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COMPOSITION OF THE LUSTRE PIGMENT USED IN THE PRODUCTION OF 13TH CENTURY AD RAQQA LUSTREWARE FROM SYRIA*

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The very rare find of the relic of the original lustre pigment attached to the glazed surface of a sherd of 13th century AD Raqqa type lustreware from Syria has been analysed using a combination of analytical scanning electron microscopy (SEM), micro-X-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS). The composition of the pigment relic inferred from these analyses is shown to match those of recipes for lustre production given in the early treatises by Jazbir Ibn Hayyan (c. AD 721–c. AD 815) and Abū'l Qasim (AD 1301). Similarities and differences between this 13th century AD Syrian pigment and pigments used in the ninth century AD in Iraq, in the 14th century AD in Islamic and Hispano-Moresque Spain, and in the 16th century AD in Renaissance Italy are discussed.

KEYWORDS: ISLAMIC, SYRIA, CERAMICS, RELIC PIGMENT, LUSTRE DECORATION, ANCIENT TREATISES

INTRODUCTION

Lustre decoration was first applied over glass objects during the seventh century AD in Syria or Egypt; later, during the ninth century AD in Iraq, the technology was transferred to decorate glazed ceramics (Caiger-Smith 1991). Lustre is a very thin layer (typically 100 nm to 1 μm) formed by the reaction between a 'lustre pigment' applied over the glaze surface and the glaze itself, resulting in the precipitation of small silver or copper metallic particles (typically 2–50 nm in diameter) in and near to the surface of the glaze. After cooling, any surviving relic of the lustre pigment is washed off from the surface, revealing the lustre layer beneath (Pradell *et al*. 2005).

Lustre decoration is a sophisticated procedure that requires pigment and glaze of a specific composition together with a controlled firing (i.e., temperature, time and atmosphere) (Molera *et al*. 2007). Skilful potters were able to produce lustre decorations of various colours (e.g., red, brown, green, yellow and orange) showing iridescences, and most remarkably, a

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golden metallic-like shine (Gutierrez *et al*. 2010; Molina *et al*. 2014). Consequently, the study of the materials and methods used in the various lustreware productions and the relationship between them is of particular interest in order to gain information about the technological connections and developments. Unfortunately, one of the main ingredients, the original raw lustre pigment, does not survive its firing, and also, in the great majority of cases, any relic of the pigment is completely washed off after firing. In a very few cases, workshop structures and, within them, samples of the raw lustre pigment, or fragments of unfired lustre-painted ceramics, have been found associated with 14th century AD Islamic and Hispano-Moresque lustreware from Spain (Molera *et al*. 2001). However, up to the present day, neither workshops nor fragments of unfired lustre-painted ceramics have been found elsewhere. Consequently, the composition of the raw lustre pigment is still unknown for most of the lustreware productions, although in some cases information has been inferred from analysis of the lustre layer itself (Padeletti and Fermo 2004; Molina *et al*. 2014).

In this paper, we present the results of the analysis of the rare finding of the relic of the original lustre pigment attached to the glazed surface of a sherd of 13th century AD Raqqa type lustreware (p620) from Syria, which was not completely washed off after firing. These results are extremely important, as they provide the first direct evidence of the composition of the lustre pigment used in the Middle East. The data obtained will be compared to the recipes for lustre production given in early treatises; to the results obtained for lustre pigment from the 14th century AD Spanish workshops; and to information on the compounds included in lustre pigment as can sometimes be inferred from the analysis of the lustre layers (Padeletti and Fermo 2004; Padeletti 2013; Molina *et al*. 2014).

MATERIALS AND METHODS

The sherd (p620) on which the relic of the lustre pigment was found comes from a Raqqa type conical shaped bowl with a greenish glaze and chocolate brown coloured lustre (Figs. 1 and 2 (a)). Details of the body and glaze analyses are given elsewhere (Pradell *et al*. 2013). The body is a characteristic stonepaste, containing some 80 wt% quartz, 10 wt% iron-rich clay and 10 wt% glass frit, which corresponds chemically (high Fe, Ca and Mg with respect to Al) to a group of pots and wasters analysed by Smith (2006), and ascribed to 13th century AD Raqqa lustreware. Both the rear and front glazes, which appear heavily weathered, are of the transparent alkali–lime type and do not contain either lead or tin oxides. The SEM surface analyses of the lustre layers showed that, as with other Raqqa wares, they are copper rich, with a Cu/(Cu + Ag) ratio close to 100%.

The lustre pigment relic found on the rear glaze has been analysed directly on the surface by SEM–EDS (INCAPentaFETx3 detector, 30 mm^2, ATW2 window) operated at 20 kV, with 120 s measuring times. The depth of the SEM analyses is approximately 5 μm, and therefore, analyses extend through the relic of the pigment, the lustre layer and into the glaze.

Micro-XRD was performed to identify the compounds present in the relic pigment. An area of the lustre glaze on which relic pigment survived was cut from the ceramic, parallel to the surface, and this cut layer was then thinned down to about 50–100 μm. Due to the small amount of relic pigment surviving, the measurements were taken at XALOC beamline (Alba Synchrotron, Cerdanyola del Vallès) to take advantage of the high brilliancy and small spot size of the synchrotron light. Measurements were taken in transmission using a focused beam of dimensions 50 μm × 6 μm (FWHM) and 12.6 keV beam energy with 1 s acquisition time in a virtually noise-free Pilatus 6M (Dectris) detector with a large (424 mm × 435 mm, 6 Mpixels) active area (Juanhuix *et al*. 2014).

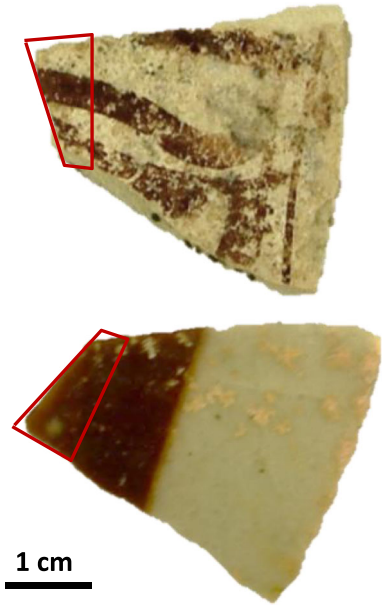

Figure 1 *The 13th century Raqqa sherd p620, showing front side (upper) and rear side (lower). The area of the sherd cut off for further analysis is outlined in red.*

RBS analysis was performed on the 5 MV tandem accelerator (CMAM, Madrid) to obtain the quantitative cross-section chemical analysis of the lustre layer. A 3070 keV energy He beam with a square section (1 mm in diagonal) was used. The sample was kept in vacuum. A careful quantification was performed by employing the simulation code SIMNRA (Mayer 1997). RBS data were fitted following a procedure described elsewhere (Gutierrez *et al*. 2010).

RESULTS AND DISCUSSION

Optical microscopy and SEM backscatter images of the lustre pigment relic are shown in Figures 2 (b) and 2 (c), and Figure 2 (d) respectively. SEM analysis of the surviving relic of the lustre pigment (~500 μm across) on the rear surface of sherd p620 was obtained directly on the surface, and therefore, it includes not only the composition of the pigment but also a contribution from the underlying glaze. The analysis shows that the pigment contains more than 5 wt% each of Al_2O_3, FeO and CuO, as well as of the order of 1 wt% each of S, As_2O_3, SnO_2 and PbO (Table 1).

The μ-XRD data, shown in Figure 3, indicate that the lustre pigment relic contains kaolinite, hematite, quartz, cassiterite (SnO_2), chalcopyrite ($FeCuS_2$), lautite (FeAsS) and marcasite (FeS_2), together with metallic copper and a copper-rich tin alloy plus various copper and sodium sulphates. Other compounds could not be precisely identified, but may be related to iron and copper arsenates.

With regard to the lustre layer, the chemical composition can be determined by RBS, the spectrum corresponding to the rear lustre layer being shown in Figure 4 (a). From this, we can see that the lustre layer is copper rich, but that it also contains silver and lead in small

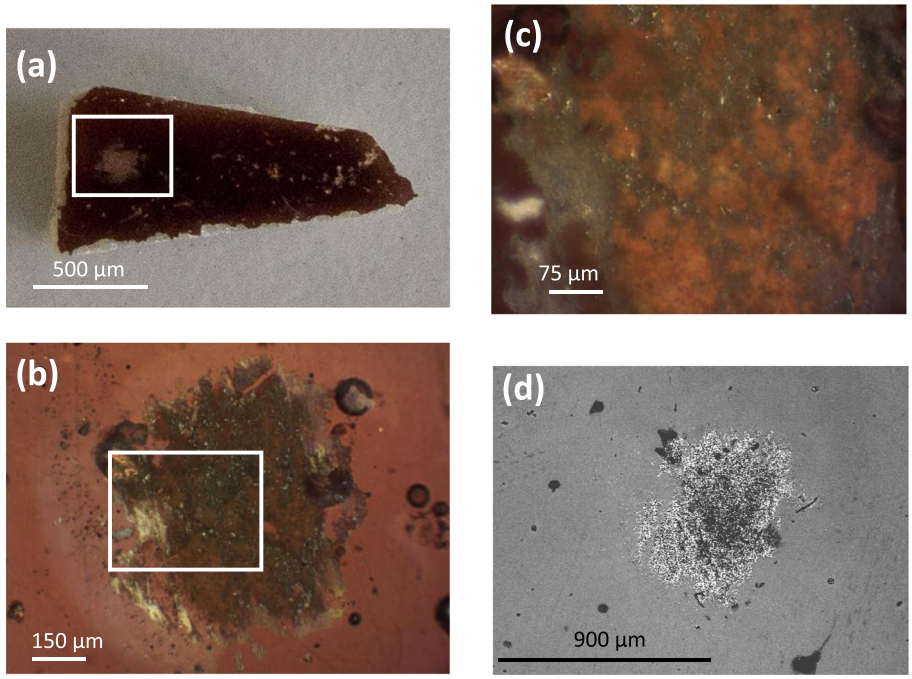

Figure 2 *A sample removed from sherd p620, showing: (a) the rear lustre surface, with the area of surviving pigment relic within the box outline; (b) an optical image of the pigment relic; (c) a magnified image of the area within the box outline in (b); and (d) an SEM backscatter image of the pigment relic.*

Table 1 *SEM–EDS analyses, in wt% (normalized to 100%), from the surface of the relic of lustre pigment surviving on the rear surface of sherd p620*

Na_2O	K_2O	Al_2O_3	SiO_2	S	CaO	MgO	TiO_2	FeO	CuO	As_2O_3	SnO_2	PbO
1.5	2.1	6.6	55.6	1.1	4.8	5.3	1.2	13.0	5.8	1.4	0.8	0.8

amounts (Fig. 4 (a), inset and Fig. 4 (b)). In fact, due to the fact that lead appears in an energy range of the RBS spectrum that is not overlapping with any other element, it can be determined even when present in very low amounts (10^{-3} at%, equivalent to about 0.01 wt%). As shown in Figure 4 (b), lead is present at the very surface of the lustre layer, and this we associate with the fact that the small amount of lead present in the pigment (Table 1) was incorporated into the lustre layer during firing. The average composition of the lustre layer, determined from the fitted RBS spectrum, is given in Table 2 in wt% oxides, normalized to 100% from a total wt% elements of 100.3; both copper and silver are kept as elements because they are mainly present as metallic nanoparticles.

Recipes for lustre production are given in a small number of treatises, among the earliest of which is the *Kitab al-durra al-maknuzna* (*The book of the hidden pearl*), by Jazbir Ibn Hayyan (c. AD 721 – c. AD 815) (Al-Hassan 2009), where a series of recipes for the production of lustre on glass are detailed. With regard to the production of ceramics, the earliest is Abū'l Qasim's

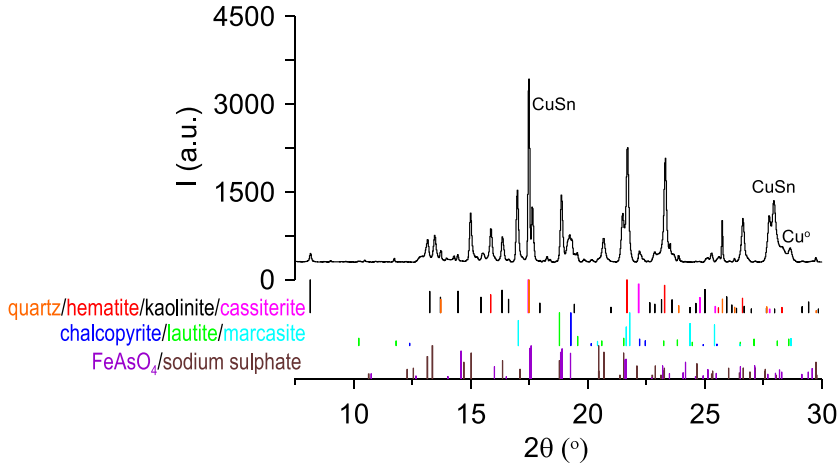

Figure 3 *The micro-XRD pattern associated with the relic of lustre pigment.*

treatise, dated to AD 1301 (Allan 1973), which describes the materials and procedures followed in the production of Kashan lustreware.

Jazbir Ibn Hayyan's treatise describes a series of 118 recipes for *talawıh* (lustre-painted or stained glass), in which the metals are mainly added as 'burned silver' and 'copper burnt with sulphur'. In addition, the inclusion of cinnabar (HgS), sulphates of metals (copper and iron), realgar (AsS), orpiment (As_2S_3) or sulphur is described. The metal compounds, mixed with some vinegar or citrus juice, are applied to the glass surface. The addition of 'ceruse' (white) of lead and/or tin is also described in some cases. Tin is known to be a powerful reducing agent if present in the glass, and the presence of lead is known to enhance the growth of metallic copper and cuprite particles.

Abū'l-Qasim's treatise describes the inclusion of pyrites (possibly chalcopyrite, $CuFeS_2$), and red and yellow arsenic (i.e., realgar and orpiment), which, with the 'burnt silver' and 'roasted copper', are mixed with vinegar. It is also stated that *sirinj*, which is interpreted as a lead–tin mixture (i.e., calx), is sometimes added.

Consequently, the composition of the relic of the lustre pigment, which includes Al_2O_3, FeO, CuO, S, As_2O_3, SnO_2 and PbO (Table 1), is in good agreement with those described in these two treatises. The compounds identified in the pigment relic are those obtained after firing. Hematite, cassiterite, quartz, chalcopyrite and lautite survive as part of the original pigment, and it is also possible that the metallic copper and copper–tin alloy was originally present in the pigment. In contrast, the sulphates, and also the possible arsenates, are products of the firing. The hypothesis so far accepted is that sulphur results in the formation of a sulphate melt, which is responsible for the ionic exchange and from which, during cooling, some mixed sulphates crystallize. The formation of mixed sulphates was also observed in the analyses of the surviving pigment from a replicated lustre (Molera *et al.* 2007).

Of particular importance is the fact that our finding matches perfectly the description of the lustre pigment used in the production of Kashan lustreware, as given in Abū'l-Qasim's treatise. There also exist other strong links between the Raqqa and Kashan lustrewares, in that they are contemporary, both use stonepaste bodies and brown-coloured lustre in combination with cobalt blue decoration, and the shapes of the bodies and the lustre designs are also similar (Watson 1985). However, in spite of these clear links between the Raqqa and Kashan productions, there are also

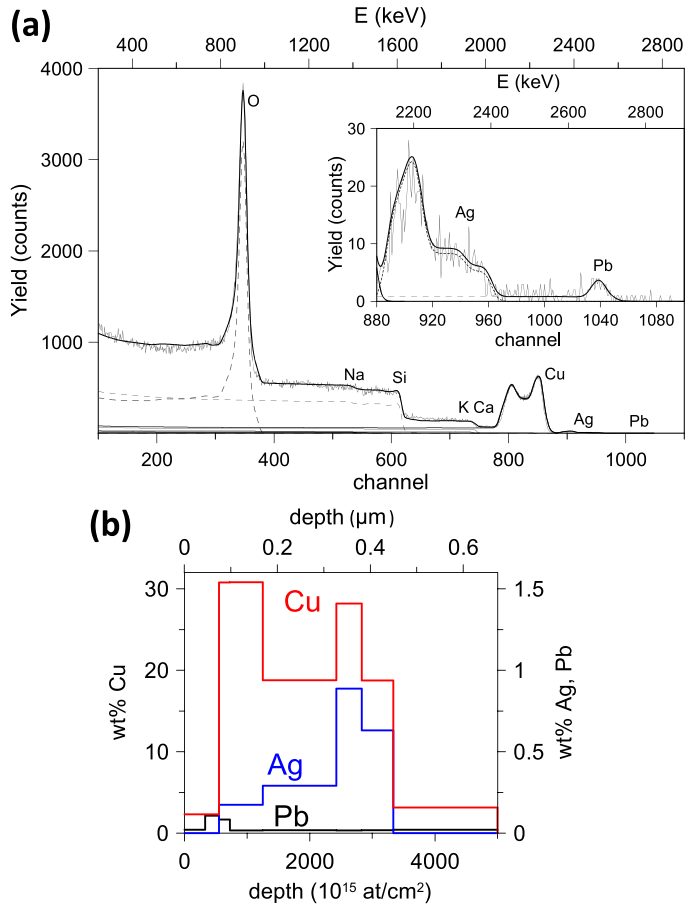

Figure 4 *RBS results for the rear lustre surface on sherd p620, showing: (a) the fitted RBS spectrum, with enlarged silver and lead peaks shown in the inset, the lower-energy copper peaks remaining outside the inset; and (b) wt% copper, silver and lead cross-section profiles for the lustre layer obtained from the fitted RBS spectrum.*

Table 2 *The RBS analysis, in wt% (normalized to 100%), for the rear lustre layer on sherd p620, averaged over the layer*

Na_2O	K_2O	Al_2O_3	SiO_2	CaO	MgO	FeO	PbO	Cu	Ag	$\%Cu/(Cu + Ag)$
3.2	1.5	1.3	65.9	4.2	2.4	0.6	0.03	20.5	0.3	98.4

many differences. For example, tin-opacified lead–alkali glazes are used in the case of Kashan lustreware (Pradell *et al*. 2008), and although both use stonepaste bodies, these have different microstructures. Consequently, the products of these two centres can be easily distinguished.

Although no pigment relic has been found in the case of earlier lustre productions, the use of lead and tin in the formulation of the lustre paint has similarly been demonstrated in some red copper lustres associated with ninth century AD polychrome lustreware from Basra in Iraq (Molina *et al*. 2014). Although in these early productions the glazes are often lead and tin free,

the analysis of the lustre layers themselves showed the presence of small amounts of lead and tin, thus demonstrating their presence in the lustre pigment.

Contrariwise, lustre pigments used in the production of some 14th century AD Islamic (Malaga, Spain) and Hispano-Moresque (Paterna and Manises, Spain) lustrewares have been found, as well as workshops and lustreware at various stages of firing (Molera *et al*. 2001). Copper and silver sulphides mixed with clay and iron oxides have been identified in these pigments, but instead of sulphur or arsenic sulphide, these pigments were found to contain mercury sulphide (HgS, cinnabar). The use of cinnabar is also indicated in some of the recipes in the Jazbir Ibn Hayyan treatise. Similarly, the Spanish treatises by Nicolau de Reyner from Barcelona, dated to AD 1514–19, describe the use of red earth, copper sulphide, cinnabar (HgS), silver coins and sulphur bars (Ainaud de Lasarte 1942; Pérez-Arantegui and Pardos 2008), and in this case the use of cinnabar is consistent with the fact that cinnabar mines are known to have been exploited in the south of Spain since Roman times. However, the addition of lead and tin calx is neither described in the Spanish treatises nor determined by analysis of the surviving pigments.

The 16th century AD Renaissance lustreware from Deruta and Gubbio was studied by Padeletti and Fermo (2004), and XRD of the lustre decoration has shown the presence of cosalite ($Pb_2Bi_2S_5$). Bismuth, which is known to be a strong reducing agent, is used in the form of the oxide or carbonate in modern lustre productions, and the deliberate addition of a bismuth compound in Italian lustreware has been thoroughly discussed by Padeletti and Fermo (2004). The relatively large amount found in lustreware, and the fact that, at the beginning of the 16th century AD, bismuth was already known as a different substance to tin, lead or silver, and was used together with lead and tin to make silver-like vessels in Central Europe, all supports the hypothesis that Italian potters deliberately added bismuth to produce lustreware. However, it should be noted that the use of bismuth is not described in the contemporary Italian ceramics treatise by Cipriano Piccolpasso (1980 [1558]). Instead, Piccolpasso describes only the use of red earth, Armenian bole (iron oxide), *ferretto* of Spain (CuS) and cinnabar (HgS) for the red lustre, with the addition of calcined silver coins for the yellow golden lustre.

CONCLUSIONS

The above analytical data for the relic of the lustre pigment surviving on the glaze of this 13th century AD lustreware from Raqqa (Syria) provide the first direct evidence for the composition of the lustre paint used in the Middle East. As inferred from its composition, the range of materials included in this lustre paint corresponds well with the lustre recipes described in Abū'l-Qasim's 13th century treatise on ceramics, as well as with some recipes given in Jazbir Ibn Hayyan's glass treatise dating to the eighth century AD. In the lustre pigment used in 14th century AD Spain, mercury sulphide (cinnabar) replaces the arsenic sulphide used in the Middle East as the source of the sulphur required to produce the sulphate melt necessary for the ionic exchange between the copper and silver from the pigment and the alkali ions from the glaze (Pradell *et al*. 2005).

As previously observed and discussed in the case of ninth century AD lustre from Basra (Iraq) (Molina *et al*. 2014), the inclusion of lead–tin calx in the pigment used for the Raqqa lustre probably helped the production of lustre through both the reducing power of tin and the role of lead in encouraging the growth of the metallic copper. This is particularly important when alkali–lime, tin-free glazes were used. Furthermore, the early addition of lead–tin calx in the case of the Basra lustre confirms the relationship between the beginnings of the lustre decoration of ceramics and the earlier lustre decoration of glass, in the production of which, according to Jazbir Ibn Hayyan's treatise, lead–tin calx was included.

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REFERENCES

Ainaud de Lasarte, J., 1942, La loza dorada y la alfareria Barcelonesa de los siglos XIV i XV, *Anales y boletín de los Museos de Barcelona, Ayuntamiento de Barcelona*, **I**, 89–104.

Al-Hassan, A. Y., 2009, An eighth century Arabic treatise on the colouring of glass: Kitazb Al-Durra Al-Maknuzna (The book of the hidden pearl) of Jazbir Ibn Hayyan (c. 721–c. 815), *Arabic Sciences and Philosophy*, **19**, 121–56.

Allan, J. W., 1973, Abū'l-Qasim's treatise on ceramics, *Iran*, **11**, 111–20.

Caiger-Smith, A., 1991, *Luster pottery*, New Amsterdam Books, New York.

Gutierrez, P. C., Pradell, T., Molera, J., Smith, A. D., Climent-Font, A., and Tite, M. S., 2010, Color and golden shine of silver Islamic lustre, *Journal of the American Ceramic Society*, **93**, 2320–8.

Juanhuix, J., Gil-Ortiz, F., Cuni, G., Colldelram, C., Nicolas, J., Lidon, J., Boter, E., Ruget, C., Ferrer, S., and Benach, J., 2014, Developments in optics and performance at BL13-XALOC, the macromolecular crystallography beamline at the Alba Synchrotron, *Journal of Synchrotron Radiation*, **21**, 679–89.

Mayer, M., 1997, SIMNRA User's Guide (IPP 9/113 1997); http://www.rzg.mpg.de/

Molera, J., Mesquida, M., Pérez-Arantegui, J., Pradell, T., and Vendrell, M., 2001, Lustre recipes from a medieval workshop from Paterna, *Archaeometry*, **43**, 455–60.

Molera, J., Bayés, C., Roura, P., Crespo, D., and Pradell, T., 2007, Key parameters in the production of medieval luster colors and shines, *Journal of the American Ceramic Society*, **90**, 2245–54.

Molina, G., Tite, M. S., Molera, J., Climent-Font, A., and Pradell, T., 2014, Technology of production of polychrome lustre, *Journal of European Ceramic Society*, **34**, 2563–74.

Padeletti, G. (ed.), 2013, *Mastro Giorgio da Gubbio: art, science and technology of lustred majolicas*, Volumnia Editrice, Perugia.

Padeletti, G., and Fermo, P., 2004, Production of gold and ruby-red lustres in Gubbio (Umbria, Italy) during the Renaissance period, *Applied Physics A*, **79**, 241–5.

Pérez-Arantegui, J., and Pardos, C., 2008, Lustre recipes for Hispano-Moreque ceramic decoration in Muel (Aragón, Spain) or 'How much a little copper weighs', in *Archaeology, history and science: integrating approaches to ancient materials* (eds. M. Martinón-Torres and T. Rehren), pp. 151–66, Left Coast Press, Walnut Creek, CA.

Piccolpasso, C., 1980 [1558], *The three books of the potter's art: a facsimile of the manuscript in the Victoria and Albert Museum, London*, translated and introduced by R. Lightbown and A. Caiger-Smith, The Scolar Press, London.

Pradell, T., Molera, J., Molina, G., and Tite, M. S., 2013, Analysis of Syrian lustre pottery (12th–14th centuries AD), *Applied Clay Science*, **82**, 106–12.

Pradell, T., Molera, J., Smith, A. D., and Tite, M. S., 2008, Early Islamic lustre from Egypt, Syria and Iran (10th to 13th century AD), *Journal of Archaeological Science*, **35**, 2649–62.

Pradell, T., Molera, J., Roque, J., Vendrell-Saz, M., Smith, A. D., Pantos, E., and Crespo, D., 2005, Ionic-exchange mechanism in the formation of medieval luster decoration, *Journal of the American Ceramic Society*, **88**, 1281–9.

Smith, D. T., 2006, Appendix 2: compositional analysis of early-thirteenth-century ceramics from Raqqa and related sites, in *Raqqa revisited—ceramics from Ayyubid Syria* (ed. M. Jenkins-Madina), pp. 221–37, The Metropolitan Museum of Art, New York.

Watson, O., 1985, *Persian lustre ware*, Faber and Faber, London.