



**Experiment title: X-rays absorption studies at the Fe and Cl K-edges on corrosion products of archeological iron objects**

**Experiment number:**  
ME-827

**Beamline:**  
ID21

**Date of experiment:**  
from: 25.02.04 to: 01.02.04

**Date of report:**  
01.02.04

**Shifts:**  
12

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*Received at ESRF:*

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## Report:

Notification : This report is written just after the end of the experiment in order to be linked with the 1st march 2004 proposals thus, some final interpretation of the results are not presented here.

The aim of this experiment was to better understand the structure of chlorinated phases in the corrosion products of archaeological artefacts. The analysed samples were cross sections or thin films on cross sections made on the artefacts in order to analyse all the thickness of the corrosion products.

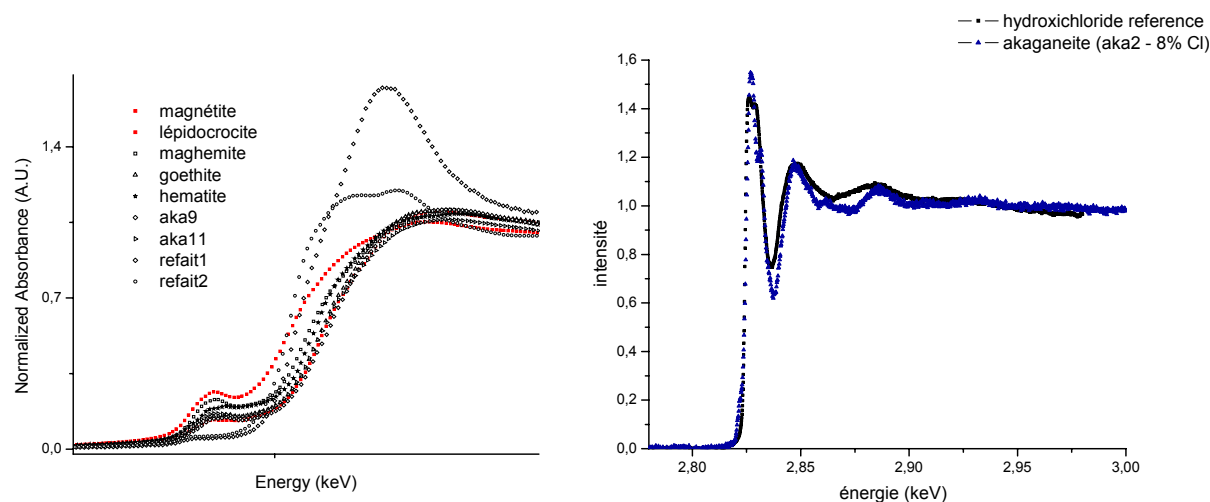


Figure 1 (a) Xanes spectra obtained at the Fe K edge on reference compounds. (b) Cl K edge

The first part of the experiment was dedicated to the collection of reference samples of iron oxides, oxyhydroxides and chlorides. This was performed on powders provided by the Alfa Aesar company for the

most common phases. Moreover, some specific phases as akaganeite containing different amounts of chlorine and a  $\text{Fe}^{2+}$  hydroxichloride were synthetised in our laboratory. These spectra (see figure 1) were collected without any focusing, first at the Cl K-edge (for the phases containing Cl), then at the Fe K-edge. For the Cl K-edge, some significant differences were observed between the phases an especially akaganeite with different chlorine content.

In a second step, the beam was focused on a  $2 \times 2 \mu\text{m}^2$  surface in order to localise and analyse the different chlorinated phases in the layers of the archaeological artefacts. Fluroescence profiles were collected in order to localise precisely the Cl in the layers. Then,  $\mu\text{XANES}$  profiles were made on the same profile at the Fe K-edge. It was possible to distinguish different preedge and edge strutures in the zones containing different amounts of chlorine. Im the low Cl zones, the XANES spectra are in good agreement with those of akaganeite i.e.  $\text{Fe}^{3+}$  valence. In the high zones, the spectra show a 2+ valence, confirming the presence in these area, of  $\text{Fe}_2(\text{OH})_3\text{Cl}$ .

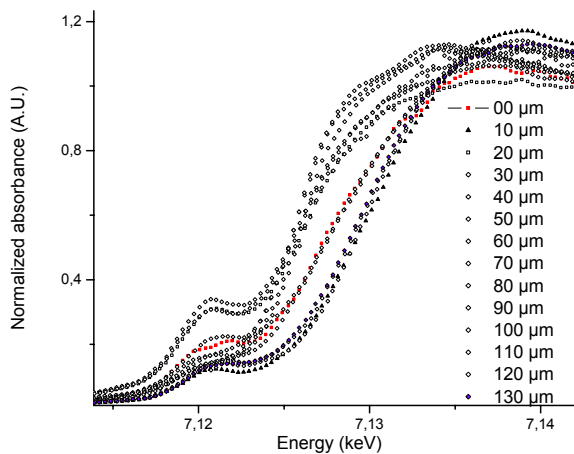


Figure 2 : different XANES spectra collected on a profile made in the corrosion products

Figure 3 shows the correlation between the Cl concentration evolution with those of the iron K-edge energy location. This also confirms that in the high Cl zones,  $\text{Fe}^{2+}$  chlorinated phases are present (edge about 7.125 keV). At the contrary, in low Cl zone,  $\text{Fe}^{3+}$  phases are present (edge around 7, 129 keV).

These experimentations confirm that  $\mu\text{XANES}$  is a powerfull technique to investigate the iron valence in transverse section off thick layers of corrosion products formed on archaeological artefacts. Moreover, coupled with other techniques as  $\mu\text{XRD}$ ,  $\mu\text{Raman}$  and  $\mu\text{EXAFS}$ , these method is very efficient to differenciate all the chlorinated phases. We wish to complete these experiments by further shifts on ID22 or ID21.

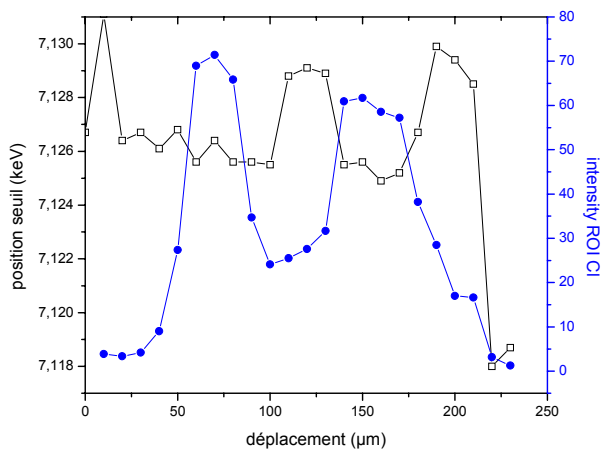


Figure 3 : Evolution of the Fe K edge and the Cl amount in the corrosion products