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10

Ion partitioning in ambient-temperature aqueous systems

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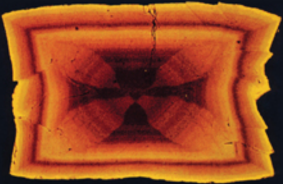

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Ion partitioning and the geochemistry of coral skeletons: solving the mystery of the vital effect

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Much of our understanding of Earth's climate history is based on interpretation of geochemical variability within the $CaCO_3$ tests and skeletons of marine organisms. Geochemical climate proxies are typically cast in terms of equilibrium thermodynamics, but there are important differences between the compositions of carbonates accreted by living organisms and predictions for carbonate minerals in equilibrium with seawater. These differences are commonly attributed to 'vital effects' thought to be caused by biological modification of the calcifying environment and of crystal-growth kinetics. If this were true, then biologically modified crystal chemistry may be unpredictable or challenging to model mathematically, making it difficult to extract accurate climate information from biogenic carbonates with any degree of confidence. Our goal with this paper is to demonstrate a systematic approach to the identification, characterization and understanding of 'vital effects' using coral skeletons as an example. We show, through insights gained from abiogenic aragonites precipitated experimentally from seawater under controlled conditions, that many of the so-called 'vital effects' in coral skeletal geochemistry are actually characteristic of abiogenic aragonites and can be described mathematically in terms of predictable physicochemical processes. By comparing elemental ratios (Mg/Ca, Sr/Ca, Ba/Ca) of abiogenic aragonite with that of coral aragonite, we show that Rayleigh fractionation and crystal-growth rate exert the dominant controls on the elemental chemistry of corals, and that the contribution of temperature is relatively small. Building on these insights, we have developed a new approach to extracting temperature information from coral skeletons that is fundamentally different from conventional palaeo-thermometry, by-passing 'vital effects' through the simultaneous use of multiple element ratios to reliably extract that small component of skeletal variability that is driven solely by temperature.

1. Introduction

The compositions of $CaCO_3$ tests and skeletons of many marine organisms vary in response to ocean conditions, and much of our understanding of past climate variability is based on the quantitative interpretation of these changes in terms of physical and chemical parameters of the ocean. For example, the magnesium-to-calcium (Mg/Ca) ratios of calcite tests of foraminifera and the strontium-to-calcium (Sr/Ca) ratios of aragonite skeletons of tropical corals are commonly taken to be geochemical proxies for temperature, and have been used to reconstruct ocean conditions during important periods in Earth's climate history, including the Last Glacial Maximum (*e.g.* Guilderson *et al.*, 1994; Elderfield & Ganssen, 2000). Such proxy-based reconstructions form the

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basis for much of our understanding of the behaviour of the Earth's climate system on decadal through orbital timescales, and provide crucial insights into the sensitivity of Earth's climate system to changes in boundary conditions, such as concentrations of atmospheric CO_2. Despite their importance and wide application, however, the majority of geochemical proxies are empirically based and we know surprisingly little about the mechanisms that control the geochemical composition of biogenic (biologically precipitated) carbonates.

Geochemical proxies are typically cast in terms of equilibrium thermodynamics, but there are important differences between the compositions of biogenic carbonates and predictions for carbonate minerals in equilibrium with seawater. For example, at 25°C the average Sr/Ca ratio of *Porites* coral skeleton, calculated on the basis of 37 Sr/Ca–temperature relationships compiled by Corrège (2006), is 9.04 ± 0.17 mmol/mol, whereas thermodynamics predicts that the Sr/Ca ratio of abiogenic aragonite in metastable equilibrium with seawater is 0.82 mmol/mol (Plummer & Busenberg, 1987). Thus, the Sr/Ca ratio of coral skeleton is more than 10 times greater than it would be if coral aragonite was precipitated in equilibrium with seawater. Abiogenic aragonite precipitated experimentally from highly supersaturated seawater provides a good morphological and compositional match to biogenic aragonite, confirming the important role played by kinetics, but significant discrepancies remain. For example, the Sr/Ca ratio of 9.43 ± 0.17 mmol/mol determined experimentally by Gaetani and Cohen (2006) for abiogenic aragonite is within the range predicted for *Porites* skeleton, but the experimentally determined relationship between Sr/Ca ratio and temperature (-0.038 ± 0.004 mmol/mol $^\circ C^{-1}$) is much weaker than is the case for *Porites* skeleton (-0.061 ± 0.009 mmol/mol $^\circ C^{-1}$).

The reliability of palaeo-temperature reconstructions derived from biogenic skeletons is further confounded by the large variability in E/Ca-temperature relationships derived from living specimens, as well as compositional variability occurring on timescales too short to be attributable to temperature. For example, Saenger *et al.* (2008) found that corals of a single genus (*Montastrea*) grown under identical temperature conditions can have very different relationships between Sr/Ca ratio and water temperature (Fig. 1). The Sr/Ca ratios, derived from four different *Montastrea* skeletons, range from 8.73 to 9.37 mmol/mol at 25°C, with Sr/Ca-temperature relationships ranging from -0.075 ± 0.010 to -0.099 ± 0.015 mmol/mol per °C. Depending on which of these relationships is used, Little Ice Age palaeo-temperatures derived from Sr/Ca ratios of fossil corals of the same species, collected at the same site, can range from 0°C to 5°C cooler than today. The application of microbeam techniques to carry out analyses of biogenic skeletons on finer and finer length-scales have revealed more and larger-amplitude discrepancies between measured coral skeletal composition and that expected on the basis of known environmental conditions at the time of crystal/skeletal growth (*e.g.* Cohen *et al.*, 2001; Cohen *et al.*, 2002; Allison & Finch, 2004; Meibom *et al.*, 2004; Meibom *et al.*, 2006). For example, Meibom *et al.* (2006) reported Mg/Ca fluctuations of 0.5–1 mmol/mol over micron length-scales (~daily timescales) within coral skeleton. Using Mitsuguchi *et al's.* (1996) Mg/Ca-SST calibration equation, this is equivalent to a temperature range of ~8°C, more than four times

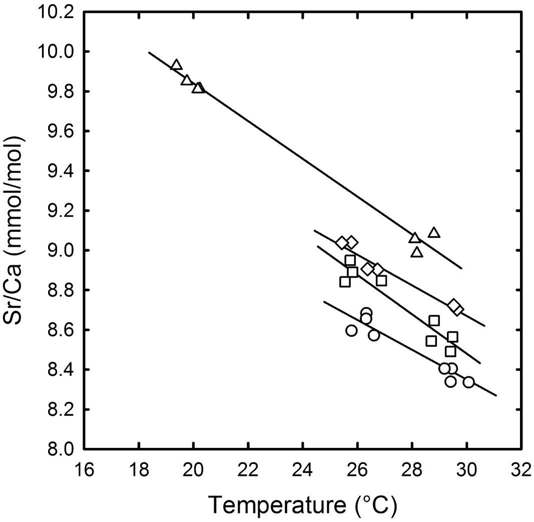

Fig. 1. Relationships between Sr/Ca ratio and temperature, derived from skeletons of the Atlantic coral genus *Montastrea* collected from St. Croix (circles, squares, diamonds) and Bermuda (triangles). These relationships vary systematically as a function of mean annual skeletal extension rate (adapted from Saenger *et al.*, 2008).

larger than the observed diurnal temperature fluctuations experienced by the coral. Such discrepancies are not limited to coral skeletons. For example, Curry and Marchitto (2008) used a secondary ion mass spectrometer (SIMS) ion microprobe to make intra-test measurements of Mg/Ca ratios in the calcitic benthic foraminfera *Cibicidoides pachyderma*. Within a single test, Mg/Ca ratios ranged from ~2.66 mmol/mol to 5.81 mmol/mol. Using the Mg/Ca-temperature relationship established from whole-test Mg/Ca averages, this represents a temperature range of >30°C.

These inconsistencies between measured and expected compositions of biogenic skeletons have been recognized for many decades and are collectively referred to as ‘vital effects’, a term for which there are two working definitions: (1) biological processes linked to skeleton building that distort the climate signal; and (2) “a name which hides the fact that we don’t understand them” (Broecker, 1982). The challenge posed by ‘vital effects’ for practitioners of proxy-based climate reconstructions is to identify and quantify the mechanisms that create them, and to use this understanding to develop reliable approaches to extracting climate records from biogenic carbonates. If the origin of ‘vital effects’ is wholly physiological, skeletal composition would probably be either unpredictable or challenging to model mathematically, making it unlikely that accurate climate information could be extracted with any degree of confidence. For example, Meibom *et al.* (2007) suggested that large variations in the Mg/Ca ratio of coral skeletons observed on micron length-scales and, importantly, unaccompanied by similarly large variations in Sr/Ca ratios must reflect “differential transport and incorporation of major and trace elements into the skeleton”. In other words, biologically induced changes in the composition of the calcifying fluid or in the availability of ions for calcification (on hourly, weekly, seasonal and inter-annual timescales) are the primary drivers of compositional variability in coral skeletons. If this were indeed the case, it might be very difficult to use coral skeletal composition as a reliable indicator of ocean conditions.

Our goal with this paper is to demonstrate a systematic approach to the identification, characterization and understanding of ‘vital effects’, with a focus on coral skeletons. We show, through comparisons of coral skeletons with data obtained from abiogenic aragonite precipitated experimentally from highly supersaturated seawater under controlled conditions, that many of the so-called ‘vital effects’ on coral composition, such as those described by Meibom *et al.* (2007) and others, are also characteristic of abiogenic aragonites and can be described mathematically in terms of predictable physicochemical processes. To date we have identified three principal factors controlling the Mg/Ca, Sr/Ca, and Ba/Ca ratios of aragonite crystals grown from seawater: (1) water temperature, (2) crystal growth rate, and (3) Rayleigh fractionation (*e.g.* Cohen *et al.*, 2006; Gaetani & Cohen, 2006; Gabitov *et al.*, 2008; Holcomb *et al.*, 2009). In abiogenic aragonites precipitated from an infinite reservoir, the impact of Rayleigh fractionation on compositional variability is relatively small. In corals however, it appears that the influence of Rayleigh fractionation is dominant, at least on seasonal timescales. By comparison, we find that the contribution of water temperature to compositional variability in both coral skeletons and abiogenic aragonites is relatively small. Despite this, we have been able to use our understanding of coral skeletogenesis to develop a new, more reliable approach to extracting ocean temperature from the composition of coral skeleton. This approach to palaeo-thermometry combines the Rayleigh equation with experimentally determined aragonite-seawater partition coefficients to solve for temperature on the basis of information derived from combining multiple element ratios (Gaetani *et al.*, 2010). Unlike conventional coral thermometers, our Rayleigh-based multi-element approach does not rely on an initial calibration of coral skeletal composition to the instrumental temperature record. Rather, by viewing coral skeletogenesis as a biologically mediated but fundamentally physicochemical process it becomes possible to reliably extract that small component of skeletal variability that is driven solely by temperature.

2. Comparison of coral skeleton with abiogenic aragonite

Coral calcification takes place at the interface between the living polyp and the existing skeleton. The schematic cross-section through a coral colony shown in Figure 2 illustrates the geometric relationships among the coral animals (polyps), the skeleton they accrete and the site of calcification located between the base of the polyp tissue and the top of the existing skeleton. In living corals, the entire surface of the skeleton is covered by several layers of tissue so that, for much of the time, the surface of the growing skeleton is not in direct contact with the external seawater. This is important because it allows the coral to isolate the calcifying medium from the external seawater and to manipulate conditions at the calcification site. Current physicochemical models of coral calcification posit that corals transport seawater to the calcification site, even

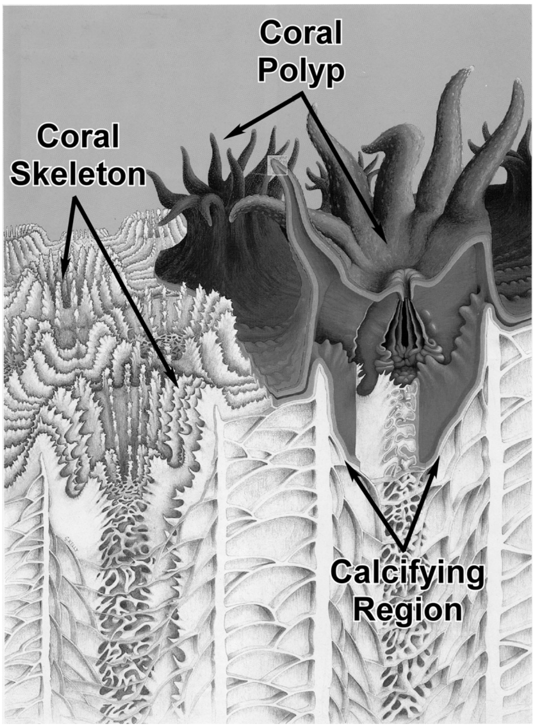

Fig. 2. Schematic cross section through a scleractinian coral showing the geometric relationship between the coral polyp, the skeleton and the calcifying region (adapted from Veron, 1986).

though the exact route or mechanism has not yet been identified (*e.g.* Cohen & McConnaughey, 2003). The most compelling evidence for the presence of seawater at the calcification site comes from the observation that when tracer dyes, such as calcein and alizarin Red-S, are introduced into the seawater surrounding the coral they are rapidly and uniformly deposited in the growing skeleton (*e.g.* Braun & Erez, 2004; Allemand *et al.*, 2010). Coral cell membranes are impermeable to these molecules, so that there must be either (1) a direct passage or channel that periodically links the calcification site with the external seawater, or (2) active transport of seawater-filled vacuoles across cell membranes to the site of calcification. Once seawater enters the site of calcification, its composition must be manipulated in order for aragonite crystals to nucleate and grow. Several lines of evidence indicate that corals achieve this by elevating the saturation state of the calcifying fluid.

Clues to the nature of the coral calcification process are found in the morphologies and compositions of the two distinct crystal types that make up the skeleton (Fig. 3). First, clusters of sub-micron sized, granular crystals occupy the centres of calcification and fine bands that are found throughout the skeleton. Second, bundles of fibrous crystals, several microns in length, make up the bulk of the skeletal mass (*e.g.* Constantz,

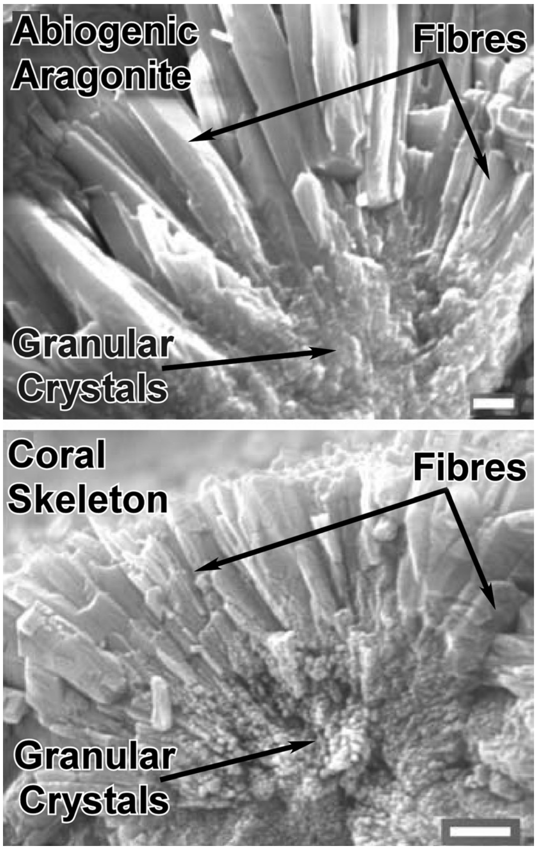

Fig. 3. Comparison of aragonite crystals produced experimentally from a highly supersaturated seawater solution (upper) and by corals (lower). In both cases, bundles of aragonite fibres radiate out from a central region occupied by aggregates of sub-micron-sized granular crystals. Granular crystals form at the highest saturation states and are thought to represent an interval of relatively rapid crystal growth (Holcomb *et al.*, 2009). Fibrous aragonite grows when the saturation state of the seawater is relatively low, indicating slower crystal-growth rates. The scale bars are 1 μm in both (adapted from Cohen & Holcomb, 2009).

1986, 1989; Cohen *et al.*, 2001; Holcomb *et al.*, 2009). Several independent studies, using *in situ* microbeam analytical techniques to selectively analyse the fine granular crystals and fibres have shown that these two crystal types are compositionally distinct (*e.g.* Cohen *et al.*, 2001; Adkins *et al.*, 2003; Allison *et al.*, 2005; Meibom *et al.*, 2006; Blamart *et al.*, 2007; Holcomb *et al.*, 2009; Juillet-Leclerc *et al.*, 2009; Rollion-Bard *et al.*, 2010). The Sr/Ca ratios tend to be slightly larger in regions of the coral skeleton occupied by fine granular crystals relative to adjacent skeleton occupied by fibrous crystals, whereas Mg/Ca and Ba/Ca ratios are significantly larger in these regions. Similarly, isotopic compositions of the two crystal types are distinct: the boron (δ^{11}B), oxygen (δ^{18}O) and carbon isotope ratios (δ^{13}C) tend to be lighter (depleted) in regions of the coral skeleton made up of fine granular crystals relative to adjacent skeleton comprised of fibre bundles. Understanding the growth conditions that produce these two distinct crystal types is a critical first step towards understanding the origin of their morphological and compositional differences in particular, and coral 'vital effects' in general.

Important insights have come from the study of abiogenic aragonite precipitated experimentally from highly super-saturated seawater. The results from these experiments demonstrate that abiogenic aragonites precipitated at low temperatures (15–80°C) from a highly super-saturated seawater solution consist of a combination of granular and fibrous crystals that are nearly identical to those found in coral skeleton (Fig. 3). In precipitation experiments carried out at 25°C, Holcomb *et al.* (2009) introduced isotope spikes (^{84}Sr, ^{86}Sr, ^{137}Ba) into the seawater at various times during the nucleation and growth of the aragonite crystals. By locating the spikes in these crystals, using the SIMS ion microprobe they were able to show that the fine granular crystals form when the saturation state of the seawater, with respect to aragonite, is almost seven times greater than ambient ($\Omega_{\mathrm{Arag}} > 25$). Conversely, fibrous aragonite grows when the saturation state of the seawater is relatively low (over an Ω_{Arag} range of ~6–20). Further, Holcomb *et al.* (2009) showed that granular and fibrous crystals are compositionally distinct in abiogenic aragonite just as they are in coral skeleton. Granular crystals have significantly larger Mg/Ca and Ba/Ca ratios than the surrounding fibres, whereas Sr/Ca ratios are only slightly elevated.

The strong correspondence between the abiogenic aragonite precipitated experimentally from seawater and aragonite accreted by corals, in terms of both their morphology and composition, suggests that corals probably produce the crystals that comprise their skeleton by a similar mechanism: seawater is brought into the region between the polyp and skeleton, isolated from the external environment, and its saturation state is elevated until aragonite crystals nucleate and grow (*e.g.* Cohen & McConnaughey, 2003). Indeed, Holcomb et *al.* (2009) proposed that diurnal cycles in the saturation state of the calcifying fluid produces the alternating layers of granular and fibrous crystals found in coral skeletons. Importantly, the similarity between experimental and coral aragonites makes it plausible to use data from abiogenic aragonite precipitation experiments to gain insights into the factors that control the composition of biogenic aragonite accreted by corals.

3. Influence of temperature on aragonite composition

Conventional element-ratio thermometry assumes that coral skeleton aragonite precipitates from an infinite reservoir of seawater, and that compositional variability is attributable to temperature-dependent element partitioning (*e.g.* Smith *et al.*, 1979; Mitsuguchi *et al.*, 1996). This is at odds with strict biological control models for coral calcification, which hold that the site of calcification is completely sealed off from the external seawater environment, and that ions are actively transported to the site of calcification *via* ion channels and enzyme pumps in the cell membranes of the coral polyp (*e.g.* Meibom *et al.*, 2007; Reynaud *et al.*, 2007). The likelihood of either process being dominant in coral biomineralization can be evaluated through comparisons of experimentally determined element partitioning for abiogenic aragonite and the composition of coral skeleton.

Gaetani & Cohen (2006) investigated the extent to which coral skeleton composition is consistent with precipitation of aragonite from seawater using experiments carried out at temperature of 15 to 75°C. They determined that the aragonite-seawater exchange coefficient for Mg/Ca ($K_D^{Mg/Ca} = (C_{Mg}/C_{Ca})^{\text{Aragonite}}/(C_{Mg}/C_{Ca})^{\text{Seawater}}$ where C_i is the concentration of element i in either aragonite or seawater) is very small, whereas $K_D^{Sr/Ca}$ and $K_D^{Ba/Ca}$ are both >1. Their results also demonstrated that $K_D^{Mg/Ca}$, $K_D^{Sr/Ca}$ and $K_D^{Ba/Ca}$ all decrease with increasing temperature. The composition of abiogenic aragonite precipitated from an infinite reservoir of seawater calculated using these exchange coefficients has important similarities with coral skeleton (Fig. 4). The Mg/Ca ratio of coral skeleton is smaller than that of the seawater by approximately a factor of 1000, which is consistent with $K_D^{Mg/Ca} \approx 0.001$, while Sr/Ca and Ba/Ca ratios are similar to or slightly higher seawater ratios, consistent with $K_D^{Sr/Ca} \approx 1.2$ and $K_D^{Ba/Ca} \approx 2.3$. However, in detail, there are also important differences. The Mg/Ca, Sr/Ca and Ba/Ca ratios calculated for abiogenic aragonite are all larger than

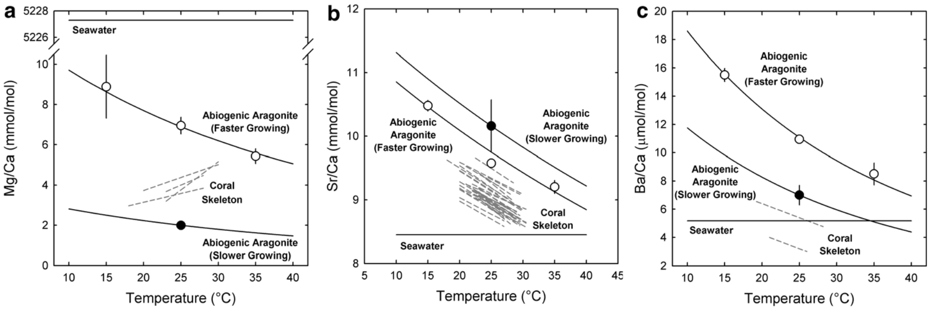

Fig. 4. Comparisons of (***a***) Mg/Ca ratios, (***b***) Sr/Ca ratios, and (***c***) Ba/Ca ratios in coral skeleton (dashed grey curves) with that of aragonite precipitated from an infinite reservoir of seawater (solid black curves) at different crystal-growth rates. The composition of abiogenic aragonite was calculated for seawater having a Mg/Ca ratio of 5.2 mol/mol, Sr/Ca ratio of 8.5 mmol/mol, and Ba/Ca ratio of 5.2 μmol/mol. Experimentally determined $K_D^{Mg/Ca}$, $K_D^{Sr/Ca}$, and $K_D^{Ba/Ca}$ values for faster crystal growth are from Gaetani & Cohen (2006), while values for slower growth were calculated from data for fibrous aragonite at 25°C from Holcomb *et al.* (2009) with temperature dependence estimated from the data of Gaetani & Cohen (2006). Relationships between the Mg/Ca ratio and temperature for coral skeleton are from Mitsuguchi *et al.* (1996), Sinclair *et al.* (1998), Fallon *et al.* (1999) and Watanabe *et al.* (2001). The relationships between Sr/Ca ratio and temperature for coral skeleton are from Smith *et al.* (1979), Beck *et al.* (1992), de Villiers *et al.* (1994), Shen *et al.* (1996), Mitsuguchi *et al.* (1996), Alibert & McCulloch (1997), Bessat (1997), Heiss *et al.* (1997), Gagan *et al.* (1998), Sinclair *et al.* (1998), Fallon *et al.* (1999), McCulloch *et al.* (1999), Corrège *et al.* (2000), Linsley *et al.* (2000), Wei *et al.* (2000), Marshall & McCulloch (2001), Quinn & Sampson (2002), Marshall & McCulloch (2002), Fallon *et al.* (2003), Allison & Finch (2004), Linsley *et al.* (2004), Felis *et al.* (2004), Zinke *et al.* (2004) and Corrège (2006). The relationships between the Ba/Ca ratio and temperature for coral skeleton are from Lea *et al.* (1989) and Gaetani & Cohen (2006).

those in coral skeleton and, more importantly, the predicted temperature dependence for the Mg/Ca ratio is negative whereas the Mg/Ca ratio of the biogenic aragonite correlates positively with temperature. In order to fully reconcile compositional variations in coral skeleton with abiogenic aragonite, factors other than temperature need to be considered. These are (1) the influence of crystal growth rate on element partitioning and (2) Rayleigh fractionation.

4. Influence of crystal-growth rate on aragonite composition

Kinetics represents the principal control on element distribution during carbonate precipitation at low temperature, so that partition coefficients vary with crystal growth rate (*e.g.* Lorens, 1981; Watson, 2004; Gaetani & Cohen, 2006; Gabitov *et al.*, 2008). The precipitation experiments conducted by Gaetani & Cohen (2006) produced spherulitic crystals, morphologically similar to those that comprise coral skeleton *i.e.* granular centres surrounded by bundles of acicular fibres. It is expected that as the crystal growth rate decreases, the Mg/Ca and Ba/Ca ratios of aragonite will decrease significantly and the Sr/Ca ratio will remain relatively constant (Gaetani & Cohen, 2006; Gabitov *et al.*, 2008; Holcomb *et al.*, 2009). This effect can be quantified using exchange coefficients calculated from the composition of fibrous aragonite reported for Experiment 1 of Holcomb *et al.* (2009) which, because of the slower rate at which Na_2CO_3 solution was added (4.8 ml/h *vs.* 60 ml/h), represent smaller crystal-growth rates relative to those studied by Gaetani & Cohen (2006). As crystal growth rate decreases, there are substantial decreases in both $K_D^{Mg/Ca}$ (from ~0.001 to. ~0.0004) and $K_D^{Ba/Ca}$ (from ~2.3- to ~1.4), whereas $K_D^{Sr/Ca}$ does not change significantly (~1.2).

Compositional differences between the granular and fibrous crystals that comprise coral skeleton are explicable in terms of differences in growth rate. Granular crystals that occupy centres of calcification and fine daily growth bands, which plausibly form at relatively large growth rates, typically have slightly larger Sr/Ca and significantly larger Mg/Ca and Ba/Ca ratios than the adjacent fibrous crystals (Holcomb *et al.*, 2009). Furthermore, the existence of large cycles in Mg/Ca ratios on micron length-scales unaccompanied by equally large variations in Sr/Ca ratios (*e.g.* Meibom *et al.*, 2008) are consistent with changes in crystal-growth rate associated with alternating layers of granular and fibrous crystals. Thus, even though in previous studies it has been concluded that these compositional differences within coral skeletons are attributable to physiologically controlled 'vital effects' (*e.g.* Blamart *et al.*, 2007; Meibom *et al.*, 2008; Juillet-Leclerc *et al.*, 2009; Rollion-Bard *et al.*, 2010), they are entirely consistent with abiogenic aragonite precipitated experimentally from seawater in the absence of any biological controls.

However, compositional variability within the bundles of aragonite fibres that make up the bulk of the coral skeleton cannot be explained solely by vaariations in crystal growth rate. The composition of abiogenic aragonite, calculated using the exchange coefficients from Experiment 1 of Holcomb *et al.* (2009), is compared with that of aragonite fibre bundles in coral skeleton in Figure 4. At this relatively small crystal growth rate, the Mg/Ca ratio of abiogenic aragonite is smaller than that of coral skeleton, while the Ba/Ca ratio is a slightly greater and the Sr/Ca ratio doesn't changed significantly. While these exchange coefficients do produce a closer match to coral skeleton, it does not appear possible that an exact match can be obtained simply by adjusting the crystal growth rate due to the differing responses of $K_D^{Mg/Ca}$, $K_D^{Sr/Ca}$ and $K_D^{Ba/Ca}$. Also, variations in crystal-growth rate cannot explain the positive correlation between Mg/Ca ratio and water temperature, combined with decreasing Sr/Ca and Ba/Ca ratios, found in coral skeleton. Therefore, while the influences of temperature and crystal growth rate on element partitioning appear to play important roles in determining the composition of coral skeleton, they cannot fully reproduce the observed compositional variability. However, the compositions of coral skeleton and abiogenic aragonite can be fully reconciled once the influence of Rayleigh fractionation is taken into account.

5. Rayleigh fractionation and compositional variability in coral skeleton

Physicochemical models for coral biomineralization implicitly require that Rayleigh fractionation play some role in determining the compositional variability in coral skeleton. In order to overcome the nucleation barrier and allow abiogenic aragonite to precipitate, the polyp must isolate seawater from the external environment and manipulate conditions at the site of calcification. As noted above, several lines of evidence indicate that corals achieve this by elevating the saturation state of the calcifying fluid, although some role for organic molecules in lowering the nucleation barrier cannot be entirely ruled out. The important point is that, in this scenario, aragonite does not precipitate from an infinite reservoir of seawater. Rather, crystal growth occurs in an isolated space and the composition of the calcifying fluid changes continuously in response to precipitation of aragonite. This process is governed by the Rayleigh distillation equation (Rayleigh, 1896).

It is the behaviour of the Mg/Ca ratio of coral skeleton that provides the key insight into the importance of Rayleigh fractionation. As discussed earlier, the relationship between Mg/Ca ratio and temperature in coral skeletons is the opposite of that predicted from abiogenic aragonite. During precipitation from an infinite reservoir, the Mg/Ca ratio of abiogenic aragonite is controlled by element partitioning and the composition of seawater. Since $K_D^{Mg/Ca}$ decreases with increasing temperature, the Mg/Ca ratio of the aragonite does also. However, it is well established that in coral skeleton the Mg/Ca ratio increases with increasing temperature (Mitsuguchi *et al.*, 1996; Sinclair *et al.*, 1998; Fallon *et al.*, 1999; Wei *et al.*, 2000; Watanabe *et al.*, 2001; Reynaud *et al.*, 2007). It is this discrepancy, more than anything else, which separates compositional variability in coral skeleton from that predicted from experimentally precipitated abiogenic aragonite. Neither temperature nor crystal-growth rate (alone or in combination) is capable of explaining the combined variability of Mg/Ca, Sr/Ca and Ba/Ca ratios in coral skeletons.

The increase in coral skeleton Mg/Ca ratio with increasing temperature, combined with decreases in both Sr/Ca and Ba/Ca ratios, can be explained by a Rayleigh process in which the mass of aragonite precipitated from an isolated 'batch' of calcifying fluid increases with increasing temperature. Such a temperature-dependent increase in the mass of aragonite precipitated is consistent with results from the *Acropora* culturing experiments of Reynaud *et al.* (2007), in which calcification rate increases by nearly a factor 6 as temperature increases from 21 to 29°C. This change in calcification rate is accompanied by a 30% increase in the Mg/Ca ratio. Therefore, the apparently anomalous temperature dependence of the Mg/Ca ratio of coral skeleton is actually related to its compatibility. Because $K_D^{Mg/Ca}$ is $\ll 1$, whereas $K_D^{Sr/Ca}$ and $K_D^{Ba/Ca}$ are both greater >1, the Mg/Ca ratio of the calcifying fluid increases continuously as aragonite precipitates, whereas the Sr/Ca and Ba/Ca ratios both decrease. The larger the mass of aragonite that precipitates, the stronger this effect becomes. Therefore, when the mass of aragonite precipitated from each 'batch' of calcifying fluid increases with increasing temperature, it produces a negative correlation between Mg/Ca and temperature and strengthens the apparent temperature dependence of Sr/Ca and Ba/Ca ratios. Results from precipitation calculations demonstrate that seasonal changes in the amount of aragonite precipitated by a coral from a fixed volume of calcifying fluid, combined with the effect of seasonal temperature cycles on element partitioning, can reproduce the Mg/Ca, Sr/Ca and Ba/Ca variations observed in the coral skeleton (Fig. 5). Therefore, the most important control on the composition of coral skeleton is Rayleigh fractionation, with temperature contributing only a small proportion of the total compositional variability.

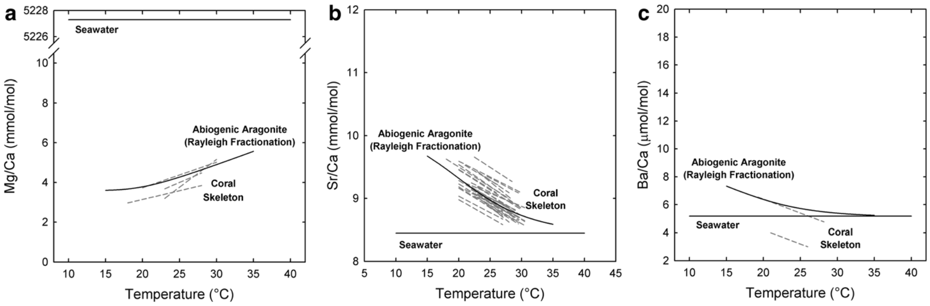

Fig. 5. Comparisons of (***a***) Mg/Ca ratios, (***b***) Sr/Ca ratios, and (***c***) Ba/Ca ratios in coral skeleton (dashed grey curves) with that of aragonite precipitated from an isolated reservoir of seawater (solid black curves). The positive correlation between Mg/Ca and temperature results from an increase in the mass of aragonite precipitated from each 'batch' of calcifying fluid. The composition of abiogenic aragonite was calculated for seawater having a Mg/Ca ratio of 5.2 mol/mol, Sr/Ca ratio of 8.5 mmol/mol, and Ba/Ca ratio of 5.2 µmol/mol. Experimentally determined $K_D^{Mg/Ca}$, $K_D^{Sr/Ca}$, and $K_D^{Ba/Ca}$ values were calculated from data for fibrous aragonite at 25°C from Holcomb *et al.* (2009) with temperature dependence estimated from the data of Gaetani & Cohen (2006). Relationships between water temperature and Mg/Ca, Sr/Ca and Ba/Ca ratios of coral skeleton are the same as in Figure 4.

6. A Rayleigh-based, multi-element approach to coral palaeo-thermometry

Recognition of the role of Rayleigh fractionation in coral biomineralization provides the basis for a new approach to coral thermometry that is fundamentally different from existing empirical calibrations. By combining analyses of multiple elemental ratios (*e.g.* Mg/Ca, Sr/Ca and 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 skeletogenesis (Gaetani *et al.*, 2010). Unlike conventional coral thermometers, this approach does not rely on calibrations involving living corals. Rather, considering coral skeletogenesis as a biologically mediated, physicochemical process provides a means to extract reliable temperature information from the skeleton using a set of experimentally determined partition coefficients and the Rayleigh equation. Moreover, because this approach is based on a model that quantitatively describes the 'vital effect', it may be applicable both across species and to corals growing in vastly different environments.

The conceptual basis for Rayleigh-based, multi-element coral thermometry is illustrated in Figure 6. The concentration of any minor element, relative to Ca, in aragonite precipitated from an isolated 'batch' of calcifying fluid is described by the following solution to the Rayleigh distillation equation:

$$\frac{\bar{C}_i^{\text{Aragonite}}}{\bar{C}_{Ca}^{\text{Aragonite}}} = \frac{C_i^0}{C_{Ca}^0}\frac{1 - FL^{D_i^{\text{Aragonite}-\text{Seawater}}}}{1 - FL^{D_{Ca}^{\text{Aragonite}-\text{Seawater}}}} \tag{1}$$

where $\bar{C}_i^{\text{Aragonite}}$ is the average concentration of element i in the aragonite, C_i^0 is the concentration of element i in the calcifying fluid as precipitation begins, FL is the mass fraction of the initial fluid remaining when aragonite precipitation ends, and $D_i^{\text{Aragonite}-\text{Seawater}}$ is the Nernst aragonite-seawater partition coefficient ($D_i^{\text{Aragonite}-\text{Seawater}} = C_i^{\text{Aragonite}}/C_i^{\text{Seawater}}$, where C_i^j is the weight concentration of element i in phase j). According to equation 1, elemental ratios in aragonite precipitated during a Rayleigh process are determined by three factors: (1) fluid composition (in this case seawater), (2) partition coefficients, which depend on both temperature and crystal-growth rate, and (3) the mass of aragonite that precipitates from a 'batch' of calcifying fluid ($1 - FL$). If it is assumed that crystal-growth rate does not vary significantly during precipitation of fibrous aragonite, partition coefficients are dependent only on temperature. In this case a given elemental ratio, *e.g.* a Sr/Ca ratio of 8.97 mmol/mol, does not represent a unique temperature but, rather, a curve on a plot of temperature *vs.* the mass of aragonite precipitated (Fig. 6). This is the reason that thermometers based on a single-element ratio are unreliable. Individual corals living at identical conditions may precipitate different amounts of aragonite at a given temperature, leading to variable relationships

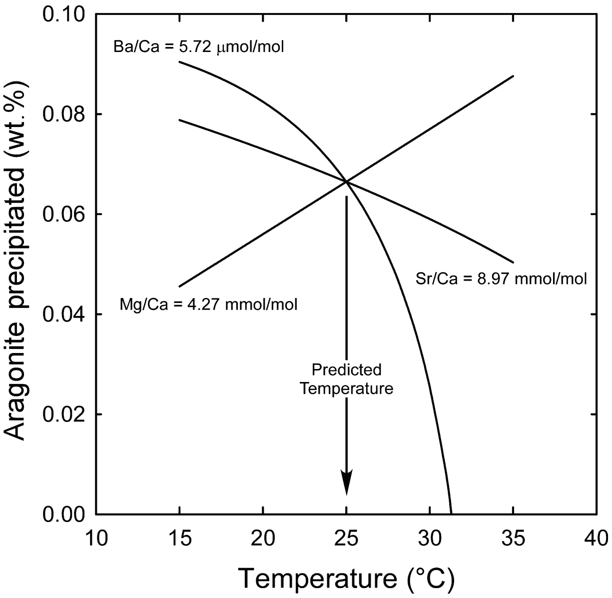

Fig. 6. Curves of constant Mg/Ca, Sr/Ca and Ba/Ca ratios calculated for aragonite precipitated from seawater using equation 1 and aragonite-seawater exchange coefficients calculated from the experimental data of Holcomb *et al.* (2009). These curves intersect at only one combination of temperature and mass of aragonite precipitated, providing the basis for Rayleigh-based, multi-element thermometry.

between Sr/Ca ratio and temperature. However, if the number of element ratios that are measured is increased, so that it is also known that the Mg/Ca ratio of the aragonite is 4.27 mmol/mol and the Ba/Ca ratio is 5.72 μmol/mol, a series of temperature *vs.* *FL* curves can be constructed that intersect at a unique point. It is this intersection that allows temperatures to be reliably extracted from coral skeleton using Rayleigh-based, multi-element thermometry. By taking the approach of solving for both temperature and *FL*, rather than assuming that Sr/Ca depends only on temperature, the uncertainty associated with single-element ratio thermometry is eliminated.

Note that equation 1 differs from the solution to the Rayleigh distillation equation used by Elderfield *et al.* (1996) and by Gagnon *et al.* (2007) to model biomineralization in foraminfera and deep-sea corals, respectively. Those studies relied on an equation that describes the instantaneous solid composition throughout precipitation of a ‘single batch’ of calcifying fluid:

$$\frac{C_i^{\text{Aragonite}}}{C_{Ca}^{\text{Aragonite}}} = K_D^{i/Ca}\frac{C_i^0}{C_{Ca}^0}\left(\frac{C_{Ca}^{\text{Seawater}}}{C_{Ca}^0}FL\right)^{K_D^{i/Ca}-1} \tag{2}$$

where C_i^j is the instantaneous concentration of element i in phase j (*e.g.* Eq. 1.5.9 of Albarède, 1995). Given that $FL \approx 1$, equation 2 was simplified to:

$$\frac{C_i^{\text{Aragonite}}}{C_{Ca}^{\text{Aragonite}}} = K_D^{i/Ca} \frac{C_i^0}{C_{Ca}^0} \left(\frac{C_{Ca}^{\text{Seawater}}}{C_{Ca}^0} \right)^{K_D^{i/Ca}-1} \tag{3}$$

Equation 1 describes the average composition of aragonite precipitated from a 'batch' of calcifying fluid. It is, therefore, more appropriate for modelling seasonal variations in the composition of coral skeleton than equation 3 because seasonal variability occurs over length scales much greater than does precipitation of a single batch of calcifying fluid. Furthermore, calculating the average composition of aragonite precipitated from individual batches of fluid takes into account the averaging that occurs naturally at the length scales on which coral skeleton is sampled.

Carrying out Rayleigh-based, multi-element thermometry using equation 1 requires a quantitative understanding of the temperature dependence of element partitioning between aragonite and seawater. Therefore, expressions describing the temperature dependence of $D_{Mg}^{\text{Aragonite-Seawater}}$, $D_{Ca}^{\text{Aragonite-Seawater}}$, $D_{Sr}^{\text{Aragonite-Seawater}}$, and $D_{Ba}^{\text{Aragonite-Seawater}}$ were derived by fitting experimental data, and substituted into equation 1 to derive a temperature-dependent Rayleigh equation for each elemental ratio. The partitioning expressions are as follows:

$$\ln D_{Mg}^{\text{Aragonite-Seawater}} = -4.86370 + \frac{1706.2460}{(T + 273.15)} \qquad r^2 = 0.9891 \tag{4}$$

$$\ln D_{Ca}^{\text{Aragonite-Seawater}} = 8.2384 - \frac{233.4766}{(T + 273.15)} \qquad r^2 = 0.8199 \tag{5}$$

$$D_{Sr}^{\text{Aragonite-Seawater}} = 2199.6710 - 7.1050 \times T \qquad r^2 = 0.8995 \tag{6}$$

$$\ln D_{Ba}^{\text{Aragonite-Seawater}} = -0.6959 + \frac{2658.4031}{(T + 273.15)} \qquad r^2 = 0.9823 \tag{7}$$

where T is temperature in Celsius.

Equation 1 cannot be solved explicitly for temperature, so that a global minimization procedure is used. First, the Mg/Ca, Sr/Ca and Ba/Ca ratios are calculated for each analysed spot on the coral skeleton using a set of initial guesses for T, FL and calcifying fluid composition. Constant values were used as starting points for T and FL, combined with the Mg/Ca, Sr/Ca and Ba/Ca ratios for Vineyard Sound seawater (Gaetani & Cohen, 2006). Element ratios predicted by the Rayleigh equations on the basis of these starting guesses are then compared to measured values by calculating the sum of the squared percentage difference between the two:

$$\Sigma(100 \times (i/Ca_{\text{Rayleigh}} - i/Ca_{\text{Measured}}) \big/ i/Ca_{\text{Measured}})^2 \tag{8}$$

where i/Ca_{Rayleigh} and i/Ca_{Measured} are the element-to-calcium ratio predicted by the Rayleigh equation and measured in the coral skeleton, respectively. The initial guesses for T, FL, C^0_{Mg}/C^0_{Ca}, C^0_{Sr}/C^0_{Ca}, and C^0_{Ba}/C^0_{Ca} are then incrementally modified using the Nelder-Mead simplex algorithm of Lagarias *et al.* (1998) until equation 8 reaches a global minimum (*i.e.* the smallest possible value). This algorithm does a better job of avoiding local minima (*i.e.* places where changing any variable increases the value of equation 8, but the smallest possible value has not been achieved) when FL is assumed to be a polynomial function of T:

$$FL = c_1 + c_2(T + 273.15)^{-1} + c_3(T + 273.15) + c_4(T + 273.15)^2 \tag{9}$$

where T is temperature in Celsius and c_i are regression coefficients.

The precision and accuracy of our Rayleigh-based, multi-element approach to coral thermometry can be demonstrated using the compositions of *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 known values is 2 × 52 (ratios) = 104 and the number of unknown variables in the Rayeigh equations is 52 (temperatures) + 7 (regression coefficients) = 59, so that the system of equations is mathematically over-constrained. The Sr/Ca ratio of newly grown *Acropora* skeleton decreases monotonically from 9.59 ± 0.02 mmol/mol at 21°C to 9.16 ± 0.01 mmol/mol at 29°C, while Mg/Ca increases from 3.76 ± 0.03 to 4.90 ± 0.04 mmol/mol. The measured calcification rate increases from 0.061 ± 0.007% day^{-1} at 21°C to 0.35 ± 0.03% day^{-1} at 29°C.

If the Mg/Ca and Sr/Ca ratios of the *Acropora* calcifying fluid are insensitive to temperature (*i.e.* they are the same in each experiment), 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 temperature. The latter should correspond to the temperature at which the corals were cultured. This is illustrated in Figure 7 using global minimization results for the culturing experiment carried out at 27°C. If the mass of aragonite precipitated from each 'batch' of calcifying fluid is held constant, both Mg/Ca and Sr/Ca ratios vary as a function of temperature alone (solid curves). If temperature is held constant, both ratios vary with the mass of aragonite precipitated (dashed curves). There is only one combination of temperature and aragonite precipitated (intersection of solid and dashed curves) that reproduces both the Mg/Ca (4.62 ± 0.08 mmol/mol) and Sr/Ca (9.20 ± 0.06 mmol/mol) ratios of coral skeleton from the culturing experiments. This corresponds to 0.155 ± 0.003 wt.% aragonite precipitated, or precipitation of ~93% of the Ca^{2+} initially in the seawater, and a temperature of 26.75 ± 0.25°C, which is within the uncertainty of the experimental temperature. Global minimization results for 21–29°C are shown in Figure 8. The Mg/Ca and Sr/Ca ratios of the *Acropora* skeletons are accurately reproduced by Rayleigh fractionation (Fig. 8a,b), and there is excellent agreement between temperatures predicted by Rayleigh-based, multi-element thermometry and those at which the *Acropora* were cultured, with a mean uncertainty of ± 0.35°C (Fig. 8c).

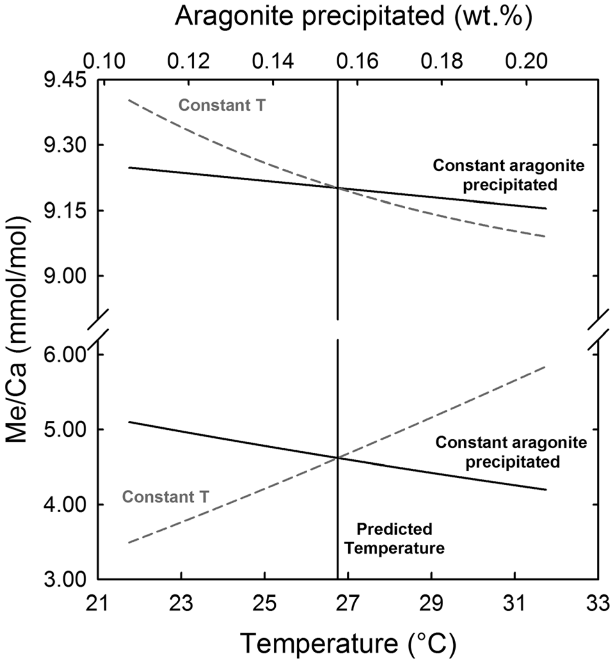

Fig. 7. Results from Rayleigh-based, multi-element thermometry on *Acropora* cultured at 27°C by Reynaud *et al.* (2007). The upper part of figure shows results for Sr/Ca and the lower part results for Mg/Ca. There is only one combination of temperature and aragonite precipitated that reproduces both Mg/Ca and Sr/Ca ratios of coral skeleton from the culturing experiments. This corresponds to 0.155 wt.% of aragonite precipitated at 26.75°C. The solid curves show how Mg/Ca and Sr/Ca ratios vary with temperature when 0.155 wt.% aragonite is precipitated. Dashed curves show how Mg/Ca and Sr/Ca ratios vary with the mass of aragonite precipitated at a temperature of 26.75°C.

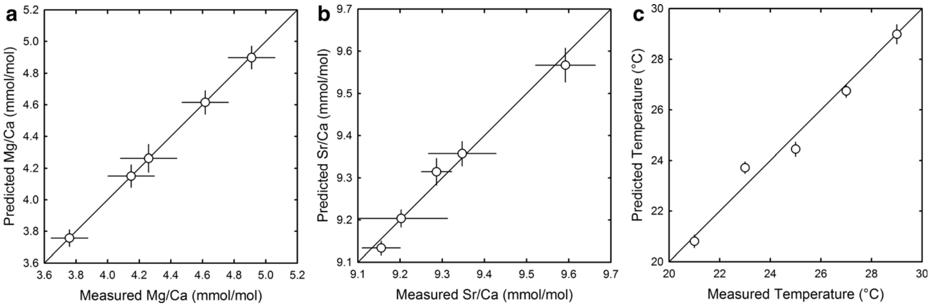

Fig. 8. Comparisons of predicted and measured (***a***) Mg/Ca ratios, (***b***) Sr/Ca ratios and (***c***) temperature from Rayleigh-based, multi-element coral thermometry carried out on *Acropora* cultured in the laboratory at 21–29°C by Reynaud *et al.* (2007). Solid lines are 1:1 relationships. All uncertainties are 2 standard errors.

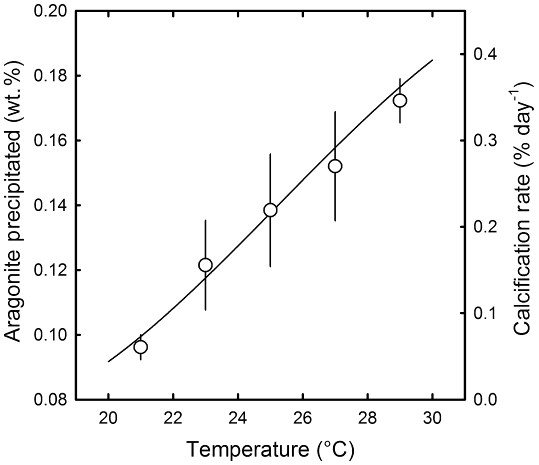

Fig. 9. Relationship between temperature and mass of aragonite precipitated from each 'batch' of calcifying fluid derived from Rayleigh-based, multi-element coral thermometry for *Acropora* cultivated in the laboratory at 21–29°C by Reynaud *et al.* (2007) (solid curve). Shown for comparison is the change in calcification rate reported for these corals by Reynaud *et al.* (2007) (open circles).

The aragonite precipitated ranges from 0.098 ± 0.002 wt.% (~81% of initial Ca^{2+} from the seawater) at 21°C to 0.176 ± 0.003 wt.% (~95% of initial Ca^{2+} from the seawater) at 29°C (Fig. 9).

6. Conclusions

Comparisons of morphological and compositional variability in abiogenic aragonites produced experimentally from highly supersaturated seawater with that of aragonites produced by corals have provided important insights to the biomineralization mechanisms and the factors governing compositional variability in coral skeletons. Through experimental manipulation of temperature and crystal-growth rates, we have identified three principal factors controlling the Mg/Ca, Sr/Ca, and Ba/Ca ratios of abiogenic aragonite grown directly from seawater. These are water temperature, crystal growth rate, and Rayleigh fractionation (through variations in the mass of aragonite precipitated from a volume of fluid). In the abiogenic aragonites, Mg/Ca, Sr/Ca and Ba/Ca ratios covary systematically and predictably, all increasing with increasing crystal growth rate and all decreasing with increasing seawater temperature. In coral skeletons, many of the compositional anomalies previously identified as 'vital effects' can be explained by the same processes *i.e.* variations in crystal growth rate and Rayleigh fractionation, without invoking differential transport of Mg^{2+} and other ions, or organic matrix control of crystal growth. Indeed, compositional differences between granular (faster-growing) and fibrous (slower-growing) crystals in coral skeletons are consistent with growth-dependent variability observed in abiogenic aragonites. On the other hand, trends in Mg/Ca, Sr/Ca and Ba/Ca ratios of coral skeletons on seasonal timescales cannot be explained solely in terms of temperature or crystal-growth rate, or the two in combination. Rather, the increase in Mg/Ca and simultaneous decrease in Sr/Ca and Ba/Ca that occur with increasing temperature are consistent with Rayleigh fractionation as the dominant control on these timescales. Identifying the processes involved in driving compositional variability in coral skeleton and the origin of the 'vital effect' has enabled us to develop a fundamentally different approach to coral palaeo-thermometry that is based on extracting the small component of the geochemical signal that is driven solely by temperature. If successful, the same approach can be applied to a broad range of biogenic $CaCO_3$ tests and skeletons: using abiogenic aragonite and calcite precipitation experiments as a framework within which to identify, understand and conquer the ubiquitous 'vital effect'.

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