



	Experiment title: XAS characterization of colorant elements in vitreous mosaic tesserae from Pompeii	Experiment number: 08-01-698
Beamline: BM08	Date of experiment: from: 17/06/05 to: 21/06/05	Date of report: 10 November 05
Shifts: 12	Local contact(s): Dr. Fabrizio Bardelli	<i>Received at ESRF:</i>
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Report:

The characterization of colorant components (usually transition elements) is essential for understanding the manufacturing technique of the coloured ancient glass. In this experiment, we have applied XAS to the study of ancient glass fragments (from Pompeii and from a number of Sicilian Roman sites) and of three copper-bearing modern glass, synthesized in laboratory under different oxidation conditions, with the aim of reproduce the ancient furnace atmosphere. Most of the analysed ancient samples were Cu-rich red opaque mosaic tesserae in good repair. All the modern samples were reproduced by adding Cu to the same batch composition (i.e. the typical silica-soda-lime composition of roman glass). One sample was produced in oxidizing atmosphere, one in reducing one, and the third in oxidising atmosphere and adding several % of Fe²⁺ (as sulphate) to test the efficiency of iron in reducing copper (Ahmed and Ashour, 1981). The aims of this work were: i) to determine the oxidation state of copper and iron in red and green tesserae; ii) to understand whether iron could play a role in the reduction of copper in the red opaque tesserae containing metallic copper clusters ;iii) to compare the results obtained between modern and ancient glass to obtain information regarding the ancient production techniques.

Before performing the XAS experiments, the glass fragments were widely investigated by electron microprobe analysis, wavelength-dispersive X-Ray fluorescence, X-Ray diffraction and SEM-EDS analyses. The Cu and Fe K-edge XANES spectra were collected directly on the glass fragments in the fluorescence mode on the GILDA-CRG beamline. In addition, for five samples, the EXAFS region of the Cu K edge was also collected, to better understand the coordination of copper atoms and to estimate the cluster dimensions. A dynamically sagittally-focussing monochromator with Si(311) crystals and a solid state detector were used (Pascarelli et al. 1996). Energy calibration was achieved with Cu and Fe foil standard and the position of the first inflection point was taken at 8984.2 eV and 7110. for copper and iron respectively. Reference spectra were also collected in transmission mode on CuO, Cu₂O, Fe₂O₃, Fe₃O₄ and on natural Olivine on powders deposited on millipores membranes. The raw XANES spectra of samples and reference compounds were subtracted of the pre-edge background with a linear function and then normalized on the high energy side of the curve. This normalization allowed the comparison of samples with different absorber content. EXAFS data processing was carried out by Fourier filtering and multi-parameter fit in the R space. Theoretical scattering amplitude and phase were generated by the FEFF8 code; the multi-electron amplitude reduction factor S₀² in EXAFS formula was fixed to the value obtained from CuO EXAFS spectrum. As concern the

iron K-edge the analysis of the pre-edge region was then performed by least-square fitting of Gaussian peaks which allowed the centroid calculation of each pre-edge peak.

The Cu edge XANES analyses of most of ancient red glass suggested the presence of both metallic and monovalent copper. In fact, the two-shells fit of the back FT of the EXAFS spectrum was obtained with both Cu-O (1.83 Å) and Cu-Cu (2.55 Å) contributions, which well agree the interatomic distance for Cu₂O and metallic copper. The coordination number obtained by the fitting procedure for the Cu-O contribution was 2.78 Å, which is higher than that of Cu₂O, where copper is coordinated by two oxygen atoms to form two collinear bond. This suggest that the monovalent copper in the red sample is incorporated in the glass framework. Only one strongly weathered red tessera (Fig 1) show a spectrum very close to that collected on Cu₂O, indicating the presence of cuprite crystals; this result is consistent with those obtained by SEM images, which previously showed the presence of large crystalline aggregates which dendritic shape, suggested they were cuprous oxide. Probably the presence of cuprite crystals could favour the glass weathering, since they contain monovalent copper and could be more alterable and subjected to oxidation processes than metallic particles. The Cu XANES analyses of modern reproduced glass showed that only the sample produced in strongly reduced atmosphere contains reduced copper (Cu⁰ and Cu¹⁺), the other two samples, also the one produced by adding Fe²⁺ to the batch, resulted to contain only Cu²⁺ (Fig. 2 and 3). This allow us to suppose that the presence of iron in the batch is not sufficient, if not coupled with a reducing atmosphere for the reduction of copper.

The Fe K- edge collected on samples revealed that all the ancient samples holding reduced copper (Cu⁰ and Cu¹⁺) contain both Fe²⁺ and Fe³⁺, whereas in the modern Fe-bearing sample only the oxidised form of iron was present. This allowed to definitively conclude that the primary role in producing red opaque glass containing metallic copper was played by strong reducing conditions in the furnace rather than by a redox reaction with iron

The Cu-XANES spectra of green glasses are virtually identical, both in the general shape and in the energy positions of the various features. These spectra show profiles similar to that obtained for Cu₂O, even if shifted of 0.8 eV toward higher energy. The peaks present in our spectra exhibit features very different from those of CuO. All the observations suggest that Cu¹⁺ is the dominant oxidation state in the green glass; nevertheless one can not exclude the presence of minor amounts of divalent copper. The analyses of the EXAFS region of the spectrum collected on the green sample provided other important information. The fit of the FT proves the presence of oxygen neighbours at 1.90 Å. This Cu-O distance, intermediate between that of CuO and Cu₂O reference compounds, suggests the simultaneous presence of both 1+ and 2+ copper in the green glass.

We can conclude that in our red sample copper is present as metallic copper accompanied by monovalent copper dispersed in the glass matrix. Only one altered red tessera shows the presence of cuprite crystals disseminated in the glass as opacifiers. In green samples copper is probably present as both Cu¹⁺ and Cu²⁺, the second one being responsible for the colour. The Fe -edge collected on modern and ancient glass allowed to conclude that the adding of iron to the batch is not sufficient to induce the copper reduction (and consequently to impart the red opaque effect) if not coupled with strong reducing condition in the furnace.

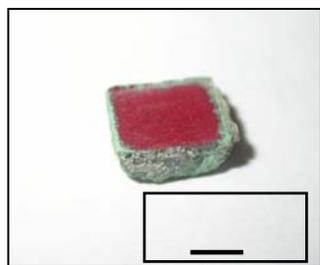


Fig. 1 weathered red tesserae

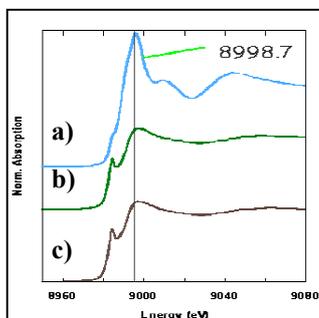


Fig 2 Cu- K Edge collected on CuO standard (a), reproduced glass obtained adding only Cu in the batch in oxidising atmosphere(b), and reproduced glass obtained adding Fe and Cu in the batch in oxidising atmosphere (c)

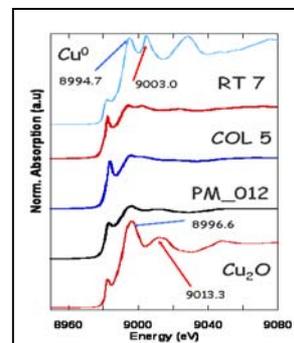


Fig. 3 Selected Cu- K edge XANES spectra of red samples and reference compounds

References

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