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Significant findings concerning the production of Italian Renaissance lustred majolica

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Abstract In the present paper the main results obtained, over a period of more than ten years, from a series of studies concerning the characterization of Italian Renaissance lustred majolicas (from Gubbio and Deruta, Umbria, Italy) are presented. Lustre decoration is a well-known technique, consisting in the application of a thin metallic iridescent film, containing silver and copper nanoparticles, over a previously glazed ceramic object. The technique had its origin in Persia (IX century), was imported by Moorish in Spain, and then developed in central Italy during the Renaissance period.

Numerous analytical techniques (among which, ETASS, XRD, UV–Vis, SEM-EDX) have been employed for the characterization of lustred ceramic shards, allowing one to acquire information on both lustre chemical composition and nanostructure. In this way it was shown how some technological parameters, such as the firing conditions, are mandatory to obtain the final result. The presence of a specific marker of the lustre Italian production, i.e., cosalite ($Pb_2Bi_2S_5$), has been also highlighted.

From the study of the ceramic body composition (by means of XRD and ICP-OES and in particular of chemometric techniques) acquired on more than 50 ceramic shards it was possible to discriminate between Deruta and Gubbio production, in this way allowing one to assign objects of uncertain provenance to a specific site.

Finally, the most interesting results obtained studying excellent lustred masterpieces from Renaissance belonging to important museums are here presented. In particular, with the use of nondestructive techniques (PIXE, RBS, and portable XRD), the production of Mastro Giorgio Andreoli from Gubbio was investigated. By means of the same analytical approach, one of the first examples of lustre in Italy (the famous Baglioni's *albarello*) was examined, and the controversial question of its attribution to Italian production was scientifically faced.

1 Introduction

Lustred majolicas produced during Renaissance period in Central Italy represent an important and very interesting ceramic production. The technique was developed for the first time in Persia (IX century) and then imported by Moorish to Spain. The know-how of the Spanish potters was then transmitted to the Italian ceramic workshops during the second half of the 15th century [1, 2]. At the beginning of the 16th century, the two important centers that specialized for this activity were Gubbio and Deruta, located in Umbria (Central Italy).

Lustred objects are earthenware ceramic coated with a white tin-opacified glaze, which was then decorated by using different pigments. To further embellish these ceramics, the ancient potters applied on the glaze a metallic decoration, known as lustre, during a third firing process [1, 2]. This metallic film appeared as a beautiful decoration characterized by shining metallic colors, gold or ruby red. In Gubbio, at the end of 1400 some potters mastered the technique (probably acquired from Deruta; still an open question). Anyway, here was developed the ruby red color that distinguishes this production from Deruta's one [2].

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In “The three books of the Potter’s Art” by Cipriano Piccolpasso [2] (1524–1579), a lot of details on the technique for majolica production are reported. Three steps can be highlighted:

1. the clay body was fired at a temperature in the range 900–1000 °C;
2. subsequently, a tin-opacified glaze was applied starting from *marzacotto* (a mixture of sand and some salts) mixed with lead and tin oxides and further sand; some decorations were painted, and then the object was fired for a second time;
3. a third firing of a previously glazed ceramic ware in a controlled reducing atmosphere was carried out, using a mixture containing metal salts of copper and silver responsible to produce, on the object surface, a thin vitreous shining layer.

The so-produced layer contains metallic copper and/or silver nanoparticles responsible to create the very particular shining aspect of the decoration called lustre.

However, it has to be pointed out that what reported by Piccolpasso could not be entirely correct since the recipes for lustre making were generally kept secret by the potters. Nowadays it is still very difficult to reproduce the outstanding effects obtained by the ancient artisans.

A large number of publications have been devoted to the study of the origin and development of lustred ceramics in the Islamic world, to their transmission to the Hispano–Moresque potters in Spain and to the majolica potters in Italy [3–12]. Among these, many researches have been devoted to the study of the technological aspects of the Italian production [4–11].

Certainly, to obtain beautiful lustre, both glaze and ceramic body compositions are important, and, as a consequence, a deep knowledge of both of them is mandatory [4, 13].

In this context, in addition to the study of lustred ceramic shards, it is also of great interest the study of well-preserved museum object by means of nondestructive techniques [8, 10]. In particular, as concerns the Italian production, majolica objects produced in the famous workshop of Mastro Giorgio Andreoli in Gubbio were investigated [8].

It is attested that the generation of nanoparticles by potters for decorative purposes dates back to some thousands of years ago when nanosized materials were used to obtain particular optical effects [11].

However, the study of lustred ceramics is not limited to the acquisition of knowledge about the technique of the ancient decoration, even if, nowadays, it is very difficult to get lustres of comparable quality to those made in the past.

In general, the lustre production technology is also of great interest for other research areas such as the production of new ceramic materials, and lustre technique can be considered as an historical example of controlled nanotechnology to be used in other fields such as optical devices [11].

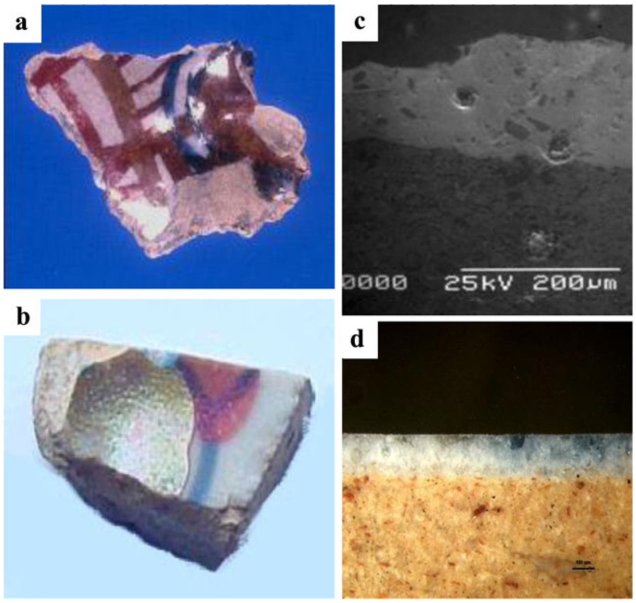

Fig. 1 Two examples of lustred shards where ruby red (**a**) and both ruby red and gold lustres (**b**) are present (sample dimensions about 2 × 2 cm); images acquired on thin sections obtained from lustred shards acquired by SEM (**c**) and optical microscopy (**d**)

2 Experimental

2.1 The analysed objects

Both lustred ceramic shards (from dishes, bowls, etc.) and lustred pieces stored in Museum collections have been analyzed. All the productions date back to the Renaissance period. The shards come from excavations carried out in Gubbio (Umbria, Central Italy). Among the objects analyzed, a representative number of them belongs to the production of Mastro Giorgio Andreoli and comes from Museo del Palazzo dei Consoli (Gubbio) and several French museums (Louvre, Musée National de la Céramique, Musée National de la Renaissance [8]). Furthermore, two *albarelli* decorated with the coat of arms of Baglioni family (one lustred and one not lustred) and a plate with the coat of arms of Montefeltro family from Louvre Museum were studied, too [10]. In Fig. 1 some examples of shards (Fig. 1a, b) are shown together with some images acquired on polished sections obtained by the fragments (Fig. 1c, d). In Fig. 2, two examples of lustred pieces are shown [8, 10]: a plate decorated by Xanto Avelli and lustred by Mastro Giorgio (Fig. 2a) and the lustred Baglioni’s *albarello* (Fig. 2b).

Fig. 2 (**a**) Majolica dish: "Phaeton fall" painted and lustred by Mastro Giorgio Andreoli; by courtesy of Museo Civico—Palazzo dei Consoli, Gubbio; (**b**) Baglioni's lustred *albarello* (inventory number OA 1885)—front; Louvre Museum

2.2 Analytical procedures

Several analytical techniques have been employed for the sample characterization of both chemical composition and structure: ETAAS and ICP-OES for the study of the elemental composition (lustre, glazes, and ceramic bodies), XRD to identify the main phases (lustre, glazes, and ceramic bodies), SEM–EDX to study both surface morphology and composition, TEM–EDX–SAED to investigate the nanostructure, and UV–Vis reflectance spectroscopy to investigate the lustre color. More details are reported in our previous works [4–7]. In particular, for the analysis of museum objects (like the plate shown in Fig. 2), nondestructive techniques, such as PIXE, RBS, and portable XRD, are used [8, 10].

Furthermore, chemometric analytical techniques, such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), have been applied to elaborate compositional data [13].

3 Experimental results and discussion

3.1 Lustres and glazes composition

What concerns Italian Renaissance lustred Italian majolicas, both glaze and lustre chemical compositions have been extensively investigated [4–7]. The analytical techniques employed for this purpose can be distinguished between those that allow one to obtain qualitative information (such as XRD and SEM-EDX) and those that allow one to obtain quantitative information (such as ETAAS and ICP-OES).

The following crystalline phases were observed through XRD analysis: cassiterite (SnO_2) present in the glaze, metallic silver and copper, copper and silver oxides (indicating that the reduction process is not complete), and cosalite ($Pb_2Bi_2S_5$), a mixture of sulfide lead and bismuth. The cosalite presence has proved to be a peculiar characteristic of the Italian lustre production [5, 7].

By means of ETAAS, Cu/Ag ratios were determined, and it has been observed that the color is not unambiguously determined by the chemical composition [4, 6]. Generally, in most of the cases, the gold color is associated with the presence of silver together with copper, whereas, the ruby red color could be associated with the presence of copper only. However, this general assumption presents several exceptions [4]. When both element are present, Cu/Ag ratio can vary in the range 0.1–10 [4, 6]. In most of the cases, high Cu/Ag values are associated with ruby red color, even if this is not a general rule, and in some cases a high ratio corresponds to gold lustres [4]. In fact, it was found that the color depends, in a complex way, on the elemental composition of the *impasto* applied on the ceramic surface, as well as on the process parameters used, such as the firing conditions (temperature, time) and the underlying glaze composition, among others. By varying these conditions the dimensions of the nanosized cluster can be changed, and, as a consequence, a different color can be obtained. The differences encountered in the lustre and glaze chemical compositions (i.e., Cu/Ag ratio) suggest experimentations by the ancient potters using different recipes.

If the Italian lustre production is compared to other kinds of productions (Hispano–Moorish or Islamic) [3, 5, 7, 12, 14] some important differences have been pointed out for the chemical composition, since different recipes were used producing different shining effects (for example, Hispano–Moorish red lustre are more brownish than Italian ones). However, the main peculiar characteristic that distinguishes Italian lustre production from the Islamic one, is the presence of cosalite ($Pb_2Bi_2S_5$) in Italian lustre [5, 7]. The presence of this phase was shown by XRD and successively confirmed by elemental analysis with ETAAS [5].

This could be related to the fact that bismuth was not known as an element for the Arabs, while in Italy, at that time, bismuth and, in particular, its use to imitate silver were well known. As a consequence, Italian potters probably intentionally added bismuth to the *impasto* for the lustre preparation in order to keep down the cost of the final product.

Furthermore, bismuth contributes to lower silver and copper fusion temperatures, and some bismuth compounds (oxide, carbonate, and nitrate) are also employed in the preparation of modern lustres [1], acting as fluxes and allowing the pigment to adhere to the glaze at temperatures that are low enough to avoid the glaze discoloration by reduction.

An interesting case is represented by samples that come from Umbria but have been defined by experts as imitation cases of Hispano–Moresque style. In particular, these samples present a ceramic body composition that is typical of Italian production (see Sect. 3.3), but they do not contain cosalite in the lustre layer, indicating that they were realized following a recipe quite similar to the one employed by the Spanish artisans. This shows how deep was the knowledge the ancient potters had.

In order to obtain a lustre film characterized by particular shining effects, the glaze composition is very important. In fact, the process of lustre formation involves an ion exchange between the *impasto* applied on the ceramic surface and the underlying glaze. In particular, there is an exchange process between Na^+ and K^+ present in the glaze and Ag^+/Cu^+ ions of the applied *impasto*. The glazes belong to the typical lead-alkali type (on average, Pb about 20 %, K about 7 %, and Na about 6 %), where tin oxide is used to obtain the glaze opacity [4]. SnO_2 (cassiterite) crystals have been shown by XRD and TEM micrographs, too [4].

At this time, the glazing mixture was commonly prepared starting from marzacotto (sintered sand and calcined wine lees providing potash and salt), which furnished a high potash (K_2O) quantity. On the contrary, the Hispano–Moorish productions were characterized by high-lead glaze containing a small amount of sodium and potassium.

What concerns the lustre technology production, the obtainment of two colors on the same object is even more complex since the temperature required for copper reduction is higher than that for silver, and the risk of over-firing the gold part damaging the object exists. The use of flux metal such as bismuth could favor the metal reduction, and in fact examining shards decorated by both gold and red, especially where the two colors were present at the same time [6], we found systematically that, in red lustres, there are always present a higher Cu concentration and a higher Bi/Ag ratio, with respect to the gold ones [6].

Bismuth, acting as an active pigment, allows the reduction of both silver and copper fusion temperatures. In particular, the reducing conditions for obtaining red lustres are more critical than the gold one due to the risk of reducing at the same time both the copper salts and the lead oxide present in the glaze, causing a darkening effect on the surface. Furthermore, as already mentioned, during Renaissance, bismuth was well known in Italy and often used to imitate silver [5, 7] with the result of keeping down the costs.

In shards decorated with both gold and ruby-red lustres, Cu, Ag, and Bi where found together with iron and mercury (which appear in the recipes as ingredients of the *impasto* in the form of Armenian bolus and cinnabar, respectively [2]). In some cases the presence of mercury has been highlighted in the red parts: it is possible to hypothesize that potters tried to obtain the red color also by adding cinnabar to the *impasto*. It has to be pointed out that this result is not in agreement with the known ancient recipes, where cinnabar is mentioned among the ingredients for the preparation of the gold lustre instead of the red one [2]. It is worth noting that Hg, as well as Bi, acts as active pigment reducing lustre-firing temperature. The presence of this element had never been highlighted before, probably because it has a sublimation temperature slightly lower than that one of the third firing.

Fe/Ag ratios higher than one were observed for all samples even if, according to Piccolpasso's recipe [2], iron oxide, as Armenian bolus, was added only at the red impasto.

All these observations confirm that the ancient potters experimented recipes different from those reported in the treaties known to us.

3.2 Lustre nanostructure

As it has been previously pointed out, lustre is constituted by a thin metallic film applied on the glaze surface during a third firing in reducing conditions. This allows the formation of copper and silver nanoparticles, which has been shown by TEM analyses [4].

In our previous studies, TEM and SAXS measurements have shown that copper and silver nanoparticle dimensions range from about 5 to 100 nm [4, 6, 15], the copper particles having generally smaller dimensions than the silver ones. By TEM-SAED it has also been demonstrated that silver and copper particles are separated instead of alloying, as it is expected from the copper–silver phase diagram [4, 11].

In general, red lustres show a structure constituted by a layer of larger nanoparticles in the outermost layer, with a

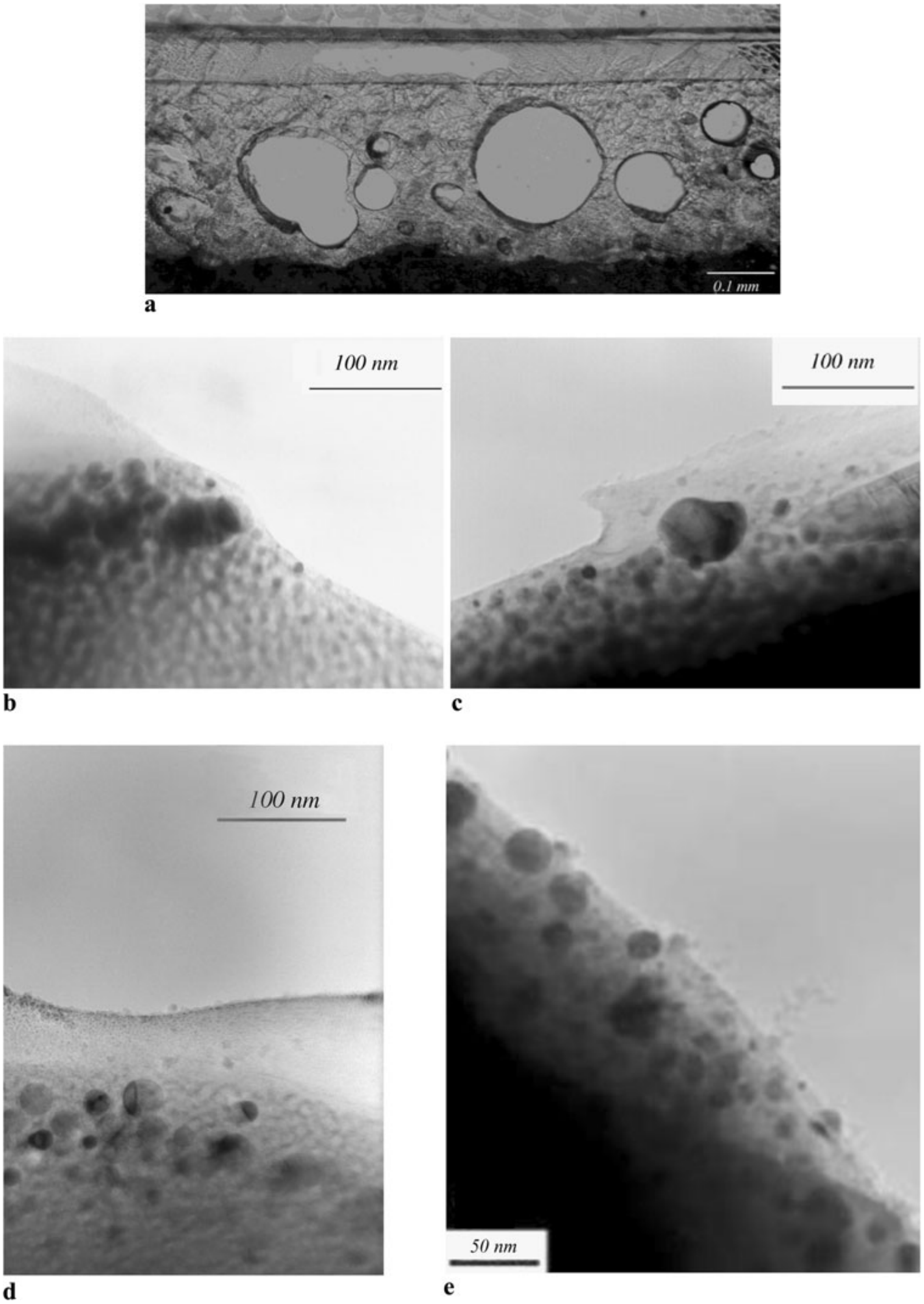

Fig. 3 (**a**) optical microscopy image of a thin section of a lustred ceramic shard (starting from the bottom: ceramic body, glaze and lustre layer); (**b**, **c**) TEM images acquired on gold lustres; (**d**, **e**) TEM images acquired on red lustres

decreasing particle dimensions moving from the surface toward the interior [11]. On the contrary, gold lustres generally show an inverted structure, where the larger particles are more diffused into the glaze, and the smaller ones remain on the surface, in the outermost layer (Fig. 3).

Lustre nanostructure is quite complex, and, depending on the kind of production (Italian or Hispano–Moresque), significant differences have been observed (for example, Hispano–Moresque have generally larger particles in the outermost layer, [12]). The color of the lustre films is strictly related to the particles dimensions. The optical properties of these films have been investigated by UV–Vis reflectance spectroscopy which has allowed pointing out the metallic colloidal nature of Cu and Ag particles [4, 6]. In particular, gold lustre samples show a maximum at about 420–440 nm, due to the silver SPR (surface plasmon resonance) band, while red lustre decorations show a maximum at about 560 nm due to the copper SPR band and, in most cases, a maximum due to the Ag SPR band. However, it is not possible to directly correlate reflectance spectra with lustre chemical composition since different parameters (i.e., composition and firing conditions) play an important role in the obtainment of the final result. For example, what concerns the firing conditions, both temperature and annealing time can influence the metallic film features. In fact, if we compare lustre of similar compositions, they can be characterized by quite different UV–Vis spectra. The process is so complex that metallic lustre decorations can be considered as a historical example of controlled nanotechnology, confirming the high technological level of the ancient masters. For this reason, lustre production technology is also of great interest for other research areas such as the production of new ceramic materials. For example, recently copper-based nanocoatings and metallic nanostructured glazes have been developed for industrial application, exploiting properties that are typical for lustre surfaces such as the shine metallic aspect and the hydrophobic characteristics [16, 17].

3.3 Lustred majolicas ceramic body

Another important aspect is represented by the study of the ceramic body chemical composition. In fact, it is well known that, thanks to the analysis of the raw materials, it is possible to identify the ceramic provenance, i.e., the production site, since ancient potters generally used local clays. In the particular case of the Italian Renaissance majolicas, XRD analyses revealed that Gubbio ceramic shards showed the presence of gehlenite ($Ca_2Al_2SiO_7$), absent in Deruta shards, a phase that forms during firing starting from a calcareous illitic clay, which is typical for the Gubbio area [13]. The presence of this phase in Gubbio shards could be due to a lower firing temperature but also could be mainly ascribed to a different chemical composition of the starting clay. On the basis of the chemical composition of the ceramic bodies (acquired by ICP-OES analyses [5]), it has been possible to discriminate between Italian and Hispano–Moresque production and, within the group formed by the Italian majolicas, between Gubbio and Deruta productions (Table 1) [13].

Examining more than 50 ceramic shards coming from both Gubbio and Deruta, we have collected a complete data set concerning the ceramic body chemical composition [5, 13]. The chemical compositional data have been treated by means of chemometric techniques such as Principal Component Analysis (PCA) and Cluster Analysis (HCA) following a procedure setup in previous works [18–20]. A good separation between the two groups of shards (Gubbio and Deruta) has been obtained (Figs. 4, 5). Furthermore, examining some local clays coming from the two sites, it was verified that they have compositions consistent with those of the shards (Figs. 4, 5). To acquire information on the firing technology employed by the ancient potters, some experiments have been carried out on the raw clay materials that have been submitted to firing processes similar to those employed during Renaissance. In particular, it has been useful to follow how Diopside/Gehlenite ratio varies with temperature. In this way it was possible to estimate that the soaking time used for the ceramic shards was probably about 2 h.

3.4 Investigation on museum objects

On the basis of the expertize acquired when analyzing lustred ceramic shards and due to the great historical and technological interest surrounding lustre, excellent pieces stored in important museums were studied with the aim to identify the composition of both pigments and lustres [8, 10]. In particular, some masterpieces belonging to the majolica production of the great master Giorgio Andreoli from Gubbio and coming from Museo del Palazzo dei Consoli (Gubbio) and important French museums (Louvre, Musée National de la Céramique, Musée National de la Renaissance) have been characterized from chemical and structural points of view [8].

In this study, nondestructive techniques such as particle-induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS) have been employed (they were carried out with the AGLAE accelerator at C2RMF, Louvre).

Mastro Giorgio's fame is due to the fact that he specialized mainly in two kinds of reflections: an intense golden yellow and a ruby red color. By optimizing the lustre technique, he obtained outstanding results, which were not possible to replicate during his time or now. In fact, the original recipes and technological procedures used at that time were and have remained a secret after his death until today since the process of lustre-making was jealously kept and handed on only within the Andreoli family to defend themselves against competition with other workshops.

The aim of the study carried out on objects lustred by Mastro Giorgio (in many cases painted by Xanto Avelli, one the most famous artists for the decoration of majolica at that time) was to investigate the evolution of the lustre technique and possible evolution in the Mastro Giorgio workshop regarding the raw materials used in the investigated period, which ranges from 1510 to about 1540.

What concerns the glaze the production techniques used, they were found to be very similar on the different objects analyzed: the glaze was a tin-opacified white lead glaze, in agreement with the recipes described by Piccolpasso [2].

For the other colors, the classic recipes used for the decoration of Italian majolica have been employed, in particular, copper (ramina) for the green (sometimes mixed with lead antimonite to obtain different tones) and cobalt oxide (zaffer) for the blue [4].

As to the blue color, it is worth noting that the studied masterpieces could be differentiated on the basis of the elements associated with cobalt. In fact, two groups are distinguishable: in the first group, the blue pigment contains mainly Co plus Fe, and these plates are dated from 1510 to 1528; in the second group, the elements associated with Co are more numerous (Fe, Ni, sometimes Cu with As and traces of Bi and Mo), and these plates are dated from 1527 to post-1540.

The main conclusion is that in the more ancient plates, As is not present, and this could be probably due to a change in the supplying source of the blue pigment during time or to a some variation in the roasting procedure of the mineral [8].

What concerns the nanoparticle distribution in the lustre layer, by means of RBS it has been observed that the lustre film can be described with a single layer or with two or more layers (in accordance with what was previously observed by analyzing the lustred shards) [4, 6, 11]. In this second case, a gradient in metal concentration occurs.

In general, the lustre thickness is about 200 nm, and it has been also observed that all the lustres are covered with a thin metal-free layer, generally strongly depleted in lead, whose thickness varies between 15 and 200 nm, this being a common feature generally observed in lustres of different provenance.

Another important observation concerning the evolution of the technique of Mastro Giorgio workshop is that, after 1527, the technique of the workshop seems to have moved toward the use of lustering pastes containing only one metal compound (silver or copper). With the aim to investigate the first step of lustre production in Italy, an emblematic lustred object, Baglioni's *albarello* conserved at Louvre museum and considered one of the very first examples of lustred objects produced in Italy, was studied [10]. Also, in this case nondestructive techniques, such as PIXE, RBS, and portable XRD, have been employed. Together with the Baglioni's *albarello*, other two objects have been investigated: another *albarello* not lustred but still decorated with the coat of arms of Baglioni's family and a lustred plate with the coat of arms of the Montefeltro family. The two Baglioni's *albarelli* are stylistically and historically considered as produced in one of the numerous workshops of Deruta.

The main interesting result obtained by XRD on the lustred Baglioni's *albarello* is the presence of cosalite ($Pb_2Bi_2S_5$). This phase, as mentioned before (see Sect. 3.1), can be considered as a marker of the Italian lustre production, and thus its presence in this object can be considered as a definitive confirmation of the Italian origin of the Baglioni's *albarello*. At this point it was interesting to establish if these *albarelli* (lustred and not lustred) were produced in the same place (Deruta or Gubbio). In fact, as stated before (see Sect. 3.3), it is possible to discriminate between the two production sites on the basis of the chemical composition of the ceramic body and on the presence/absence of ghelenite, a phase typical for the ceramics produced starting from Gubbio clays, richer in calcareous content [13]. While XRD pattern acquired on the plate with the coat of arms of the Montefeltro family clearly showed the signal due to ghelenite, allowing us to attribute this piece to Gubbio, the nonlustred *albarello* did not show this signal and, as a consequence, was attributed to Deruta production. In the case of the lustred *albarello*, gehlenite peaks showed very low intensity, not allowing a certain identification of this mineral. For this reason, the chemical composition of the ceramic body has been compared with those of ceramic of known provenance (see Sect. 3.3) and the chemical composition of the whole data set submitted to chemometric analysis in order to attribute the *albarello* to one of the two sites. On the basis of the results obtained by both cluster analysis (HCA) and classification methods such as RDA (regularized discriminant analysis), the lustred *albarello* and Montefeltro's plate were assigned to Gubbio production, while the nonlustred *albarello* was assigned to Deruta.

4 Conclusions

In this paper, we have summarized the main results obtained from researches carried out over more than ten years and having as the main topic of the study of the lustre one of the most sophisticated techniques for the decoration of majolicas during Renaissance period. Lustre is the very thin outermost decorative layer consisting of silver and copper nanoparticles that are responsible for the beautiful metallic and iridescent effects. Copper and silver nanoparticle have dimensions in the range from about 5 to 100 nm, the copper particles having generally smaller dimensions than the silver ones. The particular optical properties of the lustre are directly related to its nanostructure, confirming the high technological level of ancient masters.

The glazes underlying the lustre layers show a composition typical of lead alkali glazes. Both lustre and glaze chemical compositions as well as the firing conditions influence the color and the shining properties of the final result. Among the ingredients used for Italian lustre preparation, the presence of bismuth (and, in particular, of cosalite, $Pb_2Bi_2S_5$) has been disclosed: this element was absent in Arabian or Hispano–Moresque lustres and therefore can be considered as a marker of the Italian production. In fact, at that time, Bi was known in Italy and was used to imitate silver. Then, we cannot rule out that Italian potters intentionally added bismuth to the *impasto* for lustre preparation in order to keep down the cost of the final product. On the contrary, this element was unknown to the Arabs [5].

Within the Italian production, analyzing the ceramic bodies, it has been possible to discriminate between objects produced in Gubbio or in Deruta. What concerns the mineralogical composition, XRD analyses revealed that Gubbio ceramic shards show the presence of gehlenite, which is absent

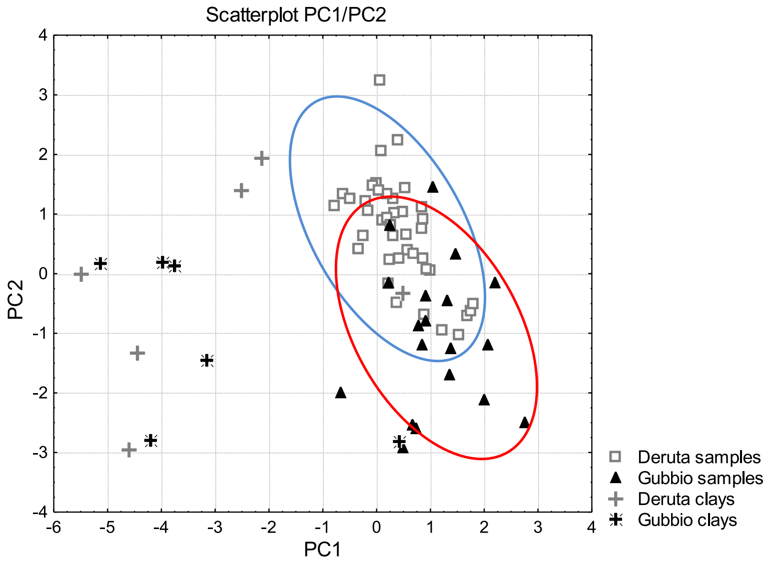

Fig. 4 Diagram of the first two principal component (scatterplot) calculated for the ceramic shards from Gubbio and Deruta and the corresponding raw materials

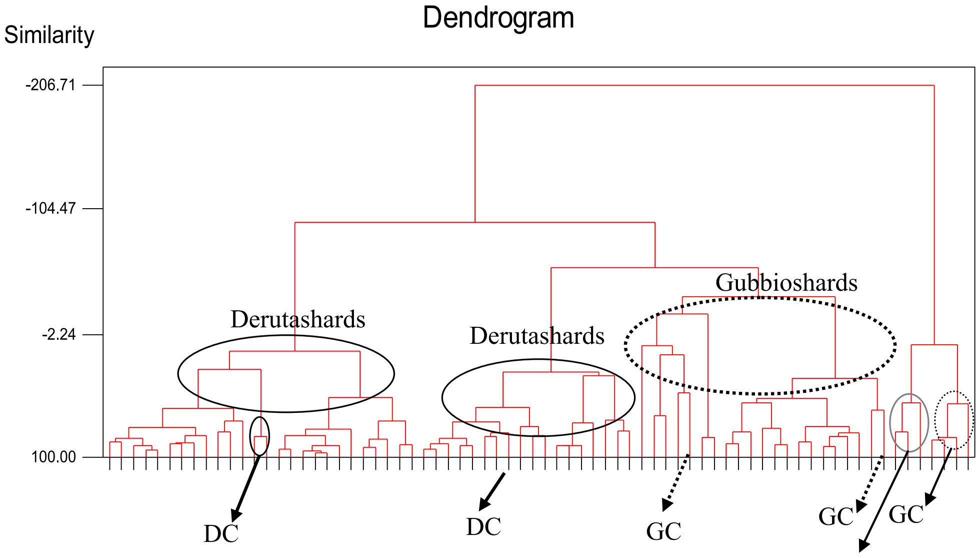

Fig. 5 Hierarchical clustering dendrogram by Ward's method for all the principal components calculated for all the examined samples (shards and clay)

Table 1 Average chemical composition by ICP-OES analysis of Deruta and Gubbio clay and of ceramic shards from the two sites

	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	TiO_2	Na_2O	MnO	Cu	Ni	Zn	Sr
Deruta samples	15.1	14.5	6.1	3.2	2.6	0.6	1.2	0.1	0.02	0.01	0.03	0.04
Gubbio samples	18.7	12.0	5.5	3.7	2.9	0.5	2.1	0.1	0.01	0.01	0.01	0.04

in Deruta shards. This distinctive feature is typical for pottery artefacts produced using calcareous illitic clay. Therefore, the presence of gehlenite in Gubbio samples could be a useful marker for the attribution of the provenance from one of these two sites, through a simple XRD analysis. In order to carry on a provenance study, the chemical compositional data acquired on a large data base formed by samples coming from the two Italian sites have been submitted to multivariate statistical treatments (PCA and HCA), and a good separation between Gubbio and Deruta ceramic shards has been obtained. Therefore, an object of unknown provenance could be attributed to a specific production site on the basis of its ceramic body chemical composition. This criterion could be very useful in the case of museum objects where the chemical composition can be acquired by PIXE analysis.

On the basis of the experience acquired by analyzing the ceramic shards, some studies have been carried out on some museum masterpieces. First, the production of Mastro Giorgio Andreoli, a great master who operated in Gubbio, was investigated. By means of nondestructive techniques the evolution of the technique in the workshop of this great artist was studied.

Then, a famous *albarello*, decorated with the coat of arms of Baglioni family and considered as one of the first examples of lustre in Italy, has been examined, and the controversial issue of its attribution has been solved thanks to the application of the criteria developed in our previous studies (in particular, the presence of cosalite as marker of Italian production).

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