	Experiment title: The prince in shining armour – Shedding light on the nanostructural arrangement of Fe mineral phases in the dermal armour of scaly snails	**Experiment number**: **SC-4890**
Beamline: ID13	**Date of experiment**: from: 04.11.2018 to: 08.11.2018	**Date of report**: 25.02.2020
Shifts: 9	**Local contact(s)**: Tilman Grünewald	*Received at ESRF:*

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Report:

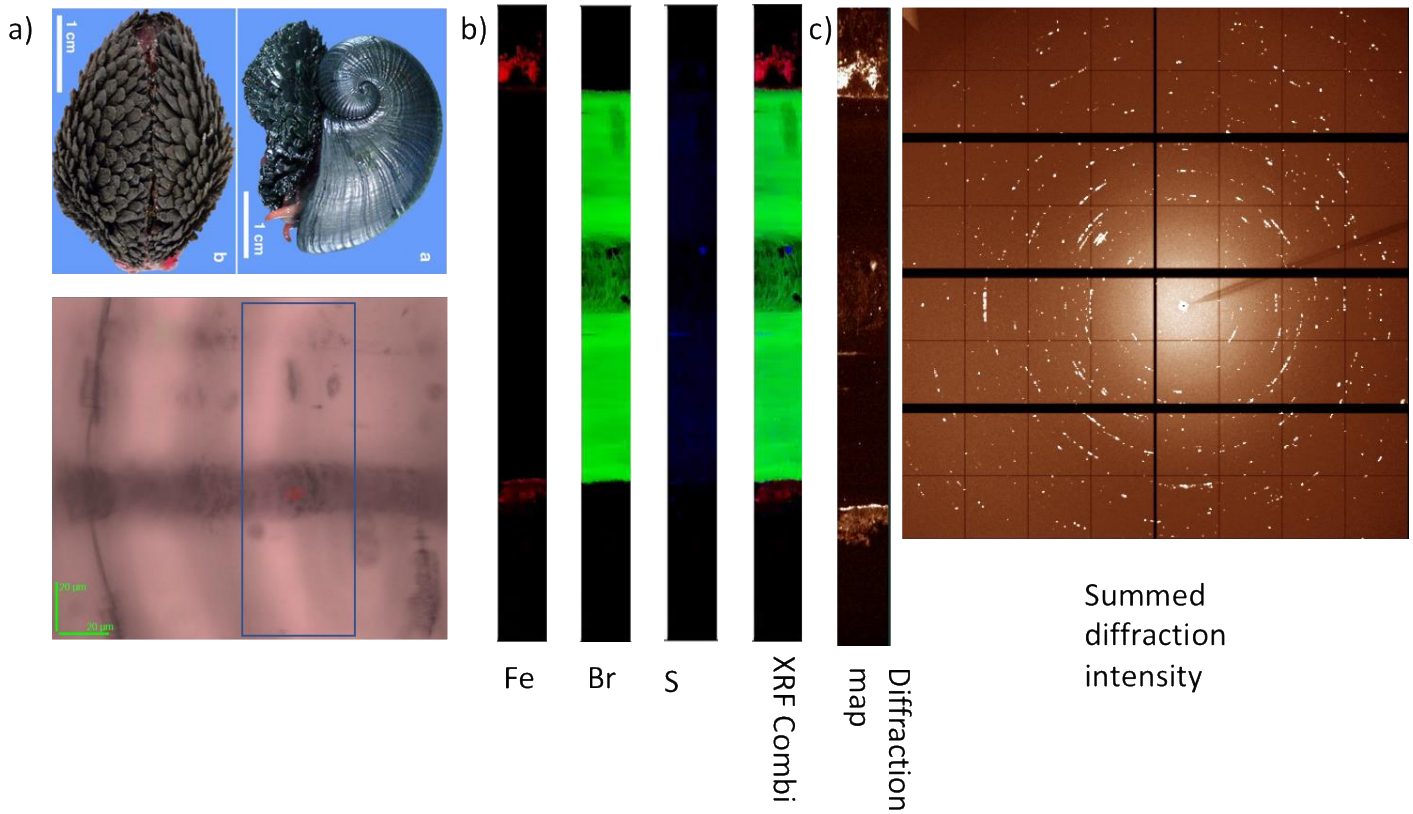
Summary:

The aim of this experiment was to understand the micro- and nanostructural arrangement of the Fe phases in the dermal armour of deep-sea vent scaly-foot gastropods (*Chrysomallon squamiferum).* Originally proposed as a double experiment that combined total scattering at ID15A with nanobeam diffraction and fluoresence mapping at ID13, we only received beamtime for the ID13 part. Therefore, we focused on the nanostructure and the distribnution of elements. We most notably managed to map the element and phase distribution in different animal sampling sites across the ocean floor. We could evidence a clear difference in the Fe content and distribution based on the site and found the Fe to be located at the very outermost side of the organism.

Samples and setup

We carried out this experiment at the nanobranch EH3 of ID13. X-rays were focused with a set of Si nanofocusing lenses and used a pre-focusing scheme to enhance the flux. This resulted in a spot size of 200x250 nm^2 with a flux of approx $2x10^9$ ph/s at 15.05 keV photon energy. We choose a 65 mm long He-flushed flight tube together with a small (250 µm diameter beampstop) to access a wide q-range from 0.5 to 35

nm^{-1}. The scanning was carried out with a three-axis PI Hera piezomotor scanner. The diffraction signal was collected with a Dectris Eiger 4M detector and the fluoresence signal with a Vortex EM detector.
As the initial proposal aimed at combing nanodiffraction at ID13 with nanobeam PDF at ID15A, we were forced to alter our experimental focus slightly as only the experiment at ID13 got beam time allocated. Due to this, we primarily focused on the nanostructural arrangement of elements and biominerals.
The sample set comprised scales from the scaly-food gastropod (*Chrysomallon squamiferum*). We were able to obtain samples from different deep-sea environments, notably the Kairei, the Longqi deep-sea vents as well as a solitaire population. Portions of the scales were embedded in epoxy resin and sliced with a microtome to a thickness between 5 and 15 µm.
The samples were mounted on SiN membranes and fixed with a droplet of nail polish on the embedding material.



Principal outcome

The experimentes could clearly help us to localize the iron-rich minerals and identify them crystallographically.
Figure 1a) shows a macrophotograph of a specimen and microscope overview of a scale cross section where the inner fibrous part of the scale attachment is clearly visible as a dark horizonal zone. Figure 1b) presents fluoresence maps of the most prominent constitutents of the scales. We can clearly identify the soft tissue periostracum based on the strong Br signature and it's notable that the Fe is only present on the outside of the scales. This observation is systematic for all the different sampling sites. The diffraction pattern unveils a rather single-crystalline diffraction pattern that could be attributed to pyrite. The most notable finding is the localization of the Fe-containing layer to top of the periostracum, the organic membrane that usually forms the outer delineation of shells. Our current preliminiary interpretation is thus that the Fe might not be structurally incorporated into the shell, but is rather deposited onto the animals during their life cycle. We however need to carry out further experiments to verify this finding.

Conclusions and further proceedings

We consider the experiment as a success as we could could collect a dataset that clearly shows the nanostructural organization of the scails and shell of the different animals, with rather surprising localization of the Fe-rich minerals on top of the organic membrane of the scales and shells. As we were unsuccesful in obtaining the PDF part of the ID15A, we envisage to apply for further beam time to add this part of the experiment to our dataset and complete our understanding of the chemical pathway of mineralization before we are able to write a conclusive publication on our experiments.

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