EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

fill in a separate form for each project or series of measurements.

type your report, in English.

include the reference number of the proposal to which the report refers.

make sure that the text, tables and figures fit into the space available.

if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: **Biogeochemical changes during biomineral diagenesis and reliability in paleoenvironmental signals**	**Experiment number**: CH1769
Beamline: ID21	**Date of experiment**: from: 10-11-2004 to: 15-11-2004	**Date of report**:
Shifts: 12	**Local contact(s)**: **M. Salomé**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*** Dauphin Yannicke - IDES University Paris XI-Orsay, France**

*** Cuif Jean Pierre - IDES University Paris XI-Orsay, France**

*** Salomé Murielle - ID21 ESRF**

Susini Jean - ID21 ESRF

Report:

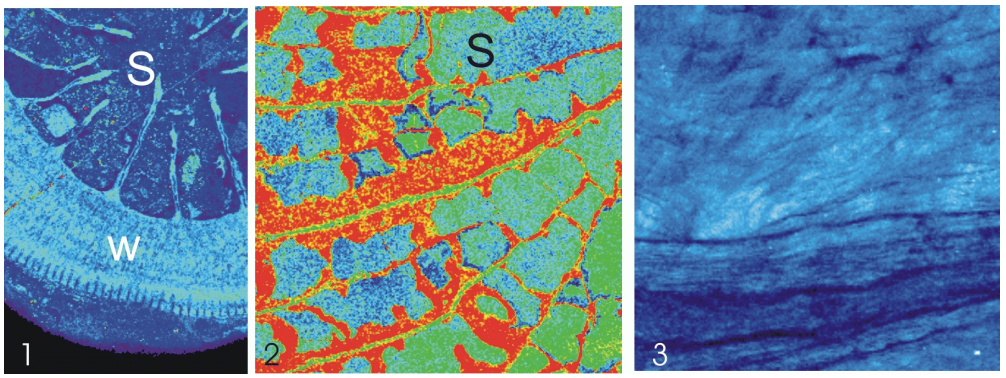
Environmental and palaeoenvironmental reconstructions are based on chemical and isotopic signals issued from calcareous hard parts built by invertebrate (i.e. coral skeletons, mollusc shells) or vertebrate organisms (otoliths, eggshells). However, it is now well known that these skeletons are composed of a mineral part (aragonite and calcite) and organic components. In these biominerals, parts of the organic components can be extracted from within the crystals. The quantity, composition and structure of the occluded macromolecules are taxonomy-linked. Most studies dealing with these organic matrices are concerned with proteins, despite that Wada (1964, 1980) has clearly shown the major role of the sulfated sugars. Previous experiments (CH721, 948, 1162, 1364, 1569) on modern samples have confirmed the presence of the sulfated sugars in the biominerals, their heterogeneous distribution within a crystal (growth lines...), and that their abundance depends upon the taxonomy.

Because of the presence of sulfated sugars, the behavior of carbonate skeletons during the fossilisation processes is variable: some taxa are better preserved than others, and within a shell, some layers are preserved whereas other layers are destroyed. These irregularities are usually neglected by geochemists for whom the only control of the mineralogical composition is sufficient to assess a good preservation. However, microprobe analyses have shown elemental chemical alterations in well preserved aragonitic samples from the Triassic period.

In the CH1769 session, we have worked on these Triassic samples to test the possible preservation of sulfated sugars (micro XANES sulfur K-edge in focussed mode). Because we have to compare with modern samples, we have selected coral skeletons. First, spectra have shown the preservation of organic sulfates in the fossils. Then maps were done to estimate the preservation of the relationships between the distribution of the organic sulfate and the microstructural data.

Various scales were used for maps. “Large” pictures (Fig. 1, horizontal field 2 mm) show that there is no organic sulfate in the secondary sediment (S), whereas organic sulfates are preserved in the skeleton (W). Medium maps in other samples have confirmed the good preservation of the skeletal parts with organic sulfate, and the absence of organic sulfate in sediment (Fig. 2, horizontal field 1 mm). Micronic maps show that the microstructure and composition are not destroyed in the skeletal part (Fig. 3, horizontal field 100 m).

These first experiments on old fossils (205-210 My) are successful.First, the absence of organic sulfate in the filling sediments inside the skeletal cavity shows that the contamination is limited and allows us to extract the organic matrices in the future to perform other analyses.



Then, such data are necessary to select the "well preserved" fossil samples for a future use as paleoenvironmental proxies. Various fossil sites and taxa have to be studied in the future.

Submitted papers:

(1) Cuif J.P. & Dauphin Y., The biochemically-driven stepping growth-mode of Scleractinian coral skeletons - J. Struct. Biol.

Abstract: Since the 19th century, it is known that coral skeletons are built by aragonitic crystals with taxonomy-linked arrangements, but the way by which each coral species controls this crystallization process remains an unsolved question. The problem became still more intriguing when it was shown that isotopic compositions of coral aragonites were also submitted to taxonomy-linked influences ("vital effect"). An organic component in coral skeletons is also long known, but presence of these compounds is admitedly restricted to these particular structures called "centres of calcifications". In this paper, it is shown that organic compounds are associated to the mineral material at every structural levels. A series of variously scaled observations and localized measurements allow the presence of an organic component to be evidenced up to the nanometer scale. Far from being a freely running process, the crystallization of coral fibres is thus on permanent control of the polyp basal ectoderm through the secreted proteoglycans. As the composition of these glycoproteic assemblages has been shown to be taxonomy dependent, hypothesis can be made that the multiple and long evidenced biological specificities of coral skeletons are linked to this biochemically driven crystallization process.

(2) Cuif J.P. & Dauphin Y.**,** The Environment Recording Unit in coral skeletons. A synthesis of structural and chemical evidences for a biochemically driven, stepping-growth process in fibres - Biogeosciences

Abstract: This paper gathers a series of structural and biochemical *in situ* characterizations carried out to improve our knowledge of the fine scale growth patterns of fibres in coral skeletons. The resulting data show a clear correspondence between the mineral subunits of fibres and the spatial distribution of organic macromolecules. New observations using atomic force microscope confirm the close relationship between mineral and organic phases at the nanometre scale.

Synthesis of these data results in a significant change in our concept of the mineralization process in coral skeletons. In contrast to the usual view of an aggregate of purely mineral units independently growing by simple chemical precipitation, coral fibres appear to be fully controlled structures. Their growth process is based on cyclic secretion of mineralizing compounds by the polyp basal ectoderm. These biochemical components of the coral fibres, in which high molecular mass sulfated acidic proteoglycans probably play a major role, are repeatedly produced. This results in a stepping growth mode of fibres and a layered global organization of coral skeletons.

Therefore, in contrast to the widely admitted geochemical interpretation, we propose a fibre growth model that places coral skeletons among the typical "matrix mediated" structures. The crystal-like fibres are built by superimposition of few micron-thick growth layers. A biomineralization cycle starts by the secretion of a mineralizing matrix and the final step is the crystallization phase, during which mineral material grows onto the organic framework. Thus, each growth layer is the actual Environment Recording Unit.

From a practical standpoint, these results may contribute to develop a new high resolution approach of the environment recording by coral skeletons.