ESRF	**Experiment title:** Organic matter mapping in aragonite and calcite skeletons of the Cretaceous scleractinian corals	**Experiment number**: EC-370
Beamline:	**Date of experiment**: from: 29-10-2008 to: 03-11-2008	**Date of report**: 01-03-2009
Shifts:	**Local contact(s)**: Dr Emilie CHALMIN	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*** Jarosław STOLARSKI**
Institute of Paleobiology, Polish Academy of Sciences, Poland
*** Maciej MAZUR**
Department of Chemistry, University of Warsaw, Poland
*** Anders MEIBOM**
Muséum National d'Histoire Naturelle, Paris, France.
Murielle SALOME, **Jean SUSINI**
ESRF - ID21 - BP 220- F-38043 Grenoble Cedex – France

Report:

In EC-370 experiment we have investigated spatial distribution of organic components in biogenic skeletons of fossil and Recent scleractinian corals using Scanning X-ray Microscope (SXM). We were following experimental setup previously used by Cuif et al. [1]. The measurements were performed with SXM, operating in the fluorescence mode. The 2D fluorescence images at fixed energies were performed pixel-by-pixel by scanning the sample in the beam. The beam was focused to 0.25 x 0.25 μm^2 microprobe using a Fresnel zone plate. The fluorescence emission of the sample was collected by a HpGe detector. XANES spectra were recorded by scanning the primary excitation energy around the sulfur K-edge (2.472 keV), using a Si double crystal fixed exit monochromator ($\otimes E/E = 10^{-4}$).

The main goal of the experiment performed at ID21 beamline was to verify our previously formulated hypothesis [2] that calcitic mineralogy of the skeleton of the Cretaceous *Coelosmilia* sp. is original - the hypothesis that breaks with a century old paradigm that all scleractinians are aragonitic. Although from the time of our publication in Science, there appeared several new arguments supporting primary calcitic mineralogy of *Coelosmilia* sp. [e.g., skeletal bioerosion pattern, see preliminary report 3], the SXM experiment at the ID 21 beamline was crucial to unequivocally confirm this hypothesis. The data collected show that the composition of organic components embedded in the skeleton is essentially the same as in other Recent corals [1] or other modern biomineralizing species [4]. In all the cases we observe characteristic banding pattern in distribution of sulphated polyssacharides. The XANES measurements performed in the fibrous skeletal regions of calcitic *Coelosmilia* sp. (Figure 1) reveal that the distribution of sulphated polyssacharides follows strictly the same pattern known for aragonitic corals: in both cases the organic-enriched growth layers and organic envelopes of the fiber bundles are clearly visible. The distribution of sulphated polyssacharides in the skeleton is independent of the presence of these components in the sediment. In the examined specimens of *Coelosmilia* sp. the sulphated polyssacharides were not present in the sediment. Our observations confirm therefore that migration of the organic molecules between the sediment and the skeleton of *Coelosmilia* is negligible – the argument that additionally supports the original calcitic nature of *Coelosmilia* sp.. The distribution pattern of sulphated polyssacharides in aragonitic skeletons of two Cretaceous corals *Rennensismilia, Trochocyathus* (the latter was included in the experiment) as well as in Recent deep-water coral *Desmophyllum* are fully comparable with *Coelosmilia* sp. The latter observation was suggested previously by acridine orange staining (Fig. 1C), however

the SXM measurements allow now to characterize the type of chemical bonds in the mapped regions the skeleton.

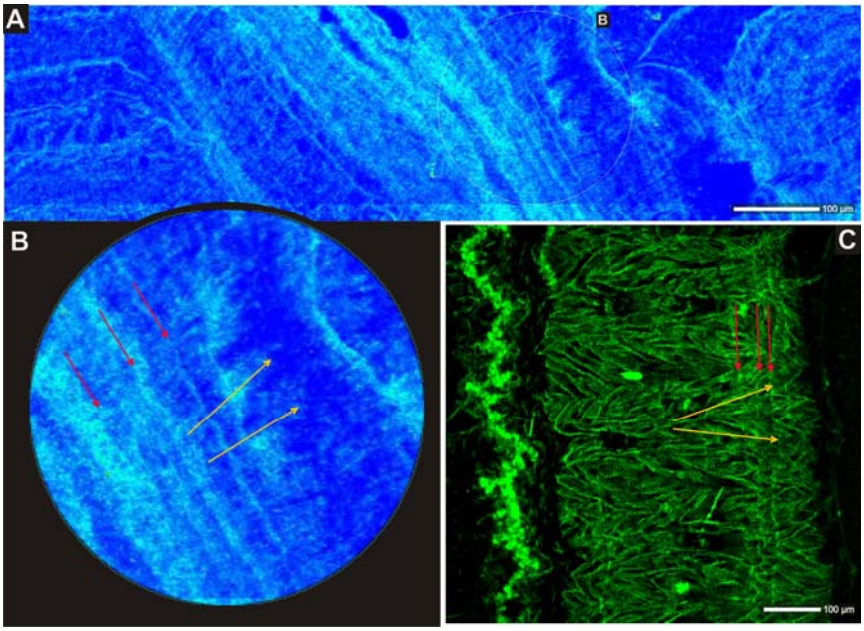

Figure 1. **A**, **B**. Distribution of the sulphated polysaccharides in calcitic skeleton of the Cretaceous scleractinian coral *Coelosmilia* sp (B enlargement). XANES map at E=2.4817 keV (sulphate). The individual growth layers of the fibrous skeleton (red arrows in B) and organic envelopes of the fiber bundles (yellow arrows) are visible. **C**. Laser confocal scanning fluorescent microscope image of aragonite skeleton of Recent *Desmophyllum* sp. that shows similar growth layers and organic envelopes.

The above results (contaning full set of illustrations) combined with the ongoing high resolution stable isotope mapping, microscopic visualization (SEM, TEM, AFM, NSOM) and analytical characterization (ESI MS, MALDI MS, FTIR) will be published in at least 2 papers [7, 8].

References

[1] Cuif, J. P. Dauphin, Y., Doucet, J., Salome, M., and Susini, J. 2003. *Geochimica et Cosmochimica Acta* 67:75-83.

[2] Stolarski, J. Meibom, A., Przeniosło, R. & Mazur, M. 2007. *Science* 318(5847): 92-94.

[3] Stolarski, J., Meibom, A., Mazur, M. & Phillips, G.E. 2008. *Geological Society of America Abstracts with Programs,* Vol. 40, No. 6, p.201 (http://gsa.confex.com/gsa/2008AM/finalprogram/abstract_144263.htm)

[4] Cuif, J.P., Dauphin, Y., Farre, B. Nehrke, G., Nouet, J. and Salome, M. 2008. *Mineralogical Magazine* 72: 233-237.

[5] Perrin C. & Smith D. C. 2007. *Journal of Sedimentary Research* 77: 495-507.

[6] Muscatine, L., Goiran, C. Land, L. Jaubert, J. Cuif, J.P. & Allemand, D. 2005. *Proceedings of the National Academy of Sciences of the United States of America* 102(5): 1525-1530.

[7] Stolarski, J., Meibom, A., Mazur, M., Salome, M., and Susini, J., in preparation (to be submitted to Nature Geoscience). Biogeochemical signatures in calcitic skeleton of the Cretaceous scleractinian corals.

[8] Stolarski, J. Meibom, A., Mazur, M., Phillips, G.E., Salome, M., and Susini, J., in preparation (to be submitted to Geology). Calcitic scleractinian corals: When, where and why.