
The colour and golden shine of early silver Islamic lustre

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Abstract - A selection of lustres including 9th century AD polychrome and 10th century AD monochrome Abbasid lustres from Iraq, and 10th to 12th centuries AD Fatimid lustres from Egypt and Syria is studied in the present paper. The selection is based on previous studies that demonstrated that all of them contain metal silver nanoparticles and copper, which, when present, appears either as Cu⁺ or Cu²⁺ dissolved in the glaze. They show different colours, green, yellow, amber, and brown, and may also show or lack a golden-like reflectivity, which results mainly from average size and concentration in the layer of the silver nanoparticles. In this paper, a depth profile composition of the lustre layers is determined using Rutherford Backscattering Spectroscopy, allowing the determination of the total silver content, concentration of silver, copper to silver ratio, and thickness of the lustre layers. We show that the enhanced golden-like reflectivity occurs only for layers with a high concentration of silver, and that the addition of PbO to the alkaline glaze helps the formation of more concentrated layers. The results obtained provide new hints concerning the lead enrichment of the glazes during this period.

1. Introduction

The first lustre decorations (Caiger-Smith 1991) on glazed ceramics can be dated to the 9th century AD in the Abbasid caliphate, and were probably produced in Bashra. The earliest examples were found in the Palace of Samarra. They are polychrome, with the most common combining green, amber, and brown, but also yellow and red. During the 10th century AD, they were replaced by a monochrome green lustre production. At the end of the 10th century AD and contemporary to the Fatimid occupation of Egypt, a new lustre production began in Fustat and in Syria, lasting until the end of the Fatimid rule. These productions are all monochrome, but show colours ranging from green to yellow and from orange to brown. The lustre decorations (Pérez-Arantegui *et al.*, 2001; Padovani *et al.* 2003) are extremely thin layers (well below the micrometre) made of small metal silver/copper nanoparticles inside the glaze

matrix (from a few to some tens of nanometres), which appear very close to the glaze surface (some tens of nanometres). The Abbasid and Fatimid lustre layers studied in this paper contain only silver metal nanoparticles, and, although they also contain copper, it appears either as Cu⁺ or Cu²⁺ dissolved in the glassy matrix (Pradell *et al.* 2008a; 2008b).

Lustre was produced following a highly ingenious procedure in which the lustre design (containing copper, silver- and sulphur- containing compounds, and clay) was painted (Molera *et al.* 2001) onto the glaze, which was then subjected to a firing at a relatively low temperature (500–600°C). Ag⁺ and Cu⁺ ions diffused into the glaze, substituting alkalis (either Na or K) (Pradell *et al.* 2005). The introduction of an external reducing atmosphere into the kiln favoured the precipitation of the metal

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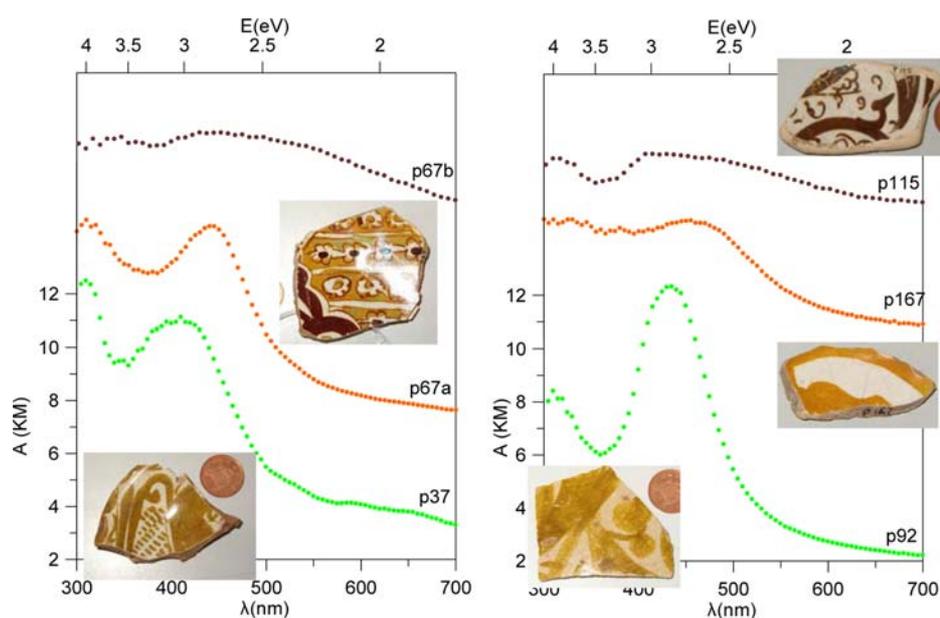


Figure 1. Images and UV-Vis spectra corresponding to some of the Islamic lustre layers showing different colours, corresponding to (left) green, amber, and brown Abbasid silver lustres and (right) green, yellow, and brown Fatimid silver lustres.

nanoparticles, which formed in a thin layer close to the glaze surface. The paint was washed off after firing to leave the colourful lustre decoration, which often exhibited a metal-like shine. Previous studies have shown that silver always appears as metal nanoparticles, while copper, being more difficult to reduce to metal than silver, often appears either as Cu^+ or Cu^{2+} ions dissolved in the glaze. Only when very reducing conditions are applied can the copper ions form nanoparticles of Cu_2O and metal copper.

The colour and shine of these layers are determined by this nanocomposite structure and produce particularly beautiful effects. The metal nanoparticles are essentially transparent to visible light, with the exception of the resonant absorption at a wavelength characteristic of the type, size, and shape of the metal nanoparticles (Berthier *et al.* 2006; Reillon and Berthier 2006; Reillon 2008). They also often show an enhanced reflectivity, responsible for the names 'lustre' given to them in English, and either 'metallic shine' or 'golden' in Spanish. This 'golden' shine may be described as resulting from the increase

in reflectivity, in a manner similar to that shown by a metallic surface. Laboratory replicas of lustre (Molera *et al.* 2007) indicated that the size of the nanoparticles, thickness of the layer, and the amount of copper or silver in the layer depend on the composition of the glaze and on the firing protocol, temperature, and atmosphere. Our laboratory replicas of copper lustres showed that the metallic shine was directly related to the presence of a high volume fraction of copper nanoparticles in the layer (Pradell *et al.* 2007), and that the composition of the glaze is the essential parameter that regulates this. The paint composition and firing temperature and atmosphere also play an important role in determining the success rate.

In the present paper, we discuss the reasons for the colour and golden shine shown by Abbasid and Fatimid Islamic silver lustre in terms of the composition and thickness of the lustre layers, which are obtained by using Rutherford Backscattering Spectroscopy (RBS); this method has been applied to the study of other lustre productions (Chabanne *et al.* 2008; Polvorinos del Rio *et al.* 2008;



Figure 2. Left, photograph of sample p99, Fatimid (11th century AD). Right, photograph of the same area with the surface tilted in order to show the reflected light. This shows the enhanced golden reflectivity of the layer.

Gutierrez *et al.* 2010; Chabanne *et al.* 2012). Optical calculations of the absorption and reflectivity of silver lustre-like layers provide direct clues about the colours and golden shine shown by the lustre layers. The voluntary modification by the Islamic potters of the glaze composition, by increasing the PbO content of the glazes in order to enhance the development of the golden shine, is discussed.

2. Materials and methods

We have analysed a set of lustre decorations which are representative of Abbasid lustre from Iraq (9th–10th centuries AD) and Fatimid lustre from Egypt (10–12th centuries AD). The selection includes lustre layers showing all the range of colours: green, yellow, orange and brown. Figure 1 shows some of the samples studied, on the left Abbasid and on the right Fatimid lustres, showing green, orange and brown colours. For all the colours, there are samples that show a golden shine and some that do not. Figure 2 shows an image of one of the Fatimid lustres showing an enhanced yellow reflectivity (golden shine).

UV-Vis diffuse reflectance (DR) avoiding the mirror reflected light was measured directly on the surface of the lustre layers by a Spectrophotometer Shimadzu UV-Vis 2401 PC. A small circular spot of 5 mm was used to collect the data. From these data, the colour coordinates and the corresponding dominant wavelength were evaluated using CIE 1931 chromaticity space. The dominant wavelength is given in Table 1 and shows an increase while red-shifting the colour, green to yellow to amber to brown. These measures are related to the total light that is transmitted through the lustre layer (neither scattered nor absorbed), reflected on the ceramic white background and transmitted back to the surface. Figure 1 shows the extinction spectra corresponding to some Abbasid and Fatimid lustres showing different colours.

The thickness and depth composition of the lustre layers are determined by means of Rutherford Backscattering Spectroscopy (RBS). RBS measurements were carried out with the 5 MV tandem accelerators at the CMAM facility (Climent-Font *et al.* 2004). The analyses were performed in vacuum using a 3035 keV He beam in order to take advantage of the $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ elastic resonance occurring at this energy, which increases the sensitivity of oxygen detection by a factor of 23. The RBS beam at the sample was square, of size $0.7 \times 0.7 \text{ mm}^2$. The backscattered ions were collected by means of two particle surface barrier detectors, at scattering angles of 170° and 165° . A careful quantification of the RBS spectra was achieved using the SIMNRA simulation code (Mayer 1997). Figure 3 shows the RBS fitted spectra from the white glaze surface and from the lustre decoration corresponding to one of the samples (p99). For the glaze, the average composition corresponds well to the Microprobe data presented elsewhere (Pradell *et al.* 2008a; 2008b), obtained from the glaze surface, but the addition of a thin lead depleted layer (of about $216 \times 10^{15} \text{ atm/cm}^2$, equivalent to 22 nm) at the surface is necessary to fit the spectrum. Modelling the RBS spectra of the lustre layer p99 reveals the same starting chemical composition as for the glaze, but with reduced quantities of Na and K, and corresponding increases of Ag and Cu, as determined from the Microprobe data (Pradell *et al.* 2008a; 2008b). As such, it corresponds to the ionic exchange mechanism responsible for the lustre formation.

To determine depth profiles, a sequence of layers has to be modelled. Figure 3 shows the depth concentration profile for the lustre layer, fitted using nine layers of varying thickness and silver content. For this sample, the total thickness of the layer approaches 500 nm, although the silver rich region is thinner, about 205 nm thick. Moreover, the maximum concentration of silver in the layer is 20.0 at%, present at a depth of 72 nm. All the lustre layers have been fitted following the same procedure.

3. Results and discussion

The corresponding depth concentration profiles for all the Islamic lustre decorations studied were also obtained, and the silver and copper profiles are shown in Figure 4. Some characteristics of the lustre layers can be determined from the fitted RBS data and are summarised in Table 1; that is, the maximum content of silver in the layer (in at%) and depth at which the maximum silver content occurs, i.e., depth at which the lustre layer forms (in nm), the total amount of copper and silver that has entered the glaze by ionic exchange per unit surface (atm/cm^2), and, finally, the thickness of the lustre layer (in nm). The silver/copper ratio in the lustre layer, wt% Ag/(Ag + Cu), is also provided.

We can observe that there is great variability in the total amount of copper and silver in the layers. Silver always appears as a well-defined layer, although the characteristics of the profile may vary greatly among samples. The profile shows some asymmetry, being steeper at the surface and showing a longer tail inside the glaze. This profile is characteristic of a diffusion controlled process.

The values corresponding to the total silver and copper in the layer are very different and are mainly related to the original paint composition and firing protocol, but do not influence the reflectivity of the layers (p67b contains a large amount of silver and does not show a metallic golden shine, while p92, containing a very low amount of silver, does show a golden shine). In contrast, the data unambiguously shows that only those layers containing a high concentration of silver show golden shine (p51a, p51b, p92, and p99). What is most interesting of the data obtained is the inverse correlation that clearly exists between the depth at which the lustre layer forms and the lead content of the glaze; this is plotted in Figure 5. This indicates that the diffusivity of silver ions into the glaze is lower for glazes richer in lead, which may explain why, broadly speaking, lustre layers tend to be very thin and contain a higher concentration of silver. It should be noted, however, that the original lustre paint composition and firing protocol followed do also play an important role (see differences between p99, p92, and p167). We know from previous replication experiments that copper enters the glaze mainly under oxidising conditions at about 500–600°C, but afterwards it needs a strong reducing atmosphere for the precipitation of metal nanoparticles; conversely, silver can reduce under less reducing conditions. Therefore, even using a glaze richer in lead, the silver in the layer may not reach the necessary concentration to produce a golden shine if a suitable firing protocol is not followed, or if the paint used does not have the appropriate composition. Finally, although the thickness of the lustre layer is a related feature, on its own it does not determine the presence of a golden shine. P51a and p37 have similar thicknesses, and only the first shows a golden shine, while

Table 1. The Islamic Abbasid and Fatimid lustre layers studied. Summary of the main characteristics of the lustre layers obtained from the fitted RBS spectra.

Samples	Abbasid (9 th -10 th century AD)					Fatimid (10 th -12 th century AD)				
	p67b	p67a	p51b	p51a	p37	p99	p92	p167		
Colour dominant wavelength (nm)	Brown 587.8	Amber 579.0	Dark green 578.1	Green 575.3	Green 577.3	Yellow 580.3	Green 577.0	Amber 581.3		
Shine	No/bluish	No	Golden	Golden	No	Golden	Golden	No		
PbO glaze (wt%)	6.9(0.3)	4.3(0.3)	13.9(2.1)	13.9(2.1)	7.9(0.4)	37.0(3.0)	34.3(1.1)	40.2(2.3)		
Lustre layer	Ag/(Cu + Ag) wt%	57	21	100	98	68	79	62		
	Max. Ag (at%)	4.7	1.1	8	4.6	20	8.9	4.6		
	Position max. (nm)	353(71.5)	488(29.7)	164(12.7)	265(43.3)	57(6.5)	34(6.8)	79(10.8)		
	Max. volume fraction Ag (%)	4.4	1.2	9	5.2	23.3	10.3	5.2		
	Total Cu × 10 ¹⁵ (atm/cm ²)	220	144	11	3	87	18	31		
	Total Ag × 10 ¹⁵ (atm/cm ²)	> 154	16	80	71	109	38	30		
	Thickness (nm)	> 660	402	275	287	206	167	120		

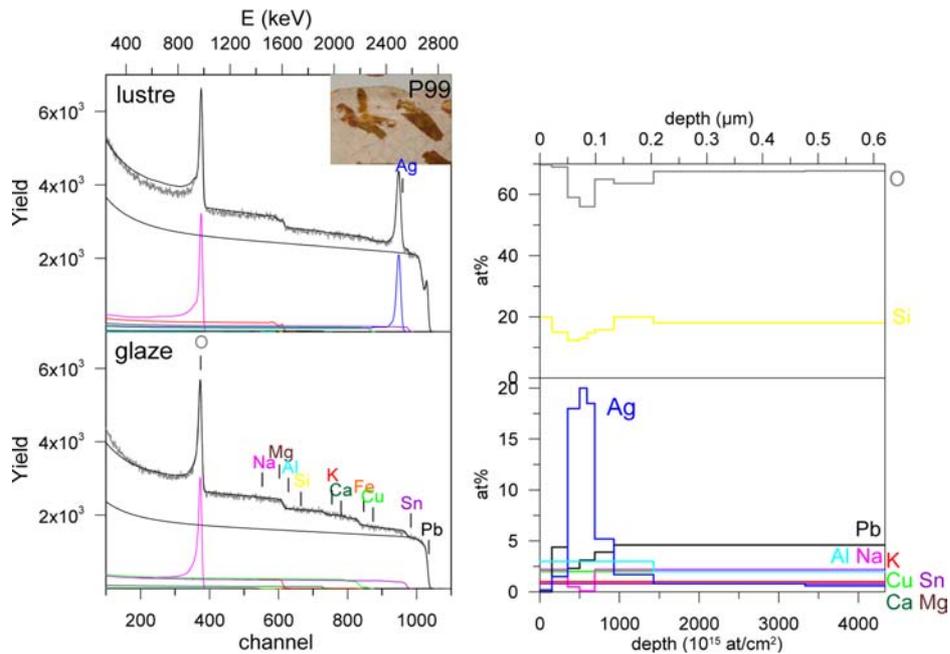


Figure 3. Left: Fitted RBS spectra corresponding to the white glaze (bottom) and to the yellow golden lustre decoration (top) for sample p99, Fatimid (11th century AD). Right: The chemical concentration depth profiles obtained by fitting the spectrum (top left) for the yellow lustre from sample p99.

p51a and p51b have different thicknesses and both show golden shine.

In an ionic exchange process, the reduced diffusivity of silver ions in lead-alkali glazes richer in lead has to be related to the reduced ionic mobility of the alkali ions

in the glaze. Some studies demonstrated that this ionic mobility is inversely related to the ionic size of the added ion for divalent ions; therefore, the addition of lead in the glaze reduces the alkali diffusivity (Doremus 1994). We can then conclude that the increase of the PbO content of the glazes from earlier Abbasid to later Fatimid lustre

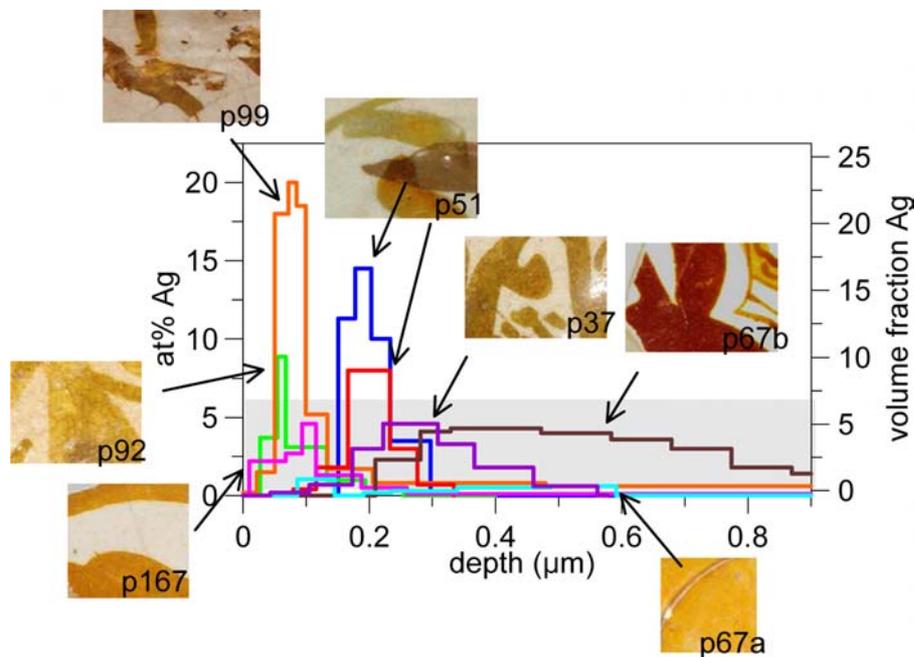


Figure 4. Silver depth concentration profiles obtained for all the Islamic lustre decorations studied. The samples showing golden shine (p51, p99, p92) exhibit a high concentration of silver in the lustre layer.

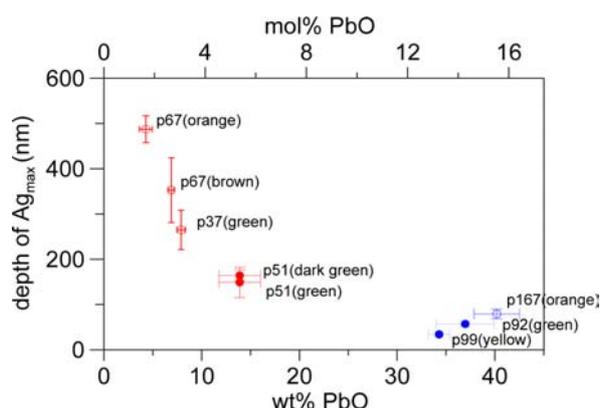


Figure 5. Depth at which the silver lustre layer forms inside the glaze as a function of the lead oxide (PbO) content of the glaze. Red symbols correspond to Abbasid lustres and blue symbols to Fatimid lustres. Solid symbols correspond to those lustre layers showing golden shine.

could have been deliberate, carried out in order to improve the success rate in producing golden shining decorations.

Concerning the colour (green, yellow, orange, and brown) shown by the lustre layers, the UV-Vis data (Fig. 1) indicate that there is a shift of the absorption peak related to the silver metal nanoparticles to longer wavelengths, as well as a broadening of the peak itself (Kreibig and Vollmer 1995; Reillon 2008). This shift is responsible for the change in colour from green to yellow and orange. This may be related to the increase in size of the metal silver nanoparticles, from 20 nm up to 40 or 50 nm. However, the peak broadening and the general flattening shown for the brown lustres has to be related to other aspect as well: on the one hand, the presence of a broad particle size distribution of silver nanoparticles, and on the other, to the presence of Cu^+ and Cu^{2+} dissolved into the glaze, which are known to respectively confer a yellowish or greenish tinge to the glaze. Finally, the presence of copper in solution into the glaze is known to produce the formation of aggregates of silver nanoparticles (Quinten and Kreibig 1993), with the consequent increase in size and a more heterogeneous distribution of sizes. The presence of copper in the lustres is therefore, directly or indirectly, responsible for the development of the yellow, orange, and brown colours.

Finally, concerning the golden shine, it is possible to calculate the reflectivity of the lustre layers using a model developed by Farbman *et al.* (1992), as a function of the concentration of metal silver nanoparticles in the lustre layer. Low concentrations of nanoparticles (up to 5% volume fraction) result in a low bluish reflectivity; with an increase in the concentration of metal silver nanoparticles (between 10 to 20% volume fractions), the reflectivity also increases and shifts to higher wavelengths, to a green-yellow colour. This enhanced yellow reflectivity is therefore responsible for the golden shine shown by the lustre layers.

4. Conclusion

We have demonstrated that the use of high lead content lead-alkali glazes in Islamic times helped the formation of

more concentrated lustre layers. This seems to indicate an intentional increase in the PbO content of the glazes from earlier Abbasid (9th–10th centuries AD) to later Fatimid (11th–12th centuries AD) lustre productions. However, the use of an adequate oxidising-reducing protocol and paint compositions is also fundamental.

The studies of Islamic lustre carried out to date have shown the high control of the process attained by its makers, allowing for ionic exchange and the precipitation of metal nanoparticles, with appropriate control of the type, size, and volume fraction of the metal nanoparticles. The Islamic potters produced a *true nanomaterial*, and their success in producing layers shining like gold may have contributed to the ancient alchemical belief in the transmutation of other metals into gold.

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