saturation state of the calcifying fluid occurs via a $\text{Ca}^{2+}\text{-H}^+$ exchange pump linked to zooxanthellate photosynthesis [e.g., Cohen and McConnaughey, 2003]. Our data suggest that *Lophelia* achieves comparable rates of skeletal extension and brings about even larger changes in the saturation state of the calcifying fluid over the annual cycle than we see in the zooxanthellate coral *Diploria* [Gaetani and Cohen, 2006]. Elucidating the mechanism(s) by which this is achieved in the absence of zooxanthellae may provide new insights into the biomineralization processes of all Scleractinia.

7. Conclusions

[22] Sr/Ca and Mg/Ca ratios in *Lophelia pertusa* oscillate systematically and inversely as they do in the skeletons of tropical zooxanthellate Scleractinia. The amplitude of the Sr/Ca oscillations is too large to be explained entirely in terms of the temperature dependence of element partitioning. Furthermore, the inverse correlation between Sr/Ca and Mg/Ca ratios suggests that factors other than temperature influence compositional variability. Results from precipitation calculations suggest that a combination of temperature-dependent partitioning and seasonal changes in the mass fraction of aragonite precipitated, driven by changes in the

saturation state of the calcifying fluid, can account for both the amplitude of the oscillations and the inverse correlation between Sr/Ca and Mg/Ca ratios in the *Lophelia* skeleton.

Appendix A: Aragonite Precipitation Calculations

[23] Aragonite precipitation calculations were carried out in 2 ways. Calculations used to explore the effects of temperature only (i.e., the mass fraction of aragonite precipitated is constant throughout the year at 0.0394 wt%) were carried out as a forward model using a base composition for the calcifying fluid containing 347 ppm Mg, 392 ppm Ca and 7.3 ppm Sr. The Mg concentration in the calcifying fluid is diluted relative to seawater, suggesting that the coral actively excludes Mg during ion pumping across the basal epithelium.

[24] Aragonite-fluid partition coefficients ($D_i^{\text{Aragonite/Fluid}} = C_i^{\text{Aragonite}}/C_i^{\text{Fluid}}$, where C is the weight concentration of element i) were calculated as functions of temperature according to the experimentally determined relationships of *Gaetani and Cohen* [2006]:

$$D_{\text{Mg}}^{\text{Aragonite/Fluid}} = \exp\left(\frac{1909}{T + 273.15} - 5.57\right) \quad (\text{A1})$$

$$D_{\text{Ca}}^{\text{Aragonite/Fluid}} = 2074 + 5.79T \quad (\text{A2})$$

$$D_{\text{Sr}}^{\text{Aragonite/Fluid}} = 2930 - 11.71T \quad (\text{A3})$$

$$D_{\text{Ba}}^{\text{Aragonite/Fluid}} = \exp\left(\frac{3635}{T + 273.15} - 3.45\right) \quad (\text{A4})$$

where T is temperature in Celsius. These partition coefficients were used to calculate the composition of aragonite coexisting with the fluid at the temperature of interest using the solution of the Rayleigh distillation equation for the composition of the mean solid:

$$\bar{C}_i^{\text{Aragonite}} = C_i^0 \frac{1 - FL^{D_i}}{1 - FL} \quad (\text{A5})$$

where C_i^0 is the concentration of element i in the initial calcifying fluid and FL is the mass fraction of calcifying fluid remaining following aragonite precipitation.

[25] Variable “precipitation efficiency” calculations were carried out using equations (A2), (A3), and (A5) through a global minimization in which both the Sr concentration and the mass fraction of calcifying fluid remaining following aragonite precipitation (FL from equation (A5)) are allowed to vary in order to derive the best match to the Sr/Ca ratio of the *Lophelia* skeleton. The functional form for FL was assumed to be:

$$FL = c_1 + c_2T + c_3T^{-1} + c_4T^2 \quad (\text{A6})$$

where T is temperature in Kelvin. The calcifying fluid composition derived from these calculations contains 392 ppm Ca and 8.4 ppm Sr. The coefficients derived for equation (A6) are as follows: $c_1 = 31.56$; $c_2 = -0.0878$; $c_3 = -3,400$; $c_4 = 7.87 \times 10^{-5}$. As noted in the text, we consider these values to represent, at best, only crude estimates that can be significantly refined through incorporation of Mg/Ca and Ba/Ca ratios into the calculations, using the methods of *Gaetani and Cohen* [2006], once such data become available. The variable “precipitation efficiency” Mg/Ca ratios presented in Figure 4b were calculated as a forward model using a calcifying fluid containing 140 ppm Mg and 392 ppm Ca, and the coefficients for equation (A6) derived from the Sr/Ca ratio global minimization calculations described above.

Acknowledgments

[26] We are indebted to Graham Layne and Pete Landry of the WHOI ion microprobe facility for assistance with the 3f. Louis Kerr at the Marine Biological Laboratory in Woods Hole assisted with photographing the *Lophelia* thin section. Max Wisshak (University of Erlangen) kindly shared his compilation of temperature data from the Kjosterfjord. Suggestions by two anonymous reviewers helped us to improve the manuscript. This study was supported in part by a WHOI Ocean Life Institute fellowship to ALC, by NSF grant OCE-0527350 to G.A.G. and A.L.C., and by the EU 6FP project HERMES, EC contract GOCE-CT-2005-511234 to T.L.

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