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.

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|---|---|---|
| | **Experiment title:**<br>High resolution XANES mapping of sulfur in cyclic secretion of sulfated sugars included in calcareous biomineralizations. Implications for the use of calcareous proxies in environmental studies | **Experiment number**:<br>CH1569 |
| **Beamline**:<br>ID21 | **Date of experiment**:<br>from: 5-09-03 to: 9-09-03 | **Date of report**:<br>16-11-2003 |
| **Shifts:**<br>12 | **Local contact(s)**: Murielle SALOME | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

**CUIF Jean-Pierre - Université Paris XI Orsay**
**DAUPHIN Yannicke – Université Paris 6 UPMC**
**SALOME Murielle – ESRF – ID21**
**SUSINI Jean – ESRF – ID 21**


**Report:** Importance of sulfated sugars in biomineralization process was illustrated by a series of spectacular mapping results concerning Scleractinian corals, Pelecypod, Cephalopod and Gastropod Mollusc shells. First studies on recent and fossil Calcareous Sponges were made. Evidencing the driving role of sugars in formation of calcareous biogenic materials finds immediate applications in paleoenvironmental studies, allowing a new interpretative and modelizing framework to be created.

**Published papers**


**DAUPHIN Y., Cuif J.P., Doucet J., Salomé M., Susini J. , Williams C.T. - 2003 - *In situ* chemical speciation of sulfur in calcitic biominerals and the simple prism concept. *J. Struct. Biol*. 142 : 272-280.**



SUMMARY:The microstructure and composition of two mollusc shells were investigated using a combination of light microscopy, SEM, EPMA, and XANES.The shells of *Pinna* and *Pinctada* are composed of calcite prisms separated by organic walls.The prismatic units of *Pinna* are monocrystalline, and those of *Pinctada* are polycrystalline with internal organic radial membranes.High-spatial resolution XANES maps for the different S species across adjacent prisms show that sulfate is the principal component in both the intraprismatic organic matrices and the outer membranes. Additionally, these maps confirm that the inner structures of the prismatic units are different for both genera.In many ways, the prisms of *Pinna* and *Pinctada* are different and invalidate the “simple prism” concept.



**DAUPHIN Y. - 2003 - Soluble organic matrices of the calcitic prismatic shell layers of two pteriomorphid Bivalves: *Pinna nobilis* and *Pinctada margaritifera* . *J. Biol.Chem.* 278, 17 : 15168-15177.**



SUMMARY: The calcitic prisms of the shells of two bivalves, *Pinna* and *Pinctada*, are considered simple prisms according to some morphological and mineralogical characteristics. Scanning electron microscopic and atomic force microscopic studies show that the micro- and nanostructures of these two shells are different. *Pinna* prisms are monocrystalline, whereas *Pinctada* prisms are not. Moreover, intraprismatic membranes are present only in the *Pinctada* prisms. The soluble organic matrices extracted from these prisms are acidic, but their bulk compositions differ. Ultraviolet and infrared spectrometries, fluorescence, high pressure liquid chromatography and electrophoresis show that the sugar - protein ratios and the molecular weights are different. Sulfur is mainly associated with acidic sulfated sugars, not with amino acids, and the role of acidic sulfated sugars is still underestimated. Thus, the simple prism concept is not a relevant model for the biomineralization processes in the calcitic prismatic layer of mollusk shells.

**Submitted papers :**

DAUPHIN Y. - Compositions of the mineralizing matrices in skeletal axes of two *Corallium* species (Alcyonacea). *Int. J. Biol. Macromol.*

SUMMARY : The soluble organic matrices extracted from the axial part of the skeletons of two *Corallium* species (Coralliidae, Alcyonacea) were analysed using FTIR spectrometry, HPLC, IEF, 2-D gel electrophoresis and XANES. All these methods show that the main characteristics of the two matrices are similar, but not identical. Both matrices are composed of proteins and sugars; they are acidic with poorly separated molecular weights. The sugars contents are low, and the matrices do not seem highly glycosylated. The differences and similarities of these matrices are also observed in the minor element contents and in the micro- and nanostructures of the samples. These results confirm the control of the morphology and the chemical composition of calcitic biocrystals. Biomineralisation processes in Coralliidae are taxonomically significant, and differ from those of Scleractinia skeletons.

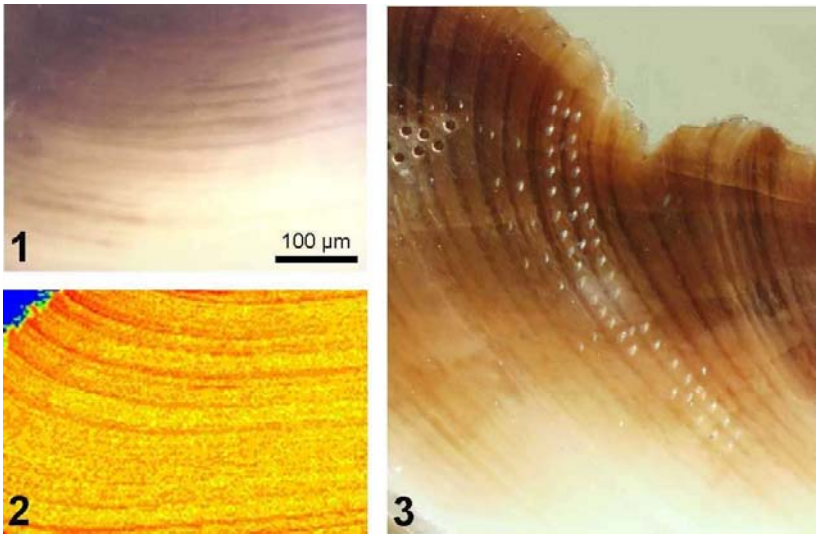
**To be submitted :**

DAUPHIN Y., Cuif J.P., Salomé M., Susini J. - *In situ* maps using X-ray absorption near edge structure (XANES) spectroscopy at the sulfur K-edge: an insight to biomineralization process in Mollusc shells – *American Mineralogist*

DAUPHIN Y., Cuif J.P. - Structures and composition of the skeletons of some Merulinidae (Cnidaria, Scleractinia) – *J. Biol. Chem.*

**Examplifying ID-21 data and application to high resolution measurement on the environmental proxy *Concholepas***

***Zonation of organic sulfate*** (2) was made visible by XANES mapping during CH-1569 experiment, demonstrating an exact correspondence with daily growth zonation banding (1). Such *in-situ* biochemical characterisations allow a reliable framework to be created for calibration of biological proxies. Continuous recording of environmental parameters (i.e. temperature, minor element concentrations, etc.) can be correlated to high resolution measurements of isotopic fractionation that were made at the CRPG Nancy (3) allowing an interpretation based on biomineralization process instead of simple chemical precipitation.




Firgure explanation: Alternance of day/night growth periods on calcein-marked *Concholepas* shells (CONCHAS IRD/ CNRS program, in collaboration with Antofagasta University, Chile).