EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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:** Analysis of marine adhesives of diatom algae with nanoprobe X-ray fluorescence	**Experiment number**: EV-212
Beamline: ID16A-NI	**Date of experiment**: from: 02.02.2017 to: 04.02.2017	**Date of report**:
Shifts: 6	**Local contact(s)**: Yang Yang, Sylvain Bohic	*Received at ESRF:*

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Report:

In our beamtime ‘Analysis of marine adhesives of diatom algae with nanoprobe X-ray fluorescence’ we aimed to investigate the extracellular polymeric substance (EPS) of the diatom *Navicula perminuta*.

The excitation energy of the beamline was tuned to 17.05 keV. We used a focus of 43 nm x 50 nm with a pixel pitch of 50 nm and an exposure time of 100 ms to acquire 2D XRF data. Beam quality, performance of the beamline, and support by the ESRF team was fantastic, some beam dumps reduced the effective beamtime by 6 hours. For the first time we were able to perfom XRF measurements of cryo-prepared diatoms, which was the in-situ extension of our previous experiment EV-182 where we investigated air-dried algae and their adhesives. After settling on silicon nitride membranes the diatoms were plunge frozen and analyzed at the ID16 beamline under vacuum. We found out that the algal shell consists besides Si of calcium, sulfur, strontium, bromine and zinc. In addition to that, the adhesive of the algae contained a high concentration of of zinc.

X-ray absorption measurements revealed that the ice thickness of the investigated samples was around 10-20 µm. Due to the thin ice even the lighter desired elements like silicon were detectable. In Fig. 1 the fluorescence signals of two algae are shown.

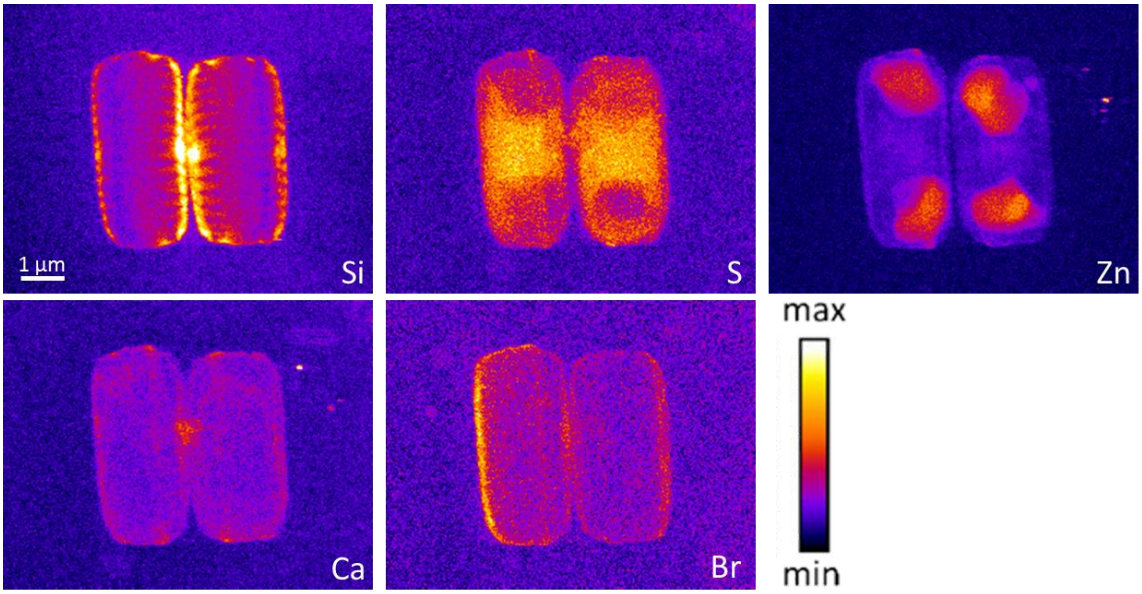

Figure 1: X-Ray fluorescence signals of the alga shell. The scale bar is 1 µm.

While the location of the elements inside the algal shell was similar to the dried cells the concentration of some elements like Cu and Zn were higher in the cryo prepared algae.
Like in the last beamtime a high concentration of Zn could be found inside the extracellular polymeric substance under the algae.

In addition to the structural analysis of adherent diatoms, we tested whether elements present in the extracellular polymeric substances secreted by the algae were initially present in the adhesive or if they are absorbed from the media. For that, algae were cultured and adhered in media with depleted metal content. After several measurements of the algae grown and attached in media with different bromine levels we were able to prove that the algae produce an EPS rich in bromine as the levels in the secreted adhesive was the same. For calcium we found the opposite behavior. Both, the algae and the EPS had a very low calcium content which is a hint that the calcium is being absorbed by the EPS from the ambient medium after secretion by the diatom. The same could was found for strontium. After culture in media without strontium, a very low signal was found in the algae and also in the EPS. This means that bromine is part of the EPS as produced by the diatoms, while Ca and Sr are ions absorbed post-secretion. Future experiments using microfluidic measurements will provide insights about the attachment strength of the algae depending on the metals in the media. The correlation with the XRF data will give further insights into the function of the elements and especially about halogens in marine adhesives.