EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

ESRF	**Experiment title: Characterizing the 3D structure of enamel at the nanoscale**	**Experiment number**:
Beamline:	**Date of experiment**: from: 9-02-2017 to: 14-02-2017	**Date of report**:
Shifts:	**Local contact(s)**: Tilman A. Grünewald	*Received at ESRF:*

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Report:

Due to measurement difficulties encountered during the beamtime, we had to revise our original scientific plans and shift to another sample material. Therefore, this report contains two parts.

Part I – The beamtime was originally dedicated to dental enamel, which is a unique hierarchical material. The aim of this experiment was to visualize the mosaic 3D crystalline organisation of individual nanorods of rat enamel (namely, the crystalline coherence, strain field and lattice rotation), using 3D Bragg nanodiffraction and ptychography. These results are fundamental in understanding the structural and mechanical properties of enamel and may further guide biomimetic models for synthetic reparative dentistry.

Unfortunatelly, the experiment on individual nanorods of rat enamel has been unsuccessful because the individual nanorods were not stable under the nanofocused beam. The diffraction spots would shift with exposure to beam. The changes in the diffraction patterns (spot positions and intensities) did not seem to be reversible. We adscribe these effects to beam induced displacements or jumps of the individual nanorods, perhaps due to charging effects.

Several strategies have been tried to stabilise the samples:

1) Individual nanorods disolved on a solvent (methanol) were drop casted on SiN membranes and let the solvent dry. Different nanorod concentrations and drop casted samples were tried.

2) After drop-casting the nanorods and the solvent was dried out, the nanorods were embedded in a cyanoacrylate-based matrix.
3) After drop-casting the nanorods and the solvent was dried out, the nanorods were coated with thin gold layers.

None of these strategies gave satisfactory results and thus, after discussions with beamline staff, we decided to shift the experiment on a different biomineral: a calcareous mollusk shell.

Part II – Calcareous mollusk shells are biominerals, which share several features with enamel: they are produced by living organisms, present a well defined hierachical structure and are composed of single-crystals. At the most local scale, *i. e.*, the nanoscale, the single crystals exibit an organo-mineral granular (50 - 500 nm) morphology, common to most of the biomineralizing systems. The back-up sample was the external part of a margaritifera mollusk shell, made of large (10-20 μm) single-crystalline calcite units, called prims. The thickness of the prims, smaller than 2 μm, allows to preserve the coherence diffraction along the beampath. Investigations of the prisms using 3D Bragg ptychography measurements have been planned, following the procedure described in [1], in order to get access to the detailed 3D image of the crystalline properties (crystalline strains, orientations and coherence).

In our previous experiments, it was found that the crystalline prismatic structure is composed of several iso-oriented and iso-strained domains, larger than several granules. Each of these domains are characterized by coherent crystalline domains extended over several granules as well. Such structural features allowed to identify two possible biomineralization models [1]. Recently, using CARS microscopy, we have evidenced the presence of an amorphous precurssor at the early stage of the prim formation. In older prisms, the amorphous precurssor remains visible at the very edge of the prism. Therefore, the reamining beamtime was dedicated to the investigation of the crystalline properties as a function of the position within a prism. About 10 positions have been selected onto the prism surface and full 3D Bragg ptychography datasets have been collected. Data analysis is in progress.

We would like to express our gratitude to our local contact (Tilman Grünewald) for assisting us with the beamline and also for helping us with sample preparation. His support during the experiment has been outstanding.

References

[1] F. Mastropietro et al., Nature Materials (2017), 10.1038/nmat4937.