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Color variations in 13th century hispanic lustre – An EXAFS study

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Abstract

Microprobe EXAFS analysis of lustre decoration from a late 13th century Hispano–Moresque potsherd has been used to examine the metallic oxide to metal ratios in different shaded copper lustre finishes. A single specimen from 13th century Paterna, exhibiting typical red and green colorations, is found to contain different copper/silver ratios depending on the color. EXAFS has been used to determine the local atomic environment of the copper and reveals a corresponding variation in the metal to oxide ratio of the copper content which is related to the visual effect.

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1. Introduction

Lustre is a metallic decoration applied to ceramics and dates from the early 9th century islamic period through to medieval and renaissance western Mediterranean. It is formed by applying a copper and silver based paint to an already glazed and fired pot. The ceramic then undergoes another firing, this time in a reducing atmosphere, during which time copper and silver ions are drawn into the glaze via an ionic exchange mechanism [1]. The metal ions are reduced and aggregate together to form nanoclusters [2–7]. Lustre finishes exhibit a wide range of colors, depending upon their chemical composition, from yellow, green and browns for silver rich lustres to orange, reds and crimsons for copper rich lustres [8,9].

Paterna was a major production center of lustreware in the late 13th through to the 15th centuries. In common with many other lustres, these show two main colors, red for thin line drawings and edges of thicker lines or motifs, and green for the thicker lines or large motifs. We selected a single specimen, shown in Fig. 1, from the 13th century workshop exhibiting the two major colors commonly seen. The main body of the decoration (circular area in the upper half of Fig. 1) is greenish[1] in color, whilst the finer lines that cross this are more red. Closer investigation shows that the edge of the green decoration is in fact red. As these changes in color occur in the same decoration, it can be expected that they were applied at the same time, using the same raw material and fired simultaneously.

A number of complementary techniques have been used in the past to characterize lustre and to understand the

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[1] For interpretation of color in Figs 1–3, the reader is referred to the web version of this article.

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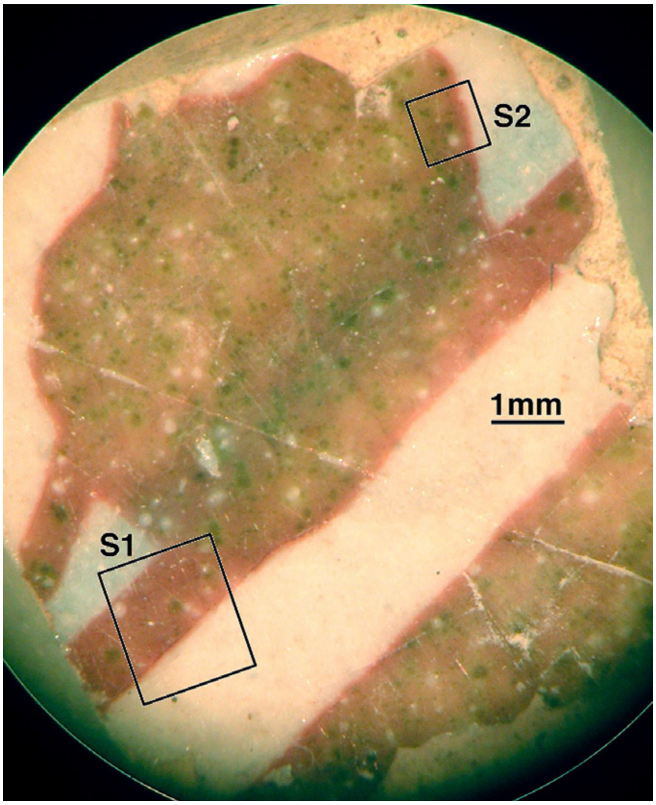

Fig. 1. Light microscope image of M11 pot sherd, showing two regions selected for data analysis. Lower left (S1) on red band (see Fig. 2) and upper right (S2) on green decoration (see Fig. 3). The scale bar is 1 mm. The blue–grey band running from lower right to upper left is a different type of decoration, found by XRF to be zinc based.

lustre making process, these have included electron microscopy to image the nanoparticles and directly measure their size [2–4,6] extending to energy dispersive X-ray analysis (SEM-EDX) [1,3,4,6,8,10,11] to determine the chemical composition and elemental distributions. Atomic force microscopy (AFM) has additionally been utilized [7] to measure the effect on surface roughness due to the growth of nanoparticles below the glaze surface. To identify the crystalline phases present and their size, X-ray diffraction has been employed [11,12]. UV–visible absorption spectroscopy is useful for giving a direct measure of the color of the lustre, rather than having to rely on a visual interpretation of that color. Moreover, the presence of surface plasmon resonances (SPR) in the absorption are characteristic of copper and silver nanoparticles, these affect the final color show by the lustre layer. The SPR peak wavelength being shifted by an amount dependant upon the nanoparticle size and the composition of the glaze [2,3,8,11] so giving indirect information on the type and size of the metal nanoparticles present. Luminescence resulting from photon stimulated emission, using visible laser, UV or X-rays can indicate the presence of Cu^+ and Ag^+ ions in the glaze [13].

EXAFS (Extended X-ray Absorption Fine Structure [14]) has been used [1,5,15–17] to provide detailed information on the local atomic configuration of the copper and identify the existence of copper in a metallic or oxidized form. As EXAFS probes the environment around individual atoms, it can determine quantitative information on the chemical bonds over very short range scales and does not need a high degree of crystallinity in the sample.

In this study, we have used microbeam EXAFS to probe the variation in copper chemistry corresponding to the color variations seen in this sample. By choosing this technique, we have been able to explore the chemical variations in the lustre on a small spatial scale and resolve differences not only between different decorations on a single potsherd sample, but also within a single decoration and be able to correlate this chemical difference with the visual effect seen.

2. Experimental

Data was collected on the microEXAFS beamline, 10.3.2, at the ALS [18]. Two modes of data collection are available: firstly, elemental imaging of the X-ray fluorescence (XRF) using an energy resolving Si(Li) detector to simultaneously record concentrations of a variety of elements by measuring the intensity of various fluorescence emission lines; secondly, Cu K-edge EXAFS measurements can also be taken at particular positions on the sample. Spatial resolution of the focal spot is approximately 20 μm × 5 μm, with the option of reducing this further but at the expense of flux. Elemental maps, such as those

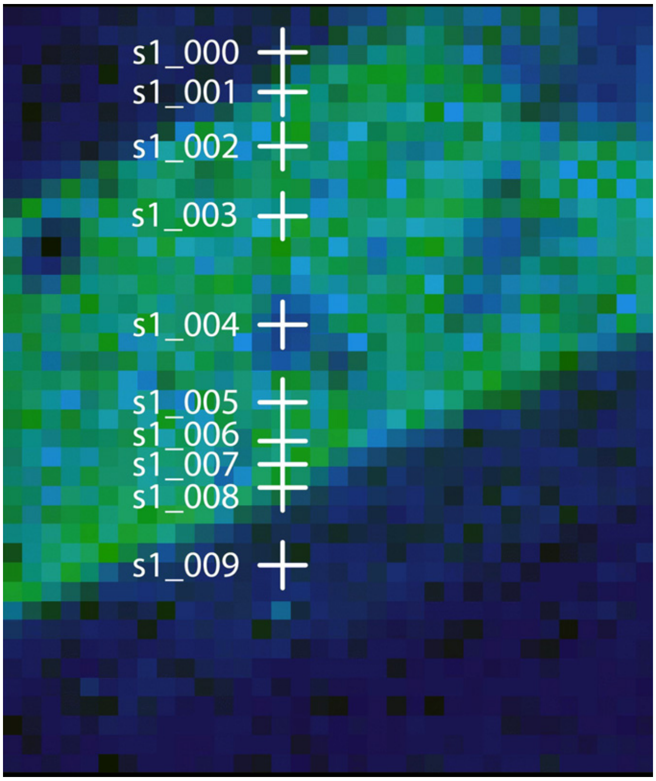

Fig. 2. Color composite of 1.7 mm × 2 mm region over red band from which S1 transect was taken. Pixel size is 50 μm. Green corresponds to copper content, blue to silver.