ESRF	**Experiment title: Analysis of calcium phopshates in ancient hairs by X-ray and infrared micro-spectroscopies**	**Experiment number**: ME1258
Beamline:	**Date of experiment**: from: 31/08/05 to: 05/09/05	**Date of report**: 16/02/06
Shifts:	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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Report:

Purpose:

The purpose of this study was to understand mineralization processes involved in very ancient tissues, particularly hairs, and to image the distribution of degradation products in the different constitutive layers of hairs. Some calcium phosphates have already been identified in some ancient Chinese mummies, principally in the core of the hair, called medulla. We wanted to extend the range of studied samples by analyzing other samples preserved in the same environment: hair from mummified animals and hair from animal skins used as clothes and found on human bodies. We also wanted to follow the degradation of sulphured molecules present in hair proteins.

The interest of performing analyses on ID21 was to access to the highly detailed images of low Z elements present in the hairs (S, P, Ca) and also to be able to measure the S and Ca speciations, with a high spatial resolution.

Experiment:

Different kinds of samples were studied:

- Camel hair
- Pelisse fur
- Fur
- Wool cloth (×2)
- Human hair (×2)
- Modern human hair (×2)

A piece of each sample was taken and embedded in a resin to prepare thin transversal cross- sections. To improve the statistic, at least three cuts of the same sample were analysed. Several thicknesses were tested and

it turned out that 4-5µm was the most appropriate thickness. As the samples were not tangential to the beam, it was necessary to limit the volumic aberrations due to the tilt.

Several experimental configurations were used:

1/ analyses at the sulphur K-edge,

2/ analyses at the calcium K-edge.

For each edge, different acquisitions were performed:

1/ elemental mappings of the endogenous and exogenous elements (Al, Si, P, S, Ca)

2/ XANES. These spectroscopic measurements were done first, with a 50µm-pinhole, in order to get an average value on the whole cross-section, and second, with a focused beam, on different regions identified thanks to elemental maps. The beam sized was reduced to less than 1µm by using a zone plate.

Results:

It was of high interest to image the distribution of elements in transversal cross-sections. This way, contrary to macroscopic techniques which may average the data on the whole sample, X-ray microscopy enables to differentiate between surrounding environment and sample as well as between the different constitutive regions of hair (cuticle, cortex, and medulla). The images revealed a great heterogeneity, with an apparent weakness of the hair in the most internal part. It was there that the main alterations were observed. On the other hand, the state of degradation was different from one sample to another.

Image 1 illustrates the distribution of sulphur, calcium and phosphorous in the cross-section of a mummified human hair. The correlation between C and P is obvious.

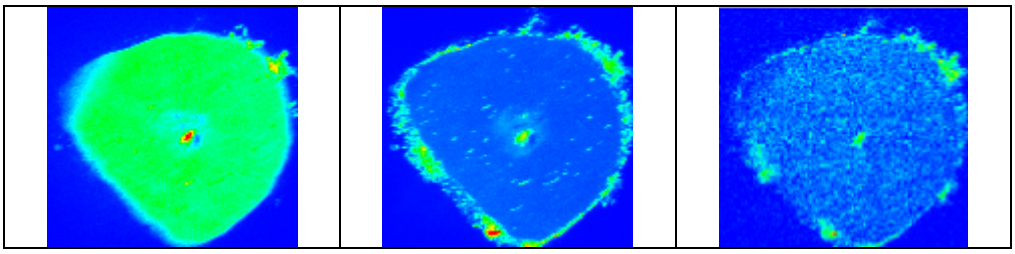

Image 1: distribution of S (left), Ca (middle) and P (right) in a transversal cross-section of a mummified hair. Map size: 100´95µm^2, beam size: 1´0.4µm^2, pixel size: 0.8´0.8µm^2. Image acquired at 4.1keV.

XANES spectra obtained in the cortex and in the “hot-spots” on the cuticle and the medulla are clearly different. Interestingly, the protein S-S bounds are still present, but some have suffered from alteration. An enrichment of phosphorous is sometimes observed with the formation of calcium phosphate. We will try to completely understand the XANES spectra and decompose them into their main components. Then, it will be interesting to search possible correlations between S and Ca degradation processes.