

Rayleigh-based, multi-element coral thermometry: A biomineralization approach to developing climate proxies

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Abstract

This study presents a new approach to coral thermometry that deconvolves the influence of water temperature on skeleton composition from that of “vital effects”, and has the potential to provide estimates of growth temperatures that are accurate to within a few tenths of a degree Celsius from both tropical and cold-water corals. Our results provide support for a physico-chemical model of coral biomineralization, and imply that Mg^{2+} substitutes directly for Ca^{2+} in biogenic aragonite. Recent studies have identified Rayleigh fractionation as an important influence on the elemental composition of coral skeletons. Daily, seasonal and interannual variations in the amount of aragonite precipitated by corals from each “batch” of calcifying fluid can explain why the temperature dependencies of elemental ratios in coral skeleton differ from those of abiogenic aragonites, and are highly variable among individual corals. On the basis of this new insight into the origin of “vital effects” in coral skeleton, we developed a Rayleigh-based, multi-element approach to coral thermometry. Temperature is resolved from the Rayleigh fractionation signal by combining information from multiple element ratios (e.g., Mg/Ca, Sr/Ca, Ba/Ca) to produce a mathematically over-constrained system of Rayleigh equations. Unlike conventional coral thermometers, this approach does not rely on an initial calibration of coral skeletal composition to an instrumental temperature record. Rather, considering coral skeletogenesis as a biologically mediated, physico-chemical process provides a means to extract temperature information from the skeleton composition using the Rayleigh equation and a set of experimentally determined partition coefficients. Because this approach is based on a quantitative understanding of the mechanism that produces the “vital effect” it should be possible to apply it both across scleractinian species and to corals growing in vastly different environments. Where instrumental temperature records are available, a Rayleigh-based framework allows the effects of stress on coral calcification to be identified on the basis of anomalies in the skeletal composition.

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1. INTRODUCTION

Resolving human-induced changes in Earth’s climate from the significant natural variability documented over the past millennium (Mann et al., 2008) requires accurate and precise reconstructions of subtle variations in sea surface temperature (SST). The scleractinian corals, many of

which grow continuously over several centuries, record this information within their aragonite skeletons, providing a valuable archive of seasonally resolved oceanographic data that is unavailable from any other source. In particular, it has long been recognized that both the oxygen isotope composition ($\delta^{18}O$) and strontium-to-calcium ratio (Sr/Ca) of coral skeleton correlate with SST (e.g., Weber and Woodhead, 1972; Goreau, 1977; Emiliani et al., 1978; Smith et al., 1979; Beck et al., 1992).

Interpretation of the skeletal compositions of corals has not proven to be straightforward. For example, the $\delta^{18}O$ values of coral skeleton are systematically lower than those of abiogenic aragonite precipitated directly from seawater

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(Epstein and Lowenstam, 1953; Weber and Woodhead, 1972) and different parts of the same skeleton accreted at the same time can have significantly different isotopic compositions. Relatively slow-growing portions of the skeleton (“valleys” and “sides”) are isotopically heavier than faster growing portions (“bumps” and “tops”) (McConnaughey, 1989a,b; de Villiers et al., 1995; Cohen and Hart, 1997).

Similarly, the relationship between the Sr/Ca ratio of coral skeleton and temperature (T) is different from that derived from abiogenic aragonite precipitated experimentally from seawater, and can be highly variable among individual corals, even conspecifics grown at the same conditions. Corrège (2006) compared 37 Sr/Ca– T relationships for the genus *Porites*, compiled from 26 different studies, and calculated T ranging from 19 to 32 °C for a Sr/Ca ratio of 9.035 mmol/mol (Fig. 1). Corrège (2006) pointed out that inter-laboratory differences in analytical techniques and standards as well as the source of T data (*in situ* versus satellite) may contribute to this variability. Nonetheless, a similar range in Sr/Ca– T relationships has also been derived in a single study. Saenger et al. (2008) calibrated Sr/Ca– T relationships for four colonies of the Atlantic coral genus *Montastrea* that predict T ranging from 20.9 to 28.5 °C for a Sr/Ca ratio of 9.035 mmol/mol. This demonstrates the significance of “vital effects”—signals attributed to physiological processes that contribute the majority of the variability in coral elemental ratios, and can overwhelm the actual climate information recorded in the skeleton (Thompson and Livingston, 1970; Weber, 1973; de Villiers et al., 1994, 1995; Cohen et al., 2002; Gaetani and Cohen, 2006).

Relationships among elemental ratios in coral skeleton provide insights into the mechanisms that produce “vital effects”. Correlations among Sr/Ca, Ba/Ca, Mg/Ca, U/Ca, and B/Ca ratios have been documented in a number of studies (e.g., Hart and Cohen, 1996; Sinclair et al., 1998,

2006; Sinclair, 2005; Montagna et al., 2007). This coherence indicates that a single process could be responsible for producing “vital effects” in coral skeleton element ratios. Recent studies have demonstrated that elemental fractionations during coral biomineralization can be described by Rayleigh fractionation, consistent with the hypothesis that aragonite precipitation occurs in an isolated or semi-isolated calcifying space (Cohen et al., 2006, 2009; Gaetani and Cohen, 2006; Gagnon et al., 2007; Cohen and Gaetani, 2010). A small percentage of these fractionations are directly dependent on T . However, the primary influence on skeletal composition is the amount of aragonite precipitated from each “batch” of calcifying fluid. This produces exaggerated or, as in the case of Mg/Ca, inverted relationships between T and elemental ratios relative to abiogenic aragonite (Gaetani and Cohen, 2006). Thus, coral colonies growing adjacent to one another can have significantly different relationships between T and elemental ratios because they differ in the amount of aragonite that they precipitate from each “batch” of calcifying fluid.

Using this conceptual model for coral calcification, we have developed a new approach to obtaining estimates of SST from the skeletons of scleractinian corals. Here we report T estimates, obtained using this approach, from the skeletons of two tropical (*Acropora* sp.; *Diploria labyrinthiformis*) and two cold-water (*Madrepora* sp.; *Lophelia pertusa*) species, spanning T of ~ 7 –29 °C. We show that a Rayleigh-based, multi-element (RBME) approach to coral thermometry can accurately capture T variability without the need to calibrate element ratios of coral skeleton to known SST.

2. METHODS

2.1. Analytical methods

The elemental compositions of the cultured *Acropora* sp. were taken from Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analyses of bulk skeleton reported by Reynaud et al. (2007). *In situ* analyses of *D. labyrinthiformis*, *Madrepora* sp., and *L. pertusa* were carried out on single corallites to determine Mg/Ca, Sr/Ca, and Ba/Ca ratios by secondary ion mass spectrometry (SIMS), using the Cameca 3f ion microprobe at Woods Hole Oceanographic Institution. A ~ 4 nA primary O[−] beam, 20 μ m in diameter, accelerated at 12.5 keV, was used for all analyses. Following a 3 min pre-burn to remove the Au coat, a single spot was occupied while measuring secondary ion intensities for ²⁴Mg, ⁴²Ca, ⁸⁸Sr, and ¹³⁸Ba within a 30 eV window centered on an 80 eV offset from the peak of the energy distribution. This energy filtering reduces molecular interferences to <0.1% (Hart and Cohen, 1996). The mass spectra for Mg, Ca, Sr, and Ba were determined to be free from significant isobaric interferences through a comparison of measured isotope ratios with natural abundances. Isotope ratios were converted to molar ratios on the basis of working curves constructed from three carbonate standards: a carbonatite (OKA), a calcite (0875), and an aragonite (AG1) with Mg/Ca ratios of 0.27–4.47 mmol/

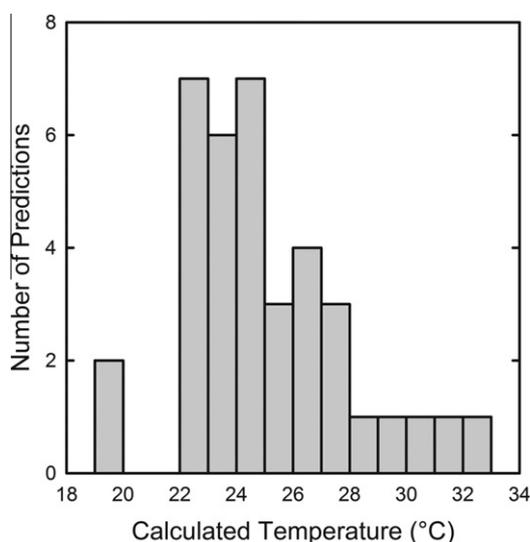


Fig. 1. Histogram showing the distribution of temperatures predicted for a Sr/Ca ratio of 9.035 mmol/mol on the basis of 37 different Sr/Ca–temperature relationships for the genus *Porites* compiled by Corrège (2006).

mol, Sr/Ca ratios of 0.56–19.3 mmol/mol, and Ba/Ca ratios of 2.2–1611 $\mu\text{mol/mol}$. The composition of each standard was determined by solution inductively coupled plasma mass spectrometry (ICP-MS). Data filtering was carried out as described in Cohen and Reves-Sohn (2004).

2.2. Coral thermometry

The principles that underlie RBME thermometry are as follows. The average Sr/Ca ratio of coral aragonite precipitated from an isolated reservoir of calcifying fluid is given by an analytic solution to the Rayleigh fractionation equation:

$$\left(\frac{\bar{C}_{\text{Sr}}}{\bar{C}_{\text{Ca}}}\right)^{\text{Aragonite}} = \frac{C_{\text{Sr}}^0}{C_{\text{Ca}}^0} \times \frac{1 - FL D_{\text{Sr}}^{\text{Aragonite-Seawater}}}{1 - FL D_{\text{Ca}}^{\text{Aragonite-Seawater}}} \quad (1)$$

where $\bar{C}_{\text{Sr}}^{\text{Aragonite}}$ and $\bar{C}_{\text{Ca}}^{\text{Aragonite}}$ are the average concentrations of Sr and Ca in aragonite precipitated from a single “batch” of fluid, C_{Sr}^0 and C_{Ca}^0 are the concentrations of Sr and Ca in the calcifying fluid as precipitation begins, FL is the mass fraction of the initial fluid that remains when aragonite precipitation ends, and $D_{\text{Sr}}^{\text{Aragonite-Seawater}}$ and $D_{\text{Ca}}^{\text{Aragonite-Seawater}}$ are the Nernst aragonite–seawater partition coefficients ($D_i^{\text{Aragonite-Seawater}} = C_i^{\text{Aragonite}}/C_i^{\text{Seawater}}$, where C_i^j is the weight concentration of element i in phase j) for Sr and Ca, respectively (e.g., Gast, 1968). The Sr/Ca ratio of coral skeleton is controlled by the Sr/Ca ratio of the calcifying fluid ($C_{\text{Sr}}^0/C_{\text{Ca}}^0$), T -dependent partitioning of Sr and Ca between aragonite and seawater, and the mass fraction of aragonite precipitated from each “batch” of calcifying fluid ($1 - FL$). Eq. (1) becomes a function of T when expressions describing T -dependent element partitioning derived from abiogenic precipitation experiments are substituted for $D_{\text{Sr}}^{\text{Aragonite-Seawater}}$ and $D_{\text{Ca}}^{\text{Aragonite-Seawater}}$ (e.g., Gaetani and Cohen, 2006).

Temperature cannot be derived from coral skeleton on the basis of Sr/Ca ratios alone unless both $C_{\text{Sr}}^0/C_{\text{Ca}}^0$ and FL are constant throughout the year, and several studies have shown that the latter is sensitive to environmental variables (Cohen et al., 2006, 2009; Gaetani and Cohen, 2006). Increasing the number of measured element ratios improves this situation because each additional Rayleigh equation adds only a single unknown. For example, if Mg/Ca, Sr/Ca, and Ba/Ca ratios are measured the unknown variables become T , FL , $C_{\text{Mg}}^0/C_{\text{Ca}}^0$, $C_{\text{Sr}}^0/C_{\text{Ca}}^0$, and $C_{\text{Ba}}^0/C_{\text{Ca}}^0$. If the calcifying fluid is assumed to be seawater, we are left with three equations and only two unknowns and it becomes possible to solve for T . In practice, however, the composition of the calcifying fluid may differ from seawater and must be treated as an unknown. If the composition of the calcifying fluid when aragonite begins to precipitate can be treated as constant throughout the year for a given coral and Mg/Ca, Sr/Ca, and Ba/Ca ratios are measured at multiple spots along the skeleton to produce a time series, the system becomes mathematically over-constrained and unique combinations of T , FL , $C_{\text{Mg}}^0/C_{\text{Ca}}^0$, $C_{\text{Sr}}^0/C_{\text{Ca}}^0$, and $C_{\text{Ba}}^0/C_{\text{Ca}}^0$ can be determined.

Aragonite–seawater partition coefficients used in this study were derived from apparent (measured) Nernst

partition coefficients determined experimentally by Gaetani and Cohen (2006) for Doerner–Hoskins-type crystallization (Doerner and Hoskins, 1925) using the relationship:

$$D_{\text{Apparent}}^{\text{Aragonite-Seawater}} = \frac{1 - FL D_i^{\text{Aragonite-Seawater}}}{(1 - FL) FL D_i^{\text{Aragonite-Seawater}} - 1} \quad (2)$$

where $D_{\text{Apparent}}^{\text{Aragonite-Seawater}}$ is the partition coefficient measured in the experiment, FL is the mass fraction of the initial fluid remaining at the end of the experiment and $D_i^{\text{Aragonite-Seawater}}$ is the true Nernst partition coefficient (e.g., Shaw, 2006).

Expressions describing the T dependence of aragonite–seawater partitioning for Mg, Ca, Sr, and Ba were derived by fitting the Nernst partition coefficients reported in Table 1 to either linear (Sr) or exponential (Mg, Ca, Ba) functional forms, depending upon the amount of curvature in the relationship:

$$\ln D_{\text{Mg}}^{\text{Aragonite-Seawater}} = -4.864 + \frac{1706}{(T + 273.15)} \quad r^2 = 0.9891 \quad (3)$$

$$\ln D_{\text{Ca}}^{\text{Aragonite-Seawater}} = 8.2384 - \frac{233.5}{(T + 273.15)} \quad r^2 = 0.8199 \quad (4)$$

$$D_{\text{Sr}}^{\text{Aragonite-Seawater}} = 2199.7 - 7.1 \times T \quad r^2 = 0.8995 \quad (5)$$

$$\ln D_{\text{Ba}}^{\text{Aragonite-Seawater}} = -0.696 + \frac{2658.4}{(T + 273.15)} \quad r^2 = 0.9823 \quad (6)$$

where T is in $^{\circ}\text{C}$.

Eq. (1) cannot be solved explicitly for T , so that a global minimization procedure is used. First, Mg/Ca, Sr/Ca, and Ba/Ca ratios are calculated for each analyzed spot on the coral skeleton using a set of initial guesses for T , FL and calcifying fluid composition. We use constant values for T and FL , combined with the Mg, Ca, Sr, and Ba concentrations of Vineyard Sound seawater (Gaetani and Cohen, 2006) as starting points. Element ratios predicted by the Rayleigh equations on the basis of these starting guesses are then compared to measured values by calculating a modified Chi-square parameter:

$$\chi_{\text{RBME}}^2 = \sum (100 \times (i/\text{Ca}_{\text{Rayleigh}} - i/\text{Ca}_{\text{Measured}})/i/\text{Ca}_{\text{Measured}})^2 \quad (7)$$

where $i/\text{Ca}_{\text{Rayleigh}}$ and $i/\text{Ca}_{\text{Measured}}$ are the element-to-calcium ratios predicted by the Rayleigh equation and measured in the coral skeleton, respectively. The initial guesses for T , FL , $C_{\text{Mg}}^0/C_{\text{Ca}}^0$, $C_{\text{Sr}}^0/C_{\text{Ca}}^0$, and $C_{\text{Ba}}^0/C_{\text{Ca}}^0$ are then iteratively modified using the Nelder–Mead simplex algorithm of Lagarias et al. (1998) until Eq. (7) reaches a global minimum. We found that the algorithm does a better job of avoiding local minima for Eq. (7) when FL is assumed to be a polynomial function of T :

$$FL = c_1 + c_2(T + 273.15)^{-1} + c_3(T + 273.15) + c_4(T + 273.15)^2 \quad (8)$$

where T is in $^{\circ}\text{C}$ and c_i are regression coefficients. An example RBME thermometry calculation for cultured *Acropora* sp. is provided in Electronic Supplement.

Table 1
Experimentally determined Nernst partition coefficients for Mg, Ca, Sr, and Ba.

Experiment	Temperature (°C)	D_{Mg}	D_{Ca}	D_{Sr}	D_{Ba}
ASW-4	15	2.7(4)	1622(5)	2030(40)	4900(200)
ASW-1	25	2.37(15)	1785(6)	2051(15)	3770(90)
ASW-2	35	2.1(2)	1819(5)	2010(30)	3000(400)
ASW-3	45	1.7(2)	1801(10)	1930(30)	2230(140)
ASW-7	55	1.4(2)	1846(10)	1740(40)	1440(130)
ASW-8	65	1.15(17)	1909(4)	1760(40)	1230(140)
ASW-9	75	1.03(16)	1911(6)	1660(60)	1110(120)

Notes: Reported partition coefficients are derived from the apparent partition coefficients reported in Table 5 of Gaetani and Cohen (2006) by correcting for the effect of compositional zoning in the crystal using Eq. (3.40) of Shaw (2006). Units in parentheses represent 1 standard error uncertainties in terms of least units cited, calculated by propagating analytical uncertainties. Therefore, 2.7(4) should be read as 2.7 ± 0.4 .

3. RESULTS

3.1. Compositional variability in coral skeletons

The *D. labyrinthiformis* specimen was collected live from a depth of 13 m, ~1 km offshore of John Smith Bay on Bermuda (32°10'N, 64°30'W) on June 1, 2001. Prior to collection, it was stained with sodium alizarin sulfonate on June 1, 2000, September 24, 2000, and January 24, 2001 to provide time markers for comparison with instrumental T records (Cohen et al., 2004; Cohen and Thorrold, 2007). This specimen was previously studied by Gaetani and Cohen (2006). Ion microprobe analyses were performed on spots spaced ~50 μm apart over a distance of 4130 μm along a straight line down a septal element in the ambulacrum. All element ratios vary systematically, with Mg/Ca ranging from ~2.8 to ~5.5 mmol/mol, Sr/Ca from ~8.6 to ~9.8 mmol/mol, and Ba/Ca from ~4.3 to ~6.4 $\mu\text{mol/mol}$ (Fig. 2).

The *Madrepora* sp. specimen was collected live from a depth of 620 m in the Gulf of Mexico (28°4'N, 89°43'W) during dive 43 of the R/V Brown cruise in September 2003. Ion microprobe analyses were performed proximal to the centers of calcification to construct a time series up the exothecal wall. Data were obtained at ~40 μm intervals over a distance of 550 μm . All element ratios vary systematically, with Mg/Ca ranging from ~2.9 to ~3.7 mmol/mol,

Sr/Ca from ~9.7 to ~10.9 mmol/mol, and Ba/Ca from ~8.6 to ~11.4 $\mu\text{mol/mol}$ (Fig. 3).

The *L. pertusa* specimen was collected live from a depth of 129 m on the Tisler Reef, NE Skagerrak (58°59'N, 10°58'E) in June 2003. It was previously studied by Cohen et al. (2006). Ion microprobe analyses were performed proximal to the centers of calcification, which provided an easily identifiable track for navigation, to construct a time series of Mg/Ca, Sr/Ca, and Ba/Ca ratios up the thecal wall. Data were obtained at ~140 μm intervals over a distance of 9800 μm , starting at the base of the calyx. All element ratios vary systematically, with Mg/Ca ranging from ~2.5 to ~4.2 mmol/mol, Sr/Ca from ~9.4 to ~10.5 mmol/mol, and Ba/Ca from ~7.1 to ~9.0 $\mu\text{mol/mol}$ (Fig. 4).

3.2. Rayleigh thermometry for tropical and cold-water corals

Rayleigh-based, multi-element thermometry was carried out for *Acropora* sp. specimens cultured at 21–29 °C by Reynaud et al. (2007). Analyses of Mg/Ca and Sr/Ca ratios were reported for 10–11 individual nubbins (small, live coral samples) in each of five experiments. The number of measured ratios is $2 \times 52 = 104$ and the number of unknown variables in the Rayleigh equations is $52 + 6 = 58$ (52 temperatures, C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , and c_1-c_4). Global minimization results are shown in Fig. 5. The negative correlation

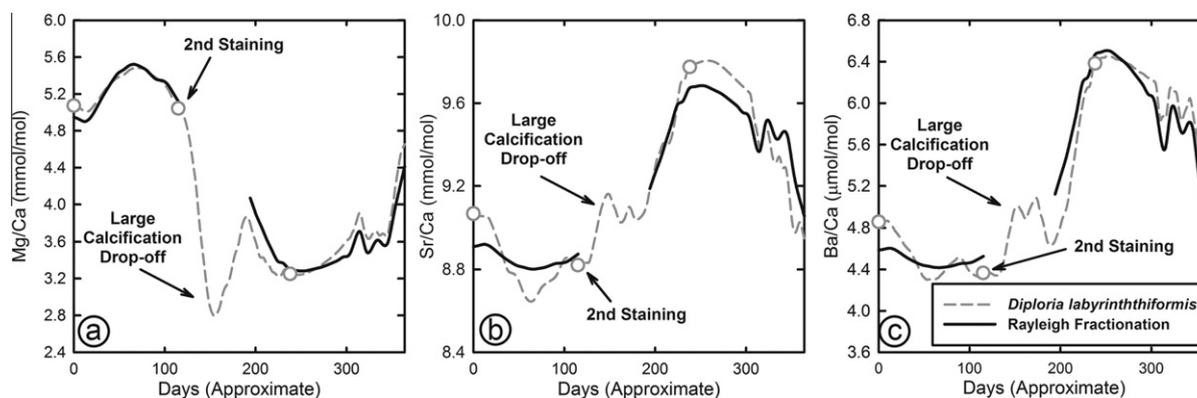


Fig. 2. Comparison of compositional variability in *Diploria labyrinthiformis* skeleton from Bermuda (dashed curves) with that predicted by RBME thermometry (solid curves). Open circles indicates days on which the skeleton was stained with sodium alizarin sulfonate.

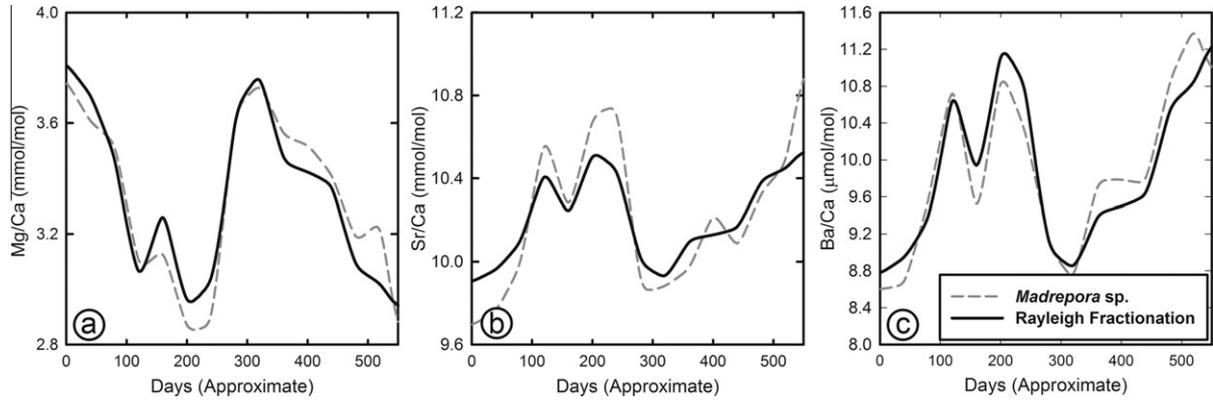


Fig. 3. Comparison of compositional variability in *Madrepora sp.* skeleton from 620 m in the Gulf of Mexico (dashed curves) with that predicted by RBME thermometry (solid curves).

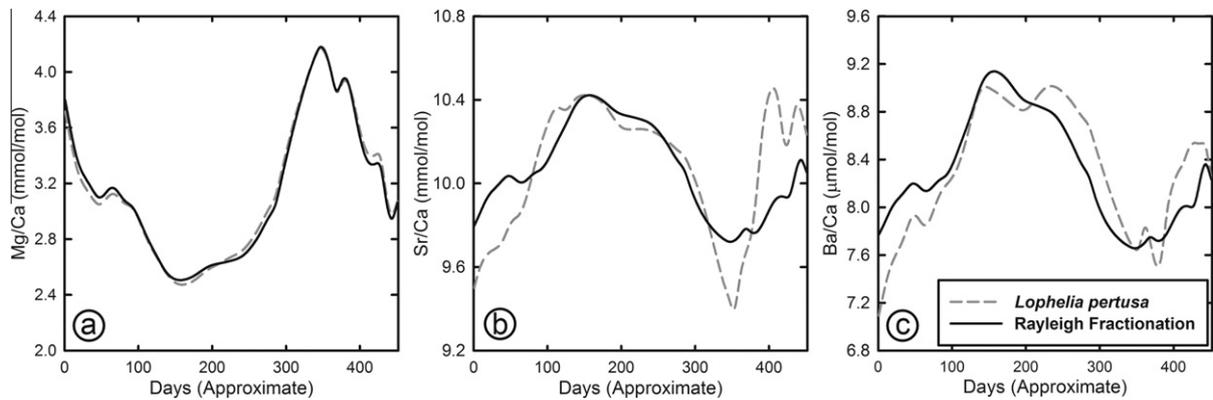


Fig. 4. Comparison of compositional variability in *Lophelia pertusa* skeleton from 129 m depth on the Tisler Reef, NE Skagerrak (dashed curves) with that predicted by RBME thermometry (solid curves).

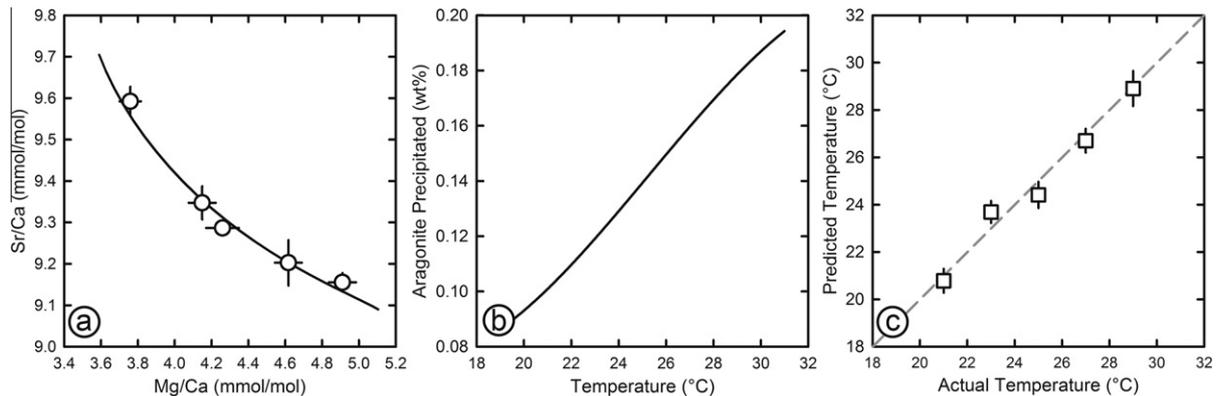


Fig. 5. Results from RBME thermometry for tropical coral (*Acropora sp.*) cultured in the laboratory at 21–29 °C by Reynaud et al. (2007). (a) Comparison of relationship between Sr/Ca and Mg/Ca ratios of cultured *Acropora* skeleton (open circles) with that predicted by Rayleigh thermometry (solid curve). (b) Relationship between temperature and mass of aragonite precipitated from each “batch” of calcifying fluid derived from RBME thermometry. (c) Comparison of temperatures predicted by global minimization of Rayleigh equations, as described in the text, with actual temperatures at which *Acropora* nubbins were grown. Dashed line is a 1:1 relationship. All uncertainties are 2 standard errors.

between Mg/Ca and Sr/Ca ratios in the *Acropora* skeletons is accurately reproduced by Rayleigh fractionation (Fig. 5a), and there is excellent agreement between T pre-

dicted by RBME thermometry and those at which the *Acropora* were cultured, with a mean uncertainty of ± 0.38 °C (Fig. 5c).

Rayleigh-based, multi-element thermometry was carried out for the *D. labyrinthiformis* skeleton on the basis of 75 Mg/Ca, Sr/Ca, and Ba/Ca ratios. Data for days 115–194 were excluded due to the presence of stress-induced compositional changes in skeletal composition, which are discussed in detail below. The number of known ratios is $3 \times 75 = 225$ and the number of unknown variables is $75 + 7 = 82$ (75 temperatures, C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , C_{Ba}^0/C_{Ca}^0 , and c_1 – c_4). The elemental ratios predicted by Rayleigh fractionation are compared with measured ratios in Fig. 2. Fig. 6 compares T derived from RBME thermometry with satellite-derived biweekly SSTs for a $1^\circ \times 1^\circ$ grid square centered on Bermuda (<http://iridl.ldeo.columbia.edu/SOURCES/IGOSS>) for the time period represented by the coral data. The predicted maximum T (28.5 °C) is nearly identical to that from the satellite-derived data (28.2 °C), as is the predicted minimum T (19.4 and 19.3 °C for predicted and satellite-derived, respectively).

Rayleigh-based, multi-element thermometry was carried out for the *Madrapora* sp. skeleton on the basis of 15 Mg/Ca, Sr/Ca, and Ba/Ca ratios. The number of known ratios is $3 \times 15 = 45$ and the number of unknown parameters is $15 + 7 = 22$ (15 temperatures, C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , C_{Ba}^0/C_{Ca}^0 , and c_1 – c_4). The elemental ratios predicted by Rayleigh fractionation are compared with measured ratios in Fig. 3. The T derived from RBME thermometry are compared with average monthly T for 600 m depth at 89.5W 27.5N from LEVITUS94: World Ocean Atlas 1994 in Fig. 7a. The predicted T reproduce both the average T for the collection site inferred from the instrumental data (7.2 °C predicted versus 7.5 °C measured) and lack of seasonal T variability expected for the collection site.

Rayleigh-based, multi-element thermometry was carried out for the *L. pertusa* skeleton on the basis of 53 Mg/Ca, Sr/Ca, and Ba/Ca ratios. The number of known ratios is $3 \times 53 = 159$ and the number of unknown variables is

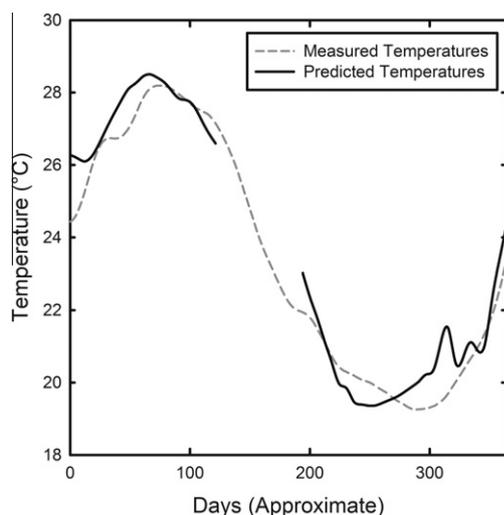


Fig. 6. Comparison of RBME thermometry results for stained *Diploria labyrinthiformis* skeleton from Bermuda (solid curve) with satellite-derived temperatures for the collection site (dashed curve). Data for days 115–194 were excluded due to the presence of stress-induced compositional changes in skeletal composition, as discussed in the text.

$53 + 7 = 60$ (53 temperatures, C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , C_{Ba}^0/C_{Ca}^0 , and c_1 – c_4). The elemental ratios predicted by Rayleigh fractionation are compared with measured ratios in Fig. 4. As discussed in detail by Cohen et al. (2006), no *in situ* T record is available for the time period over which this coral grew. Therefore, Fig. 7b compares T derived from RBME thermometry with the range of average monthly water T recorded in the NE Skagerrak (58°52'N–59°00'N; 10°58'E–11°06'E) at and near the collection site between 1967 and 2005 at depths of 125–135 m. Temperatures predicted by RBME thermometry are at the upper end of the range of average monthly values, and predict a smaller seasonal T variation ($\Delta T \sim 2^\circ\text{C}$) at the collection site than indicated by the instrumental data. This may reflect either the limitations of the instrumental dataset or that the temperature range over which skeletal accretion occurred is smaller than the seasonal temperature range (i.e., skeletal accretion did not occur at the coldest temperatures).

4. DISCUSSION

4.1. Rayleigh fractionation and coral thermometry

The conventional approach to thermometry using Sr/Ca or Mg/Ca ratios in coral skeleton is based on the assumption that aragonite precipitates from an infinite reservoir of seawater, and that compositional variability in the skeleton is attributable to T -dependent element partitioning (e.g., Smith et al., 1979; Mitsuguchi et al., 1996). The T dependence of the Sr/Ca or Mg/Ca ratio in coral skeleton is calibrated against instrumental T records, and the resulting relationship is applied, either downcore or to fossil corals, to determine paleotemperatures. The reliability of this approach is severely limited by the impact of “vital effects” (e.g., Fig. 1)—signals attributed to physiological processes that can overwhelm the actual climate information recorded in the skeleton (Thompson and Livingston, 1970; Weber, 1973; de Villiers et al., 1994, 1995; Cohen et al., 2002; Gaetani and Cohen, 2006).

A consideration of aragonite precipitation rates associated with coral calcification demonstrates that coral skeleton does not form directly from an infinite reservoir of seawater (Cohen and Holcomb, 2009). At 25 °C, aragonite precipitates from seawater with a saturation state ($\Omega_{Arag} = [Ca^{2+}][CO_3^{2-}]/K_{sp}$, where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of Ca^{2+} and CO_3^{2-} , respectively, and K_{sp} is the solubility product of aragonite) of 4 at a rate of $\sim 0.3 \text{ mmol m}^{-2} \text{ h}^{-1}$ (Burton and Walter, 1987), whereas corals typically calcify at rates of ~ 9 – $25 \text{ mmol m}^{-2} \text{ h}^{-1}$ (Gattuso et al., 1993, 1996; Ohde and van Woesik, 1999; Bates et al., 2001). This demonstrates that coral polyps exert strong control over the calcification process, which can be achieved by drawing seawater into a space between the calicoblastic ectoderm and the skeleton, isolating it from the external environment, and modifying it to achieve a higher Ω_{Arag} . A potential mechanism for increasing Ω_{Arag} of what was initially seawater is for the polyp to use the enzyme Ca^{2+} ATPase to add Ca^{2+} , coupled with H^+ removal that increases carbonate ion concentration (Cohen and McConnaughey, 2003; Holcomb et al., 2009).

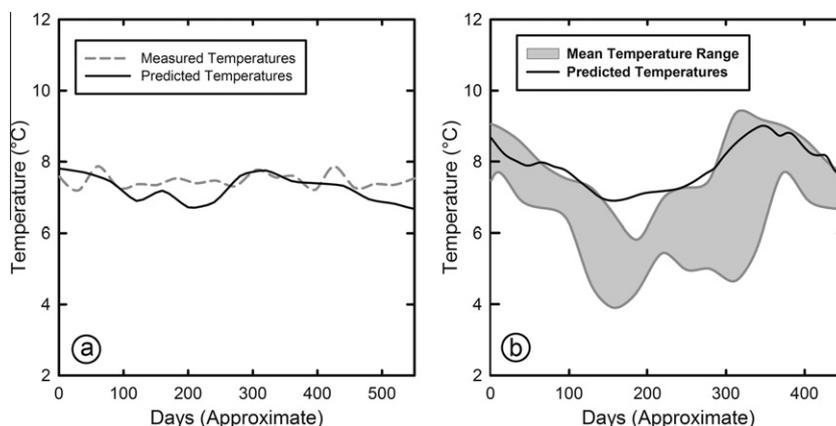


Fig. 7. Results from RBME thermometry for cold-water corals. (a) Comparison of water temperatures predicted from Mg/Ca, Sr/Ca, and Ba/Ca ratios of *Madrepora* skeleton (solid curve) with those for 600 m depth at 89.5W 27.5N from LEVITUS94: World Ocean Atlas 1994 (dashed curve). (b) Comparison of water temperatures predicted from Mg/Ca, Sr/Ca, and Ba/Ca ratios of *Lophelia* skeleton (solid curve) with the mean temperature range (2σ) recorded between 1967 and 2003 in the NE Skagerrak (58°59'N, 10°58'E) near the collection site (shaded region).

Element fractionations during precipitation of aragonite from an isolated reservoir of calcifying fluid are described by the Rayleigh distillation equation (Rayleigh, 1896). Therefore, the RBME approach to coral thermometry uses the Rayleigh equation to derive a quantitative description of the dependence of skeleton composition on T rather than relying on empirical calibrations. Because RBME thermometry incorporates a mathematical description of the mechanism that produces the dominant “vital effect” it should be applicable both across scleractinian species and to corals growing in very different environments. This is demonstrated below through application to both tropical and cold-water corals. By combining analyses of multiple elemental ratios (e.g., Mg/Ca, Sr/Ca, Ba/Ca) from a given coral skeleton with experimentally determined partition coefficients for abiogenic aragonite, it becomes possible to construct a mathematically over-constrained system of Rayleigh equations that describe element fractionations during the biomineralization process. These fractionations depend on both T and the mass of aragonite precipitated from each “batch” of calcifying fluid. The latter signal is what is commonly referred to as “vital effects”.

4.2. Considerations related to element partitioning

There are two important criteria that must be met in order for RBME thermometry to resolve the influence of T on coral skeleton composition from that of variations in the mass of aragonite precipitated, and they are related to element partitioning (Fig. 8). First, a combination of element ratios must be chosen such that one of the aragonite–seawater exchange coefficients ($K_D^{i/Ca} = D_i^{\text{Aragonite–Seawater}} / D_{Ca}^{\text{Aragonite–Seawater}}$) is either very large or very small, so that the influence of Rayleigh fractionation is very strong. We have chosen Mg/Ca because $K_D^{\text{Mg/Ca}}$ is ~ 0.001 at 25 °C. The additional ratios should have $K_D^{i/Ca}$ values reasonably close to unity in order to minimize the influence of Rayleigh fractionation and maximize the T signal. We have chosen Sr/Ca, with $K_D^{\text{Sr/Ca}}$ is ~ 1.2 at 25 °C, and

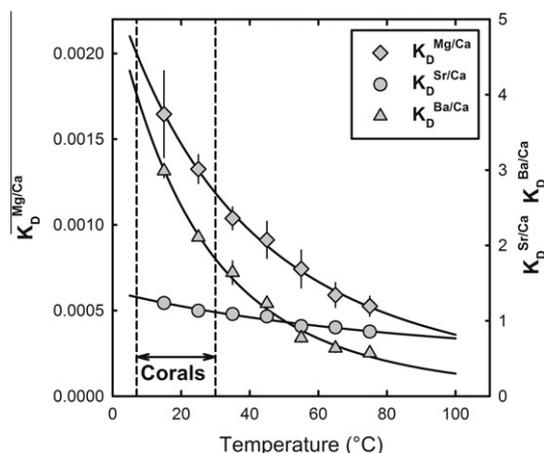


Fig. 8. Relationships between temperature and aragonite–seawater exchange coefficients for Mg/Ca, Sr/Ca, and Ba/Ca determined experimentally by Gaetani and Cohen (2006). Vertical dashed lines correspond to the temperature range over which corals used in this study grew. Note that values on the left ordinate correspond to $K_D^{\text{Mg/Ca}}$ and those on the right ordinate correspond to $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{Ba/Ca}}$.

Ba/Ca, with $K_D^{\text{Ba/Ca}}$ is ~ 3.6 at 25 °C. Rayleigh fractionation produces a strong increase in the Mg/Ca ratio of aragonite as the mass precipitated increases. Both Sr/Ca and Ba/Ca decrease with increasing aragonite precipitation, but the Rayleigh effect on these element ratios is weak relative to Mg/Ca. A second important consideration is that the element ratios with the greatest T sensitivities be chosen such that their $K_D^{i/Ca}$ values have distinctly different responses to T . For example, $K_D^{\text{Sr/Ca}}$ decreases by $\sim 14\%$ between 5 and 30 °C, whereas $K_D^{\text{Ba/Ca}}$ is much more strongly influenced by T , with a decrease of $\sim 44\%$ over the same T range. This insures that Sr/Ca and Ba/Ca ratios will change *relative to one another* with changing T . Stated another way, the Sr/Ba ratio of aragonite is T -sensitive (note, however, that because $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{Ba/Ca}}$ are different, Sr/Ba is still influenced

by Rayleigh fractionation). As shown below, it is sometimes possible to extract T from coral skeleton by combining Mg/Ca and Sr/Ca ratios only, but the addition of Ba/Ca provides a more robust estimate. Temperature estimates based on Sr/Ca and Ba/Ca ratios alone are poor because neither is sensitive enough to the mass of aragonite precipitated to allow it to be resolved from T .

4.3. Considerations related to calcifying fluid composition

An important assumption underlying the formulation for RBME thermometry presented in this paper is that seasonal variations in C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , and C_{Ba}^0/C_{Ca}^0 of the calcifying fluid are negligible. In order to explain the Rayleigh fractionation signal in coral skeleton, the mass of aragonite precipitated from each “batch” of calcifying fluid must vary over the course of a year. One possible explanation for this variation is the influence of temperature on the precipitation rate of aragonite at constant Ω_{Arag} (Burton and Walter, 1987), although seasonal variations in calcifying fluid composition may also be a contributing factor. Below we evaluate the potential for seasonal variations in C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , and C_{Ba}^0/C_{Ca}^0 by (1) showing that the amount of Ca^{2+} added to the calcifying fluid to initiate aragonite precipitation is only $\sim 8\%$ relative and (2) demonstrating that seasonal variations in the mass of aragonite precipitated from each “batch” of calcifying fluid can be accounted for by the influence of temperature on the precipitation rate of abiogenic aragonite. Therefore, seasonal variations in C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , and C_{Ba}^0/C_{Ca}^0 are not required.

Al-Horani et al. (2003) used microsensors to measure pH and Ca^{2+} concentration in fluid beneath the calcicoblastic layer of *Galaxea fascicularis*. The seawater in which these corals were held had salinity (S) of 40‰, 2400 $\mu\text{mol kg}^{-1}$ dissolved inorganic carbon (DIC), pH of 8.2, and 10 mmol kg^{-1} Ca^{2+} . These values can be used as the starting point for calculating the amount of Ca^{2+} that must be added to the seawater to reproduce the microsensor measurements of the calcifying fluid. At $\sim 21^\circ\text{C}$, with lights on, the fluid beneath the calcicoblastic layer had pH 9.28 ± 0.03 and $Ca^{2+} = 10.58 \pm 0.29$ mmol kg^{-1} . Increasing pH from 8.2 to 9.28 at constant DIC requires increasing Ca^{2+} from 10 to 10.77 mmol kg^{-1} , in excellent agreement with the microsensor measurements. This produces a calcifying fluid with $\Omega_{Arag} = 20.46$, similar to independent estimates derived from comparisons of coral skeleton and abiogenic aragonite (Cohen et al., 2009; Holcomb et al., 2009).

According to the experimental results of Burton and Walter (1987), the precipitation rate for abiogenic aragonite is 2.84 mmol $\text{m}^{-2} \text{h}^{-1}$ at $\Omega_{Arag} = 20.46$ and 21°C . Increasing T from 21 to 25°C increases Ω_{Arag} to 20.63 and the aragonite precipitation rate to 6.40 mmol $\text{m}^{-2} \text{h}^{-1}$, while Ca^{2+} remains at 10.77 mmol kg^{-1} . Therefore, seasonal variations in the mass of aragonite precipitated from each batch of calcifying fluid can be achieved without changing C_{Ca}^0 , so that seasonally constant C_{Mg}^0/C_{Ca}^0 , C_{Sr}^0/C_{Ca}^0 , and C_{Ba}^0/C_{Ca}^0 ratios can be assumed. A detailed description of Ca-pumping calculations is presented in Electronic Supplement.

Gaetani and Cohen (2006) used element partitioning and the closure constraint for aragonite to estimate C_{Ca}^0 in the calcifying fluid of *D. labyrinthiformis*, and concluded that it varies from ~ 7 to ~ 14 mmol kg^{-1} over the course of a year. A likely explanation for why the approach of Gaetani and Cohen (2006) overestimates seasonal variations in C_{Ca}^0 is that determining the composition of calcifying fluid from coral skeleton composition using partition coefficients requires a precise match of crystal growth rates, due to its impact on element partitioning. This limitation is discussed in more detail below.

4.4. Rayleigh-based, multi-element coral thermometry

The principles underlying RBME thermometry are illustrated by our results for corals cultured at known conditions. Reynaud et al. (2007) investigated the effects of T on the skeletal composition of the tropical coral *Acropora* sp. to evaluate the use of Sr/Ca and Mg/Ca ratios as paleotemperature proxies. Their results demonstrate that increasing T from 21 to 29°C increases the Mg/Ca ratio by $\sim 30\%$ and the Sr/Ca ratio by $\sim 5\%$ (Fig. 5a). The calcification rate also increases ~ 6 -fold over this T range. They concluded that: (1) coral calcification rate is influenced by external variables such as T ; (2) variations in Mg/Ca ratio are driven by changes in calcification rate and, therefore, are only indirectly related to T ; (3) the different T sensitivities of Sr/Ca and Mg/Ca indicate that Sr and Mg are transported to the site of calcification and incorporated into the skeleton by different mechanisms.

The results of Reynaud et al. (2007) can also be viewed within the framework provided by the RBME approach to coral thermometry. If the Mg/Ca and Sr/Ca ratios of the *Acropora* calcifying fluid are insensitive to T (i.e., they are the same in all experiments), each of the Mg/Ca–Sr/Ca ratio pairs measured by Reynaud et al. (2007) corresponds to a unique combination of mass of aragonite precipitated and T . The latter should correspond to the T at which the corals were cultured. These FL – T pairs can be determined by carrying out a global minimization, as described above, using the Rayleigh equation and experimentally determined partition coefficients for abiogenic aragonite. This provides a quantitative explanation for the origin of compositional variability in coral skeleton that can be rigorously tested against organisms grown at known conditions.

The RBME thermometry results derived from the data of Reynaud et al. (2007) are presented in Fig. 5. The mass of aragonite precipitated from each “batch” of calcifying fluid increases with increasing T (Fig. 5b), providing an explanation for the calcification rate increase. This change in the mass of aragonite precipitated is the dominant signal recorded in the composition of coral skeleton, producing the observed negative correlation between Mg/Ca and Sr/Ca ratios (Fig. 5a). The Sr/Ca ratio variations in coral skeleton are much smaller than those for Mg/Ca because $K_D^{Sr/Ca}$ is ~ 1.2 , whereas $K_D^{Mg/Ca}$ is only ~ 0.001 , smaller by a factor of 1000. Therefore, aragonite precipitation produces only a moderate decrease in the Sr/Ca ratio of the calcifying fluid while the Mg/Ca ratio increases significantly. A comparison of the predicted T with those at which

the corals were cultured shows excellent agreement, demonstrating that T information is accurately recorded in coral skeleton and can be resolved from the influence of “vital effects”. We conclude on the basis of these results that: (1) coral calcification rate is influenced by changes in the mass of aragonite precipitated from each “batch” of calcifying fluid which, in turn, is sensitive to T ; (2) T directly influences Mg/Ca and Sr/Ca ratios in coral skeleton, although the signal is relatively weak, and this information can be recovered using RBME thermometry; (3) there is no evidence to support the existence of independent mechanisms for controlling the transport and incorporation of Sr and Mg into coral skeleton.

Rayleigh-based, multi-element thermometry results for a second tropical coral, *D. labyrinthiformis*, are presented in Figs. 2 and 6. In this case, alizarin stain was used to provide three time markers in order to match skeletal composition with an instrumental record of SST (Cohen et al., 2004; Cohen and Thorrold, 2007). Dodge et al. (1984) examined the effects of alizarin staining on the coral *D. strigosa* and found that it produced a significant decrease in calcification rate that lasted for up to 6 days following exposure to the stain. As discussed above, RBME thermometry for cultured *Acropora* demonstrates that a relationship exists between the mass of aragonite precipitated from each “batch” of calcifying fluid and calcification rate. A drop in calcification rate due to alizarin staining should, therefore, appear in the coral skeleton as a sudden decrease in the Mg/Ca ratio combined with increases in both Sr/Ca and Ba/Ca, with no corresponding change in T , due to a decoupling of T from FL . There appears to be a small drop in calcification rate associated with the staining that took place on June 1, 2000, lasting ~14 days, that is characterized by a decrease in Mg/Ca and increases in both Sr/Ca and Ba/Ca while T is increasing. There is a much stronger signal consistent with decoupling of FL from T associated with the September 24, 2000 application of alizarin. This staining occurred while the calcification rate was decreasing due to the seasonal drop in SST, likely explaining the strength of the signal. Immediately after this staining the Mg/Ca ratio of the skeleton decreases from ~5.0 to ~2.8 mmol/mol, while Sr/Ca increases from ~8.8 to ~9.2 mmol/mol and Ba/Ca from ~4.4 to ~5.1 μ mol/mol with no anomalous drop in SST. The normal relationship between T and FL appears to have been restored by approximately day 192 (Fig. 2). There is no apparent change in calcification rate associated with the January 24, 2001 staining. This is likely due to the modest extension rate of the ambulacrum of this coral between late January and early June (see Fig. 4 of Cohen et al., 2004). Given the limited amount of skeleton accreted over this period, it is possible that a decrease in calcification rate either occurred between individual SIMS spots or was not resolvable from other high-frequency variability and, therefore, was filtered out of the data. Compositional data from days 115 through 194 were excluded from RBME analysis because the decoupling of T from FL would influence predicted temperatures. As noted above, both the maximum (28.5 °C) and minimum (19.4 °C) T predicted by RBME thermometry are nearly identical to those from the satellite-derived data (28.2 and 19.3 °C, respectively). This

example clearly demonstrates that, when an instrumental temperature record is available, it is possible to use sudden changes in skeleton composition to identify periods in which corals experienced stress-related decreases in calcification.

Cold-water corals, with long lifespans and broad geographic distribution, have gained increasing recognition as potential paleoceanographic archives (e.g., Smith et al., 1997, 1999, 2000; Adkins et al., 1998; Goldstein et al., 2001). To date, no element-ratio thermometer has been developed for cold-water corals and application of thermometers calibrated on the basis of tropical coral skeletons give unreliable results. Rayleigh-based, multi-element thermometry was carried out for samples of two different cold-water coral species: *Madrapora* sp. collected at 620 m in the Gulf of Mexico, and *L. pertusa* recovered from a depth of 129 m on the Tisler Reef, NE Skagerrak. Both of these corals experienced very limited seasonal T variations (~0.5 °C for *Madrapora*; ~2 °C for *Lophelia*) but are characterized by large variations in Mg/Ca, Sr/Ca, and Ba/Ca ratios (Figs. 3 and 4). A conventional calibration of these Mg/Sr and Sr/Ca ratios to the instrumental T record would indicate anomalously strong T dependence for all ratios. For example, the apparent T dependence of Sr/Ca in *Madrapora* is -0.36 mmol/mol/°C whereas the T dependence derived from experimentally precipitated abiogenic aragonite is only -0.038 mmol/mol/°C, different by nearly a factor of 10. Application of RBME thermometry accurately predicts the small T ranges experienced by these corals. Further, RBME thermometry accurately predicts that *Madrapora* experienced nearly constant water T throughout the year and that *Lophelia* experienced a small seasonal T variation. The large compositional variability in these deep-water corals is attributable to a stronger T response of the mass of aragonite precipitated from each “batch” of calcifying fluid relative to tropical corals.

The comparison of RBME results from tropical and deep-water corals with abiogenic aragonite precipitated experimentally in Fig. 9 demonstrates how Rayleigh fractionation produces element ratio “vital effects” in the skeletons of scleractinian corals. The relationship between T and the mass of aragonite precipitated for experimentally produced aragonite is very weak, so that the magnitude of the “Rayleigh effect” on the Sr/Ca ratio is small. For the tropical corals *Acropora* and *Diploria* the relationship between T and the mass of aragonite precipitated is stronger, so that the Sr/Ca ratio decreases more strongly with increasing T than would be inferred from abiogenic aragonite. For cold-water corals, the relationship between T and the mass of aragonite precipitated is very strong. This produces large variations in Sr/Ca in environments where there is little T variability, producing strong “vital effects”.

In addition to information about T and the mass of aragonite precipitated from each “batch” of calcifying fluid, RBME thermometry provides estimates for elemental ratios in the calcifying fluid at the onset of aragonite precipitation. Our results suggest that the fluid from which coral skeleton precipitates has a Sr/Ca ratio close to that of seawater, but is depleted in both Mg and Ba. However, Cohen et al. (2009) carried out Rayleigh-based calculations

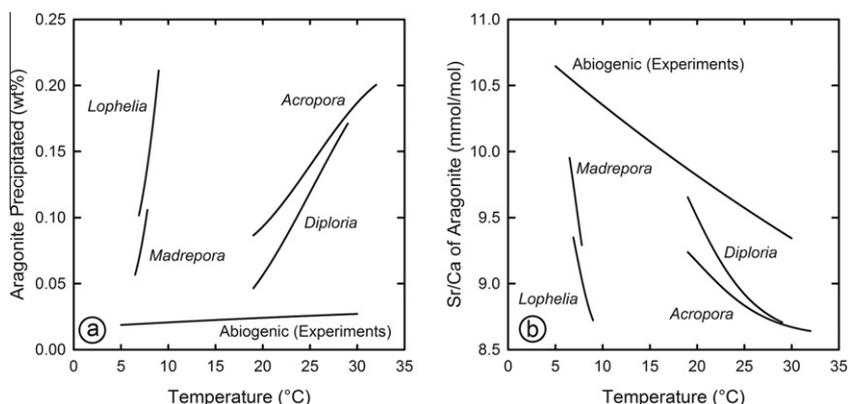


Fig. 9. Illustration of the effect of closed-system aragonite precipitation and Rayleigh fractionation on Sr/Ca– T relationships in coral skeleton. (a) Comparison of the relationships between temperature and the weight percent aragonite precipitated from a “batch” of calcifying fluid derived from global minimizations for *Acropora* sp., *Diploria labyrinthiformis*, *Madrepora* sp., and *Lophelia pertusa*. Shown for comparison is the relationship from the precipitation experiments of Gaetani and Cohen (2006). (b) Comparison of Sr/Ca-temperature relationships calculated for calcifying fluid with Sr/Ca = 8.55 mmol/mol using Eq. (1) and the relationships between temperature and the weight percent aragonite precipitated from a “batch” of calcifying fluid shown in (a), illustrating how Rayleigh fractionation is capable of producing the wide range of Sr/Ca– T relationships observed in coral skeletons.

to model compositional variability in larval Atlantic golf ball corals (*Favia fragum*) reared for 8 days at 25 °C in seawater with aragonite saturation states ranging from ambient ($\Omega_{Arag} = 3.71$) to strongly undersaturated ($\Omega_{Arag} = 0.22$). Growth-rate-dependent partition coefficients were incorporated into these calculations and the results indicate that at the start of precipitation the Mg/Ca (5.3 mol/mol) and Sr/Ca (8.9 mmol/mol) ratios of the calcifying fluid are very close to seawater. Therefore, an important next step in the development of RBME thermometry will be experimental determination of the growth-rate dependence of Mg/Ca, Sr/Ca, and Ba/Ca partitioning between aragonite and seawater over a range of T in order to improve our understanding of the extent to which seawater is modified by the polyp during the biomineralization process.

The existence of Ba/Ca “spikes” in coral skeletons related to variability in seawater Ba/Ca ratios is well documented (e.g., Hart et al., 1997; McCulloch et al., 2003). These spikes typically occur in regions where input from rivers is significant, so that periodic floods cause sudden increases in the Ba/Ca ratio of seawater and, thereby, produce sharp Ba/Ca “spikes” in coral skeleton (Alibert et al., 2003; McCulloch et al., 2003; Sinclair and McCulloch, 2004). Within the framework provided by RBME thermometry, these “spikes” correspond to large variations in the Ba/Ca ratio of the seawater that is drawn into the calcifying space, consistent with some existing interpretations. These “spikes” are many times larger than the Ba/Ca variations attributable to either Rayleigh fractionation or T , indicating that in this case variations in the initial seawater composition dominate the signal recorded in the coral skeleton. This violates the assumption that there is no seasonal variation in C_{Ba}^0/C_{Ca}^0 , so that, in this case, Ba/Ca ratios cannot be used for RBME thermometry. Therefore, T estimates would necessarily rely on Mg/Ca and Sr/Ca ratios only, until reliable experimental partitioning data become available for additional elements.

4.5. Implications for Mg incorporation in biogenic aragonite

The success of RBME thermometry in predicting water T supports the hypothesis that Mg, Sr, and Ba substitute directly for Ca in the aragonite lattice. However, these elements are present in coral skeleton in much higher concentrations than expected on the basis of thermodynamic equilibrium with seawater (Plummer and Busenberg, 1987; Pingitore et al., 1989; Gaetani and Cohen, 2006), and various studies have suggested that their incorporation into biogenic aragonite occurs through occlusion within the growing crystal or that they may be hosted in materials other than aragonite (Pingitore et al., 1989; Hart and Cohen, 1996; Gregor et al., 1997; Finch and Allison, 2008). In particular, the relatively small cationic radius of Mg (0.72 Å in 6-fold coordination with O^{2-} according to Shannon (1976)) favors incorporation into the rhombohedral structure of calcite rather than orthorhombic aragonite.

Two studies have used X-ray absorption fine structure (XAFS) spectroscopy to investigate the structural environment of Mg in biogenic aragonite (Finch and Allison, 2008; Farges et al., 2009). Finch and Allison (2008) compared Mg K-edge spectra for aragonite from *Porites* skeleton to standard materials that included aragonite, calcite and homogenized mussel tissue. They found spectra in the XANES region to be relatively featureless when compared with abiogenic carbonates and concluded that Mg is characterized by only short-range order in *Porites* skeletons. They suggested that Mg could be hosted in either organic material or a highly disordered inorganic phase, raising questions as to whether it substitutes for Ca in the aragonite lattice. Farges et al. (2009) used Mg K-edge XANES spectroscopy combined with μ -XRF to investigate the structural environment and distribution of Mg in a range of biogenic carbonates, including the skeletons of *Porites* coral. Farges et al. (2009) found significant differences in the XANES-region spectra among different corals, indicating

variations in the structural environment of Mg. On the basis of *ab initio* calculations for defect clusters around Mg in aragonite and wavelet analysis they concluded that in *Porites* skeleton Mg occurs in a rhombohedral-carbonate-type environment, similar to magnesite. However, they also found evidence that Mg occurs in a site similar to that in dashkovaite in skeleton of the cold-water coral *Desmophyllum*, implying a more organic-like bonding environment.

Given the conflicting results from these studies, it appears that existing XAFS data do not provide a quantitative and consistent picture of how Mg is incorporated into biogenic aragonite. Results from RBME thermometry presented here demonstrate that the partitioning of Mg between abiogenic aragonite and seawater successfully predicts its incorporation into coral skeleton, suggesting that it is not hosted in organics. The same conclusion can be drawn from comparisons of Mg isotope fractionations in biogenic and experimentally precipitated abiogenic aragonite. Chang et al. (2004) measured the isotopic composition of Mg in the skeleton of *Acropora* and found that $\Delta^{26}\text{Mg}_{\text{Seawater-Coral}} = -0.94\text{‰}$, while Wang et al. (2006) measured $\Delta^{26}\text{Mg}_{\text{Seawater-Aragonite}} = -1\text{‰}$ for abiogenic aragonite precipitated experimentally from seawater. Therefore, while the details of the structural environment of Mg in biogenic aragonite are not yet clear, it appears highly unlikely that it is hosted exclusively within organic material in coral skeleton.

4.6. Implications for coral biomineralization models

Some of the key questions outstanding in coral biomineralization studies relate to the source of ions for calcification, the existence of a discrete and isolated calcifying space, and mechanisms for overcoming kinetic barriers to crystal nucleation and growth. The elemental compositions of aragonite crystals that make up coral skeleton provide important insights into these questions, but there is significant ambiguity in the interpretation of these clues because the relative importance of physiological versus physico-chemical processes remains a matter of debate. There are currently at least two schools of thought regarding the interpretation of compositional variability in coral skeleton. Advocates of strict biological control hold that there is no discrete calcifying space, and that the site of calcification is completely sealed off from the external seawater environment. Individual ions are actively transported to the site of calcification via ion channels and enzyme pumps in the cell membranes of the coral polyp. Nucleation and growth are mediated by organic molecules (e.g., Meibom et al., 2007). Alternatively, biologically mediated physico-chemical models posit that the site of calcification periodically comes into contact with the external seawater environment, and that seawater provides a significant proportion of the ions for calcification. Seawater is drawn into a space, nanometers to microns in size, between the calciblastic ectoderm and the skeleton, and then isolated from the external environment. The polyp modifies the seawater to elevate Ω_{Arag} , leading to precipitation of aragonite. The polyp may elevate the saturation state by using the enzyme Ca^{2+} ATPase to add Ca^{2+} to the seawater, coupled

with H^+ removal that increases carbonate ion concentration, as proposed by Cohen and McConnaughey (2003).

The success of RBME thermometry in (1) providing a quantitative explanation for the origin of compositional variation in the skeletons of both tropical and deep-water corals and (2) demonstrating robust predictive capabilities for reconstructing water T , provides strong support for a biologically mediated physico-chemical biomineralization process. However, there are still many aspects of the process that need to be quantified. First, the role of organics in the biomineralization process is unclear. For example, it has been shown experimentally that the presence of peptides in the calcifying fluid affects the concentration of Mg in calcite (Stephenson et al., 2008), and the potential exists that the presence of organic molecules may influence the growth rate and/or composition of biogenic aragonite. Despite the remaining uncertainties, Rayleigh fractionation provides the best available quantitative explanation for element ratio “vital effects” in coral skeleton.

5. CONCLUSIONS

Accurate and precise seawater T can be derived from the skeletons of both tropical and cold-water scleractinian corals by combining the Rayleigh equation with aragonite–seawater partition coefficients derived from abiogenic precipitation experiments. This approach does not rely on an initial calibration of coral skeletal composition to the instrumental record of T . Rather, considering coral skeletogenesis as a biologically mediated, physico-chemical process provides a means to extract T information from the skeleton based on a quantitative understanding of the mechanism that produces the “vital effect”. It should be possible to apply our Rayleigh-based multi-element thermometer both across scleractinian species and to corals growing in vastly different environments.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2011.01.010](https://doi.org/10.1016/j.gca.2011.01.010).

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