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Colloquium

Ceramics in art and archaeology: a review of the materials science aspects

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Abstract. Analytical techniques developed in the field of materials science are now widely applied to objects of art and archaeology to gain information about the material composition and structure and hence to understand the way of manufacturing artefacts. Reciprocally, ancient artefacts studies show potential important contribution in the materials science field. This topical review will cover all these input and output aspects between materials science and ancient artefacts through the study of the first ceramics made by men e.g. potteries. To study these heterogeneous and complex materials, an approach based on the decomposition into sub systems of materials and the applications of traditional and novel analytical methods to scan the different scales of the material is not only mandatory but also innovative.

1 Introduction

1.1 Ceramic artefacts in archaeology

Among the archaeological remains, pottery and, more generally, ceramic artefacts are one of the most studied objects by the archaeologist community. Ceramic obtained by firing clay was the first synthetic material made by human hands with a certain ingenuity [1]. The oldest known worldwide terracotta up to date was discovered at Dolni Vestonice and Pavlov in Moravia sites (Czech Republic). It is the famous Gravettian ceramics dated between 27 000–25 000 BP and representing human and animal figurines [2,3]. Vessels in fired clay anterior to the Neolithic period were found in various parts of the world such as the potteries discovered in Jiangxi (China) dating back to 20 000 BP [4]. However it is with the settlement of human communities during the Neolithic period that the pottery is really developed intensively [5]. Early on, the pottery has not only a utilitarian function but also a cultural one. In addition to surface treatments performed for purposeful reasons such as waterproofing, decorations are also applied on the surface, which are often specific to cultural communities or civilizations. Since the Neolithic time, knowledge and know-how have improved, leading to the manufacturing of high-quality pottery, which was used as a symbol of power and social success. Actually, these potteries were not only functional objects but were also aimed at being objects of admiration and so, for the know-how of the civilization that created them. Therein these artefacts are art objects and interest also art historians.

Because of their archaeological significance, many different analysis techniques were used to determine the age, the elemental and mineral compositions of ancient ceramics in order to identify their origin (manufacturing place), the raw materials and the firing process used for their manufacturing [6,7]. Residues found inside were also analysed to clarify their use and/or to identify their contents. In fact the ancient ceramic is an ideal material for archaeometers and their physico-chemical study follows the development of the scientific field for more than a half-century. Initially confined to the elemental composition analysis by X-ray fluorescence or mineral composition by X-ray diffraction of the body they presently use state-of-the-art characterization techniques from materials science field. This is the latest analytical contribution that we are going to present in the following paragraphs.

1.2 Bridging ancient ceramics to materials science

Materials science, also called "materials science and engineering" is defined as an interdisciplinary field focused on the discovery and design of new materials. It is based on studying different classes of materials through the materials paradigm (synthesis, structure, properties and performance). In that sense, it might not seem to apply to cultural heritage materials since its main aim is the elaboration of new materials. However the basis of materials science involves studying the microstructure, crystallographic phases and defects of materials in relation to their properties which may be directly applied to heritage materials. Furthermore, ancient materials could be a source of inspiration to design new materials in the same way than biomimetic approach, which refers to human-made processes that imitate nature where, for instance, bioactive composites having a bone-like structure are developed [8]. A very good example of an archeomimetic

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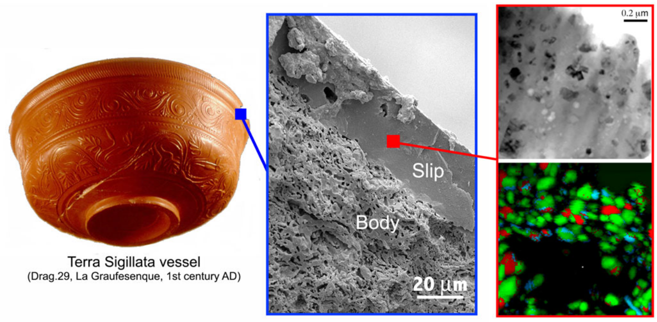

Fig. 1. Example of ancient ceramic showing a terra sigillata vessel from La Graufesenque workshop (France) with a SEM-BSE image of a cross-section (centre), a TEM image in bright field (top right) and crystalline phase map (bottom right). This phase mapping obtained from electron diffraction (ASTAR, NanoMEGAS, `http://www.nanomegas.com/`) shows the distribution of crystals (spinel: blue, corundum: green, hematite: red) contained in the glassy matrix of the slip.

material is given in the thesis work of C. Dejoie in which a zeolite cage containing an indigo molecule has been synthetized to imitate the very famous blue Maya [9,10].

From a materials science point of view, an ancient pottery (Fig. 1) is a ceramic in the sense that it is an inorganic, nonmetallic solid prepared by the action of heat (firing) and subsequent cooling. It is also a composite material combining crystalline and non-crystalline phases and often covered by one or more thin layers (slip, glaze, enamel...). These different coatings provide sealing and often better wear resistance but also they have a decorative function, in particular, the top layer which is the visible surface of the coating and defines the appearance (colour, brightness, etc.) of the pottery. Throughout the centuries, craftsmen's know-how has expressed itself in the realization of these thin decorative coatings.

As mentioned above, the analysis methods applied in cultural heritage field followed the development of the investigation techniques of materials science, especially the study of thin coatings of potteries which has significantly benefited from the development of investigation methods dedicated to small scale materials such as thin films. However, in the last few decades, specific developments have been carried out to integrate the specificity of cultural heritage objects such as the possibility to perform lab analysis of large and wide objects with complex geometry as well as large amounts of samples for statistical studies [11] or on the contrary, to perform on site analysis without moving the piece to study (portable measuring devices). These two complementary approaches are very useful in the study of masterpieces since they allow us to obtain analytical data without damaging the work of art. Mobile devices are now powerful investigation tools for studying the surface of artworks [12]. Laboratory devices or synchrotron beamlines adapted to the analysis of bulky items (large objects) allow for data logging of quality concerning the fragment surface [13]. Some strategies, by adjusting the beam focalisation or changing the incident beam energy allow us to obtain in depth information [14]. However, all these measurements are performed through the sample surface and so the in depth accuracy is not always guaranteed. Radiology tomography techniques can also be used to investigate the body of object and provide pertinent data [15–17]. Unfortunately, despite the progress made in the field, a large part of the information remains inaccessible and it might be necessary to sacrifice a piece of the object. With the development of nano-analysis methods, the specimen can be very small [18]. Moreover, in some cases it is not always necessary to perform in-depth investigations directly on the masterpiece but on equivalent pieces (made from the same material and/or with similar processes) which can be destroyed. It is especially true for pottery for which it is rather easy to have fragments of vessels or to have very small specimens coming from masterpieces [19,20]. During the restoration phase, it is recurrent that small chips are detached which can be used for analyses [21]. From these chips and from fragments of other similar potteries less valuable, one can develop an investigation method based on the current findings in materials science field.

In the last few decades, the development of complementary chemical and spatially resolved techniques, combining spectroscopy and microscopy, allows us to attain a full 2D or even 3D description of the constitution of ceramic fragments. Today, the toolbox allows us to collect information on rather large areas with high spatial resolution Synchrotron radiation based imaging techniques, especially μFTIR, μXRF, μXANES or μXRD, are (or begin to be) more and more in routinely used to analyse ancient artefacts [13]. Transmission electron microscopy begins to be also used in some cases [22]. Other nano-investigation techniques, for instance used in micro-electronic field, could be useful in the near future. Often the main difficulty is not the sampling, most of these techniques do not require large amounts of material, but the sample preparation. To be efficient, each of these techniques requires a specific shape of the sample with precise dimensions. In many cases, the preparation of suitable samples from specimens is not trivial.

2 Ceramic studies using materials science approach – some examples

Materials science applied to pottery examination can be likened to an archaeometric study. Indeed, both approaches use chemical and physical techniques to analyse and/or characterize the archaeological artefact. However, the underlying goals, even if there is some overlap, are rather different. The aim of archaeometry study is to bring answers to archaeological questions such as dating, determining the provenance or more generally assisting in "operational sequence work" [6]. In contrast, a typical materials science study is more focused on the materials constituting the object with a special attention on their physical properties. Dating is not fall under this kind of study. On the other side, specific information concerning the manufacturing process can be deduced. A materials science type approach in ceramic study will be highlighted through a few examples showing what can be brought to light.

2.1 Lustre ware

Lustre ware is a variety of glazed ceramics, with striking optical effects due to the presence of metallic nanoparticles [23,24]. This type of ceramic appeared in medieval times. The earliest known lustred ceramics were found in Mesopotamia and most of them came from the site of the Abbasid Caliphs' palace (836–883 CE) of Samarra in present-day Iraq. The use of metallic nanoparticles as a colour pigment was, however, much older and dates back to several millennia ago. Investigations using various techniques revealed that red glasses of the late Bronze Age (1200–1000 BCE) from Frattesina di Rovigo (Italy) were coloured thanks to the excitation of plasmon surface modes of copper nanoparticles [25].

Many archaeometry studies have been devoted to lustre ware and it is not the aim of this paper to present an exhaustive rundown of these works. Some review papers were already written on the various aspect of these works [26] and here we will focus on the materials science aspect and in particular on the structural, optical properties and formation of the composite thin layer containing the nanoparticles.

The majority of studies focused on the nanoparticles identification and/or the elemental compositions of body and glaze in order to determine the chemical characteristic of different productions. However the outstanding optical properties also drew the attention of physicists towards the materials science field for studying lustre.

Olivier Bobin was the first to model the optical properties of lusterware and thus to show the role of the surface plasmon resonance of metal nanocrystals in the colouring process [27]. This modelling is based on the Mie's theory and takes into account several parameters such as the copper-silver ratio, the particle size, the particle density and the nature of embedded glaze matrix. It gives rather good results for the colours observed in scattering light but does not reproduce the colour of the metallic shine which is observed in the specular direction. The modelling uses the dipole approximation and considers the particles as dielectric dipoles. This approximation is consistent with small particles (smaller than light wavelength i.e. with a radius lower than 50 nm), for which the size variation affects mainly the width and the intensity of the resonance band. For the larger particles with a size comparable to the wavelength (radius superior or equal to 50 nm), the dipole approximation is not valid and multipolar terms must be added leading to the splitting of the resonance band into several peaks: two peaks for quadrupole, three peaks for an octopole, etc. [28]. The size of the metallic particles present in the lusterware is rarely superior to 50 nm in radius and the dipole approximation gives a correct description of the surface plasmon resonance. However, the size distribution is large leading to a significant broadening of the absorption band. Since the restoring force for surface plasmons is related to the charge accumulated at the surface, it is influenced as well by the particle shape. With elongated particles, the absorption band is split into two bands: the transversal and longitudinal bands. The frequency shift is proportional to the ratio between longitudinal and transversal lengths. While the resonant frequency of transversal plasmons falls at about the same position as for spherical particles (actually, at wavelengths slightly smaller), the resonance of longitudinal plasmons shifts towards larger wavelengths when the ratio increases. The intensity of the longitudinal plasmon band increases with the ratio while the one of the transversal band decreases. Some lustres (Fig. 2) show elongated particles ("metal worms") for which the shape effect must be taken into account. Similar quantitative modellings of the surface plasmon resonances have been recently done on metal nanoclusters sandwiched between dielectric layers taking into account the influence of nanocluster size, shape and organization. It is shown that the optical response of the films in the visible range is dominated by the excitation of the surface plasmon resonance of the clusters along their in-plane long axis, while no surface plasmon resonance resulting from an excitation along their in-plane short axis can be observed due to damping effects. Moreover, the spectral position of this resonance appears to be mainly affected by the average shape of the clusters [29,30].

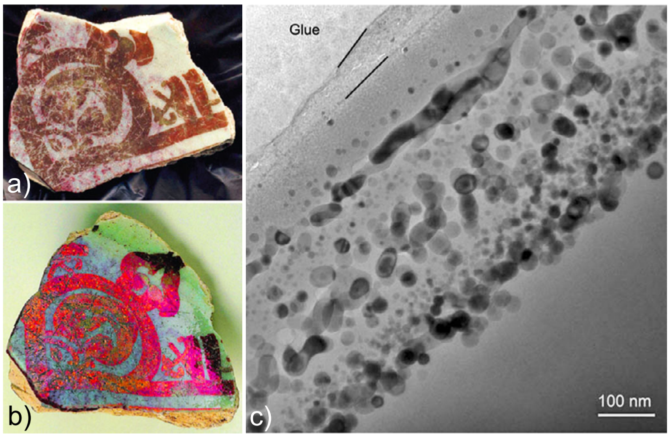

Fig. 2. (a, b) Lustre ware from Fatimid period, 12th century. AD where the colour change from brown (scattering light) to pink (specular position) and (c) TEM image of silver nanoparticle distribution responsible of the shiny aspect of this kind of lustre [37].

In addition to particle shape, other effects such as the interference phenomena must also be considered in the case of lustres. It is obvious that the interferences have a significant influence on the colour of metallic shine (the specular position) for the lustres possessing a partial multi-layer structuration. Many lustres of Abbasid and Fatimid periods shows an in depth multi-layer structuration which can be more or less complex as revealed by transmission electron microscopy (TEM) investigations [31]. A decor with a quasi-perfect double layer was even made in the twelfth century during the Fatimid dynasty [32]. A preliminary calculation demonstrated that the colour variation of the metallic shine from blue to green was due to interference phenomena between the two layers.

The first model including the interference phenomena was proposed by Vincent Reillon [33]. However, the modelling of such a complex system was not easy and it is only recently that a model integrating all phenomena such as surface plasmon absorption, interference and scattering has been published [34]. With this model, it is now possible to correctly simulate the reflection spectra recorded as well in the specular direction as in the scattering directions. The evolution of the colour between the specular and the diffusion directions can be perfectly calculated using key parameters such as the number of layers, the optical index and the thickness of each layer, the metal volume fraction, the particle size and shape, and the glass matrix composition.

To simulate the experimental spectra, the modelling uses a schematic representation of the multilayer structure of lustre decoration. Hence inversely from a modelling of a set of experimental spectra collected for different directions, it is possible to obtain basic information on the nanoparticle distribution. However the model supposes that the particles can be assimilated to small spheres (2–20 nm size range) with a metal volume fraction necessarily being inferior to 10%, which is not the case of all lustre decorations. For example, Hispanic lustre productions (13th–18th centuries) are characterized by the presence of high density of large particles (30–80 nm size range) close to the glaze surface. The particles of oriental productions (9th–12th centuries) are in general in the size range of model but the distance between nanoparticles can be too short (high metal volume fraction) for using the model. In fact, the integration in the modelling of the large and non-spherical particles, dense clusters of particles and a more realist schematic representation of the multilayer structure (rough interfaces, inhomogeneous layer thickness), is not evident. Moreover the number of parameters could be too high and a model suitable for all lusterware types could fail to give pertinent results. On the other hand, a more phenomenological approach could be considered. Despite a non-ideal structure (complex shape i.e. non spherical and broad size distribution of nanoparticles, layer thickness variations...), lustres are composite materials with very interesting optical properties and thus could be used to study the influence of structural defects on the optical properties. In order to elaborate modern devices it should be interesting to know how many defects the structure can bear without losing the desired optical property.

Lustre ware has also interested the chemist community who tried to trace the manufacturing process from the study of ceramic fragments and the base of the few ancient potter recipes come down to us [26,31,35]. Lustre manufacturing is a chemical process, which occurs from reactions between the glaze surface and a decorating paste containing various compounds such as clay, ochre, silver and/or copper salts (sulphides, sulphates, nitrates, oxides, etc.) vinegar and lyes at rather low temperatures (500–600 °C).

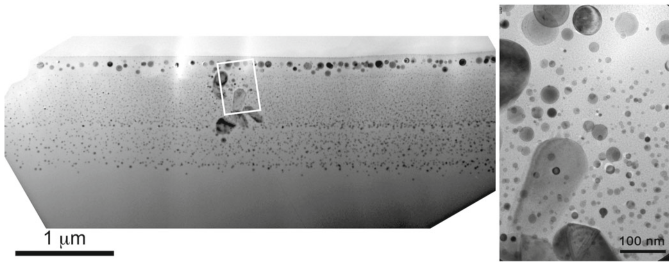

Fig. 3. TEM images of copper nanoparticle distribution in a modern creation made by Eva Haudum. The larger crystals (insert) are cassiterite compounds (SnO_2).

The chemical reactions release silver and/or copper ions, which enter into the glaze by means of ion exchange with the alkali ions of the glaze [36]. Then the reducing kiln atmosphere and/or the reducing agents present in the glaze (Sn^{2+}, Fe^{2+}...) convert metallic ions into metal state leading to the nucleation of metallic nanoparticles. In addition to the ion exchange mechanism, it has also been proposed that an extra source of local heat coming from the combustion of organic residues of the paste could play a significant role in the formation of nanoparticle layer. Size and depth distribution in multilayers of nanoparticles observed by TEM in some samples are consistent with the repetition of controlled heat flashes provoked by surface organic residue combustion. Melting of Ag/Cu metals demonstrates that glaze surface temperature close to 1000–1100 °C was achieved at the peak temperature cycle. Details of the experimental observations and formation process description can be found in [37].

Materials science type studies have greatly contributed to identify the manufacturing process thanks to the characterization at different scales of the material structure underlying lustre technology in relation to the fundamentals of their optical behaviour. Lustre replications of quality were obtained in laboratory on the base of these studies [35], while a few current craftsmen achieve very beautiful art works using decorating pastes inspired by ancient recipes but using modern kilns enabling the control of atmosphere variation [31]. For instance Eva Haudum a current artist produces lustres with nanoparticles in multilayer structure using alternative oxidising (oxygen flux) and reducing (CO or methane flux) stages during the firing (Fig. 3).

2.2 High potential compounds found in ancient potteries

Unexpected results can be revealed through the physicochemical analyses of potteries. Recently, a rare and metastable ferric oxide polymorph (ε-Fe_2O_3) was found in an ancient Chinese pottery [38]. Discovered in 1934, this phase keenly interests the materials science community for promising application in electronic storage media and magnetic stripe cards. It exhibits a giant coercive field at room temperature, millimetre-wave ferromagnetic resonance, and magnetoelectric coupling [39,40]. It is the

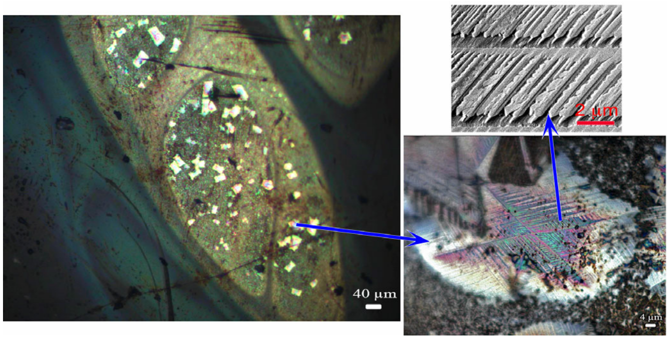

Fig. 4. Optical and SEM images of the epsilon-phase crystals observed at the glaze surface of an "oil spot" type, Song dynasty: 960–1279 AD [38].

only single metal oxide to cumulate such magnetic/electric properties. Unfortunately, this phase is metastable and its crystal growth is very difficult. Up to now, only nanoscale crystals (nanoparticles, nanowires, thin films) have been obtained [41,42].

Black-glazed Jian ware of the Chinese Song dynasty (960–1279 AD) was well-known for the lustrous black which could exhibit various coloured patterns. The variety called "hare's fur" was the most famous and common pattern [43]. Its shining black slip reveals fine radial rust-coloured streaks. Much less prevalent, the variety called "oil spot" was also sought for its silvery glints. Recently, one fragment of each type of variety was analysed using a set of characterization techniques including micro X-ray fluorescence and micro X-ray diffraction synchrotron, Raman spectroscopy and transmission electron microscopy by an international and pluridisciplinary team [38]. It was established that the coloured patterns were due to the crystallization of iron oxides in the glaze surface [43], but without considering that the predominant form was ε-Fe_2O_3. In the "hare's fur" variety the epsilon phase is associated with the alpha form (hematite) while at the surface of the "oil spot" sample only ε-Fe_2O_3 phase was found. The small crystals are concentrated in the oil spots (bubbles arrive at the surface during the firing) and organized in dendritic networks. A majority of these networks are very regular and define quasi perfect 2D gratings which behave as dispersive elements leading to the creation of structural colours by interference effects [44]. These colours which depend on angular lighting conditions, are very brilliant and iridescent with blue to red variations as shown in Figure 4.

This organization of sub-micrometric crystals can be related to 2D photonic crystals [45] where a periodic array of nanoparticles affect the motion of photons (visible light) in the same way that a tri-periodic atom arrangement (standard crystal) affects X-rays. In fact, these dendritic networks are rather similar to the structure which can be found in nature in feathers of birds or scales of butterflies showing iridescent colours [46].

Another interesting compound for the materials science community was found in fragments of ancient potteries. This concerns the pseudobrookite phase (Fe_2TiO_5), which was identified as the yellow pigment of marbled terra sigillata slips of the Roman period [47]. This compound exhibits promising properties for ceramic pigments [48] thanks to both a high refractive index (n = 2.35–2.40) and a high melting point (1550 °C). However, pseudobrookite is thermodynamically unstable with a positive enthalpy of formation, its structure being stabilised by the configurational entropy of formation due to a partial cationic disorder [49,50]. In addition pseudobrookite structure can host in octahedral sites various additional elements such as Al and Mg atoms which can increase the cationic disorder and thus improve the structure stability. Unfortunately, the cation substitution implies colour change ranging from yellow ochre to reddish-maroon. This shows the real difficulties in using this phase as ceramic pigment. The pseudobrookite synthesis with a well defined colour is not easy but moreover its colouring performance also depends on the physico-chemical properties of the ceramic matrix [48]. Various elements of the ceramic matrix can be incorporated in the pseudobrookite structure and then modify its colour. Better understanding of the ceramic behaviour of entropy-stabilised pseudobrookite is necessary to use the pigment property of this compound in an industrial context. A deeper study of marbled terra sigillata based on a multiscale approach, is in progress in order to determine the relationships between the pseudobrookite composition (presence of Mg and/or Al atoms in octahedral sites), the matrix composition and the colour. Several methods are used such as Raman spectroscopy and X-ray diffraction on a large panel of samples since no specific sample preparation is needed while TEM and synchrotron radiation methods (among them the XANES – X-ray Absorption Near Edge Spectroscopy) are done on a selected number of samples in which a dedicated preparation is mandatory. The first results revealed systematic differences between the Raman spectra of synthesized pseudobrookite and pseudobrookite present in Roman potteries (Fig. 5). The differences could be due to the presence of Mg atoms in octahedral sites. Thanks to the high sensitivity of the pseudobrookite structure to synthesis conditions, this study should provide interesting information concerning the manufacturing process of ancient marbled terra sigillata and in return could contribute to the industrial development of this compound as modern ceramic pigment.

2.3 Firing protocols of ancient ceramics

Firing protocol is an important step of the manufacturing process. It is during this stage that the clay minerals forming the vessel are fired i.e. transformed into new phases (crystallized or vitreous), thus giving new physical properties to the object.

If the first firings of the Neolithic period simply involved performing a fire around the pottery to bake it, the firing process has quickly improved and diversified [5,51]. Over time, craftsmen were able to make both functional objects of high quality but also art pieces to be admired [51]. Various complex processes were developed to

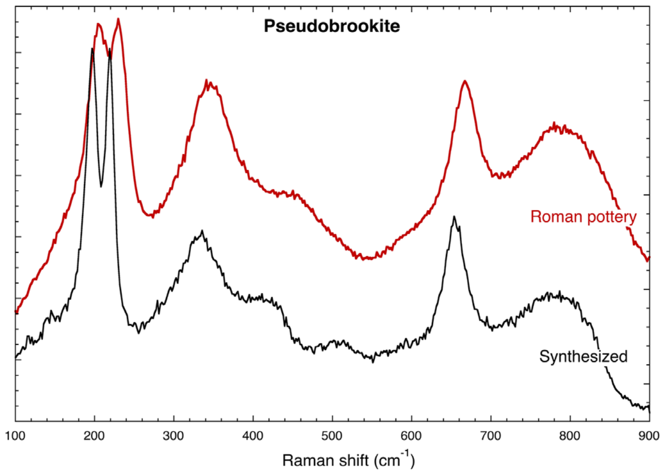

Fig. 5. Comparison of Raman spectra measured on synthesized pseudobrookite and marbled terra sigillata (Roman pottery) containing pseudobrookite crystals (Tian Wang, CEMES, private communication).

produce specific potteries which were subsequently disused or heavily modified to produce a new type of pottery. Recovering these processes is not always easy. It is in particular the case for the firing protocols used in the manufacturing of ceramics with high gloss coatings of the Greek (attic ceramics) and Roman periods (campanian, presigillata, sigillata) [52,53]. These coatings were obtained from the vitrification of an iron oxide-rich material coming from the settling and decantation of natural clays [21,54]. Controlling the colour (red or black) was achieved through the redox chemistry of iron oxides. Three key parameters determine iron state valence: the temperature and atmosphere nature – reducing or oxidising – of firing but also the permittivity of ceramics to reducing (CO) or oxidising (O_2) gases. The last parameter can be different according to the various parts of a vessel but more interestingly, it can be modified during the firing. For instance, the vitrification, which occurs when the temperature is high enough, greatly decreases this parameter. Consequently, the iron valence state of glassy zones depends on the atmosphere at the vitrification step and is only slightly affected by subsequent changes. Various more or less complex protocols were developed in order to take advantage of the differences in porosity and vitrification temperature of the main parts (slips, body) of a vessel and thus to obtain objects with red and black zones. Although these potteries were made by civilizations where writing was commonly used, no details were found up to now in antique writings concerning their firings. They are only mentioned in a few poems and drawings on terracotta slabs called "pinakes", some of them being a comminatory invocation offered to potters or giving an original inside view of a kiln, respectively. The selling price is generally stamped on the recipient foot [55,56]. Few heating structures of these periods were updated during excavations such as the large kiln for terra sigillata discovery at La Graufesenque site [57]. Unfortunately, in the majority of cases, only the kiln foundation was found which makes it difficult to retrace the operating mode. For instance, thirty years after its discovery the operating mode of the large kiln of La Graufesenque is still an open question [58,59].

In order to supplement the archaeological data, archaeologists have performed experimental firings with the help of current craftsmen [59,60]. Replications of good quality and interesting results were obtained but these experimentations also revealed that different processes could lead to very similar visual results. This type of approach is highly dependent on both the choice of materials and the know-how of the involved craftsmen. Complementary laboratory analysis are often used but even with this additional amount of information it can be difficult to understand manufacturing processes which are in fact too different from those currently used by this approach. A basic materials science study of a reverse engineering type from pottery fragments is a good way to supplement the archaeological information [54]. Indeed, these fragments (or sherds for archaeologists) are often found in great quantity during workshop excavations and can be then used in destructive surveys.

Upon firing of pottery, only the concentration of atoms (H, C, O, Cl, S...) of volatile elements (water, organic material, carbonate, chlorides, sulphites...) undergo a modification. The ratio of the other elements (Si, Al, Mg, Ca, Fe...) is slightly or not modified by the firing process. In contrast, the structural organisation (the nature of crystallographic phases) is greatly changed during the firing. For instance, clay minerals (kaolinite, illite, smectite...) begin to lose water with the elevation of temperature, leading then to structural disruptions [61–63]. The decomposition produces various new crystalline (mullite, alumina, spinel...) or disordered (glass) phases depending on the nature of clay minerals. Clay minerals can also react with other mineral phases such as hydro-oxides, oxides or carbonates present in the non-fired pottery, to form new phases such as pyroxene, plagioclase, iron oxide... The chemical reactions taking place during the firing of pottery are very diverse and, of course, depend on the chemical and crystallographic composition, but also on the size and spatial distribution of crystallites (heterogeneity) in the starting mixture. Firing atmosphere (reducing or oxidizing) has also a non-negligible influence. For instance, the nature of forming iron oxides depends directly on this parameter but also on the vitrification temperature (glass formation). Many of these reactions are irreversible and this great diversity can be considered as an advantage which can be used to obtain extensive information from the study of pottery fragments.

The size range of crystallites encountered in potteries being wide (from a few nanometres to several millimetres), a complete crystallographic study needs to use both global (or macroscopic) and local techniques with different spatial resolution in order to determine the spatial repartition of various phases. For instance, petrographic studies are suitable to investigate the majority of micrometric phases and especially tempers ("non-plastic" phases, such as quartz, feldspars...) present in the ceramic body [64]. Thus interesting results can be obtained

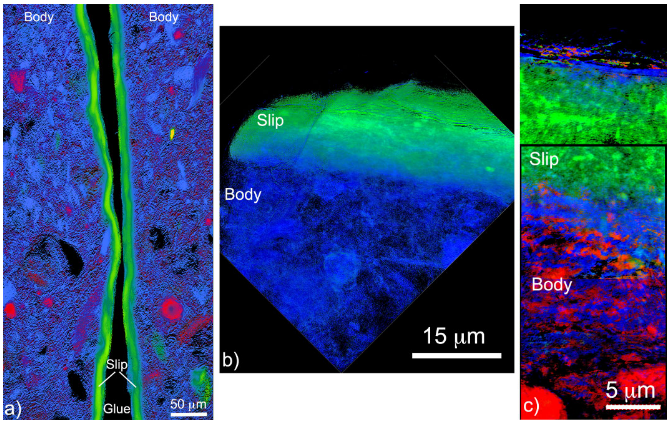

Fig. 6. Phase maps deduced from Full-field XANES analysis performed at (a) ESRF (Grenoble, France) for a campanian, and at SSRL (Stanford, USA) (b) for the same campanian and (c) for a presigillata [67].

concerning the origin of starting materials and the preparation process [65]. However firing conditions are not suitable to the formation of large crystals and only nanometric or submicrometric crystallites are formed. Global techniques such as X-ray powder diffraction can be used for qualitative and quantitative analysis of pottery body. XRD was used to accurately determine the firing temperatures of Gallic terra sigillata [66]. The study of pottery coatings requires more localized analysis because of their thicknesses (10–30 μm). μXRD allowed for identifying the yellow pigment of marbled terra sigillata [47].

More recently, the distribution of iron oxides in different parts (coating and body) of ceramics was investigated by Full-field spectro-microscopy at synchrotron facilities (SSRL and ESRF) with submicrometric resolutions [67]. Figure 6 shows the result obtained for two types of Roman ceramics. The phase maps show that dense zones (slip and some body regions) contain hercynite (Fe^{2+}), while more oxygen permeable regions contain predominantly maghemite (Fe^{3+}). Presence and distribution of maghemite, an intermediate Fe^{3+} mineral formed during re-oxidation of hercynite, is the key to some of the firing protocols. Occurrences of maghemite on the outside surface and the interface between slip and body, and especially the tendril like incursion from oxidized to reduced areas visible in Figure 7 is compelling and there is very pictorial evidence that these two vessels were once reduced and then partially re-oxidized. Furthermore, a relatively uniform hercynite slip and nearly absent re-oxidation layer on the surface indicate a successful firing protocol that allowed the body to re-oxidize while preventing most of the slip from doing so. This remarkable achievement, often not achieved in modern replications, suggests possession of uncommon skills in controlling the redox chemistry through sophisticated manipulation of clay chemistry and morphology as well as kiln firing conditions.

On the other hand, differences in maghemite/hematite distribution in the two sherds point out variations in the firing protocol by highlighting two critical differences.

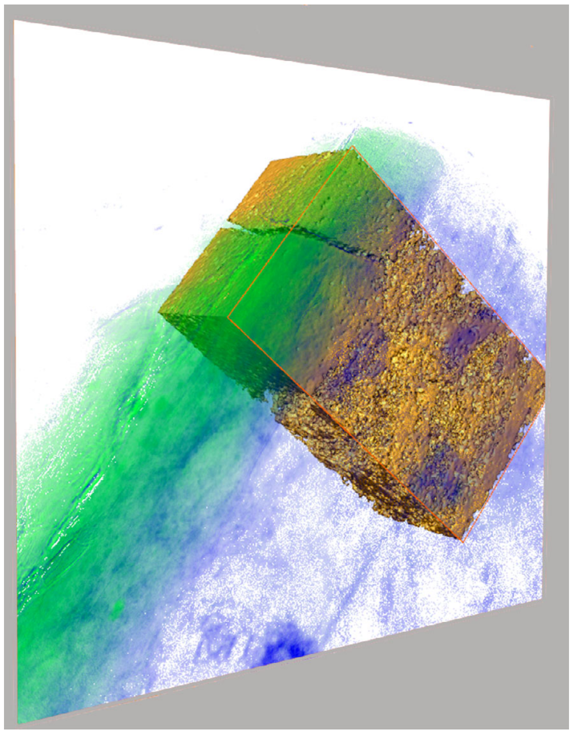

Fig. 7. 3D tomographic data obtained at SSRL (Stanford, USA) with the 2D mosaic phase map of the campanian pottery [67].

The first one is the very patchy and, when present, very thin oxidation layer at the surface of the campanian slip in contrast to a thicker and more uniform layer on the presigillata slip. The second difference is the absence of hematite, except for a few small islands centred on embedded crystals, in the body of campanian sherd as opposed to most of Hematite body of the presigillata sherd. These two distinctions, when combined with the presence of patches of un-oxidized Fe^{+2} minerals in the body (almandine particle, and small patches of hercynite) suggests that the final re-oxidation step (in the three phase firing protocol, first outlined by Noble [52]) for the campanian ceramic have occurred at significantly lower temperatures and/or shorter durations than for the presigillata ceramic. More details concerning this study can be found elsewhere [67].

A similar study has been conducted on an attic vase of 5th century attributed to Berlin Painter with an amazing result [68]. This vessel presents a complicated layered architecture of black and red gloss. The study reveals that multiple rounds of painting/firing were achieved for obtaining this type of morphology. The use of multiple firing has been previously suggested on the basis of replication investigation [69]. Another study on Greek Coral Red potteries [21] showed that, in some vessels, red and black gloss had sufficiently different compositions for being obtained using a single three-stage firing as proposed by Noble [52]. In conclusion, these materials science studies show that firing protocol used by Greek craftsmen was more diverse and complex than previously thought.

3 Further development in pottery studies

In previous sections, we brought to light the current contribution of materials science to the study of ancient ceramics. Characterizing material structures and compositions on various length scales, from the engineering level down to nanoscale, is of both fundamental and applied interest. In this framework, a strong demand is evolving toward the combination of more than one technique, in such a manner that the strengths of one complement the weaknesses of others and vice versa. The investigations are then often based on analysis performed at different scales but using different instruments and samples with connection difficulties among data. Correlations among the various data can be facilitated by using markers which allow to reliably, rapidly find and locate the region of interest when the sample is moved from one instrument to another. For instance, a crossbeam focused ion beam (FIB) equipped with a gas injection system was used to deposit Pt dots on a cross-section sample [20], which were subsequently used to correlate X-ray absorption and fluorescence measurements taken at a SSRL beamline (Stanford, USA), with X-ray microdiffraction measurements (using both mono and polychromatic X-ray beams) collected at the ALS microdiffraction beamline (Berkeley, USA) and also electron microprobe and optical microscope investigations performed at CEMES in France [47].

Now, thanks to the recent developments in both experimental – large instruments such as synchrotron facilities – and theory fields, it should be possible to go further by examining materials over a large-scale range without changing the instrument. For instance, 2D Full-field XANES at ESRF ID21 beamline allows investigating square millimetres surface with a submicrometric resolution (300–400 nm) [70] while SSRL 6-2c BL has a 10 times better resolution (30–40 nm) and the mosaic mode which allows for investigating large zones [67,71]. These two beamlines require the same sample preparation (Fig. 8) and one can then accumulate their respective advantages using for instance, FIB mark deposition. These markers can be also used to complete the observations done by TEM of smaller selected areas of interest with a much higher spatial resolution. Using the Pt registration marks, the areas of interests can be easily located in SEM/FIB and electron-transparent membranes can be cut-off by the "Lift-out" milling procedure [72]. In addition to standard TEM investigations (Bright and dark field images, HREM, TEM-EDX), these thin membranes are ideal in automating crystal orientation and the phase mapping process (Fig. 1) obtained from electron diffraction patterns [73]. Electron holography [74] can also be considered to study the magnetic properties on a nanometre scale of some phases such as ε-Fe_2O_3 detected in black-glazed Jian ware [38].

However, from 2D images it is not always possible to obtain a complete description of the material structure because of the information overlap along the projection axis. The new developments in the 3D mode from both synchrotron radiation [75,76] and TEM facilities [77] could be a way to take better advantage of spatial resolution and to obtain more complete information, in particular to be able to characterize the porosity, which is often a key parameter in firing issues. 3D reconstruction of interfacial elemental composition is achievable from nano-XRF measurement with both sub 100 nm resolution and a concentration sensibility better than 100 ppm. From this data set, we successfully complete in depth investigation of interfacial zones, which brings significant information concerning complex protocols, involving multiple applications of slip and firings. 3D tomography performed before and after K-absorption edges of more significant elements such as Fe, Ti or Mn, similarly to the study presented in a previous paragraph, is also a way to enrich the 2D XANES data waiting for 3D XANES Full-field experiments. Correlation with structural investigations which is also a very important task, is now made possible thanks to the dark-field X-ray microscopy [78]. This non-destructive microscopy technique allows for the three-dimensional mapping of orientations and stresses in crystalline materials on lengths scales from 100 nm to 1 mm. This is a very promising technique for investigating another important aspect of materials science, the mechanical properties which are more often neglected in the studies devoted to ancient materials. Indeed, residual stresses which are present in crystalline phases may give new insight as shown very recently for the making Chassey flint bladelets [79] or the damage zone of the San Andreas fault [80]. In both studies, micro Laue diffraction has been used to measure the elastic strains in quartz crystals.

There is also some progress in electron microscopy for moving from two-dimensional observations of samples in

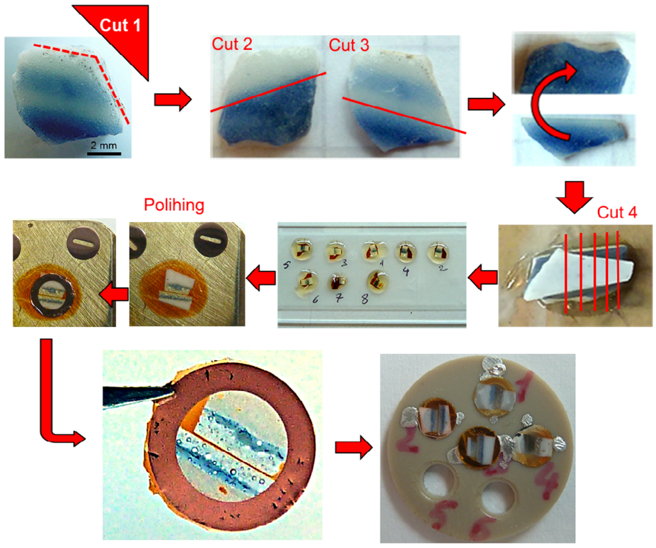

Fig. 8. The most important steps in the cross-section sample preparation process for Full-field XANES analysis belong to TEM sample preparation. The given example is related to the preparation of a Chinese porcelain for investigating the blue decor studying Mn, Fe and Co K-absorption edges (from left to right): cutting steps using a wire saw, sandwich making using glue, cutting thin lamella (300 μm), protection with glue, mechanical polishing up to 40–50 μm, adding a reinforcing Cu washer and finally, series of samples on ESRF sample-holder.

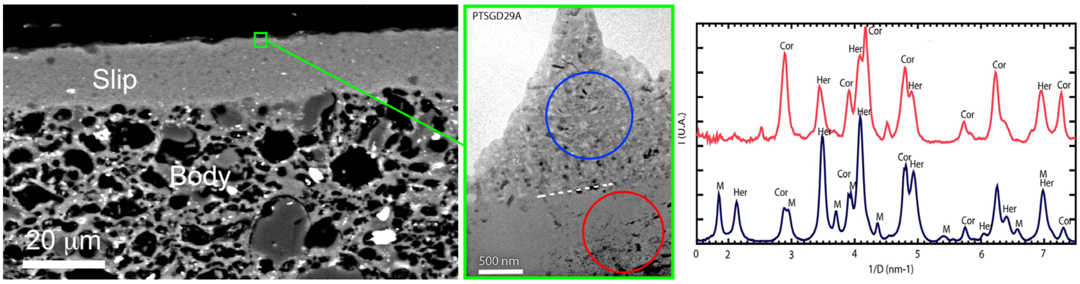

Fig. 9. Presigillata observed in cross-section by SEM-BSE (left), TEM in bright field (centre). Electron diffraction patterns (right) showing the difference in mineral composition of the two layers. The presence of mullite in the top layer reveals that the clay used for its manufacturing contained a large amount of kaolinite phase.

projection to their three-dimensional reconstruction. For instance, electron tomography is a very efficient technique to determine the nano-precipitate distributions in alloys [81] and could be an effective way to study the crystal distributions in ancient decorative coatings. In addition to the length scale complementarity between electron and X-rays microscopies, the different origin of image contrast mechanisms for the two techniques is another advantage. Therefore a combined 3D image reconstruction from these two types of high resolution microscopes would be a giant step towards deciphering the structure of large and complex heterogeneous materials.

From a whole set of data, one may expect to get a continuous description of artefacts from nanometre to centimetre length scales and using (or developing) scaling laws to link the macroscopic properties of object to its structure over the entire length scales following previous studies performed on different heterogeneous materials such as flocculated clay water suspension or hydrated cement pastes [82,83]. These two different hierarchical geomaterials exhibit complex porous structures ranging from nanometer to macroscopic scale. The authors demonstrate, for the first time, that it is possible to go beyond visualization and to extract quantitative morphological information from X-ray images in the aforementioned length scales. On the other hand, these data may be used to develop a methodological approach based on the decomposition of complex materials in sub-systems. The sub-system is defined according to the spatial distribution of the heterogeneities and all atoms forming the core of a sub-system can interact with each other i.e phase diagrams can be used. In a first approximation, each sub-system is considered as independent. Then, the interactions among subsystems are treated as perturbations and can be taken into account through the study of interfaces. During a firing process, some parameters are common to different sub-systems such as temperature and could be deduced from sub-systems for which the phase diagram is known. These parameters could then be used to clarify the formation conditions of some rare phases such as ε-Fe_2O_3 observed in Black-glazed Jian ware of the Chinese Song dynasty. From the interface study information concerning the duration of some steps of the firing protocol can be obtained. Heterogeneity in various components of a ceramic also reflects the heterogeneity of the starting mixture. Then, this kind of study could give information on the starting mixture. For instance, Figure 9 shows SEM observation of a presigillata slip prepared from the mixing of two clays. Mineral and structural analyses of the two layers show the presence of a mullite phase in the top layer. This is an indication that the raw clay used for potteries manufacturing contains a high proportion of kaolinite [63]. Inversely, the absence of this phase in the bottom layer and the large glassy phase content, indicate that this layer was prepared from an illitic clay.

4 Conclusion

Besides standard archaeometry studies whose input has been essential and is still substantial, the materials science approach can be very efficient. In addition to a conventional analysis based on chemical and physical techniques, this approach is more focussed on the materials constituting the object. It includes also other investigation fields of materials science such as material structure and morphology, the physical, chemical and mechanical properties as well as engineering aspects related to material synthesis and processing. However, there exists a main difference here with respect to standard materials science studies which holds in the research direction. While standard materials science aims to discover and design new materials, the goal here is to understand why and how materials were synthetized and to determine the adequacy between their use and their properties.

In materials science field, the structure of material is examined from the atomic level up to the macroscopic level. As shown previously through the presented examples, this approach is very well suited to the study of ancient artefacts since it provides new and original results concerning manufacturing processes and/or physical properties which are essential for the understanding of the "know-how" of ancient civilisations.

The recent advances in structural characterization of materials should improve our knowledge of the ceramic structure and thus to better take advantage of material heterogeneities by using a sub-system decomposition approach. Ceramic structure is very complex. A complete description from the atomic to the macroscopic scale is then mandatory to explain its optical and mechanical properties. This is a challenging issue, which could be beneficial in turn to the material science field. New functional materials have systematically complex structures and new knowledge in this way would be appreciated. Another interest for materials science in studying ancient materials is to gain access to a better understanding of relationships between structural imperfections and physical properties. Even if the ancient ceramic structures present a large amount of defects, their physical properties, especially optical ones, can be outstanding. For the humanities (archaeology, history), studies of materials science type provide more in-depth insight related to the technical aspects and thus, is able to detect small, but significant, process evolutions as shown recently for terra sigillata ware [84]. Better understanding of technical evolution and/or technical exchange inside or among communities or civilizations is an important challenge of the humanities.

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