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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

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Authors first thank referees for their globally positive evaluation of their manuscript. Although Ref. 3 opinion is still missing, the four documents already known (three reviews and additional comment by D. Sinclair) allow the BG Open Discussion to be started.

We will not answer personally to reviewers (anonymous or not) but thematically. To personal attached comments (presently DS only) we will make specific responses.

Comment on the global focus of the paper

Although authors are dealing with coral structures since a good while, this manuscript does not aim to make an extensive review of biomineralization process in corals. Results recently got by using atomic force microscopy has given a unique opportunity to summarize our separately published results (some of them are more than 20 years

old) and these new AFM data into a consistent scheme of the coral fibre. By starting his comment on these most recent results, one reviewer (DS) clearly emphasized the importance of AFM pictures for people already aware of arguments supporting biological control. In contrast, by starting the Results chapter with pictures concerning the monocrystalline appearance of fibres, authors adopt a demarche aiming to convince the much more numerous “mineralogy minded” peoples.

Keeping in mind that the coral skeleton unit (the fibre) is still widely admitted as an aragonite monocrystal in most of paleoenvironmental research (openly or implicitly), authors intend to give readers arguments that support a still unconventional view of the coral fibre, with respect to both its structure and environment recording mechanism. Therefore this paper cannot be considered as a “review” (Ref. 4). The word “synthesis” also suggested by R4 is more adequate with a limited sense (synthesis of “earlier author results”, as told by DS). It will be used in the title of the revised manuscript.

Remark 1: The “new microstructural model of coral skeleton formation” announced in the abstract may have misled some readers. According to our limited objective, the sentence will be changed to “a new microstructural model of the growth of coral fibres...”

Should this manuscript be “extended”

Numerous additional references have been suggested by reviewers. Taking into account our limited objective, these suggestions will be considered and included in the paper according to their immediate relevance. In this paper, the length of which already exceed the BG standard, discussion concerning all recommended citation is not always possible.

For the same reason, as noticed by R4 “this paper focuses on the aragonite fibrous growth and not on the early mineralization zone”. This is true, and first linked to the fact that in coral skeletons the fibrous part is, by far, the most quantitatively important compared with the early mineralization zone. Of course, authors are well aware of the

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importance of the so- called “centres of calcification”, specially from a biomineralization standpoint. We hope the new title and abstract changes make that immediately clear. The important question of biochemical and microstructural specificity of centres of calcification, and discussion of their rôle during skeletogenesis should make the paper too long. Remark 2: However, a short information will be given (with reference of the relevant paper) explaining why the classical expression “centre of calcification” has been replaced by “early mineralization zone”

The two step concept of fibre growth layer

“The model that the authors propose (fig. 12) invokes a matrix mediated mineralization process, but by no means proves it. May be the problem is that in my opinion the matrix mediated concept fondamentally involves a preformed framework into which crystals grow.”

Remark 3: As far as we understand the concept of “model” , we consider it as the best possible working basis, built by gathering separated results from different origins, but by no means a “proof”.

This long excerpt from the R4 report is justified because it excellently summarizes what authors consider as the key result of their long term investigation on the structure of coral fibre. In each growth layer, the secretory phase (step 2 on the model) creates the dense hydrated-organic environment - the R4 “preformed framework”- in which nanogranular crystals nucleate and grow (step 3 on the growth model).

Reading the next sentence of the R4 report “crystals grow into a hydrogel composed of a percent of so of polymers (sulfated sugars...)”, we found a serious misunderstanding of our model. The proportion of organic matrix “a percent or so” has been found by ATG measurements made directly on the calcareous skeleton itself, i.e. one percent of the total weight including calcareous material. Obviously, before crystallization has occurred, when the layer of organic framework is secreted by the mineralizing ectoderm (the secretory step), the proportion of organic compounds to water

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is certainly stronger. In the paper to be shortly published in G3 (2004 vol. 5, 1-doi:10.1029/2004GC000783), we show that, within the calcified skeleton, water and organics are broadly in a 2/1 ratio. This ratio actually corresponds to the global composition of a dense hydro-organic layer (as seen by Goreau1956, at the outer side of the ectodermal layer). From this historical observation, we hypothesized that the hydro-organic ratio shown by ATG is acceptable (without other information) as representative of the secretory step in our model (step 2).

Consequently, and this is the essential change in our mineralization model compared with the “free crystallization” concept, the crystallization medium is not sea water, but a specifically secreted hydro-organic medium.

This implies that:

1 - the composition of each crystallization medium is taxonomically dependant (i.e. each coral species produced its own hydro-organic assemblage). This provides us with a very acceptable clue for the “vital effect”, as crystallization conditions are clearly different for each coral species. NB: Importance of this result cannot be overestimated. This is the central topic of the scheduled BG2.01 session in the 2005 EGU assembly in Vienna.

2 - Reciprocally, any direct transposition of the properties of a mineral freely crystallized in sea water to mineral resulting from this biochemically driven crystallization process is irrelevant.

This point is of particular importance with respect to the focus of the DS attached document.

The mineral/organic nature of sulphate (a specific topic in the DS attached comment).

In his attached comment DS advocates the possible mineral nature of the sulphate in coral skeletons. The point is essential because a mineral nature of sulfate bounds clearly implies, not necessarily in fact but in the common opinion, the collapse of the

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“biochemically driven” crystallization model. Therefore, all what geochemists may invoke to disprove the presence of sulfated polysaccharides within coral skeletons is gathered in this long attachment.

To reach this objective, the discussion begins with a high standard methodological sentence. “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”. Authors congratulate Doctor Sinclair for this scientific attitude. They recognize they have given only a series of “circumstantial evidences” and are waiting with highest interest examples of “direct evidences” that DS will certainly present.

1- Disproving the significance of AFM pictures: DS argument: “a wide range of physical and /or chemical properties can lead to a difference in phase image (relief, composition, adhesion, friction, viscoelasticity, etc.)”. Authors : if we remark that “adhesion, friction, viscoelasticity etc. “ are various consequences of a compositional difference, we can admit that DS himself recognizes that the two components distinctly visible at the nanometric scales do not have the same composition. The presence of two different mineral phases has never been shown in corals. On the other hand, stronger interactivity (dark regions of the picture), can be admitted in first approach for organic compounds whatever the cause (composition, adhesion, viscoelasticity etc...). Consequently authors have thought (and still think) that they were allowed to suggest that interactive zones are organic.

Disproving the significance of the XANES signal: When discussing the possible mineral origin of the XANES signal, DS uses the term “a dispersed sulfated organic phase”. This is a rather unfair description of what we have shown. Multiple XANES maps have shown that the XANES sulphate signal is not “dispersed”, (a word that suggests “not controlled”, leading to the unformulated consequence mineral in nature). On the contrary, we have shown that sulfate is well linked to growth layers, i.e. linked to microstructural organization of the coral fibrous skeleton, i.e. linked the biological growth process.

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Additionally, as we have obtained the sulfated XANES signal directly from coral skeletons and indirectly from organic matrices isolated from the same coral skeletons after complete decalcification, we have admitted a common origin for these two signals.

The hypothesized SO4 = mineral ions in coral skeletons are admitted by DS as “substituting for CO3= in the aragonite lattice”. Numerous citations of laboratory co-precipitation experiments are cited. DS comments on these results by writing: “ Given the high concentration of sulphate in sea water....”. Authors kindly ask DS to give them some “direct evidence ” that under coral basal ectoderm, nanograin crystallization occurs in pure sea water, as they do in laboratory experiments.

DS concludes the discussion on the meaning of sulfur signal by writing: “Chondroitin sulfate must therefore be regarded as only one of a (potentially large) number of candidates for the skeletal sulfur”. No doubt about that. Authors may add that they ask DS to cite which of these “potential candidates” that is sensitive to Alcian Blue staining, which of these potential candidates that, after hydrolysis, is reducible to taxonomy dependant series of sugars, which such a discriminant power that we have been able to separate zooxanthellate from non zooxanthellate corals by statistical analysis of the result of polysaccharide hydrolyses. But once more, these are no “direct evidences”.

The etching method

DS comment also focuses on the result of etching techniques applied to coral skeletons. Providing us with “direct evidence” of the synchronism of fibre growth, (the micron spaced growth lines), these results strongly contrast with the geochemical concept of a “crystal growth competition”.

What is surprising for people familiar with coral studies (we mean people who are studying corals as biological objects and not simply measuring isotopic ratios as if corals were chemical products), is that growth lines in coral skeletons are known since the end of the 19° century. M. Ogilvie-Gordon has drawn these structures in a famous paper (1896) that was the first attempt to use coral microstructure as a taxonomic cri-

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terion. Micron-spaced growth lines are visible in coral skeletons under the microscope.

To illustrate this point, a microphotography was specially made and is visible at the following address:

http://biomin.geol.u-psud.fr link: Biogeosciences discussion figures (see Fig. 1)

Etching is a very usual practice among people dealing with material structures (coral skeletons but also any kind of solid structures as metal alloys etc.). Following the DS comment we should have claimed that etching "specifically target the region of the skeletal fibres which are richer in organic material". Authors should be interested in having a precise citation about our interpretation of etching limits. For their own, in a purely empirical use of the etching technique (etching solutions are very different among the cited authors), authors have only used the primary evidence that etching reveals zones of stronger solubility within an apparent compact and homogeneous material, as coral fibres appear (and other biocrystals as well).

Noticeably, addition of glutaraldehyde (a fixative molecule) should reduce the solubility of organic compounds, in contrast to DS interpretation. From a methodological stand point, why are the limits between growth layers more sensible to etching remains disputable: weaker mineralization, differences in organic constituents etc.

Banding pattern Not very surprisingly, the banding pattern has been immediately translated to daily pattern by a reviewer (DS). It is a common opinion, among people not aware of what biological rhythm is in the domain of biomineralization, to make such an interpretation. To bring some additional information (and to avoid simplistic interpretations), we attach here some documents that may contribute to a better understanding of what biomineralization process and growth rhythms actually are (Fig. 2).

Picture visible at : http://biomin.geol.u-psud.fr link: Biogeosciences discussion figures (see Fig. 2)

This is a section in the shell of a gastropod (Concholepas, Chilean seashore), the

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growth of which has been marked by fluorescent dye (the two green lines in fig. a, are separated by a week). Days and nights are well visible (b). In the external layer (calcitic prisms fig c) the microstructural study reveals a fine banding pattern fig. d) of about 50 growth layers a day (i.e. 50 distinct crystallization processes a day, i.e. 50 environment recording units a day). Elemental growth layer thickness is about 2 micrometers, a value in the range of most of mineralizing systems (compare with the Pinna banding pattern in the BG paper).

What authors may recommend to people familiar with mineral chemistry is that they do not transpose the basic rules in their domain to the living world. They have first to learn and understand that, in spite of a mineral appearance, shells, coral skeletons etc. are biologically produced materials. A direct use of mineral chemistry rules is simply irrelevant for interpretation of biological objects, whatever the scale at which observations or measurements are made.

Interactive comment on Biogeosciences Discussions, 1, 625, 2004.