



	<b>Experiment title:</b> <i>A XAS investigation of Fe and Cu speciation and distribution in the red mosaic tiles of the medieval façade of the Florence cathedral Santa Maria del Fiore</i>	<b>Experiment number:</b> 08-01/1044
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## Report:

### Aims of the experiment

The experiment consisted in an X-ray Absorption Spectroscopy (XAS) study at the Cu, Fe and Mn K edges, associated with XRF mapping, with the following aims:

- 1) Clearly define the speciation and spatial distribution of iron, copper and Mn, supporting the hypothesis on the formation of the nanoparticles: namely, we are aimed in assessing the eventual presence of copper oxide in the tile and if the whole amount of iron is converted to iron(III) species.
- 2) Verify, through the acquisition of a map at the three edges with a pencil of  $\approx 130 \times 70 \mu^2$ , attainable at LISA, what kind of spatial control was exerted during the formation of the color by the manufacturers.

Both information will be highly useful in shedding light on the modes of production and the quality of the manufacturing processes operated in Florence during the end of the Middle Age.

### Experimental procedures

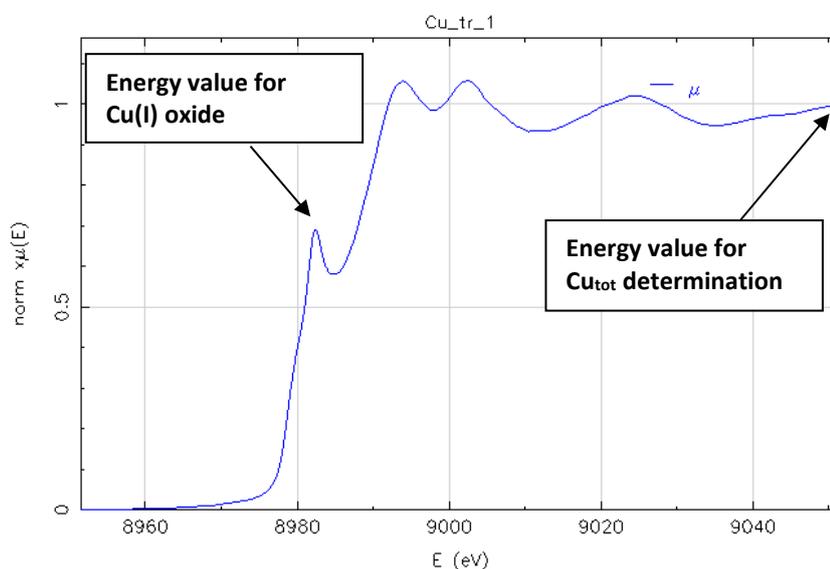
A thin polished section of a medieval mosaic tile, part of the original façade of the Santa Maria del Fiore cathedral in Florence (Italy), was prepared for the measurement with a thickness of 80  $\mu\text{m}$ . The section was fixed between 2 kapton foils and put in the experimental chamber. Measurements were carried out under low vacuum conditions, at room temperature. A fixed exit monochromator with a pair of Si [111] flat crystals was used.; Si coated focusing mirrors ( $E_{\text{cutoff}} \approx 16 \text{ KeV}$ ) were used for harmonic rejection. A reference foil (Cu, Fe and Mn) was also measured at the same time in order to accurately calibrate the energy. Both Transmission

and Fluorescence signals have been acquired, while maintaining the sample constantly oriented by  $45^\circ$  with respect of the direction of the incident beam.

Two different modalities of investigation were pursued: conventional XANES and EXAFS spectral acquisition and X-ray Fluorescence maps, obtained using a constant beam size of  $\sim 70 \times 130 \mu\text{m}^2$ .

## Preliminary Results

XAS spectra of relevant quality and  $\mu\text{XRF}$  maps were gained at the three considered edges. We started considering preliminary XAS spectra registered in optically different areas of the sample. From the micrograph of Figure 2a, these regions are mainly two: the red region, where Cu nanoparticles have been previously observed by SEM and TEM, and colorless transparent regions, characterised by the almost total absence of Cu nanoparticles. An exemplar spectrum, registered in the red region, is shown in the Figure 1. Features arising from metallic Cu and oxidised monovalent Cu (Arletti et al., 2008, J. Non-Cryst. Solids, 354-4962) are recognisable.

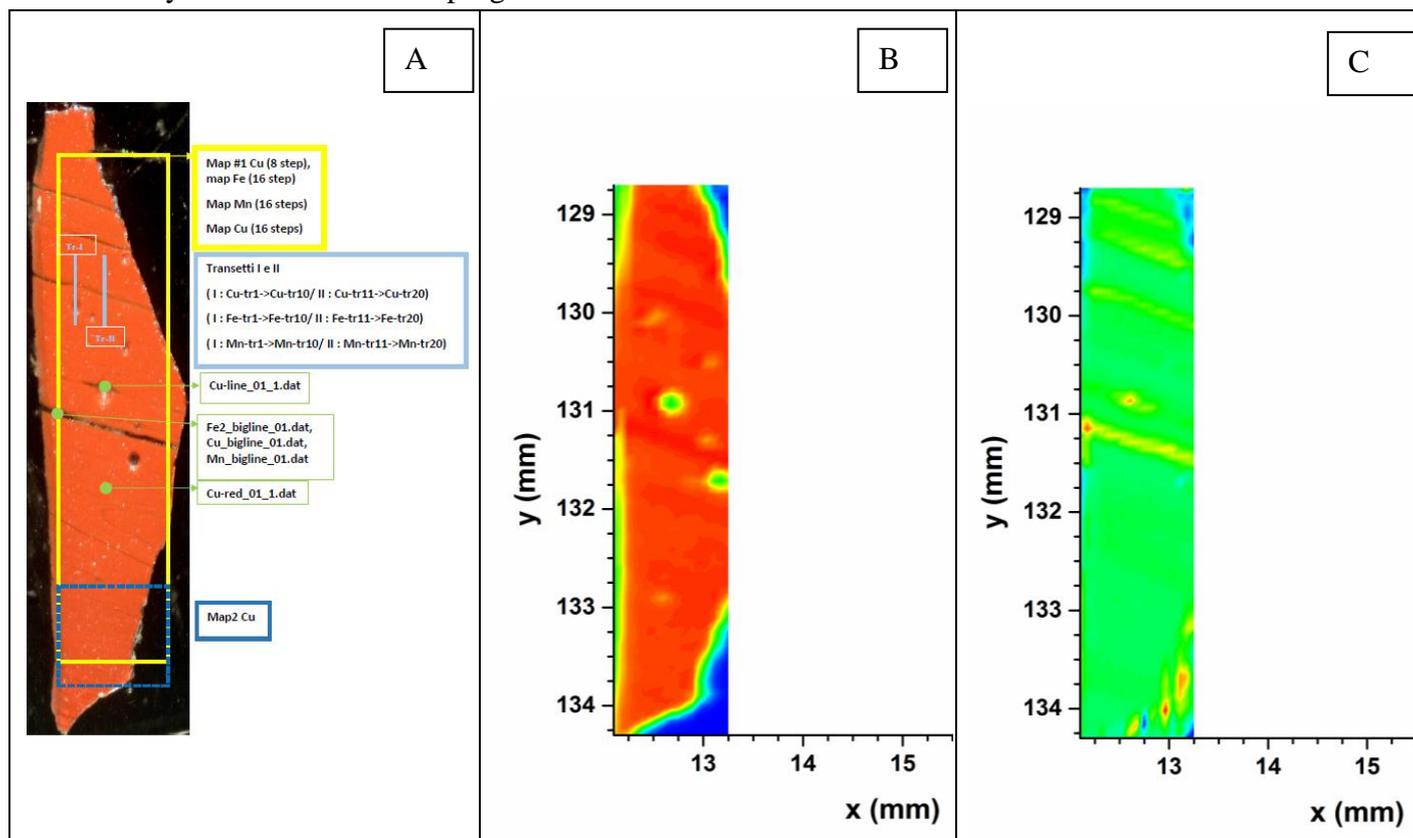


**Figure 1** – XANES Cu K edge spectrum of the investigated tile, red region of the sample. The energy values chosen for the microXRF maps of Figure 2 are indicated by arrows.

Accordingly, we decided to acquire different maps at certain energy values: a first at a value  $\sim 9.1$  KeV (map I), able to trace the overall Cu content in the sample; a second below the edge jump (8.9 KeV, map II), to normalise the total intensity of the first map; a third, located at the energy value of the main feature attributable to Cu(I) oxide, i.e. at  $\sim 8.9823$  KeV (map III). From the comparison of these three raw maps, we were able to elaborate two different combined maps: one revealing to the total Cu content distribution in the sample (Figure 2b), and the other revealing the differences in redox and structural features of the Cu in the sample (Figure 2c). From the combined map of Figure 2b, an almost constant Cu content can be devised. The only variations in the map are due to the presence of air bubbles in the section (only two are crossing the whole sample, and are visible in Figure 2a, while the other are exposed in the bottom side of the section). No or only minor changes of Cu content associated to the colorless regions (diagonal strips in Figure 2a) are identified.

Conversely, in the Figure 2c, the color contrast represents enrichment (red and warm tones) or depletion (green and cold tones) of Cu(I) versus the total Cu content in the sample. The previously mentioned diagonal stripes are enriched in Cu(I) oxide. Detailed XAS spectra carried out in selected positions in such regions confirm this trend.

Similar investigations have been carried out also at the Fe and Mn k edges, obtaining a variable presence of Fe(II) and Fe(III), and an almost constant distribution, for Mn, in terms of amount and redox state. Further analysis of the data are in progress.



**Figure 2** - A. optical micrograph of the investigated sample; B. total Cu content: image obtained combining map I and map II; C. redox/structural Cu contrast: image obtained combining map III and map II .