ESRF	**Experiment title:** Biomineralization and Diagenesis in Red Coral: Microstructure of Present Day and Fossil Samples	**Experiment number**: HS/4398
Beamline: ID31	**Date of experiment**: from: 29 June 2011 to: 2 July 2011	**Date of report**: 02/12/2012
Shifts: 9	**Local contact(s)**: Yves Watier	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Nicole Floquet *Vasile Heresanu *Daniel Vielzeuf *Angèle Ricolleau*
Centre Interdisciplinaire en Nanosciences de Marseille (CINaM) UMR7325-CNRS Campus de Luminy Case 913 - 13288 MARSEILLE cedex09

Francoise Bonneté
Institut des Biomolécules Max Mousseron IBMM UMR 5247 Faculté des Sciences 33 rue Louis Pasteur 84000 Avignon

Report

The aim of the project HS-4398 was to obtain quantitative structural information on red coral biogenic crystals from both present-day and fossil skeletons in order to understand interactions between Mg-calcite and organic matter and to determine the link with the observed variable chemical composition of Mg-calcite constituting the red coral skeleton. Thus, we performed High Resolution Diffraction (HRD) on ID31 which permits us to:
1) characterize crystal structure, crystallite size, microstrains along different crystallographic directions,
2) follow their modifications as a function of increasing temperature,
3) determine the contribution of the organic molecules within the red coral biogenic crystals, both in biomineralization process and diagenetic process.

Experimental techniques

The study was successfully carried out on five samples of red coral, namely present-day red coral (skeletons and sclerites), two different fossil red coral (2 thousand and 2 million-year old skeletons)), and iceland spar calcite as a reference sample. All samples were prepared in our own laboratory, ground gently in an agate mortar, then placed in sealed quartz capillaries, 1 mm in diameter.
High-resolution X-ray powder diffraction measurements were performed at 0.4 Å (standard) wavelength on ID31:
1) at room temperature to characterize the initial crystal structure, crystallite size, microstrains,
2) from RT to 700°C, using a hot air blower, in steps of 50°C, and again at RT after cooling to characterize the temperature-induced modifications (including loss of the organic component) to the crystal structure (lattice parameters, structural phase transition from magnesium calcite to dolomite), crystallite size, and microstrains.

Result

Red coral produces biomineral skeletons and sclerites that are made of Mg-rich calcite nano components (9 to 15 mol.% $MgCO_3$) and organic matter (OM) (1.2 to 1.7 wt%). From the high resolution diffraction data performed on ID31, we obtained:
1) accurate quantification of the magnesium calcite phase histogram constituting each red coral samples. These data highly complete our previous numerous and accurate physical (AFM, HRTEM, EBSD) and chemical (X-ray maps and EMPA) data (1-3). Consequently, the contribution of the numerous magnesium calcite phases in the broadness of the diffraction peaks (Fig.1) prevents to obtain readily, from the conventional Rietveld refinement (Fullprof software) and the Williamson and Hall method, reliable sizes and microstructural defects of the submicrometric mesocrystals constituting the red coral samples (1-3).

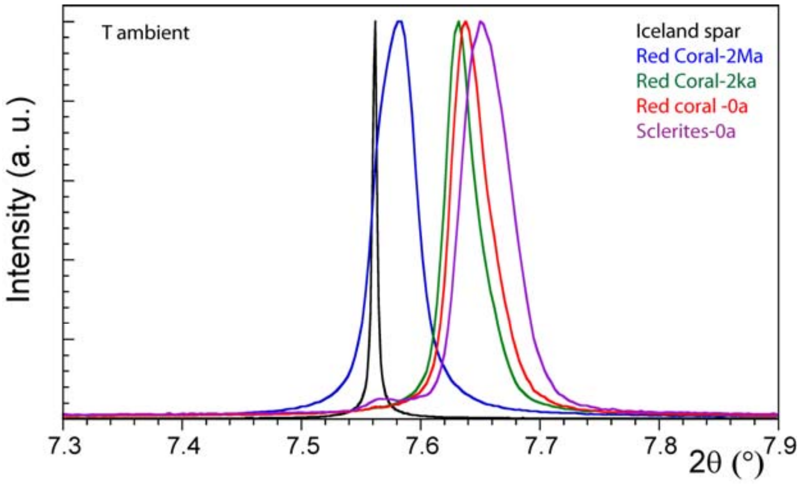

Fig.1 Experimental (104) diffraction peak of the five samples obtained at T ambient before heating.

2) signature of unexpected structural phase transition, as a function of heating temperature and the red coral analysed sample (Fig. 2). It appears that the main structural phase transition is highly correlated to the Mg quantity included in the Mg-calcite phases constituting the nanometric crystals of each red coral sample. Comparisons with the reference sample of pure calcite were very usefull: firstly, we did not observe this transition in the pure calcite, and secondly, it gave us precise thermal expansion parameters up to high temperature which helped us to quantify the biogenic calcite samples. These new results provide great insight in understanding biominerals structure.

The quantitative analysis of the data are currently under treatement. To be able to understand and quantified this phase transition, occuring in biogenic crystals, more HRD will be required. A new beamtime will be requested to perform HRD analyses on specifically identified sets of samples with choosen steps of heating and cooling temperature.

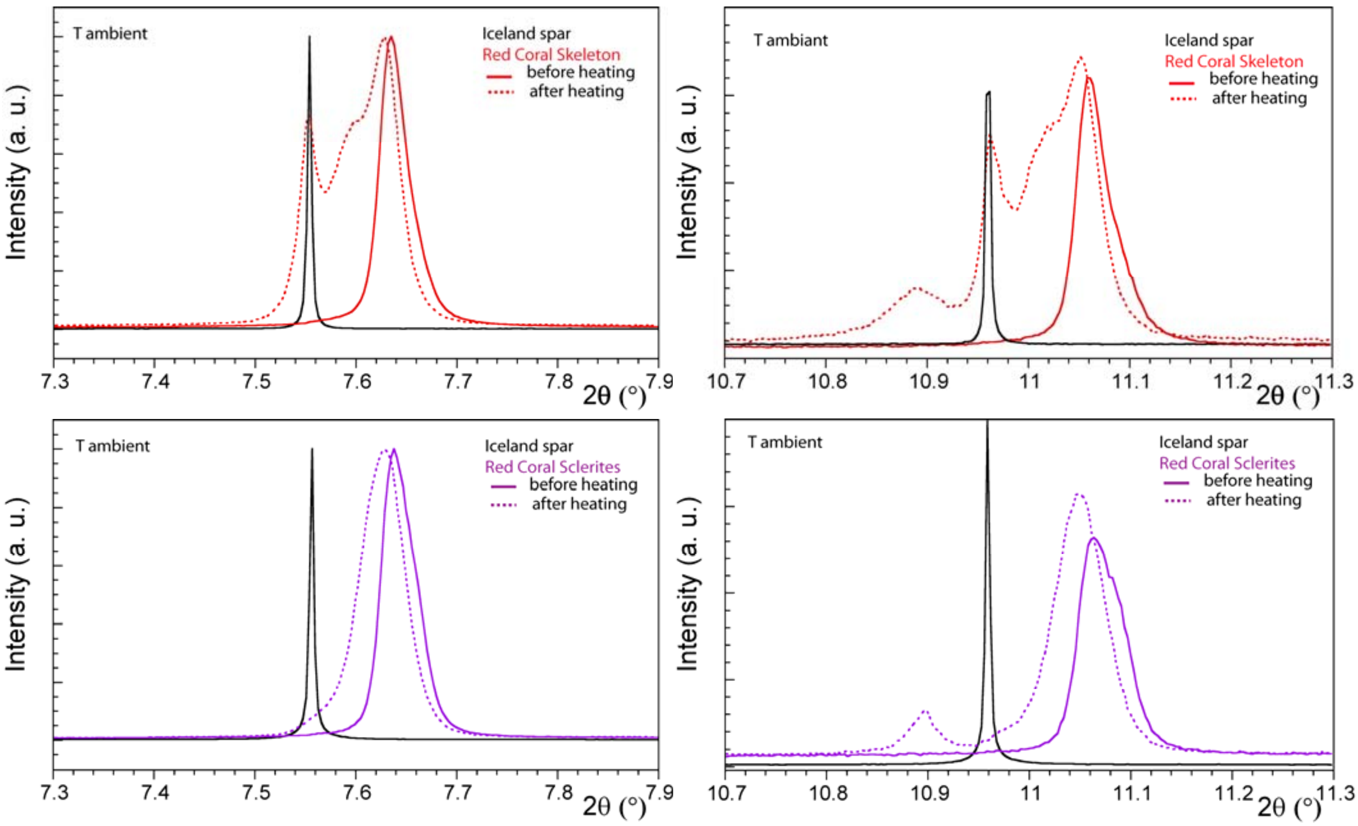

Fig.2 Annealing effect on the experimental (104) and (202) diffraction peaks for two samples of red coral (skeleton and sclerite), diffractograms recorded at T ambient. Iceland spar is also plotted for comparison.

1- VIELZEUF D., GARRABOU J., BARONNET A., GRAUBY O., MARSCHAL C. (2008) – Nano to macroscale biomineral architecture of red coral (Corallium rubrum). American Mineralogist 2008, 93, 1799-1815.
2- VIELZEUF D., FLOQUET N., CHATAIN D., BONNETE F., FERRY D., GARRABOU J., STOLPER E.M. (2010) – Multilevel modular mesocrystalline organization in red coral. American Mineralogist 2010, 95, 242-248.
3- FLOQUET N.,VIELZEUF D. – Mesoscale twinning and crystallographic registers in biominerals American Mineralogist 2011, 96, 1228-1237.