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Revisiting the beginnings of tin-opacified Islamic glazes

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ABSTRACT

The generally accepted theory is that the demand for Islamic glazed pottery started in Abbasid Iraq in the 9th century AD with the production of a range of glazed wares in response to the import of Chinese stonewares and porcelains. However, Oliver Watson has recently proposed that the demand for Islamic glazed pottery first occurred in Egypt and Syria in the 8th century AD resulting in the production of opaque yellow decorated wares. Using a combination of SEM analysis of polished cross-sections, and surface analysis using hand-held XRF or PIXE, Coptic Glazed Ware from Egypt, Yellow Glazed Ware from Syria, and comparable wares from Samarra, Kish and Susa have been analysed. The analyses show that the opaque yellow decoration was the result of lead stannate particles in a high lead glaze, which it is suggested was produced using a lead-silica-tin mixture. The use of lead stannate in the production of yellow opaque glazes is explained in terms of technological transfer from contemporary Islamic glassmakers who continued the Byzantine tradition of glassmaking. It is further argued that the introduction of opaque yellow glazed pottery into Mesopotamia could have provided the social context for the sudden emergence of tin-opacified white glazed pottery in Abbasid Iraq in the 9th century AD. However, in view of the very different glaze compositions employed for the yellow and white opaque glazes, it seems probable that the white tin-opacified glazes used for Abbasid cobalt blue and lustre decorated wares represent a separate but parallel technological tradition with its origins in the production of Islamic opaque white glass.

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1. Introduction

The generally accepted theory is that Islamic glazed pottery first blossomed in Abbasid Iraq in the 9th century AD in response to the import of Chinese stonewares and porcelains (Lane, 1947; Northedge, 2001; Tite and Wood, 2005; Wood et al., 2007) and included cobalt blue and lustre decoration on a white tin-opacified glaze. Chinese imports, as indicated by the discovery of the Belitung wreck off the Sumatra coast in 1998, were on a very large scale by the mid 9th century AD. However, Watson (2014) has recently argued that the demand for fine glazed ceramics started earlier and not in Iraq, but in Egypt and Syria. This development was a response to the drying up of the supply of fine unglazed tablewares in the eastern Mediterranean when the kilns that supplied the late Antique world with Red Slip wares were destroyed by the arrival of the Arab armies (Hayes, 1972). To fill the gap, potters in Islamic Egypt and Syria developed not only fine painted unglazed wares, but also new glazed types. Thus, Islamic glazed pottery frequently with opaque yellow and green decoration first appeared in Egypt (Coptic Glazed Wares – Scanlon, 1998) and then in Syria (Yellow Glazed Family – Watson, 1999) in the late 7th – 8th century AD. From here, the yellow glaze tradition spread to Mesopotamia where, in the 9th century AD, it could have provided the context for the emergence of a range of white tin-opacified wares, inspired by Chinese imports.

In order to investigate this recent hypothesis, a small group of sherds of Coptic Glazed Ware (CGW) from Egypt and Yellow Glazed Family (YGF) from Syria were analysed in polished section in a







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scanning electron microscope (SEM) with energy-dispersive spectrometry (EDS). These analyses were supplemented by the examination with a binocular microscope and by x-ray diffraction (XRD) measurements. The analytical data were extended by nondestructive surface analyses, using either hand-held x-ray fluorescence (HH-XRF) or proton-induced x-ray emission (PIXE), of further examples of these two wares together with comparable vellow glazed wares from Samarra. Kish and Susa. A total of twenty-seven ceramics were analysed, the primary aim being to establish whether or not the opacifiers used were tin-based (i.e. lead stannate yellow and tin oxide white) as used by Roman and contemporary Byzantine glassmakers, following the switch from the use of antimony-based opacifiers (lead antimonate yellow and calcium antimonate white) by Roman glassmakers around the 4th century AD (Turner and Rooksby, 1959; Tite et al., 2008). In addition a group of three later sherds (Fayyumi Type 1 and related wares) from Egypt were also examined since opaque yellow and green glazes were used in Egypt alongside the production of lustre ware and other white tin-opacified glazed wares introduced, probably in the 9th -10th century AD, from Iraq.

2. Experimental procedures

2.1. Glazed ceramic samples

One Egyptian CGW sherd (ALX202) from the sherd collection made from Fustat by the late Alexander Kaczmarczyk (Tite, 2011). and four Syrian YGF sherds (OLW1-4), provided by Oliver Watson, were selected for SEM and binocular microscope examination in polished section, and for XRD measurements (Fig. 1a-e). Surface analyses using either HH-XRF or PIXE were also made on a CGW dish (EA1974.48) in the Ashmolean Museum, Oxford; fourteen YGF sherds from Al Mina (Fig. 2a-b) and four comparable yellow glazed sherds from Samarra and Kish, all in the Victoria and Albert Museum; and three glazed bowls from Susa in the Musée du Louvre. In addition, one sherd (ALX66) from the collection of the late Alexander Kaczmarczyk related to Fayyumi Type 1 ware (Fig. 1f) was analysed by a combination of SEM, binocular microscopy and XRD, and two Fayyumi Type 1 sherds from the V & A (Fig. 2c–d) were analysed with the HH-XRF. The location of sites referred to in the text including those from which the ceramic samples were obtained are indicated on the map presented in Fig. 3.

The overall dating of Islamic ceramics of this period is based on the archaeological contexts in which the different ceramic types were found, and the dates for these contexts are themselves frequently of limited precision. CGW is found in late 7th and 8th century AD contexts (Scanlon, 1998); the production of the YGF was established across Syria in the second half of the 8th century AD (Whitcomb, 1989; Watson, 1999); and comparable yellow glazed wares in Mesopotamia have been found alongside 9th century AD wares of Samarra type (e.g., copies of Chinese Changsa and sancai, and tin-opacified glazed wares with cobalt blue and lustre decoration) (Watson, 2014). According to Scanlon (1993), the later Egyptian Fayyumi Type 1 wares cannot be more precisely dated than to c.850-1100 AD. Where the sherds analysed in the present paper are without precise provenance (e.g., ALX and OWC sherds), they are dated by means of typological comparison with excavated material.

2.2. Analytical procedures

The glaze-body microstructures, and the chemical compositions of the bulk glazes, individual opacifier particles and the bodies for those sherds from which polished sections were prepared were investigated using SEMs at UPC, Barcelona and RLAHA, Oxford. At UPC, a crossbeam workstation (Zeiss Neon 40) equipped with SEM (Shottky FE) column and EDS (INCAPentaFETx3 detector, 30 mm², ATW2 window) were employed, and at RLAHA, a JEOL SEM (JSM-5910) with Oxford Instruments EDS (INCA 300 System) was employed. Both systems were operated at 20 kV with 120s measuring times, and backscattered electron (BSE) images were obtained in order to study the microstructures of cross-sections through the glazes and bodies. Prior to coating for the SEM examination, the cross-sections were examined under a binocular microscope with objectives in the range $1 \times$ to $11.5 \times$. XRD measurements were made on the glaze surfaces of these same sherds using a conventional diffractometer, Bruker D8 with Cu-Ka (1.5606 Å) radiation with 4–70° two theta range, the penetration depth of the X-rays being less than about 100 µm. Identification of the compounds has been performed based on the Powder Diffraction File (PDF) database from the International Centre for Diffraction Data (ICDD).

Semi-quantitative HH-XRF analysis was performed using an Oxford Instruments X-MET 5100 X-ray fluorescence analyser equipped with a silicon drift detector, rhodium tube and 8 mm beam diameter (Casadio et al., 2012). The Soil-FP (Fundamental Parameters) mode was selected for all measurements, operating at 45 kV accelerating voltage, 15 μ A beam current with a 25 μ m iron filter. In most instances, two 30s measurements were taken from flat areas of the glaze surface. Bruker Artax software (Version 7.0.0) was used to identify spectral lines and calculate peak intensity counts. Because Pb L α counts tend to swamp the detector at high lead oxide concentrations, the Pb Ly peak intensity counts have been used, and these were calculated in Excel using the raw count data and subtracting the background counts.

PIXE analysis was performed using the new AGLAE system, introduced at C2RMF in 2012, in which four detectors consisting of Peltier-cooled SDD are dedicated to high energy X-rays (>3 keV), and another detector is optimized for the measurement of low energy X-rays (1–10 keV) (Pichon et al., 2014). Each analysis was performed by scanning the beam across one $500 \times 500 \,\mu\text{m}^2$ area, in order to minimize the influence of material heterogeneities, and a helium flow (2 l/min) was maintained in both the particle and X-ray beam paths to minimize energy losses and absorption. The glaze compositions were determined using a 3 MeV proton beam and the major, minor and trace element concentrations were calculated using the TRAUPIXE software (Pichon et al., 2010) with the GUPIXWIN code (Campbell et al., 2010). The DrN geological standard from CRPG was used to validate the results.

3. Results

The chemical compositions of the glazes, opacifier particles and bodies for the sherds analysed in polished section by EDS in the SEM, are given in Tables 1–3. The peak intensity counts resulting from surface analyses of the glazes as determined by HH-XRF are given in Table 4, and for comparative purposes, these analyses include data for sherd ALX202 also analysed in polished section by EDS in the SEM. The chemical compositions of the glazes as determined by surface analysis by PIXE are given in Table 5.

3.1. Egyptian CGW, Syrian YGF and related yellow glazed ceramics from Mesopotamia

On the basis of the analytical data presented in Table 1, it is clear that lead stannate was used as the opacifier in all the yellow CGW and YGF glazes (Fig. 1a–e), and analysis of a selection of the lead stannate particles indicated that they were of the form Pb(Sn,Si)O₃ with Sn/Si wt% ratios in the range 1.7–3.8. The green CGW and YGF glazes were all coloured by the addition of a few wt% of copper

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