

***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**

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General Comments

The authors of this manuscript present some fascinating AFM results demonstrating sub-microscale heterogeneity in coral skeletons, develop their case for XANES mapping of sulphated organic material, and synthesise a number of earlier observations into a plausible organic-matrix calcification mechanism. This is exciting and important research and certainly deserves to be published in Biogeochemistry, although I would like the authors to address a few scientific issues and to attend to some basic proof-reading matters first.

Scientific Comments

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I think this work could be extended, although not necessarily for this article, by using AFM to contrast the abundance of matrix in regions of the skeleton that are susceptible to the dilute etching with those regions which are more resistant. It would also be very interesting (and a strong confirmation of a matrix-mediated calcification mechanism) to apply AFM to examine the sub-micron crystal structure of inorganic spherulitic aragonite grains.

The authors rely heavily on the XANES mapping of organic sulphate in the skeleton to develop their case for an organic matrix within the coral skeleton (first presented in CUIF et al., 2003 and developed further in this manuscript). Here they treat XANES sulphur maps as definitive evidence for a dispersed organic phase. It is my opinion, however, that the authors have not sufficiently demonstrated that their XANES maps are organic sulphate, as opposed to (for example) inorganic SO<sub>4</sub><sup>2-</sup> substituting into the aragonite lattice. Since this is perhaps a difference of scientific opinion, as opposed to a clear flaw in the science, further exposition of these objections is not relevant here. I have therefore presented details as a separate scientific comment in the 'Open Discussion' section which I invite the authors (and other interested parties) to debate.

That said, I do not think that the authors have adequately reviewed previous work studying S and sulphate in coral skeletons (and marine carbonates). In particular, I draw their attention to the work of Pingitore et al. (1995) and Takano (TAKANO et al., 1980; TAKANO, 1985), both of whom used the same methods as Cuif and Dauphin (XANES, IR and Raman spectroscopy) to study S in coral skeletons (and other carbonates) but came to the opposite conclusion regarding the nature of the skeletal S. Some comment regarding this difference in conclusion is important.

In general, the analytical methodology section lacks detail and needs to be expanded. In particular, I would like to see some additional detail about the etching methodology used by the authors. In previous work (eg. CUIF and DAUPHIN, 1998), the dilute acid/gluteraldehyde etching has been attributed to selective dissolution of aragonite fibres containing organic material, but no further details about the selectivity or mech-

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anism of this method are presented either here or elsewhere.

Details of the preparation and polishing of 5  $\mu\text{m}$  ultra-thin sections would be helpful.

The methodology for sample preparation for AFM is absent (the authors refer to figure captions for details [p 630, line 24], but this information is missing from the captions of Figures 10 and 11).

Finally, there are no details given about the model  $\text{CaSO}_4$  mineral (or other compounds) used for characterizing XANES spectra.

With regards to the authors' calcification mechanism: I would be interested in their opinion about whether each crystal nano-grain seen by AFM is fully isolated from its neighbour by the surrounding matrix, or whether they are actually in continuous contact (essentially representing one large crystal growing through an open mesh of matrix). The latter would explain the apparent crystallographic continuity seen in larger scales, and would have implications for the mechanism of organic matrix organization and subsequent  $\text{CaCO}_3$  mineralization.

The comment regarding the possible role of Mg (as detected by SORAUF, 1997; MEI-BOM et al., 2004) in repressing crystallization at the end of the biomineralization cycle is purely speculative.

In the caption to Figure 5, the authors make the following statement: “Concentric growth layering indicates that mineralizing activity of the ectodermal cell layer is controlled at a global level, in contrast to the usual concept of “crystal growth competition”’. This seems to be a bit of a misrepresentation of the competitive growth hypothesis, which would predict a similar structure based on syntaxial fibre growth into a calcifying space.

#### Technical Corrections

The manuscript in its present form requires some careful proof-reading as it contains many (minor) typographical, spelling and grammatical errors. For the sake of brevity,

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I do not list them here; however, I strongly recommend that the authors submit the manuscript for additional proof reading and language checking before final submission. The use of 'evidenced' and 'evidencing' throughout the paper does not always seem to conform to its common usage in English. The title should read 'evidence' not 'evidences'.

Figure 13 is a little confusing to look at and a number of details and annotations are not explained adequately in the caption.

The references need to be checked. Several citations in the text do not have an entry in the bibliography (Meibom 2003, Meibom et al. 2004, Juillet-Leclerc 2004, Young 1973, Allison et al. 2001, Finch et al. 2003, Rollion-Bard et al. 2003, and maybe Jackson and Gladfelter, 1985). There are also several references in the bibliography which are not cited in the text (Hidaka 1998, Hidaka 1991, Wada and Fujinuki 1976). Finally, 'Rollion' in the text should be listed as 'Rollion-Bard'.

In conclusion, I would like to thank the authors again for a very interesting manuscript. This is important science, and I hope that the above issues can be addressed quickly so that the article makes it into broader circulation soon.

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