MicroXAFS studies into the oxidation states of different coloured glazes originating from the early Islamic world

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INTRODUCTION

The use of SR and SR based techniques to the study of old artifacts is a new research area [1]. Many of the techniques that are commonly used in the pursuit of contemporary material science are equally applicable to advancing an understanding of the material sciences exploited by peoples of an earlier age. Traditionally this information has been obtained from excavations and inscriptional evidence and in the case of many items such as the finer glazed ware has relied on the connoisseurship of art historians. An enhanced understanding of early materials processing techniques will enable archaeologists to better understand the societies that produced, traded and used the objects they have left behind.

We are particularly interested in investigating the lustre finish applied to ceramic ware first developed in the Islamic world of the 10^{th} to 12^{th} centuries[2-7]. Evolved techniques were subsequently developed in the Hispano Moresque world of the 13^{th} to 15^{th} centuries and later exported to Italy (in the Italian maiolica of the 16^{th} and 17^{th} centuries). The use of lustre decorated ceramics is one of the most exciting developments in pottery production during medieval times. This type of decoration consists of drawings with a metallic shine layer which were applied on a glaze, the production of which involved a second or third firing in special kilns in successive reductive steps to allow the reduction of Cu salts to the metallic state.

The lustre production reached a higher stage in the 13th and 14th century in Spain, following the Islamic tradition started in the East some centuries previously. That this was an advanced technique creating highly prized items is illustrated as the archaeological findings indicate that the majority of the Islamic and Hispano Moresque productions of these centuries were exported abroad

Different recipes allowed potters to obtain several colours and hues, such as those exhibited by the Italian maiolica (16th and 17th Century.) where the lustre shows colours from copper-like to gold-like or greenish. But the typical lustre recipes from the Islamic and Hispano Moresque worlds have used copper and silver, among other non metallic components. A clue to the complexity of the manufacturing process lies in the number of “non-metallic” lustre layer specimens that have been found, implying that although the potter had intended to produce a metallic lustre, he had no success. One of the questions arising about this pottery is to determine why the colour of a particular piece did not reach the metallic shine. XRD shows that metallic Cu is present in those samples which exhibit a metallic shine, but not in the “non-metallic” examples. We consider that there are two possibilities: firstly that the reduction was not enough to obtain metallic Cu, or alternatively that the metal has formed into crystals too small to exhibit metallic optical properties. Moreover, the distribution of copper and silver in the luster layers is not even. Silver appears in spots of some hundreds of microns where some copper is also found; copper and silver are not evenly distributed at the edges of the luster decorations. Both are also related to differences in the final colour and metallic shine.

The newly rebuilt microXAFS beamline 10.3.2 has been utilised to determine the spatial distributions of the Cu oxidation states both within areas of a constant colour and in different coloured specimens. Fluorescence microXAFS is an important technique and has enabled us to penetrate the predominately Al and Si surface layer (of the order of 100Å – 200 Å thick) to probe the metal glaze beneath.

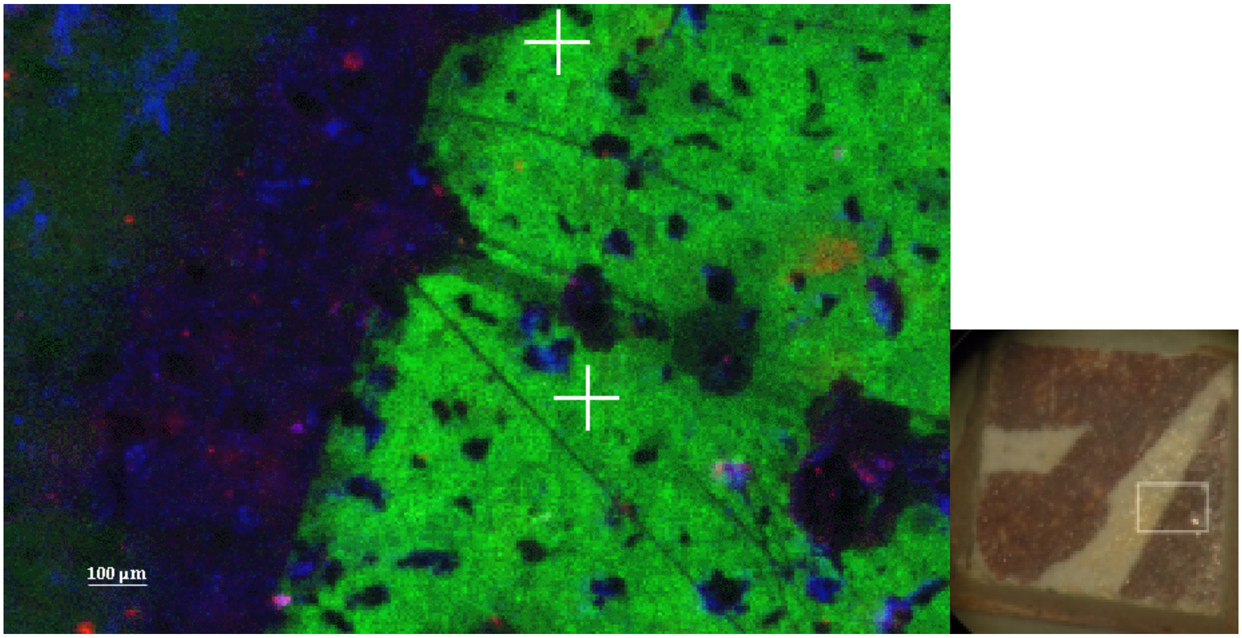

Figure 1. Tri-colour elemental map of a metal glazed strip of sample obtained from beamline 10.3.2, with (right) a larger scale visible light picture of the potsherd used. In the tri-colour map, copper is green, iron – red, calcium – blue. Shown are two locations from within the copper glaze from which copper K-edge EXAFS was recorded.

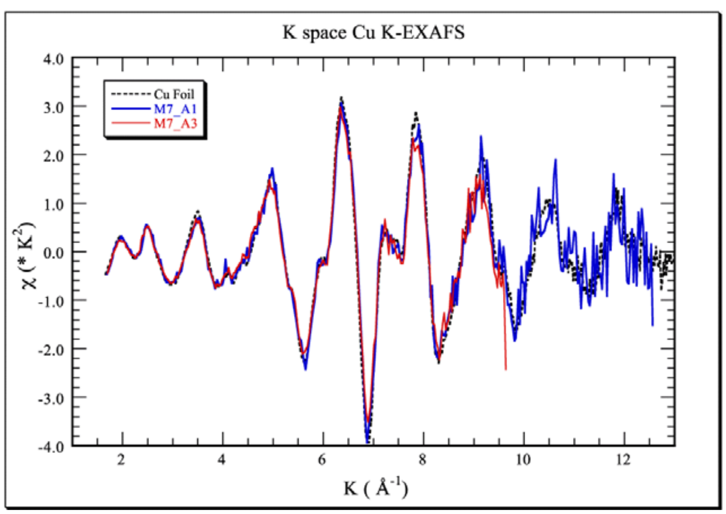

Figure 2. Cu K-edge EXAFS at two locations as shown in Figure 1 within the copper coloured part of a 'good' XXth century specimen with that obtained for a copper foil using the same instrument.

RESULTS

Examination of a number of specimens of both historical and recent providence has taken place and detailed analysis and interpretation of the results is still ongoing. Initial findings show that for good quality historical artifacts exhibiting distinct metallic glaze effects reduction to pure metal form has occurred. We present here Cu K-edge EXAFS from a 'good' Hispano Moresque 14th century specimen from Paterna (Valencia. Spain), illustrated in Figure 1. The Cu K EXAFS obtained from two sample areas within the copper glaze are shown in Figure 2, along with that for pure copper foil. Data acquisition times were of the order of 1 hour.

The fit of the experimental data to that of the pure foil is very good, demonstrating that not only was good reduction obtained in the firing process by the original potter, but also that the glaze itself has contained the copper effectively and prevented any subsequent oxidation through the centuries. Experimentally we also demonstrate the ability to collect good quality EXAFS data out to a K of 13 from small (20x20 microns) areas of these specimens, non-destructively and in reasonable time. EXAFS from "non-metallic" areas on other samples is more complex and requires further, more detailed analysis to fully interpret correctly. We hope to publish our findings shortly.

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