	Experiment title: On the cutting-edge: How beaver teeth retain sharpness and guide the wear by their nanostructure	Experiment number: SC 4504
Beamline: ID21	Date of experiment: from: 18.5.2017 to: 20.5.2017	Date of report: 23.02.2018
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Report:

Summary

The experiments aimed at the characterization of the element distribution on the cutting edge of beaver (Castor fiber) as well as the speciation of the iron-containing compounds of the teeth, as they are thought to make up the extraordinary mechanical and wear properties.

We successfully mapped the distribution of the most important elements (Mg, Al, P, Cl, K, Ca, Cr, Fe) with sub- μm resolution and carried out XANES experiments at points along the beaver teeth. Due to the small expected differences in the different Fe compounds it was decided to switch to the Si(220) monochromator to be able to resolve small changes in the pre-edge peak. We found a transition in the pre-edge peak area which we will exploit further and might stem from a changing coordination of Fe in the teeth along the growth direction. Due to the measurement of calibration standards the XRF data is quantifiable. Along with diffraction experiment at ID13 we could collect a meaningful dataset which enables us to understand the underlying iron transformation mechanisms during the tooth development.

Samples and setup

Two sets of samples were prepared, five FIB sections ($20 \times 10 \times 0.5 \mu\text{m}$) from different spots along the teeth growth direction to match the sample thickness to the beam size and one set of two large area polished samples, covering a complete tooth in three pieces with a thickness of $50 \mu\text{m}$. The samples were mounted between ultralene foils in the beamline standard sample holders.

The experiments were carried out in three setups: fluorescence scanning, $E=7.35 \text{ keV}$, Si 111 monochromator, XANES experiments, Si 220 monochromator, varying energy and for the detection of Mg, Si 111 monochromator, $E=2.2 \text{ keV}$ and excitation of Ca with higher harmonics.

Principal outcome

Fig 1 shows an overview over the complete teeth longitudinal section of $50 \mu\text{m}$ thickness. We could not detect a gradient in the amount of Fe present in the surface. Additionally and in contradiction to published theories we could not find the Mg accumulation postulated by Joester et al in the Fe rich part as an intergranular

enrichment. We could only observe a difference between enamel and dentin but no difference in the enamel across the Fe-rich layer (Fig 1b).

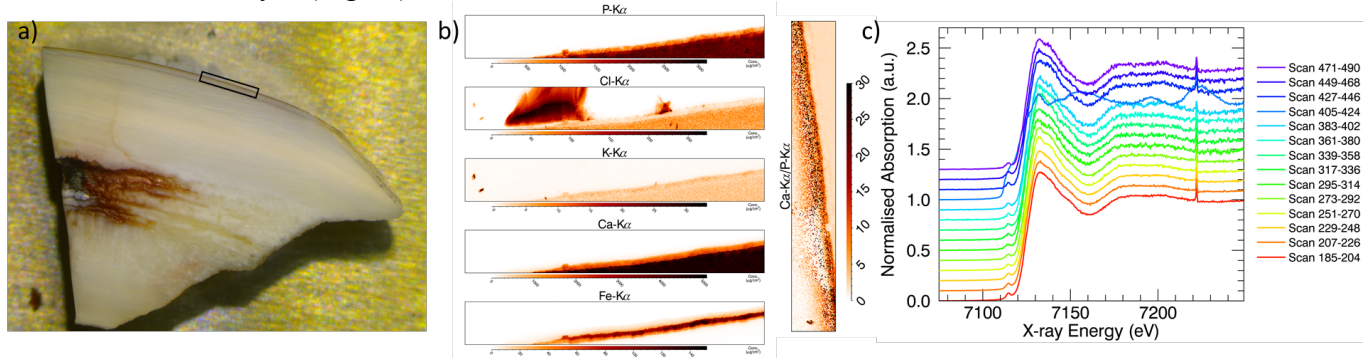


Figure 1a) Optical micrograph of a beaver tooth cross section. B) Elemental distribution of the main target elements in one scan region. It is noteworthy that the Ca/P ratio suggests a different CaP in the presence of iron. C) The XANES spectra along the Fe-rich interface

The Fe XANES experiments along the growth direction were evaluated by the pre-peak area and a set of measured standards was used for the deconvolution of the suspected phases. We found no differences in the top part of the teeth and also no difference along the pigmentation line. We however observed an transition in the earlier development stages, which by comparison to literature data could either stem from a transition from a ferrihydrite to goethite (see Fig 1c) or from 2-line to 6-line ferrihydrite. We are currently in the process of evaluating whether this is also visible in the amorphous background of the diffraction data of the same samples.

Conclusions and further proceedings

In conclusion, we were able to collect a conclusive dataset on the Fe mineralization in beaver teeth. We can clearly show that the mineralization is mostly in the form of a ferrihydrite, which is in contradiction to the claims of Dumont et al earlier. We also managed to show that there is no accumulation of Mg in the Fe rich layer, as it was proposed by Joester et al by their hypothesis of an Mg-stabilized intergranular phase. We could however see a change in the Fe structure from Goethite to Ferrihydrite in the earlier stages of development of the teeth. This very interestingly does not coincide with the change in pigmentation which is visually apparent but happens in earlier development states of the teeth. Another interesting point is the change in the pre-edge peak suggests a transformation from the more stable goethite in the the less stable ferrihydrite, which is then observed all along the rest of the tooth. We are however positive that the current data is enough to understand the processes in a conclusive fashion. We explicitly wish to point out the very good support from the ID21 team and our local contact Bernhard Hesse, enabling the quality of the data acquired, the valuable scientific discussion and the generally excellent condition of the beamline.