| ESRF | **Experiment title:** In-situ WAXS/SAXS/Raman spectroscopy characterization of the organo-mineral nanocomposite structure of the recent scleractinian coral fibers. | **Experiment number**: EC-134 |
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## Report:

The test measurements (3 shifts) have been performed in order to verify the feasibility of a more elaborated study of the composite organic-inorganic structure of coral skeletons by using microbeam SR diffraction techniques. We have selected parts of coral skeletons in the form of thin slices, so-called septa. We have used specimens extracted from different coral species: *Desmophyllum dianthus* (see our previous papers [1,2]) and *Gardineria hawaiiensis*.

The microbeam of wavelength 0.9613 Å and approximate dimensions of 1.2 μm × 1.2 μm was directed on the sample perpendicular to the septum surface. The measurements were performed in the transmission mode by using both wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) setups. The wavelength calibration and detector position adjustments were done by using the reference powder $Al_2O_3$ sample. The variation of the coral skeleton structure in space was studied by collecting a map of WAXS and SAXS measurements (the sample was moved horizontally and vertically by 1μm across a size of about 20-40μm). It was also proposed to perform micro-Raman studies on the same specimens. This part could not be done because the micro-Raman spectrometer was not yet installed at the time of our measurements.

The WAXS signals show mainly the Bragg peaks due to the crystallites of aragonite ($CaCO_3$). Our preliminary data analysis did not show substantial contributions of the organic inclusions nor traces of the amorphous calcium carbonate phase.

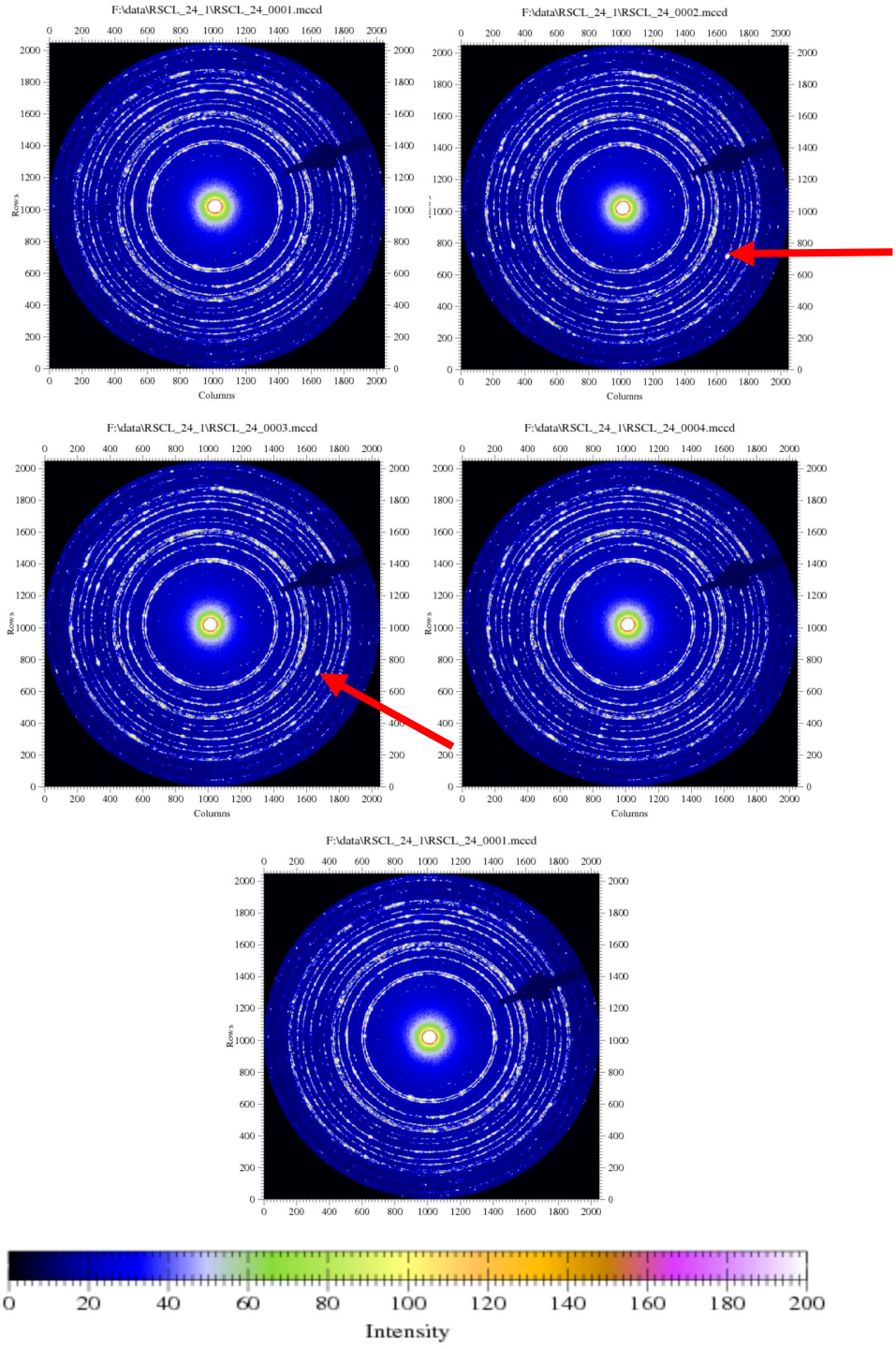


**Figure** WAXS signals obtained with a thin septum of the *Gardineria hawaiiensis* coral skeleton. The five images were obtained with the SR microbeam (1.2 µm × 1.2 µm size) pointing to neighbouring areas of the sample shifted by 1µm from each other. The strong (221) Bragg reflection spots are marked with red arrows.

The WAXS patterns indicate strong texture effects. As a matter of example we show five consecutive WAXS patterns (from areas shifted by 1μm from each other) in the figure below. There are clear spots and dark areas on many Debye-Scherrer rings. One can see the (221) Bragg reflection due to the aragonite crystallite with a very high intensity (in the middle patterns no. 2,3,4) and weak intensity (at both ends, i.e. patterns no. 1 and 5). From this data one can conclude that the spatial extent of this crystallite is about 3μm. A more detailed analysis of these WAXS patterns may provide information about the character of the aragonite crystallites' arrangement in the coral skeleton.

The SAXS signals do not show important variations within neighbouring scans. There is a monotonic decrease of the azimuthally averaged SAXS signal I(Q) with increasing Q. We did not observe the Guinier regime at low Q that could be indicative to inclusions of the organic phase embedded in the $CaCO_3$ matrix.

We have also studied one coral skeleton sample that was annealed at $300^0$C in a furnace prior to the experiment at ESRF. The annealing conditions were such that about 50% of the sample volume transformed from aragonite structure (metastable $CaCO_3$ phase) to the calcite structure (stable $CaCO_3$ phase). It is known that the composite organic-inorganic structure of the $CaCO_3$ biominerals strongly influence the aragonite-calcite phase transition [2-4]. We have measured a map of WAXS patterns on the annealed coral skeleton sample which shows Bragg peaks due to both aragonite and calcite phases. We are going to obtain information about the texture and morphology of neighbouring aragonite and calcite crystallites. The data analysis is still in progress.

## References


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