

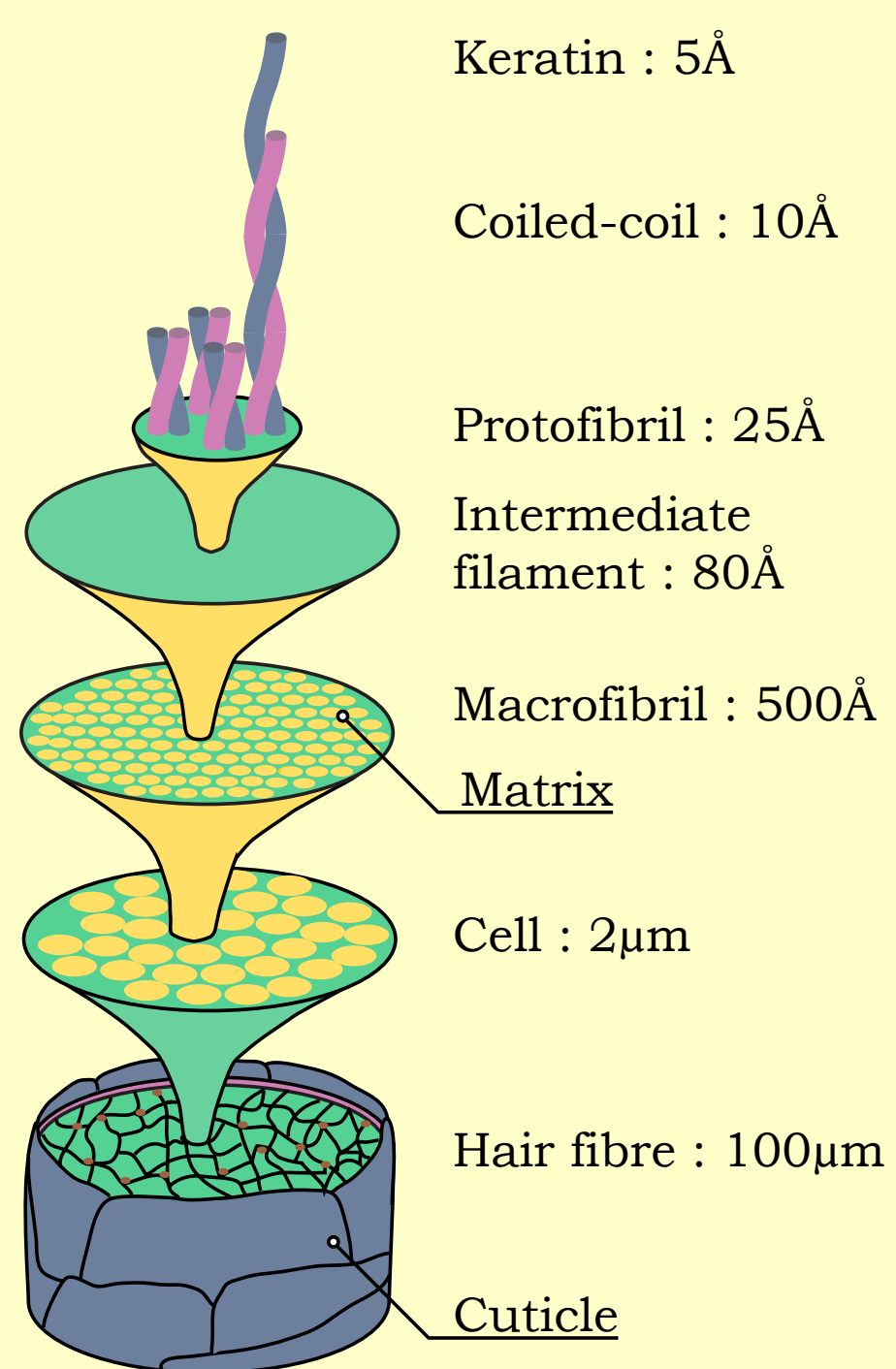
# SIMULATION EXPERIMENTS ON EARLY STEPS OF ALTERATION OF ARCHAEOLOGICAL HAIRS

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Diagrammatic representation of keratin macromolecular assembly in hair

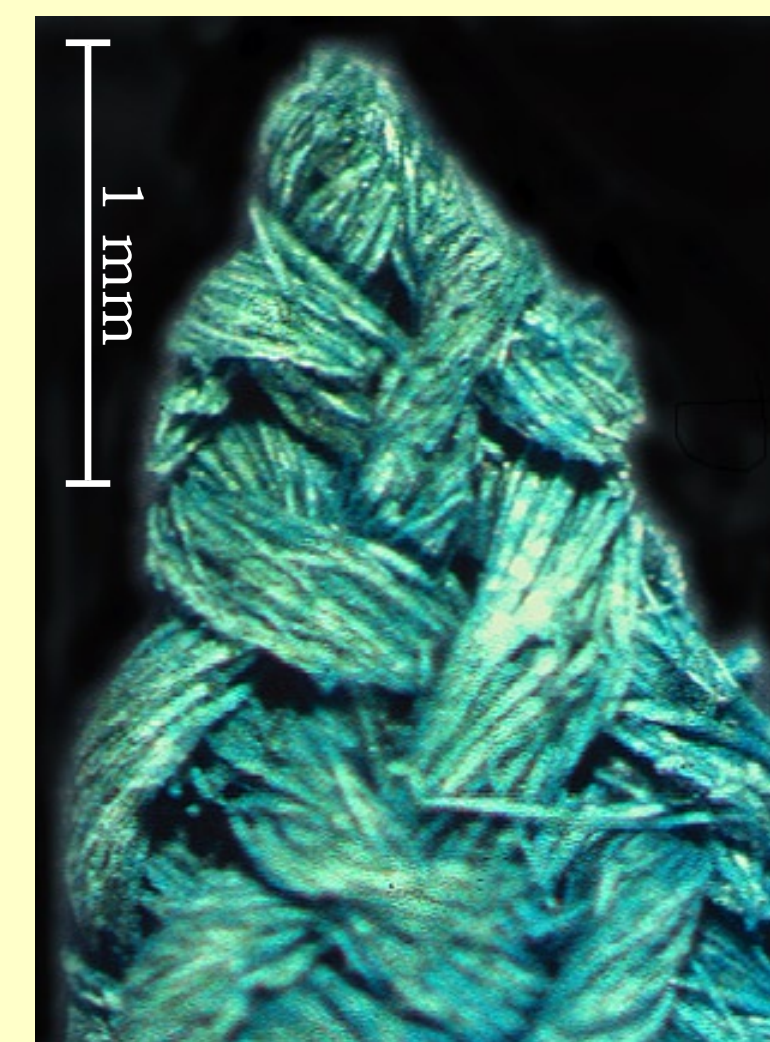
Animal and human hair is seldom preserved in archaeological contexts.

In the majority of European burial sites, in temperate climate, any observed preservation involves the **close contact with a metal object** where a corrosion layer protects the fibres against further damage.

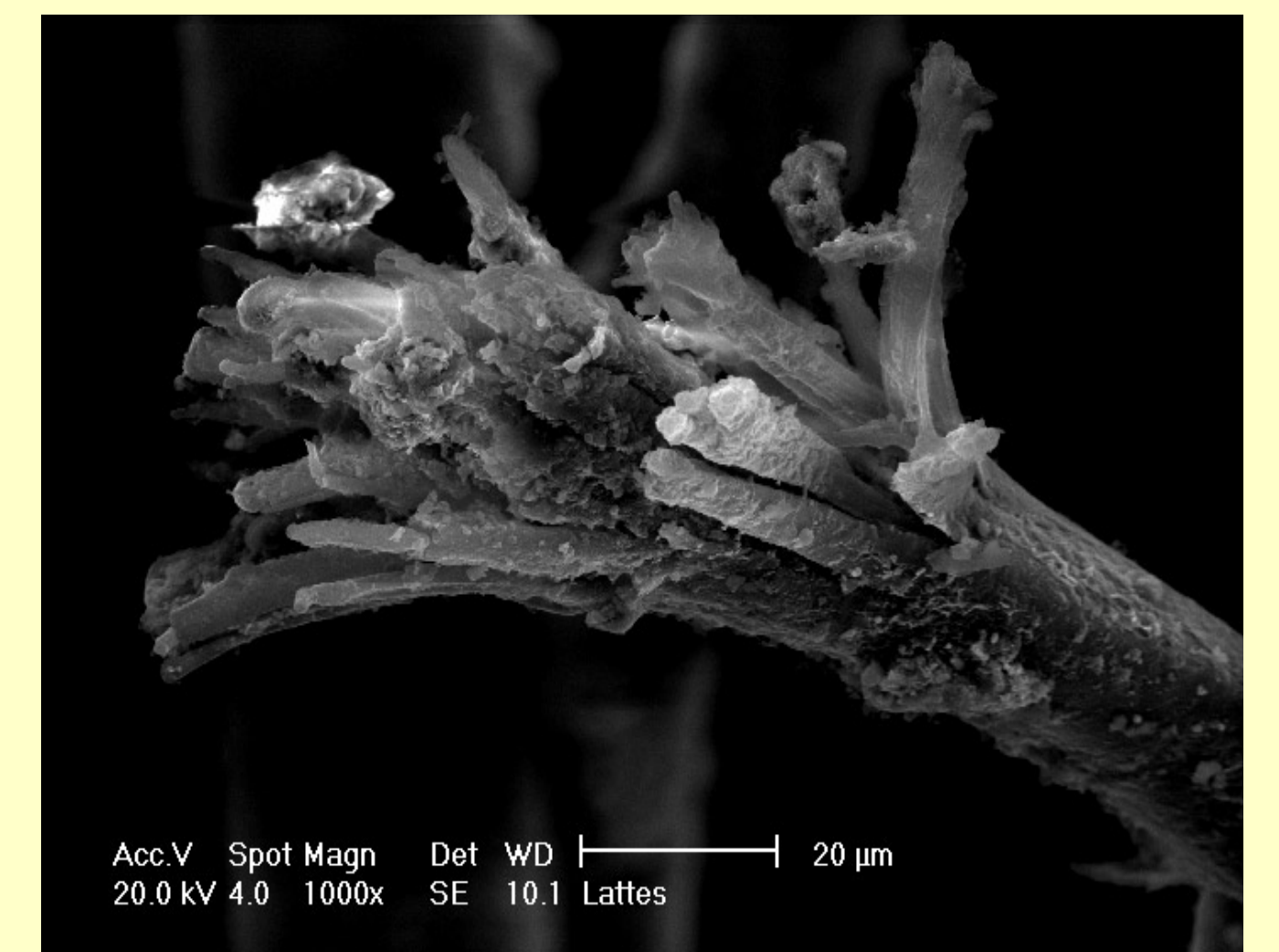
Hair structure is of particular interest as it combines :

- quasi-crystallised keratin molecules
- organized lipid bilayers

The geometrical arrangement of both can be probed by small angle X-ray diffraction.

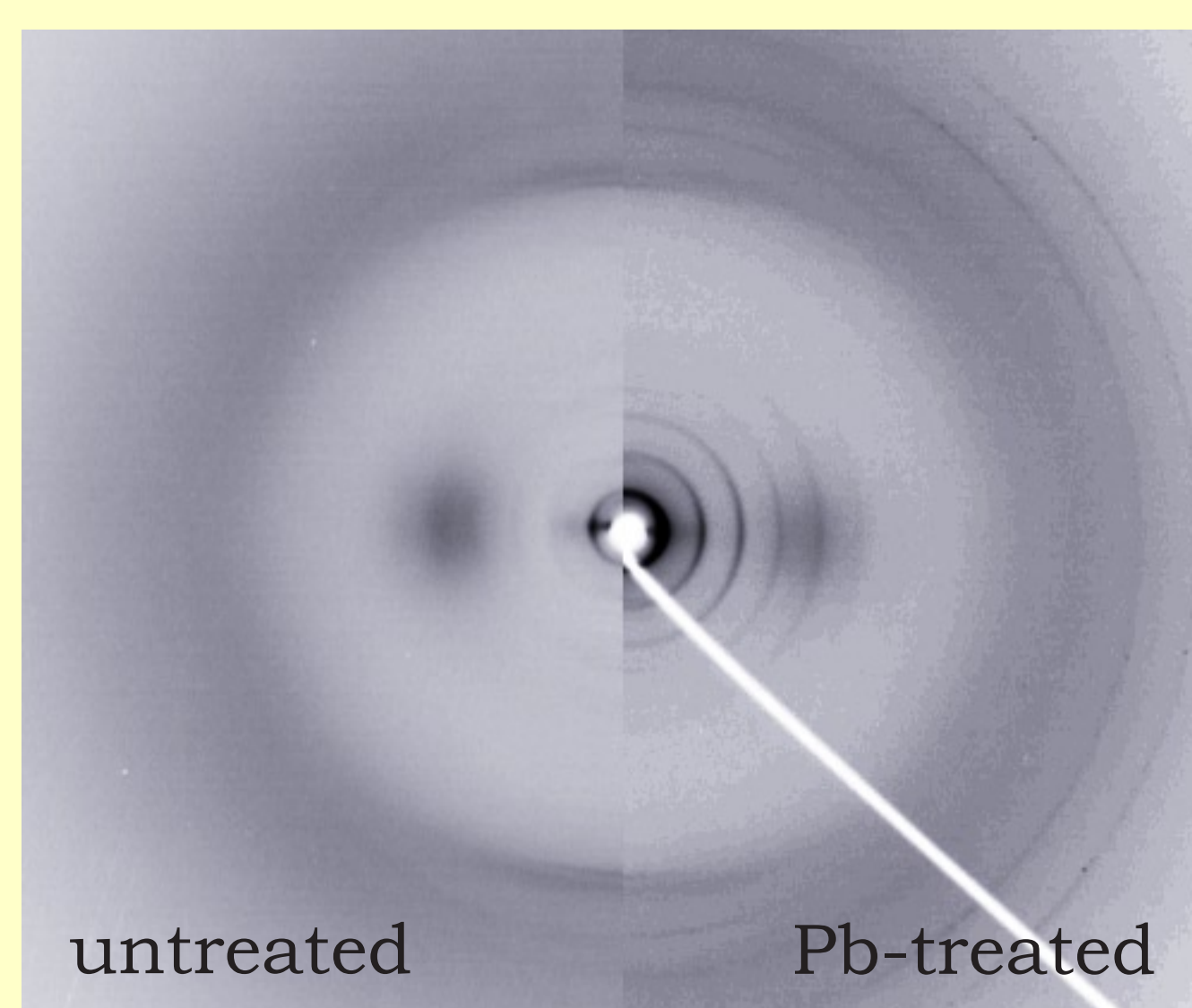


Wool textile preserved by copper mineralisation (Mardié site)



SEM image of a wool fibre (Lattes archaeological site, V° BC). The structure has been preserved up to at least a micrometer scale

Partial or total **mineralisation** of the fibre may occur, with preservation of the fibre microscopic structure.



Small angle XRD image showing the enhancement of structured lipid rings after immersion in Pb acetate solution

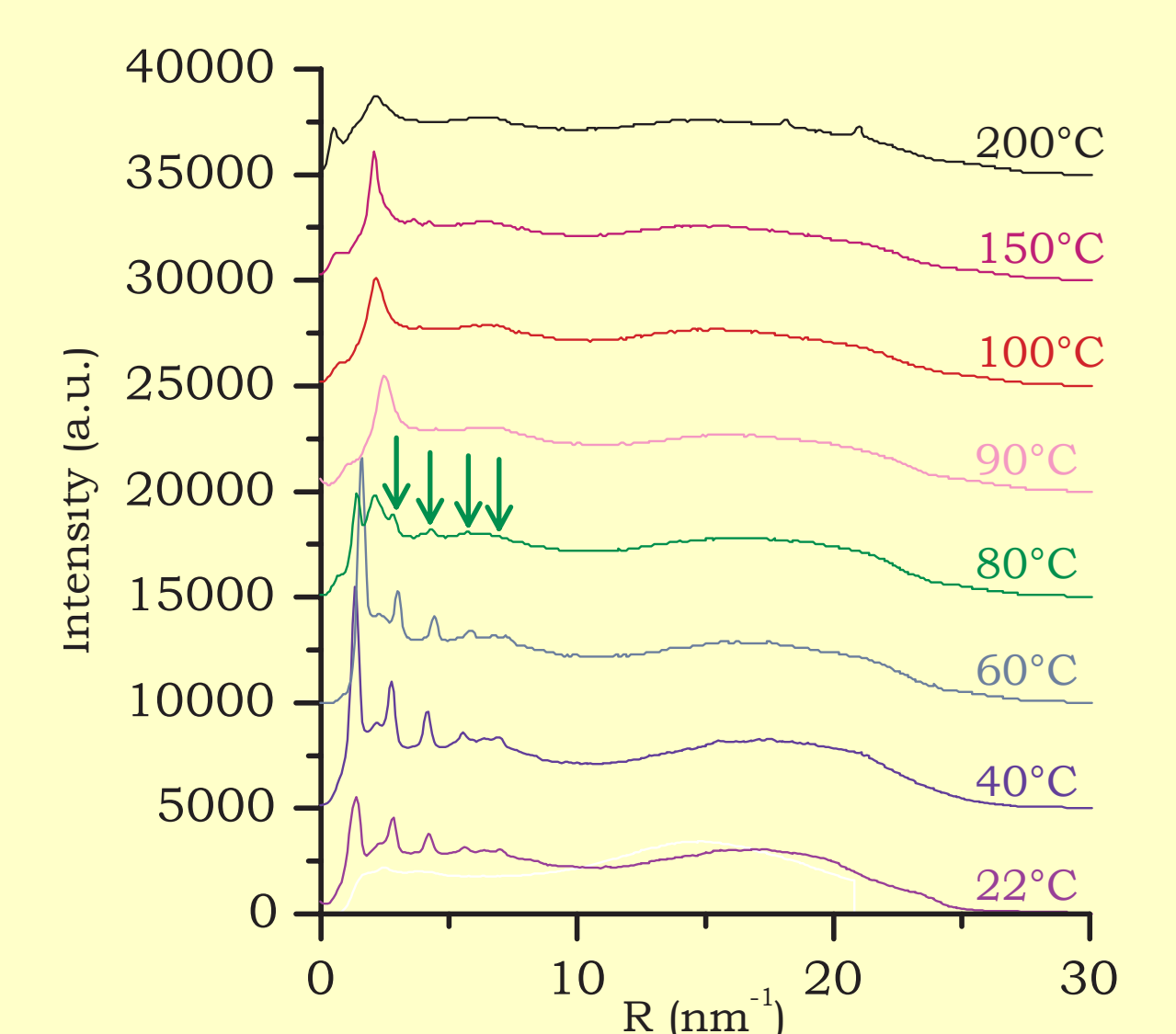
## DIFFRACTION OF STRUCTURED LIPIDS

(Pb- and Cu-treated hairs. D43 beamline, LURE)

Human and animal hairs immersed in 10mM lead aqueous solutions show :

- **strong enhancement** of the structured lipid diffraction rings
- main structural parameter of 46Å
- heating induces the destruction of Pb-lipid rings around 80°C

Similar observations have been made in concentrated copper solutions.

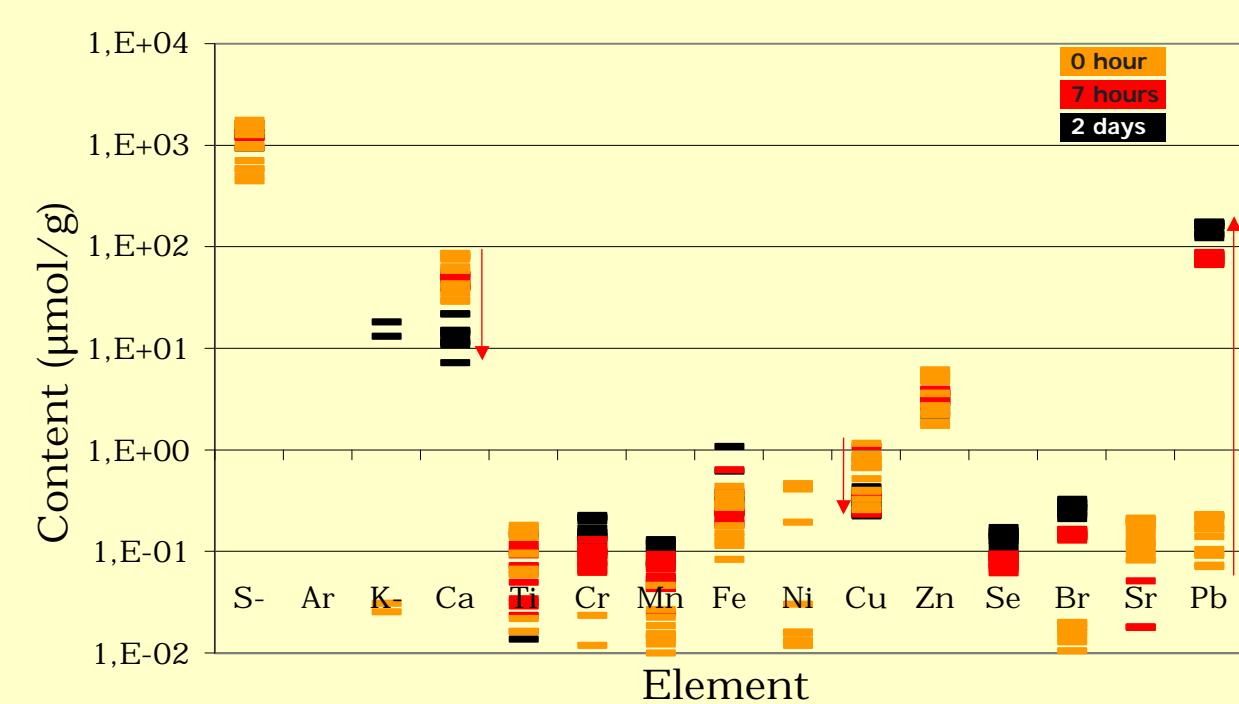


Temperature induces destruction of lipid rings on diffraction pattern of hairs immersed in Pb acetate solution

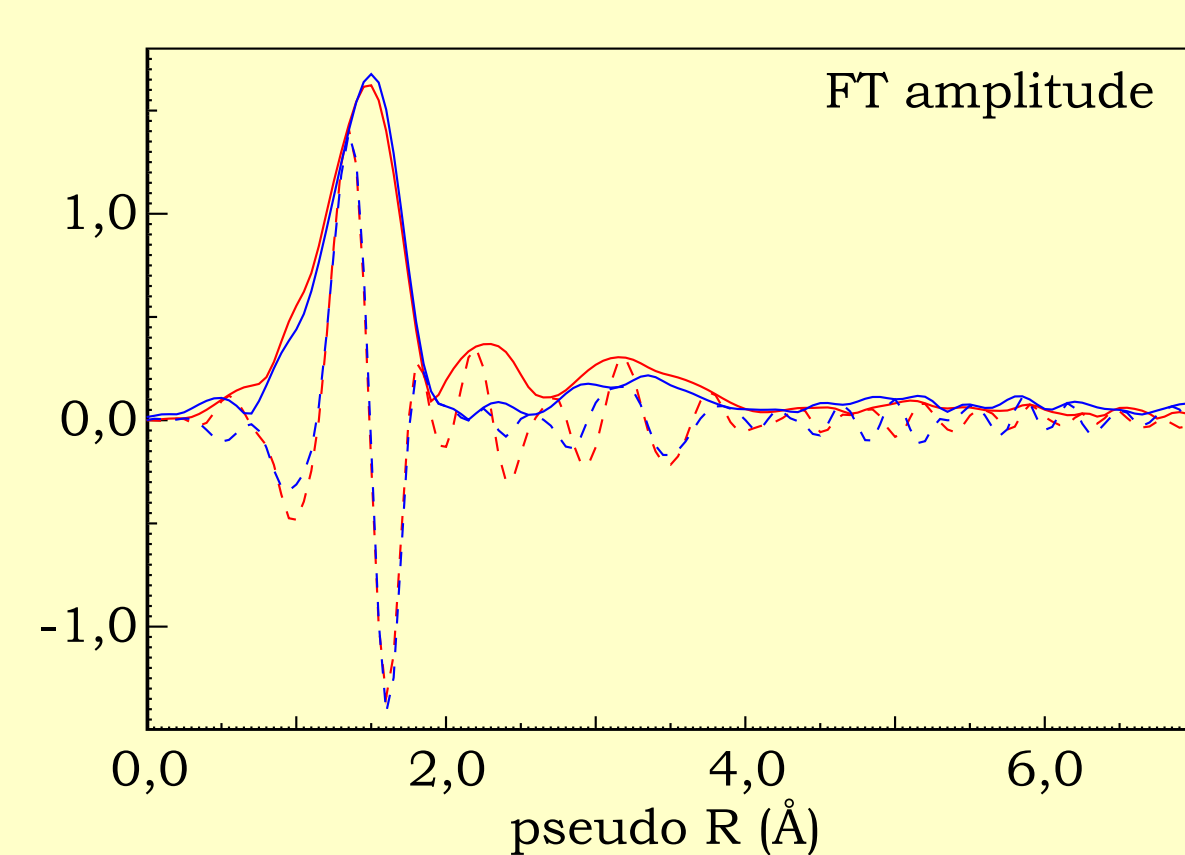
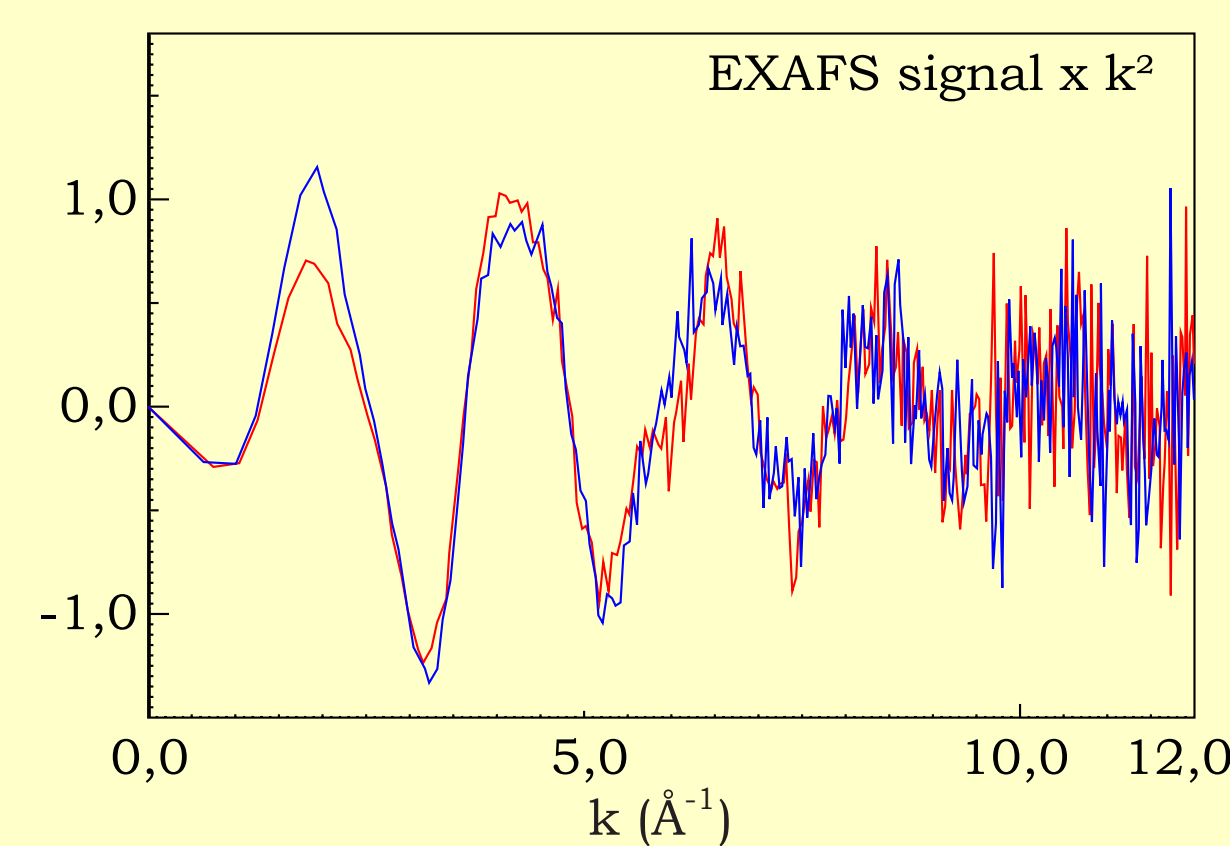
## QUANTITATIVE MEASUREMENTS

(Cu- and Pb-treated hairs)

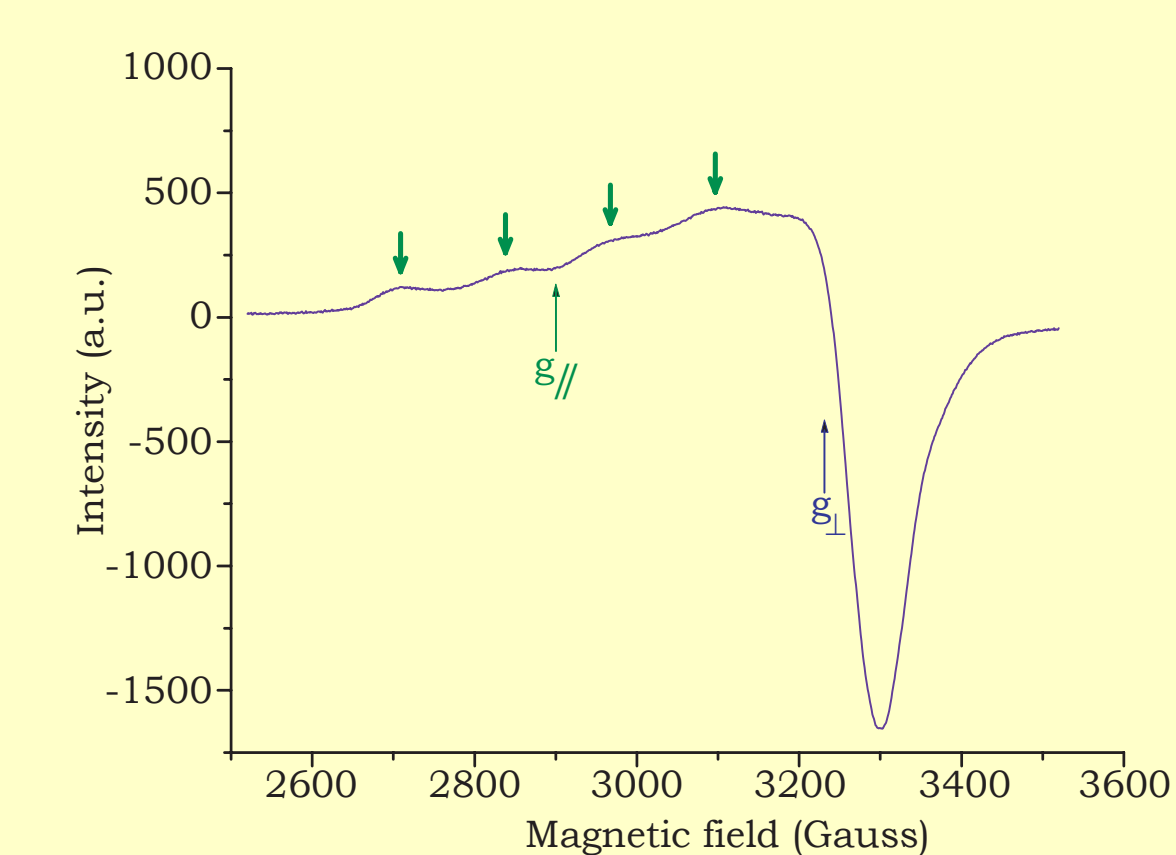
A strong decrease of calcium content is observed by X-Ray Fluorescence after immersion in metal-rich solutions.



Composition of hairs immersed in 10mM Pb acetate solution, showing decrease of Ca content



EXAFS signal and Fourier transform of hairs immersed in Cu solution and hairs coming from Naintré (IV° AD) burial site



ESR spectrum of hairs immersed in 100mM Cu nitrate solutions

## LOCAL ENVIRONMENT

(Cu-treated hairs)

Metal binding sites have been probed by :

- Electron spin resonance
- EXAFS analysis (D21 beamline, LURE)

### ESR analysis led to :

- spectrum showing Cu rigid environment
- coupling factors consistent with 4 oxygen atoms binding the Cu atom

### EXAFS analysis showed :

- 3 well-defined peaks in the Fourier transform of treated hairs spectra
- ageing induces an enhancement of the second FT peak
- consistent with binding to oxygen atoms of carboxylic groups

All these observations are consistent with the binding of Pb and Cu to structured hair lipids. Interrogations remain on Cu(I) binding site.

## KERATIN DISORGANIZATION

Immersion of hair in 100mM lead nitrate and acetate solutions leads to the decay of keratin features in XRD patterns. This fact, not observed in less concentrated solutions, could be due to the disorganization of keratin normal structure.

## CONCLUSION

A working hypothesis is that organized lipids in hair occur in the form of calcium soaps. We would therefore observe an in-situ transition to lead soaps.

We would have here a striking example of **synthetic supramolecular organization initiated specifically by lead ions within a biological sample**.

Experiments leading to the nucleation of copper- and lead-based crystallites inside the hair structure have also been performed. They are the next simulation step of the complex phenomena that occur in the preservation of archaeological samples.

## PROSPECTS

- Influence of hair supramolecular organization on crystallisation
- Complementary studies on copper oxidation state in these processes
- Understanding of the action of ancient cosmetic recipes based on lead compounds
- Lead poisoning (plumbism)