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: Tridimensional arrangement of centres of calcification in Corals and Sulfur XANES mapping of coral stepping growth patterns	Experiment number: CH-1364
Beamline:	**Date of experiment**: **November 2002** from: 14th to: 17th	**Date of report**: **15 Feb 03**
Shifts:	**Local contact(s)**: **Salomé Murielle**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Cuif Jean Pierre - Univ. Paris XI Orsay

Dauphin Yannicke - Univ. Paris VI UPMC

Salomé Murielle - ESRF ID21

Susini Jean - ESRF ID21

Report: Experiments were successful, resulting in five papers (two in press)- Pictures enphasize the rôle of sulfated sugars in biomineralization mechanisms, in addition to specific functions of protein compounds.

DAUPHIN Y. - 2002 - Comparison of the soluble matrices of the calcitic prismatic layer of *Pinna nobilis* (Mollusca, Bivalvia, Pteriomorpha). *Comp. Biochem. Physiol. A* **132**: 3, 577-590

DAUPHIN Y., CUIF J.P., DOUCET J., SALOME M., SUSINI J., WILLIAMS C.T. - 2003 - *In situ* mapping of growth lines in the calcitic prismatic layers of mollusc shells using X-ray absorption near-edge structure (XANES) spectroscopy at the sulphur edge. *Marine Biology* **142** : 299-304

Abstract

The microstructure and composition,including chemical speciation of sulphur (S),of two mollusc shells were investigated using a combination of scanning electron microscopy, X-ray absorption near-edge structure spectroscopy (XANES) and electron probe microanalysis (EPMA).The shell of *Pinna* is composed of monocrystalline, and *Pinctada*, of polycrystalline, calcite prisms separated by organic-rich walls. Sulphur speciation information from XANES spectra using a scanning X-ray microscope showed that the protein S content of the interprismatic walls is higher than the SO_4 content, whereas the reverse is true for the intraprismatic structures.High-spatial-resolution XANES maps for the different S species across adjacent calcite prisms confirm their distinctive distributions in the molluscan shells, and illustrate also the presence of narrow, sub-micron transverse growth features. On a larger scale, a series of wider growth zones, incorporating the sub-micron zones, are aligned parallel to each other and cross-cut many calcite prisms. EPMA element maps for Mg and S demonstrate that these growth increments are compositionally zoned and composed of alternating layers of high mineral (Mg-rich) and high organic (S-rich) components. Additionally, these maps confirm that the organic interprismatic walls have lower Mg and higher S than the intraprismatic structures.

CUIF J.P., DAUPHIN Y., DOUCET J., SALOME M., SUSINI J. - 2003 - XANES mapping of organic sulfate in three scleractinian coral skeletons. *Geochim. Cosmochim. Acta* **67,**1: 75-83.

Abstract

The presence and localization of organic sulfate within coral skeletons are studied by using X-ray absorption near edge structure spectroscopy (XANES) fluorescence. XANES spectra are recorded from four reference sulfur-bearing organic molecules: three amino acids (H-S-C bonds in cysteine; C-S-C bonds in methionine; one disulfide bond C-S-S-C bonds in cystine) and a sulfated sugar (C-SO4 bonds in chondroitin sulfate). Spectral responses of three coral skeletons show that the sulfated form is extremely dominant in coral aragonite, and practically exclusive within both centres of calcification and the surrounding fibrous tissues of coral septa. Mapping of S-sulfate concentrations in centres and fibres gives us direct evidence of high concentration of organic sulfate in centres of calcification. Additionally, a banding pattern of S-sulfate is visible in fibrous part of the coral septa, evidencing a biochemical zonation that corresponds to the step-by-step growth of fibres.

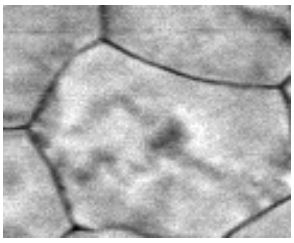
DAUPHIN Y. - in press - Soluble organic matrices of the calcitic prismatic shell layers of two Pteriomorphid Bivalves: *Pinna nobilis* and *Pinctada margaritifera*. *J. Biol. Chem.*

DAUPHIN Y., CUIF J.P., DOUCET J., SALOME M., SUSINI J., WILLIAMS C.T. - in press - *In situ* chemical speciation of sulphur in calcitic biominerals and the simple prism concept. *J. Strut. Biol.*

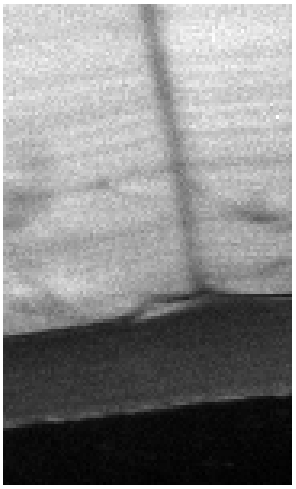
Abstract

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 polycristalline with internal organic radial membranes. High spatial resolution XANES maps for the different S species across adjacent prisms show that sulphate is the principal component in both 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.

Examples of sulfated sugar mappings in biomineralized (calcareous) materials -
Field view : 60 m wide



Pinctada prism
Transv. section



Pinna prism
Long. section