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Foreword

The book forms an excellent blueprint and a welcome step in bringing nanosciences to the tangible cultural heritage community deriving from archaeological sites and artefacts, collections in museums, masterpieces, buildings and monuments. It gives a good overview on the uniqueness of cultural heritage systems that need to be studied by physico-chemical sciences in an interdisciplinary way, with the help of specialists of pure disciplines (physics, chemistry, material sciences) associated with those practicing interface disciplines such as archaeometry, and conservation science. This complexity of approaches to investigate a large number of objects, with a large heterogeneity at different scales, explains why the nanoaspects of cultural heritage systems have only appeared fairly recently. Indeed, this book is the first attempt to review how nanoscience is bringing new insights into this area.

I find the ambitious approach to cover the whole value chain from the importance of nanoaspects in ancient technologies of cultural heritage systems, through nanotechnologies and analytical strategies to characterise cultural heritage objects, up to the stage of their conservation and protection, in addition to new technologies, as well as the implications for societies including environmental aspects, very impressively. The book covers all topics from nanoparticles, nanomaterials and nanocomponents, from fundamentals of composition, structure and properties to nanosyntheses and processing aspects, characterisation, analytical techniques, and modelling. It also covers the conservation and protection of cultural heritage with nanomaterials, e.g., aspects such as corrosion, de-acification, etc., and cleaning and restoring.

The book introduces a large panel of prospect developments, largely due to the fact that the use of suitable nano-analytical methods within a multiscale-investigation, is still in its infancy and also because possible applications in specific material science (i.e., bio-inspired materials) and conservation methods, motivates education and offers an emerging field of research and innovation. It is a source of information and pinpoints new ideas and lists a large number of recommendations for all those involved in cultural heritage and restoration of historical buildings; finally it provides an enormous potential for societal and economic benefits, including job creation.

The book is a great initiative and should receive the attention of specialists of cultural heritage, scientists interested in the application of nanosciences searching for reviews in this emerging field, but also citizens, policy-making bodies, research agencies or foundations who are searching for support of societal applications of nanosciences.

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Contents

Part I Nanostructuration in Ancient Materials

Part II Nanotechnologies and Analytical Strategies to Characterise Cultural Heritage

Part III Conserve and Protect the Cultural Heritage using Nanomaterials and Nanoscience

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Introduction

We may consider that when Theodoric the great (6th AD) listed the seven marvels of the world, this was a first but probably unconscious attempt to define a kind of Cultural Heritage. More later, in several European countries, exists the willing of stressing the value of the heritage of ancient generations. For example during the French revolution, in 1794, the "*Instruction sur la manière d'inventorier et de conserver, dans toute l'étendue de la République, tous les objets qui peuvent servir aux arts, aux sciences, et à l'enseignement*" of the *Commission temporaire des arts, Comité d'instruction publique de la Convention nationale, l'an II de la République* declared: "the objects that serve to instruction [ ] will be found in libraries, museums, in cabinets, in collections [ ], in workshops were are gathered instruments, in palaces and temples decorated by masterpieces of arts; in all places where monuments shows what were humans, people, everywhere where lessons from past can be collected and transmitted to posterity". The contemporary definition of Cultural Heritage considers both tangible heritage (such as archaeological sites and artefacts, collections in museums, masterpieces, buildings and groups of buildings, monuments, landscapes, etc.[1]) and also intangible attributes of human groups (languages, folklore, traditions, biodiversity, etc.[2]) inherited from past generations. As stated by International Council of Museums (ICOM[3]) the main international organisation representative of museums and professional of museums, or the International Council of Monuments and Sites (ICOMOS[4]), both linked to UNESCO, this heritage must be protected and preserved for future generations.

Concerning tangible Cultural Heritage, in addition to other approaches (historical, ethnographical, archaeological, art history, conservation, etc.), physico-chemical

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[1] Convention Concerning the Protection of the World Cultural and Natural Heritage: http://whc.unesco.org/en/conventiontext/; and Convention on the Protection of the Underwater Cultural Heritage: http://www.unesco.org/new/en/culture/themes/underwater-cultural-heritage/2001-convention/.

[2] Convention for the Safeguarding of the Intangible Cultural Heritage: http://www.unesco.org/culture/ich/en/convention.

[3] http://icom.museum/.

[4] http://www.icomos.org/en/.

sciences can be used to study what can be considered as Cultural Heritage systems (in the physico-chemical sense). Contrary to a large part of systems that are studied in experimental sciences and that can be synthetised, authorising reproducibility of measurement, heritage systems (as the other one studied in natural sciences or geology for examples) present several particularly as their uniqueness, their heterogeneity at different scales or their variability. For that reason their study using physico-chemical methods needs a high interdisciplinarity and the involvement, in addition to specialists of pure disciplines (physics, chemistry, material sciences, etc.), of "intermediaries" as scientists practicing archaeometry, conservation science, etc.

Moreover, the challenges on the one hand of understanding and preserving objects and buildings of the past and, on the other hand linked to the difficulty of setting adapted methodologies and scientific concepts, leaded scientists to implement, since the beginning of positive sciences during the nineteenth century, new analytical methods or disciplines on heritage systems. For example, one of the first experiment proceeded after the development of metallographic microscope and metallurgy was to observe damasked swords and to try to decipher their structure (see for example the works of G. Pearsonen, P. Anossov, Faraday and J.-R. Bréant). Besides, Willhelm C. Röntgen, the inventor of X-rays, has very early used his invention to investigate painting, polychromed sculptures and metallic archaeological artefacts. Soon after the discovery of X-rays, they were employed to better understand the structure of archaeological artefacts. After the Second World War, the development of analytical techniques (as neutron activation, X-ray fluorescence, magnetism, etc.) was quickly followed by applications to heritage artefacts; furthermore some specific methods dedicated to heritage problematics were invented, as radiocarbon dating (for which Willard Frank Libby received the Nobel Prize in 1960) or thermoluminescence dating (proposed by Martin J. Aitken). The development of these researches, with dedicated laboratories, leads to the first scientific journal dedicated to this field: "Archaeometry", which is published since 1958. Still at the end of the twentieth century and today, scientists follow the development of analytical techniques to implement their performances to enhance the deciphering of challenges (ancient techniques, materials, conservation) offered by Cultural Heritage systems. Nowadays because of their pluridisciplinarity and impacts in various fields, researches dealing with cultural heritage are accepted for publication in diverse categories of journals. It could be "multidisciplinary sciences", general or specialised journal in a scientific field (as chemistry, physics, earth sciences, analytical sciences), or journals dedicated to heritage problematics which more recently flowered with the multiplication of journals and publications [e.g. some of the most ancient ones: Studies in Conservation (since 1952), Journal of Archaeological Science (since 1974), ArcheoSciences-Revue d'archéométrie (since 1977), Journal of Cultural Heritage (since 2000)]. Sometimes the recall of new analytical techniques are only "one-shot" tries with low significant added-value in the domain of heritage, but often the use of these cutting-edge methods brings key results to the understanding of ancient systems. Some examples of this dynamic trend are the following journals special issues corresponding to papers given in international conferences: Synchrotron Radiation in Art and Archaeology (SR2A) (Journal of Analytical Atomic Spectroscopy, issue 3, 2015), International Conference on Particle Induced X-ray Emission (Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, volume 363, 2015). Thus, naturally, with the development of nanosciences and nanotechnologies at the end of the twentieth century and the beginning of the twenty-first century, scientists tried to benefits of these new approaches, methodologies and concepts for studying systems of Cultural Heritage. First attempts could be sometimes clumsy or artificial, but they have the merit to open the doors of nanoscale to conservation scientists and archaeometers.

Nanoscience and nanotechnology are based on the control of the knowledge, structure and function of materials on the nanometer scale, i.e. on the scale of one billionth of a metre. The gateway to this domain has been opened since 100 years, when W.C. Röntgen discovered the X-rays which allowed us to unravel the nanoscale structure of matter and when M. Planck, W.K. Heisenberg, E. Schrödinger and A. Einstein developed the language of quantum mechanics. Indeed, the nanometer world is governed by quantum mechanics and represents the interface between quantum and classical physics. As material systems and device structures become nanosized and nanostructured, new challenges have emerged: how to grow and design these artificial material structures in a precise and reproducible way and how to analyse their three-dimensional structure, properties and functions with the highest level of precision. In the past 40 years, the development of analytical techniques, capable to investigate the chemical, electronic and magnetic structure of any given material structure in any possible environment in a non-destructive way, has been spectacular. Among them, synchrotron radiation facilities providing micro-sized X-ray beams has a specific position because diffraction, diffuse scattering, tomography, spectroscopy, microscopy have produced unprecedented information in the nanoscale world. Generally, nanoscience and nanotechnology is an interdisciplinary ensemble of several fields of sciences such as materials science, physics, chemistry, biology and engineering. It is producing a true revolution because there are opportunities of connecting nanostructures with various functions and macroscopic properties as well as designing and fabricating new objects with specific functionalities. This explains why major consequences are expected in health and medicine, energy and environment, transport and space, communication and information.

Considering this short definition of nanoscience and nanotechnologies, one can think that “nano” is only a contemporary reality. Nevertheless, nanoscale can be addressed by looking ancient nanosystems. As illustrated by the various chapters of this book, “nano” plays a role at various step of the “ancient object life”. Nanoscaled systems have been manufactured since a long time, or nanostructures of natural materials are anciently exploited during manufacturing processes. The understanding of the processes to form such nano-features could reveal the selection of some specific raw materials and/or the setting of precise know-how. These impacts on the knowledge and organisation of ancient societies answer or renew some historical questions. Part I of this book dedicated to “Nanostructuration in

Ancient Materials" illustrates from diversified examples (materials, periods) such relations between nano-features and Cultural Heritage. This is demonstrated for multiple artificial materials and their related manufacturing techniques with: metallic-lustre ware (Chapter "Lustre and Nanostructures-Ancient Technologies Revisited"), nano-crystallisation in decorative layers of Greek and Roman ceramics (Chapter "Nano-crystallization in Decorative Layers of Greek and Roman Ceramics"), natural nanosized raw materials and sol-gel technology in pottery (Chapter "Natural Nanosized Raw Materials and Sol-Gel Technology: The Base of Pottery Since Millenniums") or for a more recent technique one of the first photographic process at the beginning of the XIXth century: daguerreotypes (Chapter "The Science Behind the Daguerreotype: Nanometer and Sub-micrometer Realities On and Beneath the Surface"). Besides, natural biomaterials (bones, ivories, antler) intensively used by men along their history are complex organic/mineral composites which must be studied down to the nanoscale in order to ensure their identification (nature and associated species), to understand their properties, to reveal treatments and to undertake adapted conservation strategies (Chapter "Informative Potential of Multiscale Observations in Archaeological Biominerals Down to Nanoscale"). Through scales the understanding of the influences of the nanoscale on the macroscopic properties (aesthetic, mechanic, durability, etc.) is challenging. Ancient societies prepared some objects with nano-features to obtain some "macro" properties, readily evaluable at these periods. One can even consider that ancients were practicing nanotechnologies but with no means to observe the results of their "trial-and-error" approach with probes revealing the nanoscale and models explaining the properties. The challenge offered nowadays is to understand the effects of "nano" on the macro-scale in quite complex samples prepared in the past by an often currently unknown process or of natural ones not already fully understood. It has to be stressed that these concerns about relations between structures from the nanoscale and properties are the same than the current challenges in new material design. Tackling these challenges in ancient artefacts could inspire modern material designs, as one searches some concepts in "bio-inspired materials" (see for example: Sanchez et al. 2005; Nicole et al. 2010).

Besides, the needs to investigate objects at the nanoscale level (especially through the chemistry and material scientific aspects), conducted scientists to use new suitable characterisation techniques. These analytical techniques which open the "nano world" and which can be of great interest for the study of heritage systems are discussed in Part II "Nanotechnologies and Analytical Strategies to Characterise Cultural Heritage" with the Chapters "Surface-Enhanced Raman Spectroscopy: Using Nanoparticles to Detect Trace Amounts of Colorants in Works of Art" and "From Archaeological Sites to Nanoscale: The Quest of Tailored Analytical Strategy and Modelling". Nevertheless, some specific precautions should be taken for an efficient and significant use of nanotechniques. Lastly, new insights at nanoscale bring other point of views and new challenges concerning the bridging of the gaps between functional scale (macroscopic scale) and nanoscale, as especially discussed in Chapter "From Archaeological Sites to Nanoscale: The Quest of Tailored Analytical Strategy and Modelling".

A third aspect linked to heritage artefacts and systems is the understanding and the management of the alteration processes. First because it is needed to properly identify and differentiate anthropic information from alteration effects; second to propose suitable and efficient conservation (preventive or curative) and restoration strategies. These aspects are presented in Part III "Conserve and Protect the Cultural Heritage using Nanomaterials and Nanoscience". Altered materials are heterogeneous at all scales, and the setting of a global mechanism requires starting from the nanoscale at which the chemical reactions occur. Studying transport mechanisms or reactivity underlines the role of nanostructures or interfaces in the complex thick layers of alterations. Moreover heritage systems give an unique opportunity to explore the very long time span, for which mechanisms are specific and with given material characteristics produced over long periods which could not be reproduced by accelerated processes in laboratories. Studying ancient artefacts as "analogues" of modern ones in order to predict their very long term behaviour could answer: on the one hand questions about modern material durability; and on the other hand issues on the ways to conserve the heritage artefacts, gathering for the future the becoming of ancient and present objects. An illustration is given in Chapter "Nanoscale Aspects of Corrosion on Cultural Heritage Metals" with the case of the corrosion of metallic heritage artefacts and their protection.

As stated in the beginning of this introduction, a crucial aspect is the protection of cultural heritage objects by setting adapted treatments. As indicated by the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM[5]), the restoration or protection treatment must be adapted to the specific case of heritage systems, must easily be removable and should not alter the aspect of the artefact or heritage system. Additional requirements are also practical ones, as a quick preparation, a relatively low cost and a straightforward use, because the global costs should be controlled and accordingly only few museum laboratories have the extensive sample preparation capabilities of university-based facilities. Besides, dealing with archaeological artefacts on the field or monuments requires procedures adapted to on-site work. Two chapters will present several cases where the nanotechnologies propose innovative solutions for preserving the Heritage. The systems presented are linked to paper with alkaline nanoparticles for deacidification and pH control (Chapter "Alkaline Nanoparticles for the Deacidification and pH Control of Books and Manuscripts"), or cleaning procedures using gels and nanofluids (Chapter "Confined Aqueous Media for the Cleaning of Cultural Heritage: Innovative Gels and Amphiphile-Based Nanofluids").

The studies around cultural heritage systems, dealing with nano-aspects, are obviously relatively recent. One could expect many developments with the current possible increasing access to the nanoscale, through analytical approaches or mechanisms description across scales from the element, the molecules, to the functional scale of the artefacts or the system. Thus the aim of this book, mixing general review and some more specific case studies, is to provide a global overview

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[5] http://www.iccrom.org/.

of the up-to-date and significant aspects of nanoscience and nanotechnologies in the domain of Cultural Heritage to give examples of potentialities and good practice of these axis of researches, integrated in the large panel of approaches and scales dealing with the study of tangible cultural heritage for the next decades.

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Part I
Nanostructuration in Ancient Materials

Lustre and Nanostructures—Ancient Technologies Revisited

Trinitat Pradell

Abstract *Lustre* is a glaze decoration with a colourful metallic and iridescent appearance of sparkling beauty. It is among the first technologies which made use of the peculiar optical properties of nanostructures, and in particular, of metallic nanoparticles. It involves also a scientifically advanced method of production which is able to trigger the lustre optical properties (colour and shine) of the decorated object. Consequently, among the various technologies developed in historical times able to generate nanostructures and modify the physical properties of the materials, *lustre* is unquestionably the one involving the utmost technological advance. The chapter unveils the science behind lustre, how the nanostructure is obtained, how it is related to the lustre colour and shine, and explores the main features of historical lustre productions.

1 Introduction

Metallic and iridescent glazes containing metallic particles (gold, silver, copper, iron) were produced since early medieval times with the object of either imitating metal objects to give to the ceramics an extra value or simply producing objects of sparkling beauty. Many different methods for producing metallic and iridescent glazes and glaze decorations have been developed since then but, among them, *lustre* decorations (Figs. 1, 2 and 3) are unquestionably those involving the utmost technological advance and are distinguished fundamentally by the total absence of relief.

In fact, *lustre* is a micrometric layer made of silver and/or copper metallic nanoparticles lying beneath the glass surface of an artefact (Fig. 1b, c) which shows a large variety of colours (green, yellow, amber, red, brown, white) (Fig. 2) and metallic (golden, coppery, silvery) (Fig. 3a) and iridescent (bluish, purplish)

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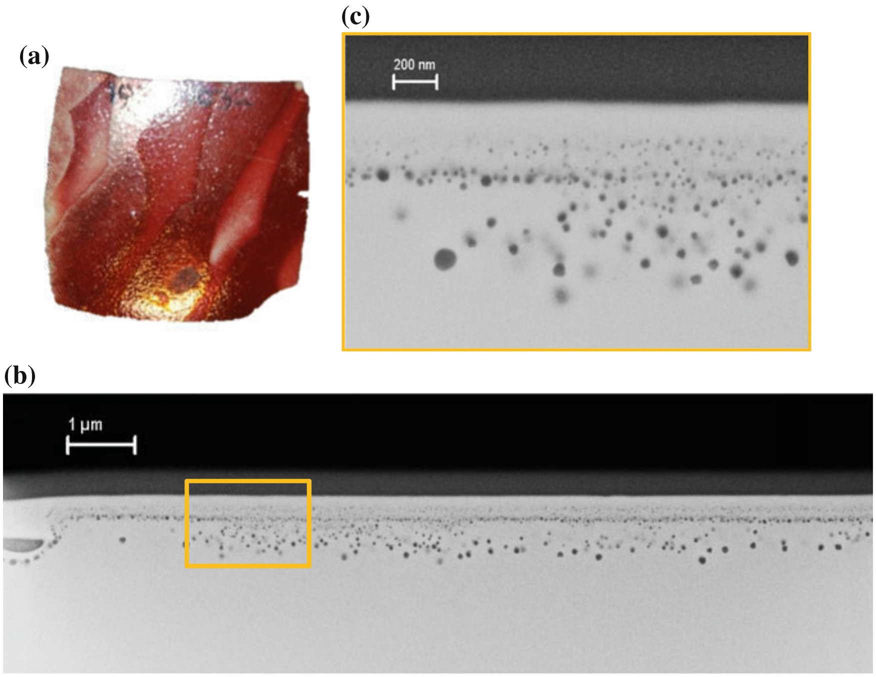


Fig. 1 **a** Red coppery lustre (Iraq, 9th century AD); **b** Nanostructure of the lustre layer; **c** Magnification of the *yellow square area* in **b**

appearance (Fig. 3b). Among them, a most remarkable feature is the high specular reflectance which conveys to the decoration a metallic-like shine (Fig. 3a). Although all this may suggest a product of modern nano-science and technology, the fact is that the first *lustre* was produced at least 1300 years ago. Consequently, the study of historic *lustre* layers, the materials and processes used in their production, as well as their optical properties and in particular the link between the optical properties and the lustre nanostructure have attracted much interest among the scientific community. (Pérez-Arantegui et al. 2001; Jembrih-Simbürger et al. 2002; Bobin et al. 2003; Padovani et al. 2003; Padeletti and Fermo 2004, 2013, Pradell et al. 2005, 2006, 2007, 2012; Bethier and Reillon 2006, Reillon and Bethier 2013; Molera et al. 2007; Polvorinos del Rio et al. 2008; Colomban 2009; Sciau et al. 2009; Gutierrez et al. 2010; Delgado et al. 2011; Chabanne et al. 2012).

Although *lustre* is not the only historic material where metallic nanoparticles are present, it is the one implying the utmost scientific and technological achievement. Among the many materials containing metallic nanoparticles we can mention the dichroic Roman glass, i.e. Lycurgus cup (Barber and Freestone 1990), which appears red in transmitted light and green in reflected light as a consequence of the presence of gold and silver nanoparticles; the red glasses, glazes and enamels (Freestone et al. 2003; Kunicki-Goldfinger et al. 2014; Wood 1999), the colour of which is due to the

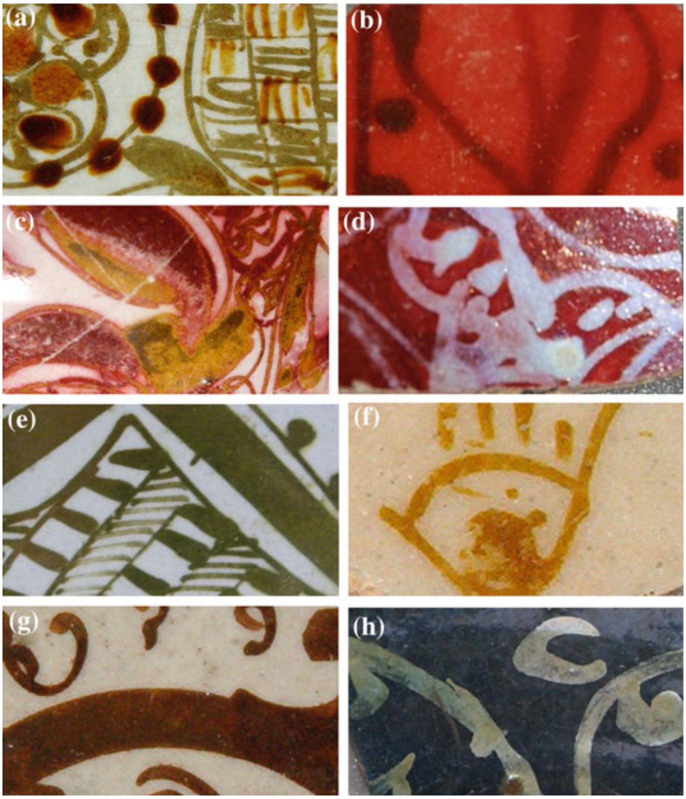


Fig. 2 Colours of lustre. **a**–**d** Iraqi polychrome 9th century; **e** Iraqi monochrome 10th century; **f**, **g** Fatimid late 10th–12th century; **h** Syrian or Egypt 14th century

presence of metallic copper and cuprite nanoparticles; and also, the gold ruby glasses whose colour is due to the presence of metallic gold nanoparticles. However, none of them has a lustrous appearance and the nanoparticles are present in the whole glass thickness.

The term *lustre* is often used among the potters to define any type of metallic-iridescent glaze, and *clay-paste lustre* or *transmutation lustre* is used to distinguish the *historic lustre* from other types of lustrous glazes (Clinton 1991; Caiger-Smith 1991; Hamer and Hamer 2004). In fact, metallic-iridescent glazes were also made following other methods of production. For instance, in *raku ware*, copper, silver or other metals are added to the glaze mixture, the ceramics are covered with clay and combustible material which produces a strong reducing atmosphere during the firing after which the ceramic is cooled in an oxidising atmosphere in flowing water when metallic particles precipitate in the glaze (Hamer and Hamer 2004). Another method consists in applying a *resinate* over the glaze, a *resinate* being a low temperature glass mixture which contains metals and reducing

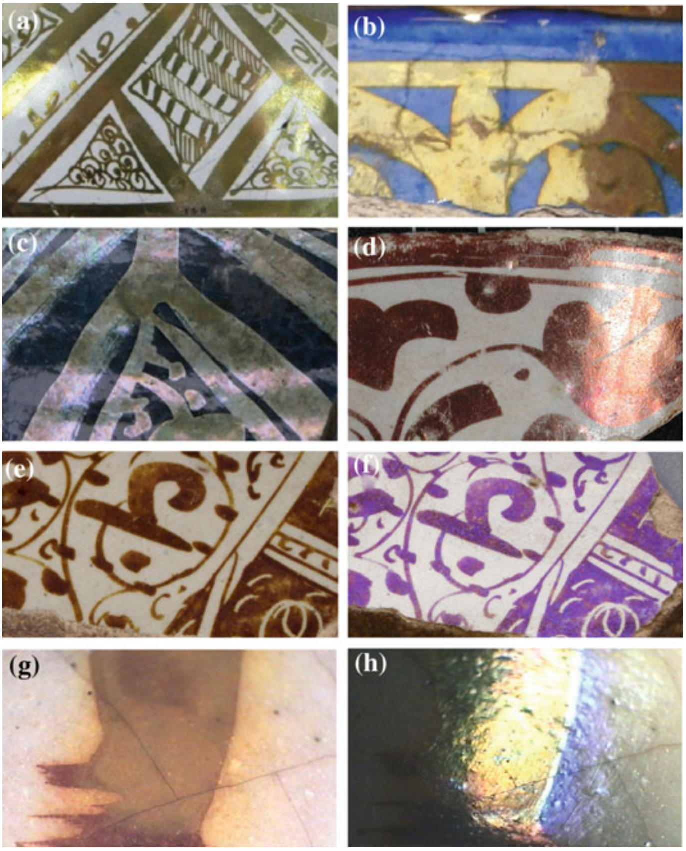


Fig. 3 Metallic like shine of lustre: **a** Green-golden (Iraq 10th century AD); **b** yellow golden (Syrian 14th century AD); **c** white-silvery (Syria, 14th century AD); **d** Red coppery (Barcelona, 16th century AD). Iridescent lustre (Fatimid, Egypt, 11th–12th century AD): **e** and **f** Brown-purplish; **g** and **h** yellow golden-bluish iridescences

agents which after firing forms a glass layer attached to the glaze surface like an enamel, but containing metallic nanoparticles (Clinton 1991). Furthermore, a metal foil may be fused onto the glaze surface after firing. In all the cases a metallic surface finishing may be obtained provided that the adequate firing conditions are applied. *Resinates* and metal foils are distinguished from *lustre* because they protrude or stand in relieve above the glaze surface in contrast to *lustre* which shows a total absence of relief. *Raku* and all types of reduced glazes are also distinguished from *lustre* because the metallic particles are present in the whole glaze thickness.

All of them are characterised by a production process where simply the mixing of metals into the glass and the control of kiln temperature and atmosphere induce the development of the nanostructures. Contrariwise, *lustre* is the result of a complex process with very close connections to modern nanotechnologies.

Consequently, *lustre* will be more precisely defined by the method of production rather than by the small thickness of the layer or the presence of metallic nanoparticles.

A lustre pigment is constituted basically by salts of copper and silver and a sulfur compound all of which are finely ground and mixed together with some organic medium or clay. The lustre pigment is painted over the glass surface and placed in the kiln at relatively low temperatures to avoid the glass softening. After firing the lustre pigment relic is rubbed off revealing the lustre layer beneath.

From this description, two important facts are revealed, on the one hand that the lustre layer is the result of some kind of reaction between the lustre pigment and the glass surface and, on the other hand, that the lustre pigment is missing from the finished objects. Moreover, the lustre layer microstructure, i.e. nature and size of the nanoparticles, position and thickness of the layer and distribution of the particles in the layer, depends on the materials (lustre pigment and glass substrate) and firing protocols. Therefore, variation on the materials and firing protocols in different epochs and places is responsible for the various appearances shown by the lustre decorations.

We will first give some historical background and describe the historical context of the main lustre productions; then we will explore the historical information available about the lustre technology. We will discuss the science behind lustre, including the chemistry (materials and reactions) and physics (nanostructure and optical properties) and how they are connected. We will present what is known about the materials and methods used in the various historic lustre productions, how they changed and how the changes relate to the appearance of the objects. A final section will be dedicated to the link existing between lustre and Alchemy.

2 Historical Setting

The first *lustre* decorations were applied on glass, the earliest identified objects dating to between 772 AD and 779 AD (Brill 1979; Jenkins 1986; Carboni 2002). Those *lustr*e painted glass objects were produced in Egypt or Syria (there is not full agreement between scholars about the place) and probably dated earlier (there is no agreement either but it has been suggested that as early as the 6th century AD). Lustre glass continued being produced by the Fatimid (10th–12th centuries AD) and also Byzantine glassworkers (10th–13th centuries AD) (Pilosi and Whitehouse 2013). Later, in the 13th century, lustre paints were also used to produce the so-called yellow stained glass for the windows of the cathedrals in central Europe. Soon after, in the Renaissance (15th–16th centuries) the palette of colours was expanded and not only yellow but also amber, orange and red stained glasses were produced.

Actually, lustre painted glass is often referred as stained glass due to the fact that it rarely shows distinct metallic lustre (Brill 1979). Robert H. Brill studied a large amount of lustre painted glass fragments (above 700 fragments) from an excavation in Fustat (Cairo) and less than 15 % showed any metallic lustre effect. Only a few showed a mirrorlike effect, what we call silvery, and most of the lustre appeared only ephemeral, although they all appeared in very good conservation conditions. Here lated this to a possible loss of the lustrous effect over the centuries. However, as we will see when discussing about lustre technology, this is not wholly unexpected.

Following Lamm (1941), (Carboni 2002) lustre painted glass is classified into three main periods. The earliest, amber-brown lustre, often two sided, painted over clear or lightly tinged glass dates to the 8th century. Opaque deep yellow-orange lustre painted over a cobalt blue transparent glass, opaque red ruby lustre painted over a dark olive glass as well as polychrome glass, date to the 9th or 10th century. Finally, amber, brown or greenish lustre paintings applied over a clear glass with a high artistic quality were produced during the Fatimid period (10th–12th centuries). Actually, the rich range of colours shown by the lustre painted glasses seems more the desired purpose than the lustrous effect itself. Later on, we will see that, in fact, the *lustre* painted glass and *lusterware* decoration nanostructures also show distinctive microstructural features.

There is quite wide agreement between scholars that lustre decorated glaze ceramics started being produced in the 9th century in Iraq, under the Abbasid rule (750–1258) (Watson 1985; Caiger-Smith 1991). Künel (1934) dated the polychrome (brown-green-amber) lustres as the earliest (Fig. 2a), followed by the bichrome (red-black, red-yellow or red-silvery and brown-green) (Figs. 1, 2b, 3c, d) and then by the monochrome green lustres (Fig. 2e). Green and yellow often show a golden shine (Fig. 3a, b) while red lustre sometimes shows a coppery shine (Fig. 3b). Generally speaking polychrome and bichrome lustres are dated to the 9th century while the monochrome lustres to the 10th century. This dating corresponds well with the lustre painted glass studied by Brill (1979) as mentioned above with the sole difference that the lustre painted glasses were found in Cairo and attributed to the Egyptian glass workshops. Nevertheless, besides this large lustre painted glass production there is no evidence of a contemporary Egyptian lusterware production (Figs. 2f–h and 3e–h). Lustreware stopped being produced in Iraq by the end of the 10th century. Some theories suggest the fracture of the Abbasid caliphate that was forced to cede authority to the Fatimid in Egypt and which may have been accompanied by the migration of the potters. In fact the complexity of the lustre production suggested that copying is unlikely and that direct transmission of knowledge is more probable, as a consequence, the migration of potters has traditionally been considered the main mechanism of geographical expansion of lustre. However, this seems not to apply for the transmission between lustre painted glass and lustre decorated ware, as the early Egyptian lustre glass production mentioned above is not accompanied by a contemporary lustreware production.

After the Abbasid lustreware, the next unquestionable lustre production was set in Egypt (Fustat) during the Fatimid rule (909–1171), earliest datable objects being around the year 1000. Fatimid lustre is monochrome green-yellow later shifting to stronger orange (Fig. 2f, g) and brown (Figs. 2g and 3e–h) colours and showing often a golden shine (Philon 1980) (Fig. 3g, h). The Fatimid lusterware stopped probably due to the take-over of Egypt by Saladin who established the Ayyubid dynasty, although the political and social instability at the end of the Fatimid dynasty may have helped an earlier movement of potters to other more peaceful areas (Watson 1985).

A clear direct connexion between the end of the Fatimid production and the beginning of lustre production in Iran (Kashan) can be established (the earliest object dates 1179). Watson firmly states, that the sudden start of Iranian lusterware was due to the migration of Egyptian potters after the Saladin destruction at Fustat (Watson 1985). A large lustre decorated tile production started in the second half of the 13th century and 14th century. After this period lustre nearly disappears in the Middle East until the 17th century under the rule of the Safavids. Well fired Kashan lustre is brown with golden shine and often appears combined with cobalt blue and copper turquoise decorations, and is also applied over cobalt tinged transparent glazes. Safavid lustre is red with golden and coppery shine often combined with cobalt blue and yellow decorations and also applied over cobalt tinged transparent glazes.

Besides the Iranian production, during the Fatimid regime lustre appears already spread all over the Islamic lands. Some recent findings suggest the existence of local productions in Tunisia dating before second half of the 11th century (Waksman et al. 2014) and in Al-Andalus, second half of the 11th and 12th century (Albarracín, Almeria, Zaragoza) (REMAI 2015). Yellow golden and red lustre are found in Zaragoza and Albarracín, and red coppery lustre is found in moulded objects from Almeria (Rosser-Owen 2010).

Syrian lusterware begins in the first half of the 12th century, it is called *Tell Minis* lustre (Porter and Watson 1987) showing a clear Egyptian influence (i.e. similar colours and designs). At the end of the 12th century, without clear continuity between them, a very distinct lusterware production (red-brown lustre) appears in Raqqa (Porter 1981; Jenkins-Madina 2006). Raqqa lusterware is contemporary to, and shows also clear stylistic similarities with the Iranian lusterware; it ends in 1260 due to the destruction of the city by the Mongols invasion. Again without continuity with the earlier lustres, it reappears in Damascus by the end of the 13th century, with a yellow golden over cobalt tinged transparent glaze (Figs. 2h and 3b).

The next production in importance, mainly due to the high quality of the few objects preserved, is the 13th–14th century lustre from Malaga (Rosser-Owen 2010). Contemporarily, a mass lustre ware production, the first outside the Islamic lands, begins in Manises (second half of the 14th century and 15th century) (Fig. 3d). Hispano-Moresque lusterware (Fig. 3d) was exported all over Europe and can be found in all the noble and rich houses in central Europe. 14th century lustres are brownish golden. Lustre does not disappear but continued being produced in other places in Spain until the first half of the 20th century although the objects tend to be of low quality and with a coppery finish.

During the 16th century, lustre was introduced in the Italian majolica produced in Deruta and Gubbio (Caiger-Smith 1991; Padeletti and Fermo 2004; Padeletti et al. 2004; Padeletti 2013). The most remarkable characteristic of Gubbio lusterware is the reintroduction of the red ruby lustre which is found together with the characteristic Italian yellow golden lustre. This is the first time that red ruby lustre and polychrome lustre is produced since the 9th century.

During the second half of the 19th century lustre is rediscovered by some companies (red ruby lustres from William de Morgan in England, Vilmos Zsolnay in Hungary or Clément Massier in France) (Clinton 1991; Caiger-Smith 1991). By the turn of the 20th century, various potters all over Europe reintroduced lustre to obtain beautifully coloured, iridescent and metallic surfaces for their objects (Allan Caiger-Smith, Margery Clinton, Said El Sadr, Jordi Serra Moragas among many others). With them lustre became an art object appreciated by the beauty and singularity of each piece and the great difficulty in producing them.

3 Chemistry and Physics Behind Lustre Nanotechnology

3.1 The Chemistry of Lustre

As we have mentioned above, the lustre layer is the result of some kind of reaction between the lustre pigment and the glass surface. Moreover, the lustre pigment is rubbed off from the finished objects and consequently missing. In a very few cases, workshop structures and within them, samples of the original lustre pigment, or fragments of unfired lustre-painted ceramics have been found; for instance those associated with 14th century AD Islamic and Hispano-Moresque lusterware from Spain (Molera et al. 2001a, b).

Consequently, the composition of the lustre pigment is still unknown for most of the lusterware productions, although in some cases information can be inferred from analysis of the lustre layer (Brill 1979; Padeletti and Fermo 2004; Molina et al. 2014; Pradell et al. 2016). 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. 721–c. 815 AD) (Al-Hassan 2009) where a series of recipes for the production of lustre on glass are detailed.

Jabir 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 “*burnt silver*” and “*copper burnt with sulphur*”. In addition, cinnabar (HgS), *vitriol,* sulphates of metals (copper and iron), realgar (AsS), orpiment (As_2S_3) or sulphur and magnesia are added. Finally, in some cases “*ceruse*” (white) of lead and/or tin is also described (probably lead carbonate $PbCO_3$ and tin oxide SnO_2). The ingredients mixed with some vinegar and citrus juice and thickened by small amount of Arabic gum, are applied to the glass surface.

With regard to the production of ceramics, the earliest treatise is Abu’l Qassim (Abd Allah Ibn Ali Al Qashani) dated to 1301 AD (Brill 1979; Allan 1973) which describes the materials and procedures followed in the production of Kashan lustreware. The pigment is made of silver or gold marcasite (probably chalcopyrite—

$CuFeS_2$) and red and yellow arsenic (i.e., realgar and orpiment) with "*burnt silver*" and "*roasted copper*"; everything being ground very fine and mixed with vinegar and grape juice. It is also indicates that *sirinj*, which is interpreted as a lead-tin mixture is sometimes added. It has to be fired with little smoke in a second oven made especially for this purpose. After cooling the pigment has to be rubbed off with wet earth.

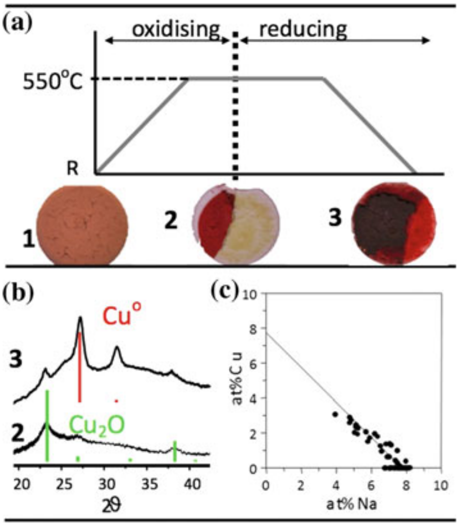
Later Islamic treatises on lustre painting on glass appear to be a compilation from earlier treatises (Heaton 1948). The earliest European text where a recipe of lustreware is given in "El llibre de les fornades" from Nicolau de Reyner, Barcelona dated to 1514–1519 AD (Ainaud de Lasarte 1942) and Cipriano Picolpasso's "Three books of potters art" dated to 1558 AD (Caiger-Smith and Lightbown 1980). They describe the same basic recipe which includes cinnabar, an earth rich in iron oxides, copper sulphide, sulphur and silver. In fact the lustre pigment found in the excavation of workshops from Paterna and Manises, show also the same ingredients (Molera et al. 2001b).

In summary, the basic ingredients are silver and copper salts, obtained after burning silver and copper (some indicate with sulphur) and a sulphur containing compound such as cinnabar, copper, iron and arsenic sulphide or iron/copper sulphates. Earlier recipes indicate also the addition of some tin/lead compound (probably mixed lead-tin oxides) together with Arabic gum, substituted in later recipes by an earth rich in iron oxides. The ingredients have to be ground and mixed with vinegar and grape juice or citrus juice before application.

Replication of the process using any of the previous recipes has been undertaken (Brill 1979; Jembrih-Simbürger et al. 2002; Delgado et al. 2011 for lustre painted glass and Molera et al. 2007 also for lustreware) and the science behind lustre has unfolded. The mechanism by which silver and copper react with the glass surface is what is known as "ionic exchange" which happens between the silver ions (Ag^+) but also copper ions (Cu^+ or Cu^{2+}) from the lustre paint and the sodium (Na^+) and potassium (K^+) ions from the glass. Ag^+ is very similar in size and also has the same electric charge as Na^+, but it may also substitute K^+ and the same happens with Cu^+. Figure 4 shows how the process takes place. A copper lustre pigment containing 30 % HgS, 10 % CuO, 60 % clay in water is applied over a modern glass (Fig. 4a-1) and fired at 550 °C for 10 min under oxidising conditions; after removing the lustre pigment the glass appears yellow tinged (Fig. 4a-2) due to the precipitation of cuprite (Cu_2O) nanoparticles (Fig. 4b-2); if a reducing gas is introduced for 5 more minutes, the glass appears red tinged (Fig. 4a-3) due to the precipitation of metallic copper (CuO) nanoparticles as a result of the reduction of most of the cuprite (Fig. 4b-3). Chemical analysis of the red lustre (Fig. 4c) shows an inverse linear correlation between sodium and copper atoms demonstrating that each sodium ion has been replaced by a copper ion, the so called "ionic exchange", which happens during the lustre firing.

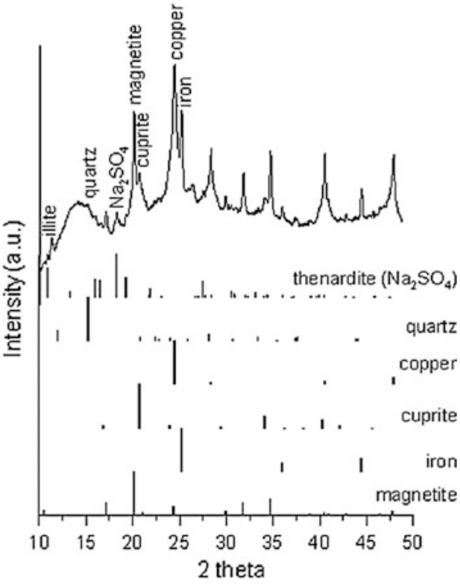
Moreover, Fig. 5 shows the X-ray Diffraction pattern corresponding to the lustre pigment after firing; among the compounds expected to be formed during the firing, sodium sulphate (thenardite) is most probably formed during the cooling. Its presence gives a good clue that the compound responsible for the ion-exchange mechanism is a mixed sulphate melt. As a consequence, sulphur needs to be present

Fig. 4 **a** Firing protocol (10 °C/min heating rate, 20 min at 550 °C and free cooling). *1* copper lustre pigment (10 % CuO, 30 % HgS, 60 % clay; *2* After firing for 10 min under oxidising conditions; *3* then after firing for 5 more minutes under a reducing firing. **b** XRD-patterns of the glass surface *2* and *3* after removing the lustre paint. **c** Analysis of the glass surface *3* showing the substitution of sodium by copper



in the lustre pigment. In the case studied, sulphur has been added as cinnabar (HgS), and a more complete study of the reactions taking place (Pradell et al. 2004) shows how at temperatures above 400 °C the sulphur reacts with the copper and silver compounds producing copper and silver sulphates and sulphides. Moreover, the decomposition of cinnabar produced a sulpho-reducing atmosphere able to reduce Cu^{2+} to Cu^{+}, and result in the formation of a silver-mercury amalgam.

Fig. 5 XRD-pattern obtained of the lustre pigment from Fig. 4 after firing



Looking at the recipes we can see that sulphur was also added as copper sulphide; and other recipes indicate that the silver (and also copper) was sometimes previously burnt with sulphur. Finally, the addition of sulphur itself to the pigment mixture is also sometimes indicated, and its role would be to generate a sulpho-reducing atmosphere and produce copper and silver sulphides and sulphates.

Although all the lustre recipes found or described in the ancient treatises add sulphur as main ingredient in the lustre pigment, other silver and copper salts, such as silver and copper chlorides (AgCl, CuCl) and silver nitrate ($AgNO_3$), may also act as vehicles for ionic exchange, if they become molten at the right temperature range. It is not improbable that some chlorides could be present in the lustre pigment resulting from the complex preparation procedures described in the treatises. However, silver nitrate was not yet discovered in early Islamic times. What is true is that later, with the industrial revolution (18th and the 20th century) both AgCl and $AgNO_3$ were used in the production of the silver yellow lustre paints (Caiger Smith 1991; Jembrih-Simbürger et al. 2002). Some replication experiments of silver painted lustre glasses (Jembrih-Simbürger et al. 2002) demonstrated that modifying the glass paint, using either silver nitrate, sulphate (Ag_2SO_4), chloride and phosphate (Ag_3PO_4) together with different optimal firing temperatures, resulted in larger or smaller silver nanoparticles. However, only $AgNO_3$ gave rise to a homogeneous yellow colour.

The addition of clay or Arabic gum is related to the need of a dispersal medium that gives some plasticity to the paint, although some clay minerals may also act as an ion-exchange medium. Other compounds such as tin and iron oxides could act as a redox buffer, controlling the reducing process, in the pigment during firing.

The recipes also often describe very finely grinding together at the compounds with vinegar, grape or citrus juice to obtain a fine homogeneous pigment. The reason for the addition of vinegar has been discussed in terms of either producing copper and silver acetates which during firing would presumably generate a reducing atmosphere; assisting the drying of the painted pigment; acid attacking the glass surface and generating more free surface for the lustre to form in; or acting as a deflocculant preventing the particles in the paint from agglomerating or settling (Brill 1979). The last is the most probable reason, as laboratory replications showed that copper and silver acetates are not decomposed during the firing and lustre does not take in those areas where acetates are present (Molera et al. 2007).

Once copper and/or silver ions enter the glass surface they diffuse inside the glass, the inter-diffusion process depending on the cations from the glass involved in the ionic exchange. We have to mention that the firing temperature has to be higher than the glass transition temperature (T_g, temperature at which the viscosity of the liquid is 10^{12} Pa s) of the substrate glass. This is necessary because at temperatures above T_g, the glass behaves as a liquid and, as a consequence, atomic diffusion coefficients show a great increase (Doremus 1994). However, T_g depends on the heating rate and is lower at low heating rates, so that heating a soda-lime glass (16 % Na_2O and 10 % CaO) at 20 °C/min, T_g is 578 °C, while heating it at 2.5 °C/min the T_g is reduced by 33°. Finally, the glass softening temperature should not be reached to avoid the pigment sticking onto the glass surface. These restrictions leave a relative narrow range and a dependence on the composition of the substrate glass for the lustre firing temperature.

The glass transition temperature decreases with increasing the alkali (Na_2O and K_2O) and contrariwise, it increases with increasing CaO, MgO or Al_2O_3. Finally, the incorporation of PbO results in a decrease by more than 100 °C in the glass transition temperature. Most of the early Islamic glasses are of the soda-lime type (between 17–20 % Na_2O, 7–15 % CaO, 1–5 % MgO, 1–3 % K_2O and 1–3 % Al_2O_3) which means typical glass transition temperatures between 550 and 650 °C, and therefore optimal firing temperatures above 600 °C. This agrees with the firing temperatures found to be adequate by Brill (1979). Moreover, soda-lime and potash-lime glasses were tested to replicate lustre painted glass (Delgado et al. 2011), and for a soda-lime glass firing temperatures between 600 and 650 °C were required while for potash glasses the optimal firing temperature was 550 °C. On the contrary, the composition of the glazes may vary a lot between productions and large amounts of PbO are incorporated in many cases. Consequently, the firing temperatures are expected to be lower than for glass, in particular, replication experiments have shown that 550 °C is the most frequent optimal firing temperature.

One of the most astonishing results from the replication work (Molera et al. 2007) is undoubtedly the difference in the lustrous appearance shown by lustres produced over lead-free and lead-containing glazes. The composition of the glaze was found to be strikingly important. Lustres produced following the same firing protocol on lead free glazes did not show metallic shine in contrast to those obtained on lead containing glazes (32 % PbO). Moreover, for lead free glazes, lustres produced at higher temperatures (up to 600 °C) and longer reducing times (up to 30 min) showed a similar, but more intense colour as a result of increases in the size of the nanoparticles and the total amount of the metals but the metal shine was not achieved. On the contrary, for the lead containing glaze, the metal shine was always obtained provided that temperatures close to or higher than 550 °C were reached even for shorter reducing times (5 min). The explanation could be related either to the presence of large metallic particles or to a higher concentration of metallic particles in the lustre layers.

In order to check which one was the right explanation, detailed chemical composition of the lustres was obtained by Rutherford Backscattering Spectroscopy (Pradell et al. 2007, 2012). The chemical cross section profiles of copper and silver lustres produced over lead free and lead containing glazes are shown in Fig. 6a, b respectively. The copper lustres, j6 for a lead free glaze and j65 for the same glaze to which 32 % PbO was added, were obtained following the same firing protocols (50 °C/min heating ramp, dwell at 550 °C, 20 min under oxidising conditions and 10 min reducing conditions, free cooling). The silver lustres, j126 for the lead free glaze and r254 for the lead containing glaze, were obtained following same firing protocol as before for j126 but with a shorter reducing stage for r254; this was done to obtain a nanostructure with similar nanoparticle sizes for both glazes. j6 is red ruby and j126 green with neither showing metallic shine, while j65 is red coppery and r254 green golden.

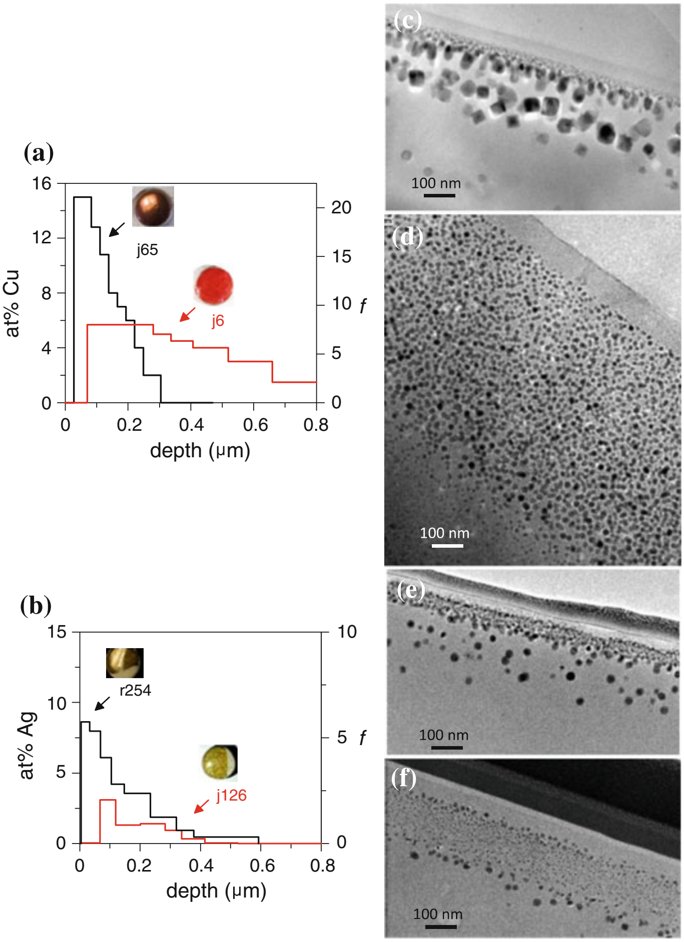


Fig. 6 Atomic concentration profiles corresponding to **a** copper lustres produced on a lead free glaze (j6) and on a lead containing glaze (j65) and the corresponding TEM images **c** j6, **d** j65, **b** silver lustres produced on a lead free glaze (j126) and on a lead containing glaze (r254) and the corresponding TEM images **e** j126, **f** r254

Figure 6a, b shows that the lustres obtained over lead containing glazes are more concentrated, the layer appears closer to the surface and is also thinner. Moreover, the nanoparticles are larger for the lead containing glaze, as is shown in the TEM images of the nanostructures for the copper lustres obtained on a lead-free and a lead containing glaze respectively (Fig. 6c, d). However, nanoparticles of similar size can be obtained by shortening the reducing stage of the lustre firing for the lead containing glaze. This was done for the silver lustres, and we can see the nanostructures formed on a lead-free and a lead containing glaze in Fig. 6e, f respectively. This demonstrates that the metallic shine observed is mainly due to the high