EUROPEAN SYNCHROTRON RADIATION FACILITY
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ESRF	**Experiment title:** Testing a biomineralisation model : structural comparison of PILP-induced CaCO3 film and pearl oyster shell based on x-ray Bragg ptychography data.	**Experiment number**: EV191
Beamline: ID13	**Date of experiment**: from: 15/06/16 to: 17/06/16	**Date of report**: 1/03/20
Shifts: 12	**Local contact(s)**: M. Burghammer and M. Rosenthal	*Received at ESRF:*

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Report:

This experiment proposed to take advantage of the unique features of lens-less coherent x-ray imaging to test a current hypothesis on biomineralization, which claims the existence of a polymer-induced liquid precursor (PILP) at the early stages of the biomineralization process. We proposed to test this assumption by fully characterizing the crystalline structure of oriented $CaCO_3$ films, synthetically produced through a PILP driven growth process in the presence of poly(aspartic acid), and comparing this structure to that of a recently investigated biomineral. We expected to be able to conclude how similar the synthetic growth process is to the natural one. In addition, the data will help to identify the mechanism that drives the amorphous-to-crystalline transformation in synthetic PILP films classically obtained in biomimetic mineralization.

For this experiment, the samples were grown in liquid phase onto Si3N4 membranes (500 mu frame width, 200 nm thick). The films thickness was estimated to be smaller than 1 mu (around 500 nm). Preliminary optical microscopy observations with crossed-polarizors allowed to confirm the existence of large single crystalline domains (Figure 1).

The whole experiment was dedicated to the analysis of the Pilp11f film. Our aim was to obtain a detailed characterization of different regions of the domains and a statistically relevant domain information. As a starting point, we performed extensive nanodiffraction scanning experiments with the Eiger detector located close to the sample (0.13 m) in order to observe several diffraction peaks at once (Figure 2). 3D nanodiffraction data were measured with typical angular steps of about 0.1°. The sample was scanned across the beam to provide the spatial description (typically 50 x 50 μm^2 with 0.2-0.5 μm step).

The data have been analysed and several information have been extracted: peak intensity, crystalline orientation along the azimuth direction, shift position along q (strain), for the different Bragg peaks accessible. Figure 3 shows a typical set of maps obtained in the vicinity of a crystalline domain center.

Finally, Bragg ptychography was attempted. In order to compensate for the loss of intensity in the coherent beam, the exposure time was dramatically increased (by a factor of 100). This long lasting illumination condition resulted in the degradation of the sample under the beam. Hence, we could not perform further coherent diffraction imaging investigation.

Note that since this experiment, our sample preparation procedure have been improved and we expect that the actual PILP induced crystalline films are able to resist to radiation damage even with the ESRF-EBS beam.

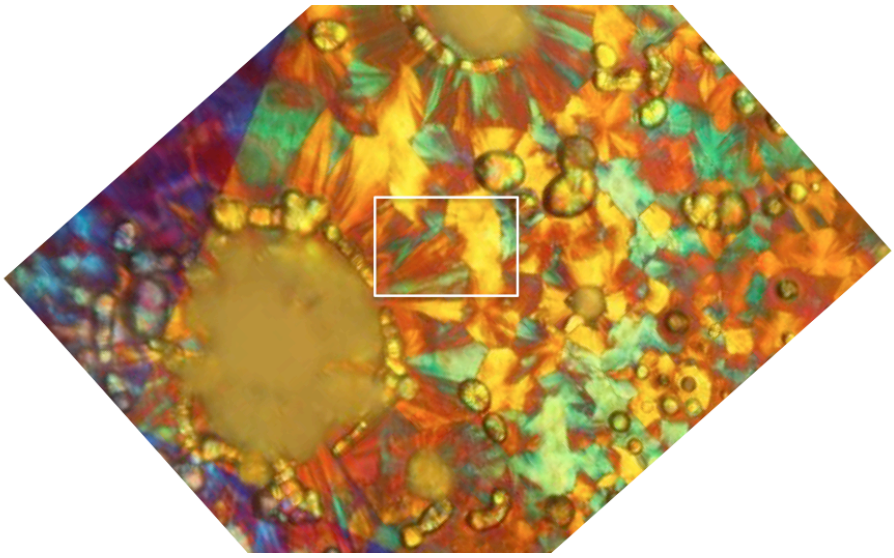

Figure 1: Investigated sample (PILP11f) as seen with crossed-polarized optical microscopy. The white rectangle corresponds to one of the investigated areas. The Si3N4 membrane border is visble on the left.

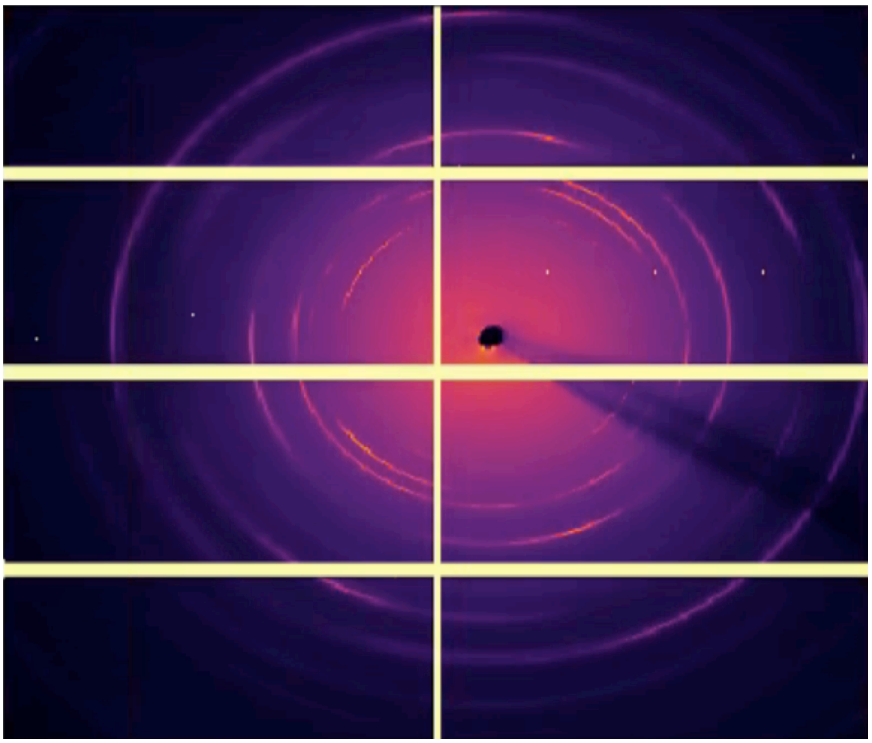

Figure 2: Typical diffraction pattern acquired with the Eiger 4M detector and integrated along the rocking curve. Note the azimuthally ectended Bragg peaks.

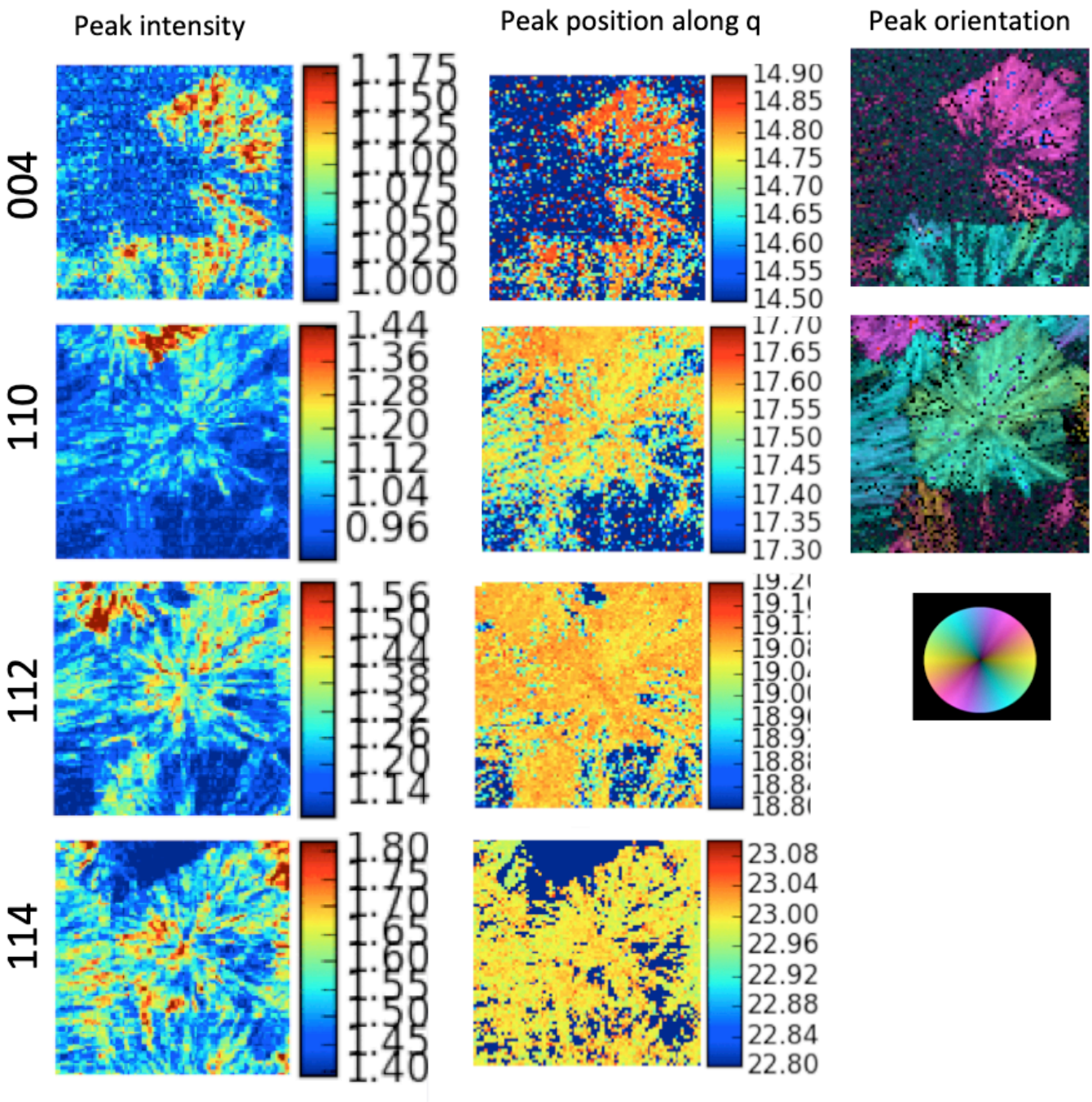

Figure 3: Some extracted information, for different Bragg peaks. From left to right: integrated intensity, peak position along the Bragg vector direction (strain information) and orientation of the Bragg peak along the azimuthal direction.