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ORIGIN OF RED AND ORANGE COLORATION IN ROMAN GLASS TESSERAE

Before the 17th century, almost all red and orange glasses were colored by precipitates rich in copper, in the form of metallic copper or cuprite (Cu₂O). In particular, colorations with cuprite, often correlated with high concentrations of copper and lead, are specific to archaeological glass. Studying the composition and microstructure of archaeological glasses allows a better understanding of the ancient manufacturing processes, still poorly known. We have investigated the color heterogeneity in red and orange glass tesserae, in relation with the glass composition and copper precipitation to unravel the technology used by Roman glass masters.

GLASS TESSERAE FROM THE LARGEST ROMAN MOSAIC

Floor mosaics were developed in the Hellenistic times and enjoyed great popularity during the Roman era. They consist mainly of near-cubic pieces of natural stones (so-called tesserae), but glass tesserae were occasionally used to accentuate the brilliance of particular motifs. Glass has the advantage of being available in a wide range of colors across the visible spectrum, and it interacts differentially with light. Among the colors, the manufacture of red/orange tesserae has attracted a lot of scientific attention because of the technical challenges in making them. These colors require careful control of the

melting conditions (furnace atmosphere, melting temperature, cooling treatment) and mastery of the glass composition. Here, we report the compositional and structural results of glass tesserae found in the Roman villa of Noheda (Cuenca, Spain) dating from the 4th century CE. This exceptional site hosts one of the largest Roman floor mosaics, which is exceptionally well preserved, and shows numerous mythological scenes. A previous paper reports a detailed compositional study of 420 tesserae and their possible provenance [1]. From these samples, we have selected different red and orange glass tesserae characterized by different hues or textures (Figure 1) and, in particular, samples with alternating stripes of red/orange, often observed in Roman or early Christian and Byzantine glass tesserae. These striated tesserae have been little investigated so far, although they can shed new light on the production processes and techniques.

CHARACTERIZATION OF NANOCRYSTALS IN GLASS TESSERAE

The nature of the crystalline precipitates responsible for the red or orange colorations was determined by XANES spectroscopy and confirmed by electron microscope imaging. Metallic copper nano-particles (Cu⁰) are identified in the red samples, while crystals of cuprite, Cu₂O, are responsible for the orange hue. Similar analyses were also carried out on the striated samples by probing the different stripes separately (Figure 2). Peak A indicates that Cu²⁺ ions are present, especially in the red bands, and in various amounts depending of the samples. The evolution in the position of peak B can differentiate Cu⁺ in the red zones at high energy from Cu⁺ in cuprite crystals (orange zones) at low energy.

Compositional analysis has revealed that both red and orange bands are obtained from the same base glass. Additional elements, Cu, Sn, Pb and probably Fe, were added to this base glass in different amounts for the red and orange glass. The red hues observed in monochrome or banded tesserae correspond to glasses with low-copper and low-lead contents (CuO > 4 wt%, PbO < 10 wt%). In the case of the orange monochrome and orange stripes, the coloration is due to cuprite crystals resulting from a high copper content (>5 wt% CuO) and a high variability in the lead content. Based on our observations and the literature review, we were able to propose a new classification for ancient red and orange glasses. Lead is usually added to enable the crystallization of cuprite. Its role is not yet fully understood but it might favor the formation of large dendritic Cu₂O crystals (> 1 μm), giving a red coloration similar to that of Cu⁰ nanoprecipitates but requiring a less reduced atmosphere.

TECHNOLOGICAL IMPLICATIONS

The question remains whether the orange/red striped tesserae were intentional or accidental, but they were frequently used in Roman and Byzantine mosaics to imitate marbles such as *cipollino rosso* [2]. A striking aspect in our characterization is the mixing of stripes containing either Cu⁰ nanoprecipitates (red) or Cu₂O crystals (orange) within the same sample. For this purpose, two glass batches with different copper and lead contents were mixed together. The alternating bands are probably due to the stirring of the molten glasses. Careful control of the furnace atmosphere is required to maintain redox conditions that allow both the precipitation and growth of Cu⁰ nanoparticles or cuprite crystals when

mixing the two glass melts. Suitable reducing conditions may have been achieved by the addition of charcoal and plant ashes, which explains the high magnesia and potash contents in these tesserae. A short duration of the melting process probably also prevents a complete mixing of the two glasses. Our investigation thus reveals that Roman glass makers had an excellent command of the reducing conditions in the furnace, as well as the melting time and glass compositions.



Figure 1

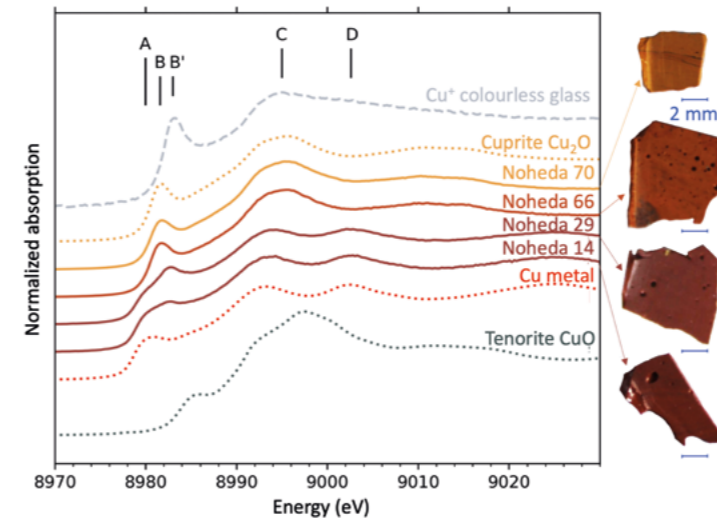
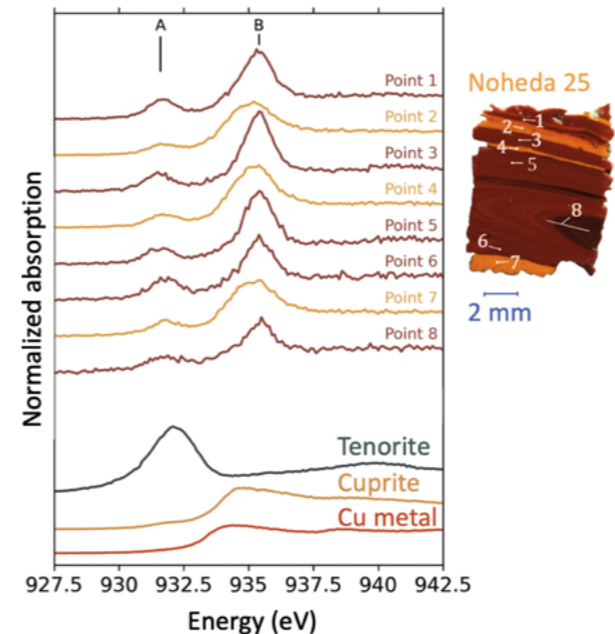


Figure 2



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Associated publication

Comparative Investigation of Red and Orange Roman Tesserae: Role of Cu and Pb in Colour Formation.



C. Noirod, L. Cormier, N. Schibille, N. Menguy, N. Trcera & E. Fonda.

Heritage, 5, 2628 (2022).



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Captions

Figure 1: Cu K-edge XANES spectra, obtained on SAMBA beamline, for tesserae with orange (Noheda 70 and 66) and red (Noheda 29 and 14) colors, compared with reference materials.

Figure 2: Cu L3-edge XANES spectra, obtained on LUCIA beamline, at selected points for a red/orange striated tessera. The color of the curves represents the color of the selected point. Reference materials are plotted in the bottom.