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Biological forcing controls the chemistry of reef-building coral skeleton

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[1] We present analyses of major elements C and Ca and trace elements N, S, Mg and Sr in a *Porites* sp. exoskeleton with a spatial resolution better than ~ 150 nm. Trace element variations are evaluated directly against the ultra-structure of the skeleton and are ascribed to dynamic biological forcing. Individual growth layers in the bulk fibrous aragonite skeleton form on sub-daily timescales. Magnesium concentration variations are dramatically correlated with the growth layers, but are uncorrelated with Sr concentration variations. Observed (sub)seasonal relationships between water temperature and skeletal trace-element chemistry are secondary, mediated by sensitive biological processes to which classical thermodynamic formalism does not apply. **Citation:** Meibom, A., S. Mostefaoui, J.-P. Cuif, Y. Dauphin, F. Houlbrequé, R. Dunbar, and B. Constantz (2007), Biological forcing controls the chemistry of reef-building coral skeleton, *Geophys. Res. Lett.*, 34, L02601, doi:10.1029/2006GL028657.

1. Introduction

[2] Coral-derived paleoclimate reconstructions are empirically based on observations that skeletal oxygen isotopic composition and certain trace-element abundances (e.g., Sr and Mg) vary in response to changes in water temperature. Traditionally, equilibrium thermodynamics has been invoked to explain these relationships [Epstein *et al.*, 1953; Mitsuhashi *et al.*, 1996; Smith *et al.*, 1979; Swart and Leder, 1996]. However, a detailed understanding of the biomineralization process is lacking and a critical question is the role of biological processes in controlling skeletal composition. Without such knowledge, it is difficult to quantitatively assess the general applicability and precision of coral-based paleoclimate reconstructions.

[3] Reef-building coral skeletons consist primarily of fibrous aragonite. Understanding the level of biological influence over the chemistry and growth of this skeletal component is the focus of this study. A number of recent micro-analytical studies of coral skeletons have uncovered large amplitude chemical variations that cannot be ascribed to external environmental variability [Allison, 1996; Allison *et al.*, 2005; Cohen *et al.*, 2001; Cuif *et al.*, 2003; Hart and

Cohen, 1996; Meibom *et al.*, 2003, 2006; Sinclair, 2005]. Until recently it has not been possible to perform sensitive chemical analysis at the sub-micrometer length scales that are characteristic of the skeletal ultra-structure, which could provide a deeper insight into the skeletal growth processes.

2. Results

[4] *Porites* is the most frequently used coral genus for paleoenvironmental reconstructions. With the NanoSIMS N50 ion microprobe at the Muséum National d'Histoire Naturelle a chemical analysis of a *Porites* sp. skeleton has been carried out. Materials and methods are discussed in the auxiliary material¹. As a guide to the analyses, the *Porites* sp. skeletal architecture is shown in Figure 1. Figure 2 shows the NanoSIMS data accompanied by an SEM image of the corresponding skeleton. The NanoSIMS traverse starts at the edge of the skeleton and proceeds to the right - towards the interior. It passes close to, but does not cross a center of calcification (COC), which is visible in the right hand side of the SEM image.

[5] Magnesium exhibits dramatic variability in the layered fibrous aragonite. Over length scales of 2–5 μm , the Mg/Ca ratio changes from ~ 4 mmol/mol to >7.5 mmol/mol (Figure 2). Qualitatively, these variations are similar to those observed previously in *Pavona* sp. [Meibom *et al.*, 2004], but the Mg/Ca variations recorded in this *Porites* specimen are of larger magnitude: the total range in Mg/Ca spans a factor of three. These oscillating Mg/Ca variations are not due to large variations in the $^{40}\text{Ca}^+$ signal, which typically varies less than $\sim 5\%$ on similar length scales and does not correlate with the Mg signal (Figure 3c). Mg/Ca oscillations therefore reflect variations in Mg concentration within the skeleton. Furthermore, the Mg/Ca oscillations are spatially correlated with components of the layered ultra-structure of the fibrous aragonite. While previous studies have investigated the distribution and speciation of Mg in biogenic calcite [Davis *et al.*, 2004] very little work has focused on the role that Mg plays in aragonite biomineralization. Dissolution experiments on coral skeletons suggest that Mg occurs in a dispersed mineral phase that is more soluble than aragonite [Amiel *et al.*, 1973]. It has also been suggested that the Mg/Ca fluctuations might be a signature of the production of an amorphous calcium carbonate phase [Meibom *et al.*, 2004] that is transiently stable during skeletal formation [Weiner *et al.*, 2003]. The identification of a distinct high-Mg phase in the fibrous aragonite skeleton is an important research objective. Combined NanoSIMS,

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Figure 1. Architecture of the *Porites sp.* skeleton. (a) Macroscopic morphology of the skeleton after removal of the tissue layer. Growth direction is towards the viewer. The skeleton consists of aligned calices, each consisting of a near circular wall, from which individual septa protrude towards the center. Scale-bar: ~1 mm. (b) SEM image of a broken septa surface showing the characteristic central COC overgrown by fibrous aragonite. Scale-bar: ~100 μm . (c) Optical microscope image in transmitted and polarized light of a polished thin-section of a septa cut transversely to the growth direction. The fibrous aragonite appears to be organized into bundles (one is indicated by arrows) radiating away from the COC. These fiber bundles are conventionally considered to be the product of 'free crystal growth' from a supersaturated solution [Bryan and Hill, 1941]. (d) SEM image of a septa (cut transversely to the growth direction, polished and etched) reveals that the fibrous aragonite is in fact a complex, layered structure, formed by a cyclic formation of layers each 2–5 micrometers in thickness [Cuif et al., 2003]. Scale-bar: ~10 μm .

TEM and synchrotron-based X-ray spectroscopy are under way in an effort to investigate this issue further.

[6] The Sr/Ca ratio also exhibits significant fluctuations along the traverse. Near the edge of the skeleton (left-hand side in Figure 2) several clear Sr/Ca oscillations are observed over length scales of 2–5 μm , with amplitudes up to ~15% relative to the average Sr/Ca ratio. In general, the Sr/Ca ratio does not correlate with Mg/Ca, nor does it correlate clearly with the ultra-structure of the fibrous aragonite. Around 43 μm into the traverse there is a sharp positive spike in the Sr/Ca ratio that coincides with a broad negative fluctuation in Mg/Ca and with positive fluctuations in N/C and S/C, respectively. After this feature, the Sr/Ca ratio decreases in the right hand side of the traverse, in the vicinity of the COC.

[7] The distribution of organics in the skeleton is elucidated by the observation that the $^{40}\text{Ca}^+$ signal correlates negatively with the $^{12}\text{C}^+$ signal (Figure 3a). A relatively high $^{12}\text{C}^+$ signal is obtained in the vicinity of the COC, indicating that the abundance of organics increases close to the COC. Sulfur, which is thought to be present in the skeleton primarily as sulfated polysaccharides, is known to increase towards the COC region [Cuif et al., 2003] and our data are consistent with this observation. The S/C ratio increases significantly in the right hand side of the traverse (i.e., in the vicinity of the COC), supporting the interpretation that S is associated primarily with organics. Further-

Figure 2. NanoSIMS profiles of Mg/Ca and Sr/Ca (calibrated), and $^{32}\text{S}/^{12}\text{C}$, $^{12}\text{C}^{14}\text{N}/^{12}\text{C}$ (uncalibrated) across a segment of a *Porites sp.* skeleton. A SEM image of the polished and etched surface of the skeleton traversed by the NanoSIMS is shown below. The hatched line indicates the position of the NanoSIMS traverse. The coral formed this skeleton by adding layers of aragonite onto a skeletal structure that was first formed around the COC [Cuif and Dauphin, 2005]. The general growth direction is therefore from right to left. Error-bars, shown to the left of each profile (in frames), are $\pm 1\sigma$.

Figure 3. Inter-element relationships from the NanoSIMS traverse in Figure 2. Solid lines are linear fits through the data.

more, the S concentration exhibits clear oscillations (with amplitudes of about 20% on length scales as short as $1 \mu\text{m}$) and exhibits large spikes around $43 \mu\text{m}$ (Figures 2 and 3b). In contrast, N, which is primarily associated with proteinaceous molecules [Constantz and Weiner, 1988], exhibits a flat and featureless distribution with the exception of the positive fluctuation around $43 \mu\text{m}$. Thus, in general, N is homogeneously distributed in the fibrous parts of the

skeleton, at least on length scales comparable to the beam-size of the ion microprobe, here about 100 nm .

3. Discussion

[8] The annual extension rate of the *Porites* coral studied here is $\sim 11 \text{ mm}$, which corresponds to an average daily linear extension rate of $\sim 30 \mu\text{m}$. Seasonal fluctuations in extension rate range from 16 to $46 \mu\text{m/day}$ [Meibom et al., 2003]. The lateral (thickening) growth rate is comparable, certainly for the fibrous skeleton formed close to the COC. Thus, as a first order estimate, assuming a nearly linear growth rate, the growth-time represented by the analyzed skeleton is 1.5 to 3.5 days. There are eight full Mg/Ca oscillations corresponding to eight growth layers in Figure 2. This provides a strong indication that individual growth layers are deposited on a timescale significantly shorter than 24 hours. Within the plausible uncertainty of this estimate, it is possible that up to five growth layers are formed in 24 hours. In contrast, it is very unlikely that only one growth layer is formed within a full diurnal cycle. Individual growth layers are therefore the result of a continuous and active biological forcing of the skeletal growth process, as opposed to a passive biological response to the diurnal cycle, a conclusion also reached in several other recent studies [e.g., Clode and Marshall, 2003; Cuif et al., 2003; Meibom et al., 2004; Raz-Bahat et al., 2006; Stolarski, 2003]. Furthermore, the short growth timescale recorded in the skeleton are driven by changes in the external marine environment. Hourly measurements of ocean temperature on a nearby Kenya reef during 1995/1996 reveal diurnal variability of less than 1°C . In thermodynamic equilibrium between seawater and inorganically precipitated aragonite such temperature variations can induce Sr/Ca variations of about 1% [Kinsman and Holland, 1969], far less than the variations measured here.

[9] Non-biological models for trace element variation in the coral skeleton predict inter-element correlations that are not observed here [e.g., Cohen et al., 2006; Gaetani and Cohen, 2006]. Such ‘inorganic’ models invoke kinetic fractionations and/or changing levels of super-saturation of a hypothetical reservoir that is assumed to exist between the calicoblastic ectoderm and the surface of the growing skeleton, the so-called “extracytoplasmic calcifying fluid”. However, all modern observations of the interface between the skeleton and the calicoblastic ectoderm clearly demonstrate a tight physical contact between the skeleton and the calicoblastic ectoderm, leaving no space for such a reservoir [Brown et al., 1983; Clode and Marshall, 2002; Domart-Coulon et al., 2006; Johnston, 1980; Muscatine et al., 1997; Le Tissier, 1990]. Furthermore, none of the non-biological models offer an explanation of the general observation that skeletal chemical and isotopic composition are not uniform over the skeleton. It is an observational fact that COC and fibrous aragonite are distinctly different (compositionally as well as isotopically) and that COC are further away from thermodynamic equilibrium than fibrous aragonite [Meibom et al., 2006; Rollion-Bard et al., 2003a; Sinclair et al., 2006]. In absence of a non-biological model that offers an explanation for these recent micro-analytical observations, it is proposed instead that the data indicate differential trans-

port and incorporation of major and trace elements into the skeleton.

[10] Strontium is in solid solution in the CaCO_3 structure [Allison et al., 2005] and a strong correlation is observed between Ca and Sr (Figure 3c). Towards the COC, the $^{88}\text{Sr}^+$ signal drops because the carbonate phase is increasingly diluted by the embedded organics. However, if the carbonate-to-organics abundance ratio was the only changing parameter along the traverse, the Sr/Ca ratio should be essentially constant. Nonetheless, there is a significant residual Sr/Ca variability (on the order of 15–25%) that is much larger than the analytical precision (± 2 –3%; 1σ) and that cannot be explained by changes in the carbonate/organics ratio (Figure 3c). These Sr/Ca variations, which are not correlated with Mg/Ca, most likely result from biological processes capable of changing the Sr/Ca ratio of the skeleton on sub-daily timescales. It has been argued that Sr^{2+} and Ca^{2+} are transported across the calicoblastic cell layer through the same voltage sensitive, transcellular channel [Ferrier-Pages et al., 2002; Tambutte et al., 1996]. However, because the Sr/Ca ratio fluctuates both positively and negatively relative to the mean and does not correlate with the skeletal ultrastructure (Figure 2), we propose that biological processes other than this particular transport mechanism are important on short timescales; perhaps on timescales characteristic of cellular metabolic turnover rates. The observed lack of correlation between Mg and Sr strongly suggests that these two elements have dramatically different transport mechanisms or pathways from the environment into the skeleton. Similarly, S is not correlated with Mg. The S distribution shows clear oscillations in the fibrous aragonite but, unlike Mg, there is no obvious correlation with the layered ultra-structure. The factors that control the incorporation of sulfated polysaccharides into the skeleton are unknown. However, it is clear that these organic molecules are incorporated into the skeleton with a high degree of spatial and temporal control because COC and fibrous aragonite systematically have different concentrations of S [Cuif et al., 2003; Meibom et al., 2006].

[11] From this and other recent micro-analytical studies it is evident that the chemistry of the bulk coral exoskeleton is under very strong biological influence and that chemical (and stable isotope) variations are strongly coupled with the skeletal ultra-structure [Allison, 1996; Allison et al., 2005; Cohen et al., 2001; Cuif et al., 2003; Meibom et al., 2004, 2006; Rollion-Bard et al., 2003b; Sinclair, 2005]. This raises a fundamental question. Why are correlations often observed between seasonal time-series of skeletal trace-element concentrations and environmental factors (e.g., sea-surface temperature) when, at the ultra-structure level, the incorporation of these trace-elements is clearly not controlled directly by these environmental factors? Transportation of different elements into the skeleton likely takes place across trans-cellular, often protein-mediated pathways and/or in vesicle shuttles [Allemand et al., 2004; Erez, 2003]. These transport mechanisms are sensitive to temperature variations. In general, cellular properties such as membrane composition, fluidity, membrane-protein activities and metabolic processes are temperature sensitive [McKinley and Hazel, 2000; Tchernov et al., 2004; Vigh et al., 2005]. Most likely, it is the complex biological response to changes in water temperature (and other envi-

ronmental parameters, such as nutrition) that introduces seasonal and sub-seasonal variations in skeletal chemistry. Importantly, the classic, physio-chemical formalism for inorganic carbonate precipitation does not offer an adequate or relevant description of these processes. A fundamentally new conceptual approach to coral-derived paleo-environmental proxies is therefore needed. The intimate relationship between biological processes at the cellular level and exoskeletal composition must be understood because it carries the potential for greatly improved paleoclimatology.

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