



	Experiment title: EXAFS study of the polychrome lustre decoration in Italian renaissance pottery	Experiment number: 08 01 326
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Report:

EXAFS measurements at the Cu and Ag K-edges have been carried out to study polychrome luster decorations in original samples of glazed Renaissance pottery (end of XV-XVI century) from Deruta and Gubbio.

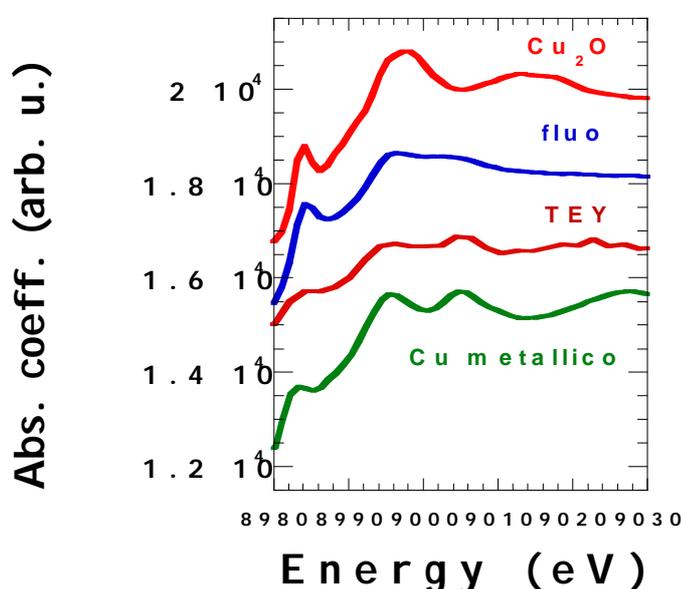
Luster is one of the most important decorative techniques of the Medieval and Renaissance pottery of the Mediterranean basin. It consisted of a metal deposition on a tin-opacified lead glaze which produced brilliant metallic reflections of different color and iridescence [1]. Examples of luster pottery from Deruta and Gubbio are conserved in many important international museums, such as the Louvre in Paris, the Metropolitan Museum of Art of New York, the National Gallery of Art of Washington, the British Museum and the Victoria and Albert Museum of London and many others. Very recently, studies of the same authors of the present work demonstrated that luster consists of a heterogeneous metal-glass composite film, some hundreds of nanometers thick, analogous to that present in the modern metal-glass nanostructured composites synthesized for high technology applications [2,3]. In the luster, separate silver and copper nanoclusters appear dispersed within the outer layers of the glaze. Although heterogeneous, the nanocluster distribution can be locally homogeneous, being characterized in specific regions by constant cluster dimensions and constant densities.

Aims of the measurements were to collect X-ray absorption spectra at Cu and Ag K-edges, for different luster decorations (gold and red), with the goal to establish states and local environment of copper and silver into the glaze matrix, and to correlate these data to the luster properties.

It has been found that, in the case of red luster, the color is mainly due to the presence of copper nanoclusters, while in the case of gold luster the color is mainly due to nanoclusters of silver. However, copper and silver are significantly present in the glaze also in oxidized

forms; specifically: in gold luster, Ag^+ , Cu^+ and Cu^{2+} ions are present, while in red luster, where no silver is present according to the historical recipes [4,5], the dominant ion is Cu^+ . It has been found that, in the luster, the nanoclusters are confined in the more external glaze surface layer, while oxidized forms are more deeply penetrated. This was put in evidence, in the case of red luster, by the absorption spectra at the Cu K-edge (8979 eV) recorded both in fluorescence mode (fluo), probing depths of about 50 microns, and in total electron yield (TEY), capable to collect signals only for the first 0.1 microns. As reported in the figure, the TEY spectrum shows the presence of metallic copper, while that collected in fluorescence mode (fluo) shows the dominant presence of oxidized Cu_2O .

Quantitative analysis of the EXAFS spectra obtained for red luster, in the fluo- mode, indicates that copper coordinates oxygen atoms at 1.86 Å, which is a distance very close to the interatomic distance for the first shell of Cu_2O (1.85 Å). The Cu-O first shell coordination number is 1.3, which is a value not very far from 2, the value shown by the Cu_2O standard. The low coordination number (1.3 instead of 2) can be explained taking into account that a fraction of copper atoms is in the reduced metallic phase.



States and local environment of Cu ions are similar to those found in copper-alkali ion-exchanged silicate glass samples [6]. This finding strongly supports the view that luster formation is mediated by a copper- and silver-alkali ion exchange as a first step, followed by nucleation and growth of metal nanocrystals as a spontaneous process due to the supersaturation of the elemental concentrations in the region where clustering occurs [7,8].

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