



	Experiment title: Archaeometrical analyses of ancient glass of the imperial age	Experiment number: 08-01-641
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Report:

It is known that colours in glass can be determined by the oxidation state and electronic configuration of the metal ions in them. They are usually elements belonging to the transition row of the periodic system, which absorb characteristic frequencies of visible region as a result of the d-d electronic transitions. Since the characterization of colorant components is important in understanding the manufacturing technique of the ancient glass samples, we applied synchrotron X-ray Absorption Spectroscopy to the study of ancient glass fragments from Western Emilia Romagna and from Pompeii excavation. The majority of the selected samples are transparent while, some of those are opaque. They represent a broad pattern of the production of glass in Roman times. The aim of this work was to determine the oxidation state and the coordination of copper in green and red glass fragments and to test the influence of its oxidation state on the colour of studied glass.

Before performing the XAS experiments, the glass fragments were investigated by electron microprobe analysis and by wavelength-dispersive X-Ray fluorescence. Moreover, for the opaque sample additional analyses were performed to investigate the origin of the opacity: X-ray diffraction and SEM-EDS analyses evidenced the presence of crystalline phases dispersed in the glass matrix. In particular, crystals of calcium antimonate and cluster of metallic copper have been found for green and red opaque glass, respectively. From the chemical point of view, all the samples resulted to be 'low-magnesia' glasses, with a composition typical of the Roman period.

The Cu K-edge XANES spectra were collected directly on the glass fragments in the fluorescence mode on the GILDA-CRG beamline. In addition, for two samples, the EXAFS region of the spectrum 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 foil standard and the position of the first inflection point was taken at 8989.7 eV. Reference spectra were also collected in transmission mode on CuO, and Cu₂O, standards 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 multiparameter fit in the R space. Theoretical scattering amplitude and phase were generated by the FEFF8 code; the multielectron amplitude reduction factor S_0^2 in EXAFS formula was fixed to the value obtained from CuO EXAFS spectrum.

The XANES spectra of selected samples and the standard compounds are reported in Figure 1. Figure 2 shows the Fourier transform and the best fit for the EXAFS region for red and green samples.

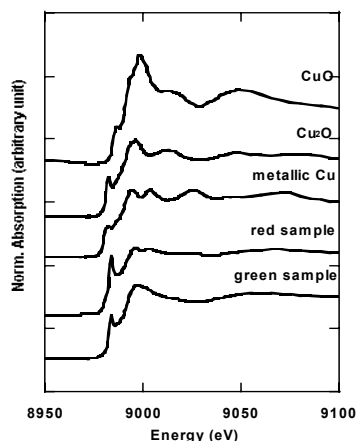


Figure 1: Cu K-edge XANES collected on standard compounds and on selected samples.

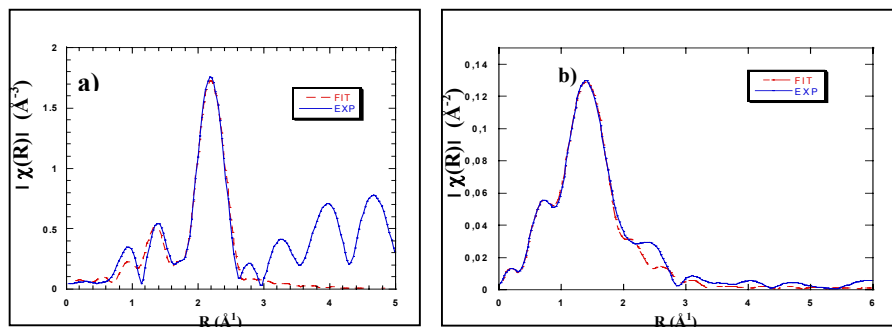


Figure 2: Moduli of Fourier transform at Cu K edge and best fit for RED (a) and green (b) samples

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 Cu_2O even if, shifted of 0.8 eV toward higher energy. Although the green colour in glass has always been attributed to the presence of Cu^{2+} , the peaks present in our spectra exhibit features very different from those of CuO . All the observations suggest that Cu^{1+} is the dominant oxidation state in the green glass; nevertheless one can not exclude the presence of minor amount 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 Cu_2O reference compounds, suggests the simultaneous presence of both 1+ and 2+ copper in the green glass.

The XANES analyses of red glass suggested the presence of both metallic (dominant) and monovalent (subordinate) 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 Cu_2O 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 Cu_2O , 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.

We can conclude that our ancient glasses contain copper in different oxidation states:

- i) in red samples there are metallic Cu clusters accompanied by monovalent copper linked with the oxygen atoms in the glass framework;
- ii) for green samples the situation is more uncertain, due to the interatomic distance obtained for the Cu-O path, which is nearly the average between those characteristic of Cu_2O and CuO . However, the shape and the position of the XANES edge in green samples spectra reinforce the hypothesis of the dominating presence of the monovalent specie.

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