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Biogeosciences Discussions

Interactive comment on "The environment recording unit in coral skeletons: structural and chemical evidences of a biochemically driven stepping-growth process in coral fibres" *by* J. P. Cuif and Y. Dauphin

D. Sinclair (Referee)

djsweb1971@yahoo.com.au

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I very much enjoyed reading this manuscript, and I believe that the work presented here, and the work that preceded it, represent a very significant contribution to the field of coral biomineralization. The observations presented in this manuscript allow the authors to draw a number of lines of evidence from their earlier work and that of their colleagues into a plausible organic matrix calcification mechanism.

The importance of this work, however, warrants a fairly detailed examination of the supporting evidence, especially that concerning the presence and distribution of organic material within the skeleton. The most direct evidence for a possible nanometer scale organic matrix comes from the AFM observations. The phase imaging clearly shows two distinct phases, and there seems to be little doubt that coralline aragonite fibres

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must be regarded as being structurally heterogeneous at a scale much smaller than previously thought.

However, a wide range of physical and/or chemical properties can lead to a difference in phase images (relief, composition, adhesion, friction, viscoelasticity, etc), and the interpretation that this matrix is organic material rests upon several other lines of evidence, all of which are indirect and open to some degree of debate. The juxtaposition of several independent lines of circumstantial evidence can amount to a powerful argument, but until direct evidence is available, it is appropriate to maintain at least a basic level of scepticism.

The case for the phase observed being organic material relies heavily upon XANES spectra of coral skeletons (initially presented in CUIF et al., 2003 and expanded in this MS). The authors take this as definitive proof that a dispersed sulphated organic phase is distributed throughout the skeleton. The principal pieces of evidence for XANES sulphur being organic material are:

1) The XANES spectrum of corals does not match that of mineral sulphate (this MS). 2) The XANES spectrum of corals closely matches that of the sulphated sugar chondroitin sulphate (CUIF et al., 2003 and this MS). 3) In laser-Raman spectrums of corals there is no peak at 1007 cm-1 (which would indicate CaSO4) (CUIF et al., 2003).

Here I argue that this evidence is not sufficient to eliminate the hypothesis that the bulk of the sulphur detected by XANES mapping of the corals is (inorganic) SO42- as a dispersed ion substituting for CO32- in the aragonite lattice. Given the high concentration of sulphate in seawater, SO42- would be expected to be a semi-major trace substituent in marine carbonates (see TAKANO et al., 1980; BUSENBERG and PLUMMER, 1985; TAKANO, 1985; PINGITORE et al., 1995).

Examining the observations in the order presented above:

1) Poor match with mineral sulphate Firstly, in this MS, the authors show that a pure

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mineral CaSO4 phase (which appears to be gypsum from the XANES spectrum) does not provide a good match with coralline S. A similar result was observed by Pingitore et al. (1995) who showed that the XANES spectra of gypsum and anhydrite did not match those of the corals they analysed.

While this certainly eliminates small discrete domains of gypsum and anhydrite as being a significant source of skeletal S, it does not eliminate the possibility that the S is in the form of (inorganic) SO42- substituting for CO32- in the aragonite lattice. The XANES spectra for S are very sensitive to the local environment around S, including electronic influence of near-neighbour atoms and local symmetry. Thus Gypsum (which is monoclinic) and Anhydrite (which is orthorhombic but has very different unit-cell dimension to aragonite) would not necessarily be expected to produce the same XANES spectra as SO42- dispersed as a trace substituent in aragonite (which presumably experiences the smaller orthorhombic configuration of the aragonite lattice). The fact that Gypsum and Anhydrite have distinctly different XANES spectra (PINGITORE et al., 1995), despite both being CaSO4, demonstrates that there is a strong mineralogical control over the X-ray spectra.

In fact, Pingitore et al. (1995) noted that the primary control over the sulphur XANES spectra in carbonates seemed to be mineralogy, with each CaCO3 mineral (aragonite, calcite, dolomite) having a different sulphur XANES spectrum, while different examples of the same CaCO3 mineral had very similar spectra despite different origins. On the basis of this and other evidence Pingitore et al. (1995) conclude that the S in corals must be SO42- substituting for CO32-.

2) Close match with chnodroitin sulphate In the 2003 paper, Cuif et al. show that the near-edge spectrum of S in coral skeletons is a good match to that of the sulphated sugar chondroitin sulphate. A close match, however, is not a definitive proof: Pingitore et al. (1995) examined seventeen model compounds, and found a number which had a good match with the Post-K-edge region of the XANES spectrum, including potassium sulphate, magnesium sulphate monohydrate, copper sulphate pentahydrate, and even

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dolomite.

While Pingitore et al. (1995) do not propose that these phases actually exist within the coral (there being insufficient K, Mg, or Cu) these observations illustrate that a number of sulphate compounds exhibit post-K-edge XANES spectra which are similar to corals. Chondroitin sulphate must therefore be regarded as only one of a (potentially large) number of suitable candidates for the skeletal sulphur.

3) Laser Raman Spectra Cuif et al. (2003) examined the Raman spectra of corals and compared this to the spectra of CaSO4 (Figure 8 of that paper). The authors did not detect this peak, and concluded that all SO42- must therefore be organic. It should be noted, however, that the y-axis in this figure is scaled such that the peaks for SO42- in the pure CaSO4 phase, and CO32- in aragonite, are full scale. As the S content of coral aragonite is around 0.4%, the peak for CaSO4 would have been around 200 times smaller - approximately the same size as the thickness of the line on the page. In fact, 400 ppm is below the detection limited listed by Takano (1985) for this technique.

In addition, the authors did not run the Raman spectra of a sulphated sugar, and thus there is no way to demonstrate that there was detectable chondroitin sulphate present. Raman spectra for a range of mono and di-saccharides (ARBOLEDA and LOPPNOW, 2000) show strong peaks in the 600 - 1200 cm-1 range (corresponding to the range in Figure 8 of CUIF et al., 2003). D-Glucuronic acid, the monomer that makes up Chondroitin, displays especially strong peaks in the 1000 - 1200 cm-1 range (spectra by Søren Balling Engelsen (Food Technology, Dairy and Food Science, Royal Vet. and Agricultural University, Denmark) can be found at http://www.models.kvl.dk/users/engelsen/specarb/glcpa.html). None of these peaks are visible in the spectra of Cuif et al. (2003). Thus, their conclusion that the “whole sulfate content is in the organic skeletal matrix”, is invalid - or at least is not supported by the spectra they presented in their paper.

It is worth noting that Takano (1985) specifically searched for the signature of Chon-

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droitin sulphate in a coral skeleton (using conventional IR techniques) and did not find it. This author, like Pingitore et al. (1995), concluded that sulphate was present as an inorganic substituent for CO32-.

Other indirect evidence for organic S:

With these three principal pieces of evidence in doubt, it is worth considering several other pieces of evidence linking organic S to the XANES S map.

4) XANES and ion microprobe maps show high S in the centres of calcification, while UV autofluorescence indicates high organic concentrations. 5) Light etching in formic acid + fixatives reveals daily banding. This differential etching is attributed to the preferential dissolution of organic-rich aragonite. At the same time, XANES maps show simultaneous alternation of high and low S regions. 6) There is a semi-quantitative correlation between the height of sulphated sugar peaks in infrared spectrums of the organic matrix extracted from corals, and the visible intensity of staining in isoelectric focalization electrophoresis gels.

The juxtaposition of fluorescence and SO42- in the centres of calcification is consistent with an organic source for S. The daily banding in SO42- (CUIF et al., 2003) would therefore suggest an alternation of organic rich and organic poor regions. However, Cuif and Dauphin (1998) did not find an alternating pattern of UV autofluorescence within the fibrous skeleton (perhaps due to the limitations of the technique), weakening the interpretation that this SO42- is organic.

This brings attention to the etching method. The light etching by formic (or acetic) acid and gluteraldehyde, used by Cuif and Dauphin (1998) and others (SORAUF and JELL, 1977; SORAUF, 1980; SORAUF, 1997; CUIF et al., 1999; SORAUF, 1999; PERRIN, 2003) to show the daily banding, is claimed to specifically target the regions of the skeletal fibres which are richer in organic material. I have tried to track down further details of this method, to understand why organics are selectively targeted rather than simply more soluble CaCO3 domains - such as amorphous CaCO3 or regions of arag-

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onite which incorporate high amounts of Mg (such as those seen by SORAUF, 1997; MEIBOM et al., 2004), which would result in distortion of the lattice and an increase in crystal solubility (as seen for calcite in BUSENBERG and PLUMMER, 1985). See also reviews in Speer (1983) and Viezer (1983). Although my review of this literature is by no means exhaustive, I have not been able to locate a reference to the etching method which discusses its mechanism and demonstrates its specificity for organic material. I would be grateful if the authors could expand a little on their etching methodology or direct me to a source so that I can examine this method in a little more detail.

As for the correlation between the sulphated sugar peaks in infrared spectrums of the organic matrix, and the intensity of staining in electrophoresis gels: the presence of sulphated sugars, such as chrondroitin sulphate, in coral skeleton is probably now widely accepted. What has not been demonstrated is that they are dominant or even significant contributors to the total coral sulphur budget. Given that the authors are now routinely extracting soluble organic matrix from the corals by careful demineralization, I would like to see some quantitative mass-balance analysis (perhaps using HPLC, GCMS or similar methods) of the overall distribution of S amongst the different chemical forms. Even if the exact organic form containing the S could not be clearly identified, these methods should be able to exclude ionic SO42- as being the dominant form.

As a final note: the approximate volume proportion represented by the intergranular material seen in AFM images of the fibrous aragonite accords with the measured amounts of organic material in coral skeletons only if the abundance of organic material is taken to be around 2.5 - 3% (by weight). This estimate by the authors is significantly larger than values quoted in the past (which typically range from 0.1% to 1.0%), especially since much of the organic material appears to be concentrated in the centres of calcification (CUIF and DAUPHIN, 1998) and not the aragonite fibres. The amount of organic material in corals has been the focus of some debate recently, focusing on the methodology for organic analysis. It will be interesting to watch the next stage of this debate when the paper by Cuif et al. (2004) is published in G3.

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In summary, the authors have built up a plausible and consistent case that submicron domains in fibrous coral aragonite are the dispersed organic matrix of sulphated glycoproteins they claim to have detected by XANES spectra. While a number of pieces of indirect evidence link the sulphate detected by XANES to organic material, it is my opinion that the authors have not adequately dismissed the possibility that this sulphate is an inorganic SO42- lattice substituent. The XANES evidence supporting their interpretation of the submicron matrix must therefore be treated with some caution.

Daniel Sinclair, GEOTOP (UQAM-McGill), Université du Québec à Montréal

References Cited:

Arboleda P. H. and Loppnow G. R. (2000) Raman spectroscopy as a discovery tool in carbohydrate chemistry. Analytical Chemistry 72, 2093 - 2098. Busenberg E. and Plummer N. L. (1985) Kinetic and thermodynamic factors controlling the distribution of SO42- and Na+ in calcites and selected aragonites. Geochimica et Cosmochimica Acta 49, 713 - 725. Cuif J.-P. and Dauphin Y. (1998) Microstructural and physico-chemical characterization of 'centers of calcification' in septa of some recent scleractinian corals. Paläontologische Zeitschrift 72(3/4), 257 - 270. Cuif J.-P., Dauphin Y., Doucet J., Salome M., and Susini J. (2003) XANES mapping of organic sulfate in three scleractinian coral skeletons. Geochimica et Cosmochimica Acta 67(1), 75 - 83. Cuif J.-P., Dauphin Y., and Gautret P. (1999) Compositional diversity of soluble mineralizing matrices in some recent coral skeletons compared to fine-scale growth structures of fibres: discussion of consequences for biomineralization and diagenesis. International Journal of Earth Sciences 88, 582 - 592. Meibom A., Cuif J.-P., Hillion F., Constantz B. R., Juillet-Leclerc A., Dauphin Y., Watanabe T., and Dunbar R. B. (2004) Distribution of magnesium in coral skeleton. Geophysical Research Letters submitted. Perrin C. (2003) Compositional heterogeneity and microstructural diversity of coral skeletons: implications for taxonomy and control on early diagenesis. Coral Reefs 22, 109 - 120. Pingitore N. E. J., Meitzner G., and Love K. M. (1995) Identification of sulfate in natural carbonates by X-ray absorption spectroscopy. Geochimica et Cosmochimica Acta

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59(12), 2477 - 2483. Sorauf J. E. (1980) Biomineralization, structure and diagenesis of the coelenterate skeleton. Acta Palaeontologica Polonica 25(3-4), 327 - 343. Sorauf J. E. (1997) Geochemical signature of incremental growth and diagenesis of skeletal structure in Tabulophyllum traversensis (Winchell, 1866). Boletin de la Real Sociedad Espanola de Historia Natural (Seccion Geologica) 92(1-4), 77 - 86. Sorauf J. E. (1999) Skeletal microstructure, geochemistry, and organic remnants in cretaceous scleractinian corals: Santonian Gosau beds of Gosau, Austria. Journal of Paleontology 73(6), 1029 - 1041. Sorauf J. E. and Jell J. S. (1977) Structure and incremental growth in the ahermatipyc coral Desmophyllum cristagalli from the North Atlantic. Palaeontology 20(1), 1 - 19. Speer A. J. (1983) The Kinetics of Calcium Carbonate Dissolution and Precipitation. In Carbonates: Mineralogy and Chemistry, Vol. 11 (ed. R. J. Reeder), pp. 145 - 190. Mineralogical Society of America. Takano B. (1985) Geochemical implications of sulfate in sedimentary carbonates. Chemical Geology 49, 393 - 403. Takano B., Asano Y., and Watanuki K. (1980) Characterization of sulfate ion in travertine. Contributions to Mineralogy and Petrology 72, 197 - 203. Veizer J. (1983) Trace Elements and Isotopes inn Sedimentary Carbonates. In Carbonates: Mineralogy and Chemistry, Vol. 11 (ed. R. J. Reeder), pp. 265 - 299. Mineralogical Society of America.

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