



Experiment title: Investigation on iron chlorinated phases of cultuage heritage artefacts by μ XANES, μ EXAFS and μ XRD

Experiment number:
ME-949

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Report:

The aim of this μ XANES experiments, performed at the iron K edge was on one hand to better understand the structure of chlorinated phases in the corrosion products of archaeological artefacts (they are complementary to shifts at the Cl K edge realised in april 2005, ME-1104). On the other hand investigations were made on corrosion layer of heritage iron artefacts corroded in atmosphere since several centuries.

In this kind of corrosion products it is necessary to clearly determine and localise at the microscopic scale, the presense of reactive iron phase that could play an important role in the corrosion processes. Theses phase could be more or less crystallised. The analysed samples were cross sections or thin films in order to analyse all the thickness of the corrosion products.

To this purpose, a complete set of reference powder synthetised in our laboratory (goethite, lepidocrocite, akaganeite with different Cl amounts, magnetite, maghemite, ferrihydrite 2 and 6 lines, ferroxihite), was anlysed with macrobeam (figure 1). To our knowledge, it seems that it is the first time that some of these phases (ferrihydrite) are investigated with this technique. In the case of atmospheric corrosion, ferrihydrite and maghemite could have different electrochemical reactivity in the corrosion processes, thus it is of primary importance to clearly identify and distinguish this two phases and locate them at the microscopic scale in the corrosion layer. It appears that the spectrum of ferrihydrite can be clearly differentiate from the spectrum of maghemite. Thus, μ XANES is one of the only method avaible to differentiate these two phases at the sub-microscopic scale. Indeed, because ferrihydrite is not well crystallised, μ XRD is not suitable to proceed to this discrimination and, μ IR investigation can not be performed on so small areas.

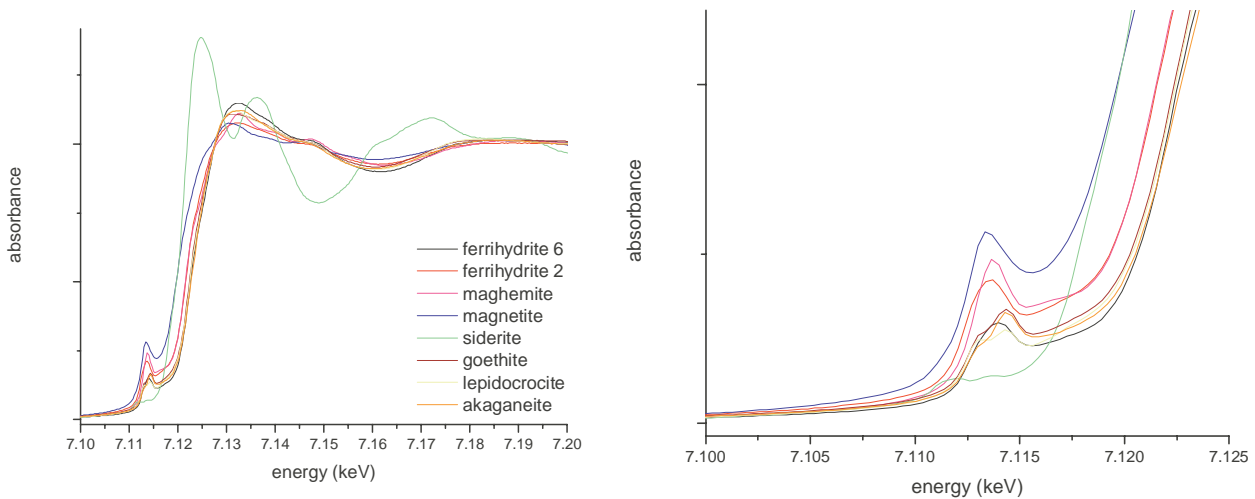


Figure 1: XANES spectra obtained on several reference powders.

In a second step, the beam was focused on a $0,6 \times 1 \mu\text{m}^2$ surface in order to localise and analyse the different iron phases in the layers of the archaeological artefacts. Two different methodology were adopted to study on one hand the chlorinated phases and in the other hand to distinguish maghemite and ferrihydrite.

For samples containing Cl-phases, fluorescence profiles were collected in order to localise precisely the Cl in the layers. Then, μXANES profiles were made on the same profile at the Fe K-edge. It was possible to distinguish different preedge and edge structures in the zones containing different amounts of chlorine. In the low Cl zones, the XANES spectra are in good agreement with those of akaganeite i.e. 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 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, Fe^{2+} chlorinated phases are present (edge about 7.125 keV). At the contrary, in low Cl zone, Fe^{3+} phases are present (edge around 7, 129 keV).

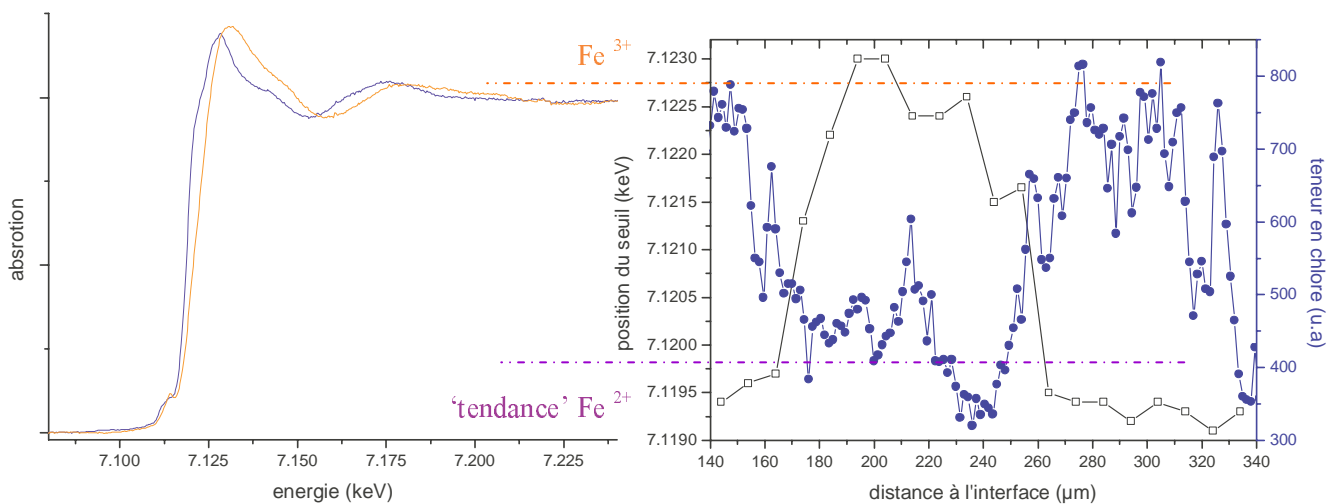


Figure 2: XANES spectra and evolution of the Fe K edge and the Cl amount in the corrosion products

For the samples where maghemite and/or ferrihydrite are searched, it was possible to clearly evidence with the microbeam the presence of ferrihydrite (see figure 1). This first tests on such kind of sample reveal the great potential of this techniques to understand the fine microstructure (at the microscopic scale) of the corrosion layers of heritage artefacts altered in atmosphere. Because this topic of research is of great interest up to day for the conservation of iron elements of the cultural heritage, future proposal will be made in order to investigate more museum and ancient objects.