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## Distribution of magnesium in coral skeleton

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[1] Ion micro-probe imaging of the aragonite skeleton of *Pavona clavus*, a massive reef-building coral, shows that magnesium and strontium are distributed very differently. In contrast to strontium, the distribution of magnesium is strongly correlated with the fine-scale structure of the skeleton and corresponds to the layered organization of aragonite fibers surrounding the centers of calcification, which have up to ten times higher magnesium concentration. This indicates a strong biological control over the magnesium composition of all structural components within the skeleton. Magnesium may be used by the coral to actively control the growth of the different skeletal crystal components. **INDEX TERMS:** 4215 Oceanography: General: Climate and interannual variability (3309); 4267 Oceanography: General: Paleooceanography; 3620 Mineralogy and Petrology: Crystal chemistry; 4825 Oceanography: Biological and Chemical: Geochemistry; 4294 Oceanography: General: Instruments and techniques. **Citation:** Meibom, A., J.-P. Cuif, F. Hillion, B. R. Constantz, A. Juillet-Leclerc, Y. Dauphin, T. Watanabe, and R. B. Dunbar (2004), Distribution of magnesium in coral skeleton, *Geophys. Res. Lett.*, 31, L23306, doi:10.1029/2004GL021313.

### 1. Introduction

[2] Scleractinian corals are among the most prolific biomineralizing organisms on Earth [Lowenstam and Weiner, 1989] and massive, reef-building corals are used extensively as proxies for past variations in the global climate. It is therefore of wide interest to understand the degree to which biological versus inorganic processes control the chemistry of the coral skeleton. Early workers considered aragonitic (CaCO<sub>3</sub>) coral skeleton formation as a purely physiochemical process; essentially an inorganic precipitation of aragonite from a supersaturated solution [Bryan and Hill, 1941]. More recent studies have increasingly emphasized the role of a skeletal organic matrix, or intercalated organic macro-molecules that control the macroscopic shape and size of the growing crystals. It is now well established that organic compounds play a key role in controlling the morphology of crystals in a wide variety of calcium carbonate biomineralization processes by binding

to specific sites and thereby causing direction-specific binding energies on the crystal surfaces [Aizenberg *et al.*, 2002; Berman *et al.*, 1993; Cuif *et al.*, 2003; Gotliv *et al.*, 2003; Johnston, 1980; Lowenstam and Weiner, 1989; Orme *et al.*, 2001; Weiner *et al.*, 2003]. Macro-molecules, such as aspartic acid-rich or glutamic proteins [Constantz and Weiner, 1988; Mitterer, 1978; Young, 1971] and sulfated polysaccharides [e.g., Cuif *et al.*, 2003] are known to be embedded within the aragonitic skeletal components of coral. In addition, endosymbiotic algae and the layer of cells adjacent to the mineralizing surface, the calcicoblastic ectoderm, are believed to play important roles in driving and controlling hermatypic coral skeletogenesis [Barnes, 1970; Clode and Marshall, 2002; Johnston, 1980]. However, until recently, it was not possible to obtain trace-elemental analyses of a coral skeleton with sufficiently high spatial resolution and sensitivity to correlate chemical variations with the micrometer (μm) scale organization of its different structural components.

[3] In coral skeletons, individual corallites are composed of two primary structural components (Figure 1). Centers of calcification (COC) are μm-sized, rounded aggregates of randomly oriented, nanometer-sized calcium carbonate crystals embedded in an organic matrix of sulfated polysaccharides and acidic proteins [Constantz and Weiner, 1988; Cuif and Dauphin, 1998; Cuif *et al.*, 2003; Gladfelter, 1982]. The spatial organization of individual COC determines the macroscopic morphology of the skeleton. The COC are overgrown by the second skeleton component, a composite of fibrous aragonite crystals and organic macro-molecules organized into growth layers [Constantz and Weiner, 1988; Cuif *et al.*, 2003] (Figure 1c). This fibrous aragonite composite, of which organic macromolecules constitute on the order of 1 wt% [Cohen and McConnaughey, 2003; Cuif *et al.*, 2004, 2003], constitutes the bulk of the skeleton and gives it mechanical strength. The processes involved in the formation of COC and fibrous aragonite are not well understood in detail.

### 2. Materials and Methods

[4] Using a NanoSIMS NS50 ion microprobe (SIMS: Secondary Ion Mass Spectrometry) [Hillion *et al.*, 1993], we produced images of the Mg and Sr distributions in the COC and adjacent fibrous aragonite in a specimen of the massive, hermatypic shallow water coral *Pavona clavus*, which is used frequently for paleo-climate reconstructions. Our coral specimen was collected live at Bartolomé, Galápagos Islands in January 1995 at a water depth of 3 meters [Wellington *et al.*, 1996]. A thick-section of this coral was cut perpendicular to the growth direction, mounted in epoxy and polished to a 0.25 micrometer surface finish using diamond and silica colloidal suspen-

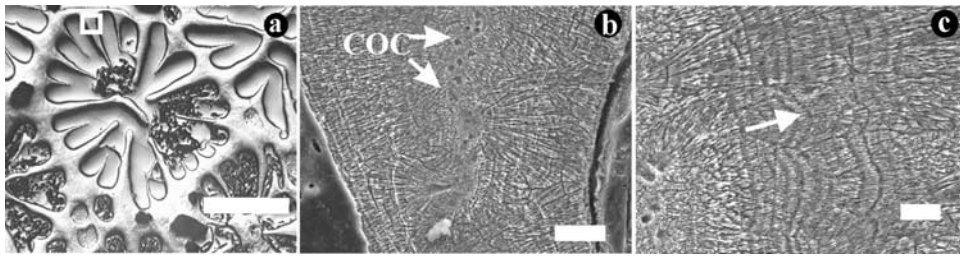
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**Figure 1.** *Pavona clavus* skeletal architecture and ultra-structure. a, Reflected light image of a section of the Bartolomé *Pavona clavus* coral cut perpendicular to the growth direction, mounted in epoxy and polished. Individual corallites consist of a near-circular wall with septa protruding from it and pointing towards the center of the corallite. b, SEM image of a lightly etched [Cuif and Dauphin, 1998] region of a septa (outlined in a) showing the COC overgrown by layers of fibrous aragonite. c, Higher magnification SEM image of an etched surface showing the distinctly layered fibrous aragonite. Each fibrous layer is 2–6  $\mu\text{m}$  wide, depending on the exact orientation of the cut. Arrow indicates direction of growth of fibrous aragonite layers away from COC. Scale bars: a, 1 mm; b, 20  $\mu\text{m}$ ; c, 10  $\mu\text{m}$ .

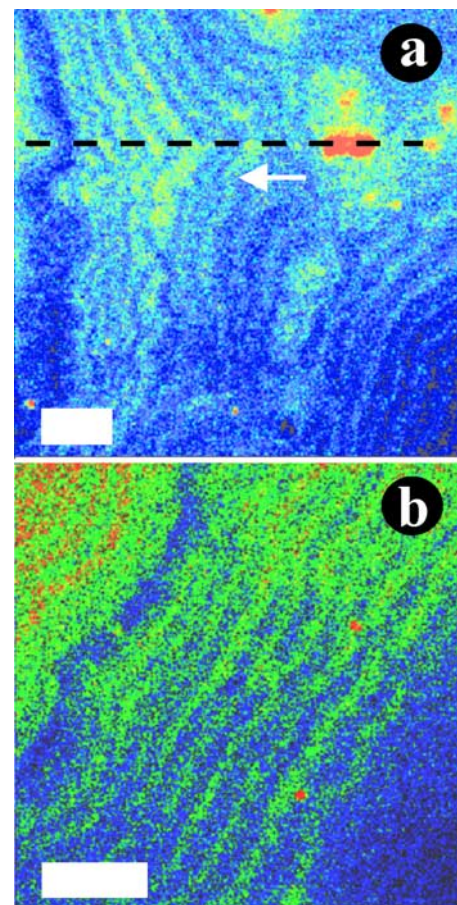
sions. During analyses a 16 keV  $\text{O}^-$  beam of about 10 pA, focused to a diameter of about 0.4  $\mu\text{m}$ , was rastered across a pre-sputtered area on the gold coated sample. Secondary ions of  $^{24}\text{Mg}^+$ ,  $^{40}\text{Ca}^+$  and  $^{88}\text{Sr}^+$  were collected simultaneously in electron multipliers. The mass resolving power ( $M/\Delta M$ ) of the mass spectrometer was about 3000 during all analyses; no mass-interferences on the measured peaks were observed. Magnesium and Sr data were calibrated against electron microprobe analyses of the average Mg and Sr concentration in the fibrous aragonite. We used the JEOL Superprobe 733 at Stanford University operated at 15kV with a beam current of 15nA; dolomite, calcite, and strontianite crystals of known composition were used as standards.

### 3. Results and Discussion

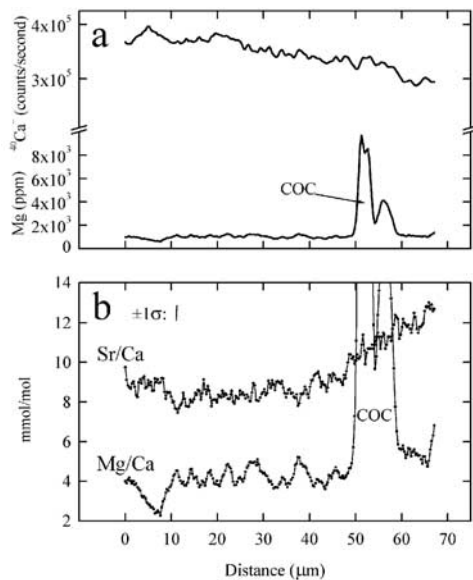
[5] Results are shown in Figures 2 and 3. Several observations arise from these data. First, there is a striking  $\mu\text{m}$ -scale zoning in Mg concentration in the fibrous aragonite composite (Figure 2) that corresponds closely with the layered structure of this material (Figure 1c). Within the regular zoning pattern the Mg concentration varies by as much as a factor of two on a characteristic length scale of a few  $\mu\text{m}$  (Figure 3b). This distinct Mg zoning pattern is ubiquitous in the skeleton. Second, the COC (Figure 2a) have up to one order of magnitude higher Mg concentration than the surrounding fibrous aragonite composite (Figure 3a) and the very high Mg concentrations are strongly localized to the COC (Figure 2a). Such high Mg concentrations in COC have not previously been observed, most likely because of the limited spatial resolution of the analytical techniques applied, which may not have allowed the COC to be completely resolved. Third, in contrast to Mg, the distribution of Sr is more smooth and does not display the same degree of zoning; the distributions of Mg and Sr are not correlated on shorter length scales. Consistent with previous observations [Cohen and McConnaughey, 2003], the Sr concentration increases smoothly towards the COC, forming a “halo” of relatively high Sr surrounding the COC (Figure 3b). In contrast with Mg, the higher Sr concentrations are not strongly localized to the COC (Figure 3b).

[6] It is not likely that the observed variations in Mg concentration in the *Pavona* coral are simply due to localized organic matter in the skeleton; i.e., a strong matrix effect affecting the yield of secondary ions. If this was the

case, variations in the Mg and Ca signals would be correlated. This is not observed (Figure 3a). Figure 3b demonstrates that normalizing Mg to Ca preserves the clear oscillatory banding in the Mg signal evident in Figure 2.



**Figure 2.** The distribution of Mg in different parts of the *Pavona clavus* skeleton. Dark blue colors correspond to relatively low Mg concentrations; green, yellow and red colors correspond to increasingly high Mg concentrations. COC have the highest concentration of Mg (Figure 3). Calibrated transect (dashed line in a) is shown in Figure 3. Arrow indicates direction of growth; c.f. Figure 1c. Scale bars are 10  $\mu\text{m}$ .



**Figure 3.** Magnesium, Ca and Sr analyses along the transect indicated by the dashed line in Figure 2a. a, On short length scales the variations in Ca along the transect are small (<10%), statistical in nature and uncorrelated with the much larger, systematic variations in the Mg concentration. This rules out matrix effects as the cause of the measured Mg variations. A monotonic decrease in the Ca signal towards the right hand side of the plot is likely due to gentle curvature of the sample surface. b, Expanded view of the layered Mg distribution and the Sr distribution.

Instead, the banded Mg micro-distribution might reflect either systematic differences in the amount of Mg in solid solution within the aragonite crystal structure and/or the preferential concentration of Mg at the surfaces of individual aragonite fibers at the initiation or termination of each fibrous growth layer (Figure 1c), as it has been observed in mollusks [Rosenberg *et al.*, 2001] and in foraminifera [Eggins *et al.*, 2004; Erez, 2003]. The presence of surface adsorbed Mg in the COC would be consistent with their high Mg concentration, compared with the surrounding aragonite fibers (Figure 3), due to the larger surface to volume ratio of their constituent nanometer-sized crystals. Another possibility is that the small crystals making up the COC in *Pavona clavus* are calcitic, as observed in *Mussa angulosa* [Constantz and Meike, 1988]. However a recent Raman spectroscopy study of 15 coral species, including *Mussa angulosa*, did not find evidence for calcite [Cuif and Dauphin, 1998].

[7] The time-span involved in formation of the skeletal structures mapped in Figure 2 is on the order of hours to one day [Barnes, 1972; Risk and Pearce, 1992], too short for any external environmental parameters to change significantly. Diurnal temperature changes of up to 1–2°C are possible at Bartolomé. Such temperature variations would correspond to changes in the Mg concentration of less than 5% in thermodynamic equilibrium between aragonite and sea-water [Mitsuhuguchi *et al.*, 1996]; even smaller variations would be expected for Sr. Therefore the Mg and Sr concentration variations documented in Figures 2 and 3 can not be explained by changes in the thermodynamic equilibrium

between aragonite and sea-water. These variations are more likely to result from a strong biological control over the flux of both Mg and Sr to the surface of the growing aragonite skeleton.

[8] Cuif *et al.* [2003] observed a layered distribution of sulfur associated with sulfated polysaccharides embedded within the fibrous aragonite layers and corresponding to the structural growth layers; i.e., similar to the distribution of Mg (Figure 2). It was inferred that cyclic secretion of polysaccharides is directly involved in the mineralization process [Cuif *et al.*, 2003]. Qualitatively similar observations of banded or layered S and Mg distributions have been observed in bivalves [Rosenberg *et al.*, 2001] which are forming their shells under strict biological control [Lowenstam and Weiner, 1989] and in the absence of symbiotic algae. In the bivalve shell, Mg and S are preferentially concentrated at the termination of elongated calcite crystals. Furthermore, these elongated calcite crystals are aligned in a way similar to the aragonite fibers shown in Figure 1c, which give rise to distinct Mg and S banding [Rosenberg *et al.*, 2001], very similar to that observed in corals ([Cuif *et al.*, 2003] and this study). For the bivalve it was inferred that Mg and S-rich organic components are used actively by the organism to control crystal size and morphology [Rosenberg *et al.*, 2001].

[9] Magnesium is known to play a crucial role in regulating the formation of different calcium carbonate phases [Davis *et al.*, 2000; Raz *et al.*, 2000]. Recent advances in the study of calcium carbonate skeletons formed by a variety of organisms have revealed the widespread presence of amorphous calcium carbonate (ACC), either as a stable structural component in the skeleton, or as a transient precursor phase to crystalline polymorphs of calcium carbonate [Addadi *et al.*, 2003; Aizenberg *et al.*, 2002; Raz *et al.*, 2000; Weiner *et al.*, 2003]. Magnesium is an important component of ACC, which can have different degrees of short range order [Raz *et al.*, 2000; Weiner *et al.*, 2003]. In conjunction with organic macro-molecules, Mg is known to stabilize this otherwise inherently unstable phase [Addadi *et al.*, 2003]. ACC can therefore either act as nucleation sites for calcium carbonate crystals, or cause their formation by subsequent transformation into crystalline polymorphs [Addadi *et al.*, 2003; Aizenberg *et al.*, 2002; Weiner *et al.*, 2003]. The unstable and amorphous nature of ACC makes its identification in crystalline calcium carbonate skeletons difficult [Weiner *et al.*, 2003]. However, it is entirely possible that Mg-rich ACC is transiently present in the coral skeleton, where it provides a controlled environment for the nucleation and growth of individual aragonite crystals in the fibrous aragonite layers as well as in COC [Cohen and McConnaughey, 2003]. The Mg-rich bands in the layered fibrous aragonite composite and the high magnesium concentration in COC (Figure 2) might in part be the trace element signature of transient ACC in both skeleton components. Isotopic labeling and wash-out (efflux) experiments using <sup>45</sup>Ca have provided strong evidence for the presence of an unstable calcium carbonate phase in newly formed coral skeleton [Tambutté *et al.*, 1996]. Thus, we propose that temporally and spatially controlled release of Mg to the mineralizing surfaces plays a key role in the formation of the coral skeleton.

[10] The main feature of the Sr profile shown in Figure 3b is the gradual increase in Sr concentration from the fibrous

aragonite crystals into the domain of the COC, forming a "halo" of relatively high Sr concentrations around the COC, qualitatively consistent with previous observations [Cohen and McConnaughey, 2003]. Isotopic labeling experiments have demonstrated that  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  are delivered to the mineralizing surface through the same voltage-sensitive, transcellular pathway located in the calcicoblastic ectoderm [Ferrier-Pages et al., 2002; Tambutté et al., 1996]. Furthermore, incorporation of Sr into the skeleton is inversely correlated with the rate of calcification [Ferrier-Pages et al., 2002]. As a consequence of the enhanced calcification rate, aragonite precipitated during the daytime is characterized by lower Sr/Ca ratios than aragonite precipitated during the night. The COC are believed to be precipitated at night and expected to be characterized by relatively high Sr/Ca ratios, as observed [Cohen and McConnaughey, 2003].

[11] More importantly, the observations presented here indicate that Mg is delivered to the surface of the growing skeleton by a different and more actively controlled mechanism. Magnesium can either be actively pumped through the calcicoblastic ectoderm to the mineralizing surface, or be introduced by allowing sea-water to enter the mineralizing zone directly, such as it has been observed in foraminifera [Erez, 2003]. Either way provides a mechanism for the coral to dynamically control the Mg concentration in the mineralizing zone.

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## References

- Addadi, L., S. Raz, and S. Weiner (2003), Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization, *Adv. Mater.*, **15**, 959–970.
- Aizenberg, J., G. Lambert, S. Weiner, and L. Addadi (2002), Factors involved in the formation of amorphous calcium and crystalline carbonate carbonate: A study of an ascidian skeleton, *J. Am. Chem. Soc.*, **124**, 32–39.
- Barnes, D. J. (1970), Coral skeletons: An explanation of their growth and structure, *Science*, **170**, 1305–1308.
- Barnes, D. J. (1972), The structure and formation of growth-ridges in scleractinian coral skeletons, *Proc. R. Soc. London, Ser. B*, **182**, 331–350.
- Berman, A., J. Hanson, L. Leiserowitz, T. F. Koetzle, S. Weiner, and L. Addadi (1993), Biological control of crystal texture: A widespread strategy for adapting crystal properties to function, *Science*, **259**, 776–779.
- Bryan, W. H., and D. Hill (1941), Spherulitic crystallization as a mechanism of skeletal growth in the hexacorals, *Proc. R. Soc. Queensland*, **52**, 78–91.
- Clode, P. L., and A. T. Marshall (2002), Low temperature FESEM of the calcifying interface of a scleractinian coral, *Tissue Cell*, **34**, 187–198.
- Cohen, A., and T. A. McConnaughey (2003), Geochemical perspectives on coral mineralization, in *Biomineralization*, edited by P. M. Dove, J. J. D. Yoreo, and S. Weiner, pp. 151–187, Mineral. Soc. of Am., Washington, DC.
- Constantz, B. R., and A. Meike (1988), Calcite centers of calcification in *Mussa angulosa* (Scleractinian), in *Origin, Evolution and Modern Aspects of Biomineralization in Plants and Animals*, edited by R. E. Crick, pp. 201–208, Springer, New York.
- Constantz, B. R., and S. Weiner (1988), Acidic macromolecules associated with the mineral phase of scleractinian coral skeletons, *J. Exper. Zool.*, **248**, 253–258.
- Cuif, J.-P., and Y. Dauphin (1998), Microstructural and physio-chemical characterization of 'centers of calcification' in septa of some recent scleractinian corals, *Paläontologische Z.*, **72**, 257–270.
- Cuif, J.-P., Y. Dauphin, J. Doucet, M. Salome, and J. Susini (2003), XANES mapping of organic sulfate in three scleractinian coral skeletons, *Geochim. Cosmochim. Acta*, **67**, 75–83.
- Cuif, J.-P., Y. Dauphin, P. Berthet, and J. Jegoudez (2004), Associated water and organic compounds in coral skeletons: Quantitative thermogravimetry coupled to infrared absorption spectrometry, *Geochem. Geophys. Geosyst.*, **5**, Q11011, doi:10.1029/2004GC000783.
- Davis, K. J., P. M. Dove, and J. J. D. Yoreo (2000), The role of  $\text{Mg}^+$  as an impurity in calcite growth, *Science*, **290**, 1134–1137.
- Eggins, S. M., A. Sadekov, and P. D. Deckker (2004), Modulation and daily banding of Mg/Ca in *Orbulina universa* tests by symbiont photosynthesis and respiration: A complication for seawater thermometry, *Earth Planet. Sci. Lett.*, **225**, 411–419.
- Erez, J. (2003), The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies, in *Biomineralization*, edited by P. M. Dove, J. J. DeYoreo, and S. Weiner, pp. 115–149, Mineral. Soc. of Am., Washington, DC.
- Ferrier-Pages, C., F. Boisson, D. Allemand, and E. Tambutté (2002), Kinetics of strontium uptake in the scleractinian coral *Stylophora pistillata*, *Mar. Ecol. Prog. Ser.*, **245**, 93–100.
- Gladfelter, E. H. (1982), Skeletal development in *Acropora cervicornis*: I. Patterns of calcium carbonate accretion in the axial corallite, *Coral Reefs*, **1**, 45–51.
- Gotliv, B.-A., L. Addadi, and S. Weiner (2003), Mollusk shell acidic proteins: In search of individual functions, *ChemBioChem*, **4**, 522–529.
- Hillion, F., B. Daigne, F. Girard, and G. Slodzian (1993), A new high performance instrument: The Cameca Nanosims 50, in *Proceedings of the 9th SIMS Conference*, edited by A. Benninghoven et al., pp. 254–257, John Wiley and Sons, New York.
- Johnston, I. S. (1980), The ultrastructure of skeletalogenesis in hermatypic corals, *Int. J. Cytol.*, **67**, 171–214.
- Lowenstam, H. A., and S. Weiner (1989), *On Biomineralization*, 324 pp., Oxford Univ. Press, New York.
- Mitsuguchi, T., E. Matsumoto, O. Abe, T. Uchida, and P. J. Isdale (1996), Mg/Ca thermometry in coral skeletons, *Science*, **274**, 961–963.
- Mitterer, R. M. (1978), Amino acid composition and binding capability of the skeletal protein of corals, *Bull. Mar. Sci.*, **28**, 173–180.
- Orme, C. A., N. Noy, A. Wierzbicki, M. T. McBride, M. Grantham, H. H. Teng, P. M. Dove, and J. J. D. Yoreo (2001), Formation of chiral morphologies through selective binding of amino acids to calcite surface steps, *Nature*, **411**, 775–779.
- Raz, S., S. Weiner, and L. Addadi (2000), Formation of high-magnesium calcites via an amorphous precursor phase: Possible biological implications, *Adv. Mater.*, **12**, 38–42.
- Risk, M. J., and T. H. Pearce (1992), Interference imaging of daily growth bands in massive corals, *Nature*, **358**, 572–573.
- Rosenberg, G. D., W. W. Hughes, D. L. Parker, and B. D. Kay (2001), The geometry of bivalve shell chemistry and mantle metabolism, *Am. Malacol. Bull.*, **16**, 251–261.
- Tambutté, E., D. Allemand, E. Mueller, and J. Jaubert (1996), A compartmental approach to the mechanism of calcification in hermatypic corals, *J. Exper. Biol.*, **199**, 1029–1041.
- Weiner, S., Y. Levi-Kalisman, and L. Addadi (2003), Biologically formed amorphous calcium carbonate, *Connective Tissue Res.*, **44**, 214–218.
- Wellington, G. M., R. B. Dunbar, and G. Merlen (1996), Calibration of stable oxygen isotope signals in corals, *Paleoceanography*, **11**, 467–480.
- Young, S. D. (1971), Organic material from scleractinian coral skeletons. I. Variation in composition between several species, *Comparative Biochem. Physiol.*, **40B**, 113–120.

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