Appl Phys A (2010) 100: 771–784
DOI 10.1007/s00339-010-5689-x

Applied Physics A
Materials Science & Processing

A scientific approach to the attribution problem of renaissance ceramic productions based on chemical and mineralogical markers

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Received: 28 September 2009 / Accepted: 9 March 2010 / Published online: 22 April 2010

Abstract Renaissance lustred majolica shards from Gubbio and Deruta (Central Italy) were investigated in order to point out differences in chemical and mineralogical composition between these two very similar Italian potteries and furthermore to find correlations with the local raw clay materials probably used for their production. Chemical and mineralogical analysis on the ceramic body were performed by ICP-OES (inductively coupled plasma optical emission spectroscopy) and XRD (X-ray diffraction), respectively. Investigation of the ceramic body revealed significant differences on calcium content indicating that it could be used as a marker for the two different productions.

A separation of the ceramic shards in groups, on the base of their provenance, has been achieved applying to the data set formed by the chemical compositional data some multivariate techniques, such as PCA (principal component analysis) and HCA (hierarchical cluster analysis).

Even the mineralogical composition of the groups shows very interesting features, differing Gubbio production from Deruta one for the presence of several mineralogical species.

The investigations carried out on clays that were collected in the two geographical places have confirmed these differences. In fact, the clay materials have a chemical composition coherent with that one found in the shards. Firing tests performed by heating these clay in different conditions (temperature and soaking time) have shown a different behaviour as concerns the formation of the minerals and it is compatible with the shard composition found. From the comparison between the fired clay and the ceramic shards, some assumptions about the firing conditions applied by the ancient potters have been drawn.

1 Introduction

Ceramics appear already in Prehistoric age. The Neolithic civilizations probably perceived by chance the potential of clay that in contact with fire produces materials which are particularly hard and resistant.

At that time, the furnishing production was based on raw, not purified clay, and the objects were forged by hand with very simple techniques, without the use of potter's wheel.

During centuries, the production of artefacts is becoming more and more complex and refined, for what concerns the working processes on raw materials as well as for the decorative techniques and motifs used.

The ceramic artefacts are particularly resistant and do not suffer great alteration during time and weathering. For these reasons their study is fundamental for archaeologists in order to go back up the habits, the commercial relationship and the economy of ancient civilizations.

Traditional ceramics are made from natural materials, such as clay, that have been hardened by heating at high temperatures (driving out water and allowing strong chemical bonds to form between the flakes of clay). In fact, the word "ceramic" comes from the Greek *keramos*, whose original meaning was "burnt earth." When artists make ceramic works of art, they first mould clay, often mixed with other raw materials, into the desired shape. Special ovens called kilns are used to *fire* (heat) the shaped object until it hardens.

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Clay consists of a large number of very tiny flat plates, stacked together but separated by thin layers of water. The water allows the plates to cling together but also acts as a lubricant allowing the plates to slide past one another. As a result, clay is easily moulded into shapes. High temperatures drive out water and allow bonds to form between plates holding them in place and promoting the formation of a hard solid. Binders such as bone ash are sometimes added to the clay to promote strong bond formation, which makes the ceramic resistant to breakage.

In Italy, the more remarkable evolution took place during the XIV cent., when a new technique concerning the glaze preparation was developed. Due to the contemporary presence of tin and lead oxides, a white and waterproof coating was obtained and it was possible to use it as a canvas by the pottery painters. For this reason, real works of art were produced representing noblewomen and noblemen's portraits, mythological and religious scenes, sayings, loving dedication, heraldic symbols and coat of arms. All these motifs were inspired by the masterpieces of Renaissance artists and were requested by cultured and refined customers.

This moment represents the origin of "majolica" in the actual meaning, which is referred generally to glazed production. It is characterised by a ceramic body with a porous structure, and covered by a glazed layer, generally white, that is decorated. During the XV and XVI cent., the Italian potters named "majolica" (*de Maiorica*) only the objects decorated with metallic reflections (i.e. *Lustre*), reminding the beautiful pieces of this kind, firstly obtained by Arabs and Hispano-Moors, and imported in Italy through Majorca island.

Lustred majolicas produced during Renaissance period in Central Italy represent an important and very interesting ceramic production. These objects (dishes, bowls, jars, etc.) are earthenware ceramic coated with a white tin-opacified glaze which was then decorated by using different pigments. Furthermore, in order to embellish these ceramics, the ancient potters from Gubbio and Deruta (Umbria, Central Italy) applied on the glaze a further decoration, known as lustre, during a third firing process [1, 2]. This metallic film appeared as a beautiful decoration characterized by shining metallic colours, gold or ruby-red. In particular Gubbio masters specialized themselves in the production of red lustres [2]. Thanks to the treatise "The three books of the Potter's Art" by Cipriano Piccolpasso [3] (1524–1579), the technique for majolica production is well known. The clay body was fired at a temperature in the range 900–1000°C. 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. An interesting and complete reassessment concerning the production technology of Italian majolica has been recently published [4, 5].

Many production centres flourished in Italy, particularly during Middle Ages and Renaissance, and today it is not easy, even for experts, to assign an object to a certain production centre.

The aim of this study is to investigate local raw clay materials and ancient shards of certain origin, from Renaissance time, in order to find if it is possible to establish a correlation between them defining criteria that could be useful for the attribution of other works of art of uncertain origin, discriminating pottery production sites in Central Italy.

The ceramic body analysis is of great interest since it allows acquiring information both on the production technology and on the provenance of the ancient ceramics.

In particular, chemical analysis for major and minors elements provides a fingerprint that allows to group together pottery made starting from the same raw material and to distinguish groups of ceramics made from different raw materials. The analytical methods employed include ICP-OES (inductively coupled plasma optical emission spectroscopy), used also in the present paper, XRF (X-ray fluorescence) and more sensitive techniques such as ICP-MS (inductively coupled plasma mass spectrometry) [5].

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) represent the most widely used statistical techniques to identify compositional groups [6].

Italian majolicas generally were realized starting from calcareous clay with lime content higher than 10%. A comparison with the chemical composition of the local clay may be of great help even if it is important to consider the eventual treatments to which the clay were submitted and a possibly slight change in composition during the centuries.

The characterization of the ceramic body microstructure and mineralogical composition allows to acquire additional information concerning the production technology such as the firing procedures used by the potters [5].

The present paper is focused on the possibility to approach the problem of attribution of a ceramic to a specific site (Gubbio or Deruta) on the base of chemical and mineralogical markers.

For this purpose 60 ceramic shards coming from the two sites of Gubbio and Deruta have been investigated and characterized by means of ICP-OES and XRD in order to evidence eventual differences in both chemical and mineralogical composition.

In order to better clarify the technological features of these two productions, raw clay materials coming from both sites have been examined, too.

The chemical data acquired on the shards and the clay have been treated by means of multivariate techniques.

Firing tests carried out on the raw clay materials, following what reported in the old treatises [3], have allowed to clarify some aspects of the firing technology employed by the ancient potters. In particular, the comparison with the ceramic shards has allowed to asses the pottery firing conditions.

2 Experimental procedures

2.1 Ceramic shards and clay samples

Samples of ceramic shards both from Gubbio and Deruta and clay samples from these two sites were examined in this study. The ceramic shards are dated to XV and XVI centuries and consist of fragments of dishes, bowls, jars, etc. They were found during archaeological excavation carried out in Gubbio and Deruta. We used for this study only shards, such as lustre tests, second firing pieces and shards that, from a stylistic point of view, were unequivocally assigned to one of the two town by experts.

On the whole, 60 ceramic shards have been examined as concerns the ceramic body: 41 samples were from Deruta and 19 from Gubbio. The raw clay materials used in the past for ceramic production in Gubbio and Deruta came from the sedimentary basin defined by some authors as belonging to the Middle Miocene marly-arenaceous formation [7] and by other authors as Pliocenic continental deposit of lacustrine origin [8]. On the whole, 9 raw clay samples have been examined: 3 from Deruta and 6 from Gubbio. The 3 samples from Deruta are named DRA, DRB and DRC and come from 3 different clay banks surrounding Deruta, where quarry activities were present during Renaissance period. The 6 samples from Gubbio come from 3 different locations and are named GPA1a, GPA1b, GPA2 and GPA3 (all of them coming from the quarry of Ponte d'Assi), GCP (coming from a site named Cipolleto Pozzo) and GML (coming from a site named Montelugliano). Also these samples come from places where quarry activities for ceramic production were attested in the past. These raw clay materials were submitted to a depuration procedure and then dried in air. Then, the air dried samples were submitted to firing tests, at different temperatures and for different times.

2.2 Firing test on clay samples

The raw clay materials were submitted to some firing tests in order to simulate the processes occurred in the objects during the firing procedure. Later on, in the text, the details of the firing procedures used are reported.

2.3 Chemical analysis

The chemical composition of the shard ceramic bodies was already determined in a previous work [9] while in the present paper X-ray powder diffractions (XRD) have been acquired.

X-ray analysis have been performed by a Bragg–Brentano diffractometer (SEIFERT ID 3000) equipped with a Ge focusing primary monochromator ($\lambda = \text{Cu K}\alpha$).

The diffractograms have been acquired on the inner part of the shard ceramic body and reduced in powder. In particular, 3–4 g of material was collected, grinded and homogenized; from this amount, 500 mg were analysed.

Clay samples were submitted to both X-ray powder diffraction and chemical analysis carried out by Inductively coupled optical emission spectroscopy (ICP-OES) using a thermo instrument (model Iris Intrepid) equipped with a low-noise CID detector and an echelle spectrometer. Twelve elements were determined: Ca, Al, Fe, Mg, Ti, Na, K, Mn, Cu, Ni, Zn and Zr.

The data were acquired and elaborated using TEVA software. The analytical data produced are given with a precision of 5%. The concentrations of the major elements (Ca, Al, Fe, Mg, Ti, Na, K and Mn) have been reported as oxide % while the concentrations of minor elements (Cu, Ni, Zn and Zr) have been reported as element %.

The analyses were performed on solutions obtained submitting about 100 mg of sample to a digestion procedure (in Teflon crucibles using an heating plate), using about 3 mL of a mixture of nitric and hydrochloric concentrated acids (in a ratio of 1:3) and 2 mL of hydrofluoric acid (for the silicates dissolution), followed by the addition of about 2 mL of perchloric acid in order to eliminate HF that not reacted. Then the solutions were diluted to 25 mL and analysed.

The raw clay materials were also analysed by infrared spectroscopy (FT-IR) in the range 4000–400 cm^{-1} using a thermo instrument equipped with an ATR (attenuate total reflection) accessory.

2.4 Statistical study of chemical composition

ICP data were treated by means of chemometric analytical techniques, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA). Both of them are well-known multivariate methods of analysis [10, 11].

Principal component analysis involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components.

Hierarchical cluster analysis refers to a group of techniques of multivariate analysis whose objective is to select and group together homogeneous data. All these techniques are based on the concept of distance between two elements. The algorithm used for the analysis groups together the elements on the base of their reciprocal distance and therefore one element belongs to a group depending on the distance from that group.

In the literature, these two techniques have been successfully applied in archaeological applications to solve provenance problems [9–13].

Table 1 Mineralogical composition by XRD analysis of some ceramic shards from Gubbio (G) and Deruta (D)

	provenance	quartz	plagioclase	diopside	gehlenite	hematite	calcite
L1	G	++++++	+	++	++++	tr	+
L2	G	++++	+	+	++	+	+
L5	G	+++	+	+	++	tr	
L6	G	+++++	+	++	+++	+	
L7	G	++++	+	+	++	+	
L8	G	+++++	+	++	+++	+	+
L9	G	++	+	+	+	+	
L10	G	++++	+	++	+++	+	+
L11	G	+++++	+	++	+++	tr	
L12	G	+++++	+	+	++	+	+
L 14	G	++++	+	++	+++	tr	
L15	G	++++	+	+	++	+	
L16	G	+++++	+	++	+++	+	
L17	G	++++	+	+	++	+	+
L18	G	++++	+	+	++	+	
L21	G	++++++	+	+	++	+	
L22	G	++	+	+	+	+	+
L24	G	+++++	+	+	++	+	+
G50	G	+++++	+	++	+++	+	
L3	D	++++++	+++	+++	−	+	+
L4	D	++++++	+++	++++	−	+	+
L19	D	++++++	+++	+++	−	+	+
L20	D	++++++	+++	+++	−	tr	
L23	D	+++++++	+++	++++	−	+	+
L25	D	+++++	++	+++	−	+	+
D 24	D	++++++	+++	+++	−	+	+
D 29	D	++++++	+++	+++	−	+	+
D 40	D	++++++	++	+++	−	+	+
D 42	D	++++++	+++	+++	−	+	+

Another useful chemical and compositional data representation used in this paper is the box and whisker plot that highlights specific features as median value, quartiles and outliers in the data set for each variable, i.e. each analyzed element.

Principal component analysis (PCA) has been performed after a data transformation consisting in a closure procedure (the sum of the new chemical data is equal to 100) [9].

All the graphs reported in the text (box and whisker plots, scatter plots in two and three dimensions and dendrograms) were realized by using the statistical packages Minitab Inc. 15.1 and STATISTICA 7.1.

3 Results and discussion

3.1 Chemical and mineralogical composition

From the point of view of the mineralogical composition, XRD analyses have evidenced that Gubbio ceramic shards are characterized by the presence of quartz, plagioclase, emathite, diopside, calcite and high quantities of gehlenite. On the contrary, Deruta samples show quartz, hematite, calcite and high content of diopside and plagioclase (see Table 1 and Figs. 1, 2).

The std patterns reported in Fig. 1 come from RRUFF Project website (http://rruff.info/) containing an integrated database of Raman spectra, X-ray diffraction and chemical data for minerals.

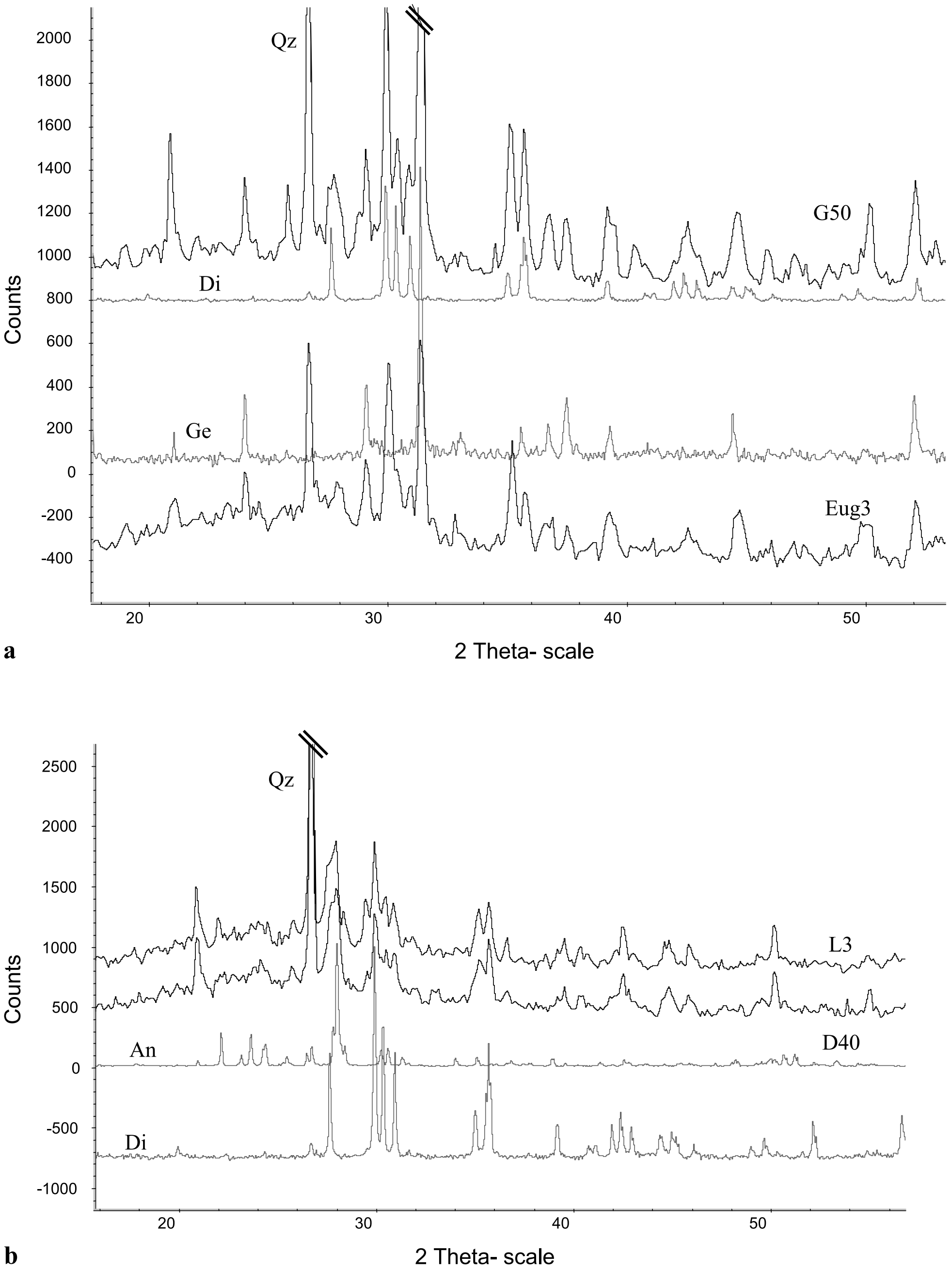
The mineralogical phases present in the XRD patterns of Figs. 1a and 1b are those which typically form when calcareous illitic clay, such as those used for the production of the ceramics here examined, are fired.

Here are reported the main reactions that occur when a raw material, such as clay, is fired [14].

The first reaction, occurring in the range of temperature 650–850°C, is the decomposition of calcite:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \text{(reaction 1)}$$

Fig. 1 (**a**) XRD patterns acquired on Gubbio samples together with the two references gehlenite (Ge) and diopside (Di) (note that in G50 spectrum Ge signal is out of scale); (**b**) XRD patterns acquired on Deruta samples together with the two references diopside (Di) and anorthite (An), a kind of plagioclase (note that in both spectra Qz signal is out of scale)



Then, starting from a temperature of 850°C, the formation of gehlenite (Ge) occurs:

$$SiO_2 + 2CaO + Al_2O_3 \rightarrow Ca_2Al_2SiO_7(Ge) \quad \text{(reaction 2)}$$

If the temperature is increased at values higher than 1000°C, Ge can react and form two other phases, namely calcium pyroxene (wollastonite, Wo) and plagioclase (anorthite, An):

$$2SiO_2(Qz) + Ca_2Al_2SiO_7(Ge) \rightarrow CaSiO_3(Wo) + CaAl_2Si_2O_8(An) \quad \text{(reaction 3)}$$

if the clay is rich in calcium this reaction can takes place already at 1000°C and, if the firing duration is long enough, only anorthite can be found.

Diopside (Di, $CaMgSi_2O_6$) can also forms starting from about 1000°C [14].

These minerals of neo formation can be used as firing temperature indicators, even if temperature is not the only parameter to be taken into account.

In fact, in order to establish the firing conditions, in addition to the maximum temperature, other parameters, such as the heating rate, time of stay at the maximum temperature and the raw clay material composition, must be considered.

Table 2 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 clay	1.998	6.263	5.122	0.325	2.124	0.311	0.744	0.067	0.001	0.001	0.019	0.012
Gubbio clay	3.986	4.293	7.549	0.686	1.921	0.278	0.522	0.063	0.003	0.007	0.020	0.016
Deruta samples	15.104	14.486	6.139	3.197	2.560	0.579	1.168	0.090	0.022	0.010	0.029	0.035
Gubbio samples	18.753	12.000	5.550	3.674	2.953	0.492	2.080	0.126	0.011	0.010	0.014	0.041

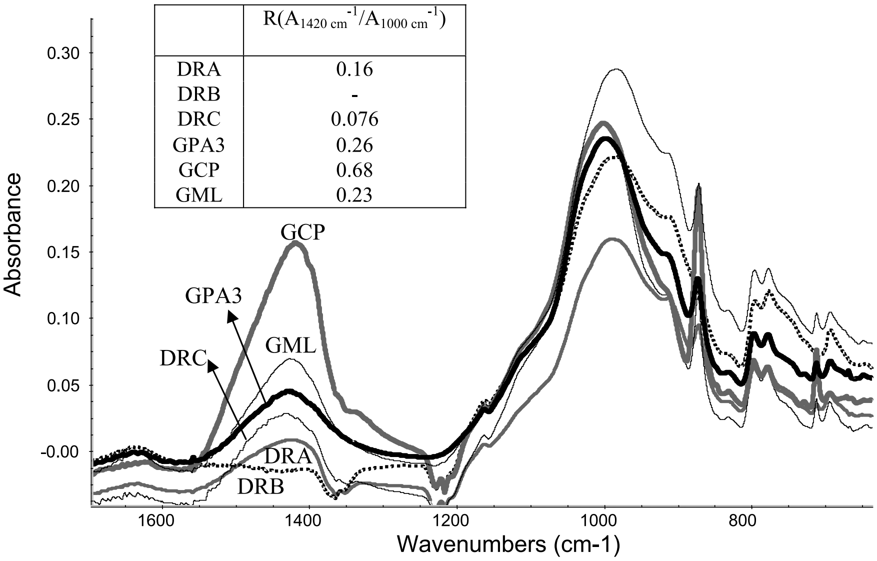


Fig. 2 FT-IR spectra acquired on clay from Gubbio (GPA3, GCP and GML) and Deruta (DRA, DRB and DRC); in *the insert*, the ratio *R* between carbonate and silicate component, calculated taking into account the absorbance of these two species, is reported

Gehlenite presence in the Gubbio samples could be due to a lower firing temperature (probably, gehlenite formed in the Deruta samples disappeared quickly due to higher temperatures used) but it could be also attributed to a different chemical composition of the starting clay.

In fact, from a geological point of view, the raw clay materials found in the neighbourhood of Gubbio are Ca-rich calcareous clay due to the presence of carbonaceous massif at West, close to the marly areas. It is typical for other localities too, from the Adriatic ridge, in Marche region, while the clay materials from the Tirrenic ridge as Deruta are poorer in calcium.

It is worth noting that, among the samples assigned to Gubbio, the second firing pieces, certainly produced in Gubbio furnaces, show gehlenite signal, too.

It has been observed that, firing clay with or without carbonates, the mineralogical phases which forms are different. In particular, gehlenite formation has been observed for a rich carbonate clay (about 9%), while this phase is absent for clay with a carbonate content very low (about 0.5%) [15].

It is also known that, in presence of higher quantities of quartz and amorphous silica, Ge and Wo destruction can take place earlier and diopside and plagioclase formation is favoured at lower temperature. This could be another hypothesis that justifies gehlenite absence in Deruta shards [16].

In any case, we can hypothesize that the presence of gehlenite in Gubbio samples could be a useful marker for the attribution of the provenance of ceramic lustred samples from one of the two sites, through a simple XRD analysis.

As far as the chemical composition of the examined shards is concerned (Table 2), it is possible to observe that samples from Deruta show, on average, a lower Ca content (about 15%) and a higher Al and Fe content, while Gubbio shards are characterized by a higher Ca content (about 19%). If we look at the chemical compositions of the clay coming form the two sites we observe a higher calcium content for Gubbio clay confirming the hypothesis that the raw clay material employed in Gubbio ceramic production were richer in calcite.

The differences among the clay are confirmed also by the infrared spectra (Fig. 2), from which it appear that the signal due to calcite at 1420 cm^{-1} is higher for Gubbio raw materials (GCP, GPA3 and GML). For this purpose, it is useful to look at the ratios (reported as insert in Fig. 2) between the absorption at 1420 cm^{-1} and the absorption at about 1000 cm^{-1} due to the silicates, present in the clay, as well. It is worth noting that Gubbio clay are characterized by higher values of this ratio.

Among Deruta clay, DRB shows a low calcium content, coherent with the absence of calcite signal in the infrared spectrum. This fact is confirmed also by the elemental analysis: 0.6% of CaO for DRB against about 3% for DRA and DRC (in Table 2 the average value for Deruta clay is reported). For this reason, this kind of clay was probably not suitable for ceramic production. In fact, it is well known that clays with low calcium content are not suitable for pottery production [15]. The trend observed by infrared spectroscopy has been also confirmed by XRD analysis from which it results that the main crystalline phases common to all the clay are quartz, illite, chlorite, plagioclase and calcite (with the exception of DRB where calcium carbonate is absent), still evidencing a more quantity of $CaCO_3$ in Gubbio clay.

The calcium carbonate content for the clay examined in this work falls in the range typical for the calcareous clay ($CaCO_3$ between 2 and 10%).

Comparing the Ca content in the clay and in the shards, it is quite evident that the raw clay materials employed were refined in order to obtain pastes more suitable for the ceramic production.

Clay refinement was a quite common procedure and also Piccolpasso in his fundamental treatise *Li Tre Libri dell'Arte del Vasaio* [3] refers to the refinement procedure of the clay. Nowadays, it is, in fact, commonly accepted that the ancient potters submitted the clay to such procedures, after having drawn it from the quarry or taken it from rivers banks, as attested by Piccolpasso for what concerns Umbria region. In fact, fine clays suitable for ceramic production are not so common and the hypothesis of a refinement procedure applied by the ancient potters is accepted [17, 18].

The collected clays were, at first, submitted to a drying process, just exposing them to sunlight, in order to improve their plasticity [18]. Then a refinement step followed to eliminate fragments, vegetable remains, etc. [18]. Among the most common methods of purification there was the sedimentation in still water and the sieving during which the clay was passed through one or more sieves.

After the sedimentation the fine clay on the surface was accurately drawn while the heavier material deposited on the ground were discarded [18].

In some cases, it could be necessary to add some materials in order to correct or to improve the characteristic of the clay. For example, a clay too much plastic required the addition of degreasing agent (quartz or sand materials). On the contrary, when a clay was too much slim (i.e. sandy), as in the case of the raw materials considered in this work, the possible corrections were two [17]:

- addition of a highly plastic clay
- depuration procedure in order to eliminate the sandy fraction.

The depuration procedure (refinement), as previously described, generally consisted in the decantation of a suspension of clay and water where the coarse materials deposit on the ground of the container, while the fine clay, lying on the surface, is collected and successively employed by the potter. Even if Piccolpasso seems to refer to a more simple sieving procedure ("Sogliono molti, per fare il bianco allatato, convertire la terra quasi in aqua, e quella colare per certi panni grossi e radi; altri per certi crivelli tondi di cuoro forati; altri per staccio largo. E quella colatura servano in certi vasi cotti una volta e, cossì asciutta alla bastanza, la lavorano" [3]), we can hypothesize a depuration of the sandy component with a consequent enrichment in carbonate content increasing the clay plasticity. This could justify the higher Ca concentration found in the ceramic samples. It is also noteworthy that the high lime content contributes to help the matching formation between the glaze and the ceramic body. Furthermore, since CO_2 evaporates during firing the material results more porous and therefore suitable to be glazed [16].

Coming back to the ceramic shards chemical composition, a quite useful method to represent the samples is given by the box and whisker plots (Fig. 3a, 3b, 3c and 3d) which allow to evidence the data dispersion, the possible presence of anomalous values (outliers) and the symmetry of the distribution.

In this plot, each box encloses the 50% of the samples (25 and 75° percentile range) while the media, (i.e. the central value of each variable), is represented by a small square inside the box. The lines extended from each end of the box, called whiskers, are calculated from each end of the box $\pm 1.5^{*}H$ (where H is defined as the inter-quartile distance, i.e. the distance between the 25° and the 75° percentile, the first and the third quartile, respectively). Values which fall outside the whiskers are considered as outliers if they fall beyond the whiskers but within three interquartiles distance. The points which are more distant are considered as extreme values.

Looking at the chemical composition of the major elements (Figs. 3a and 3b), it appears that Gubbio shards, besides to show a higher Ca content, with respect to this element are also more scattered with an outlier showing a Ca concentration of about 41% (Fig. 3a). This higher dispersion may be due to a major differentiation inside the production probably related to the use of different recipes for the preparation of the paste, depending on the workshops. On the contrary, Deruta samples are less scattered and show lower CaO values (with a minimum of 6% against 10% for Gubbio shards, Figs. 3a and 3b). Deruta samples show also slightly higher Al and Fe contents. The small difference in iron concentration hardly would explain the different colours of the ceramic bodies from the two sites: more pink and yellowish for Gubbio shards and more reddish for Deruta shards. This difference can be better explained taking into account the different calcium content. In fact, it is known that lime rich clay at enough high temperature develop a yellow colour.

Fig. 3 Box and whiskers plots for Gubbio and Deruta shards: major elements reported as oxides % (**a**), (**b**) and minor elements reported as the logarithm of the % concentration of the elements (**c**), (**d**)

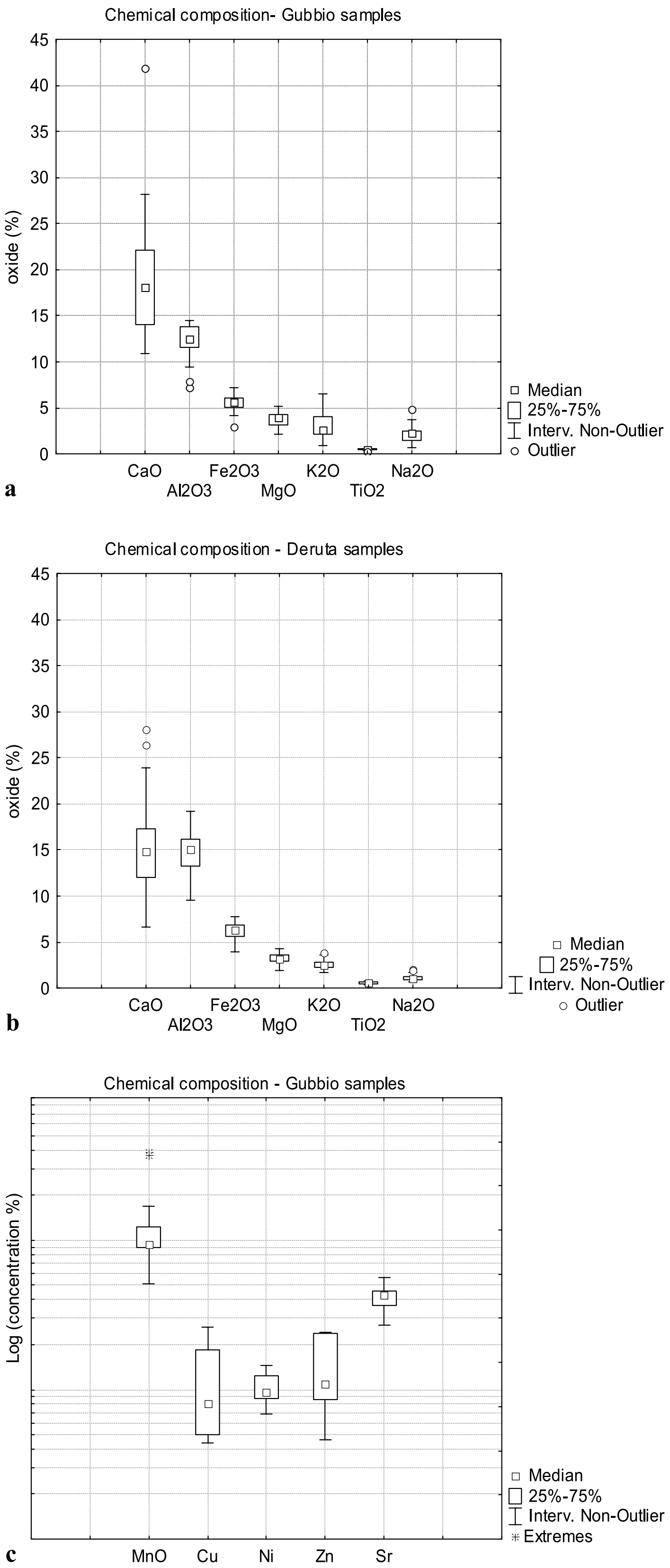


Fig. 3 (*Continued*)

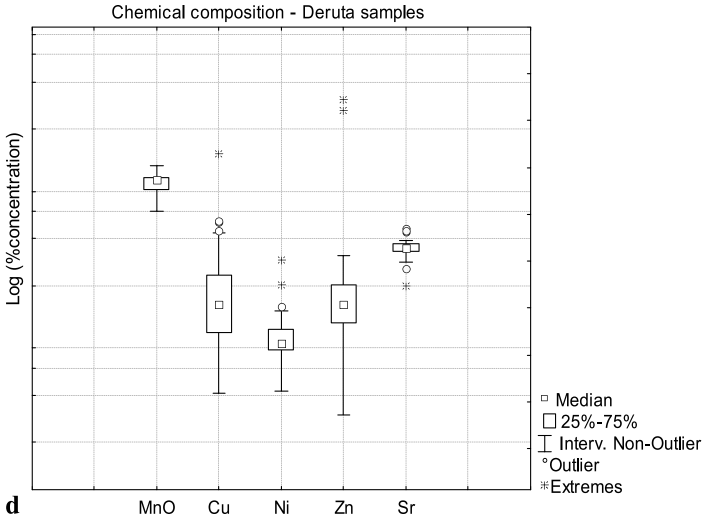
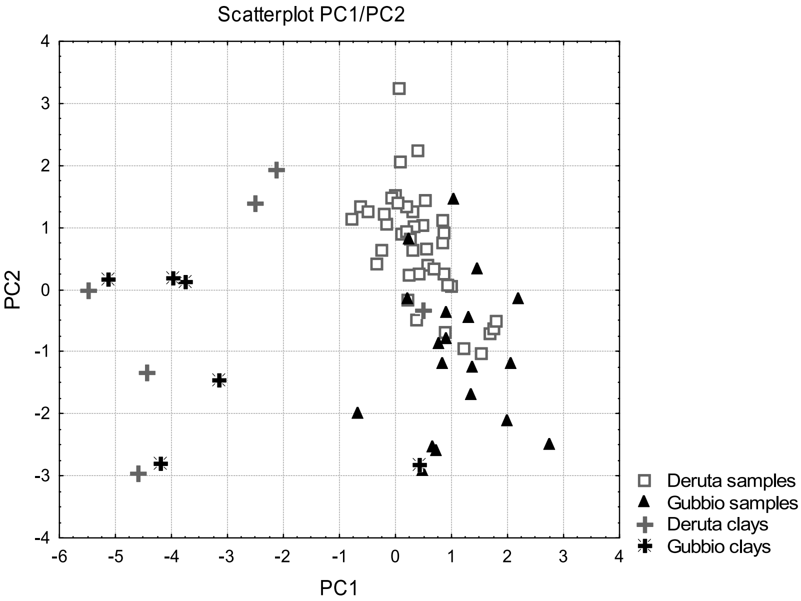


Fig. 4 Diagram of the first two principal components (scatterplot) calculated for the ceramic shards from Gubbio and Deruta and the corresponding raw materials



This is probably due to the incorporation of trivalent iron in the crystal lattice of diopside, wollastonite and mullite [14]. This phenomenon is also more evident when calcite grains are fine [17], since this fact promote diopside formation instead of anorthite which is not able to incorporate Fe^{3+} in its lattice. As a consequence, when diopside/anorthite ratio is low, the shard is more red.

Moreover, Gubbio samples show a higher alkali content. It is known that compounds containing Na and K could be add to the clay as fluxes in order to obtain a material suitable to be modelled and fired [18]. Since Gubbio clay are poorer in Na and K (see Table 2), with respect to Deruta clay, the hypothesis of a flux addition, in order to favour the fusions of the materials at a lower temperature, can not be ruled out.

Looking at the minor elements (Figs. 3c and 3d), the trend is quite similar for both sites with some small differences (minor Cu concentration for Gubbio samples and more outliers and extreme values for Deruta shards).

Referring to the major and the minor elements, it is also possible to carry out a provenance study submitting the chemical data to a multivariate statistical treatment. In this way the origin of a shard can be established/confirmed. One of the most common ways to proceed is also to consider, together with the ceramic shards, the raw clay materials probably used to realize them. In fact, the raw clay materials may represent a control group of certain provenance. Nevertheless, it can not be excluded that during the centuries the composition of a clay could be slightly changed.

As concerns the clay, together with the nine samples available, we have included in the data set also three samples coming from Deruta quarries that have been analyzed in a work published in the literature [8].

The results of the principal component analysis (PCA) are reported in Figs. 4 and 5. In the space defined by the first two components, which accounts for the 41% of the total

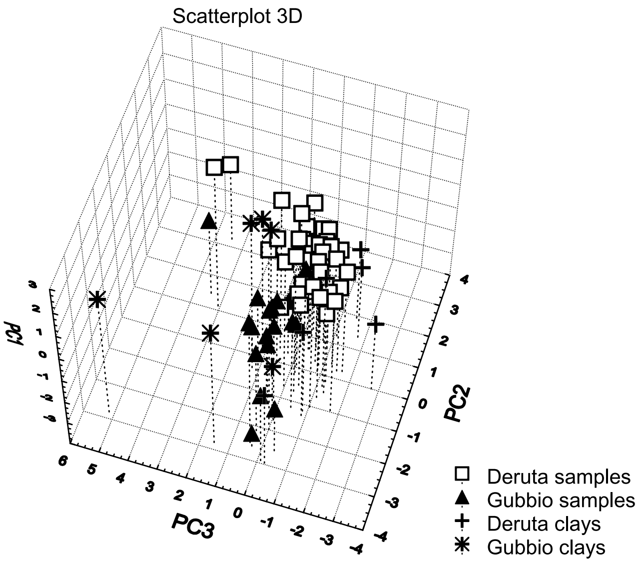


Fig. 5 Diagram of the first three principal components (scatterplot) calculated for the ceramic shards from Gubbio and Deruta and the corresponding raw clay materials

Table 3 Variables loadings for the first three components for the data set examined (ceramic shards and clay)

Variable	PC1	PC2	PC3
%CaO	0.501	−0.223	0.145
%Al_2O_3	−0.129	0.534	−0.445
%Fe_2O_3	−0.463	−0.179	0.258
%MgO	0.378	0.221	0.013
%K_2O	−0.420	−0.151	−0.023
%TiO_2	−0.330	0.337	0.048
%Na_2O	0.002	−0.309	−0.227
%MnO	−0.221	−0.249	0.126
%Cu	0.082	0.422	0.287
%Ni	−0.097	0.333	0.405
%Zn	−0.112	−0.034	0.258
%Sr	0.109	0.014	0.575

variance, Gubbio and Deruta shards appear as two groups partly superimposed (because of the quite low value of the variance explained by PC1 and PC2), while a more clear separation is observed between the ceramic shards and the clay. Nevertheless, two clay (GCP among the Gubbio clay and a clay named DE taken from data present in the literature [8] among Deruta clay) are quite similar to the samples (in particular the Gubbio clay GCP is very similar as composition to some Gubbio shards).

To better understand the separation between the different groups, it is useful to consider the loadings of the variables for the first components (Table 3). It allows to identify the chemical elements which are more efficient in determining the separation between groups.

In the first component, for example, CaO and MgO have the higher positive loadings indicating a higher content of these oxides in the ceramic shards (and in the two previously mentioned clay). Looking at the second component, Al_2O_3, TiO_2 and Cu have the higher positive loadings and, therefore, are in part responsible for the separation among Gubbio and Deruta shards along this component. The Deruta shards are therefore characterized by higher values of Al, Ti and Cu as already observed (see Fig. 3 and Table 2).

Since the variance explained by PC1 and PC2 is not so high, to obtain a good representation of the samples it is useful to consider a tri-dimensional one, taking into account the first three components (Fig. 5).

In the graph (corresponding to a variance of 55%), a clear separation between the two groups is achieved and it is also interesting to note that Deruta clay are closer to Deruta shards while Gubbio clay are closer to Gubbio shards (in particular the clay sample named GPA3 is positioned nearby Gubbio shards together with the clay GCP).

A hierarchical cluster analysis (HCA) has been performed, too (Fig. 6). In this case, taking into account all the 12 components, a good separation between Gubbio and Deruta ceramic shards is observed. In particular, clusters 1 and 2 are formed by Deruta shards, while Gubbio shards are grouped in cluster 3. In the two first clusters (1 and 2), we find also the three clay whose compositional data have been taken from the literature and already referred to Deruta (C3, C4 and DE [8]), while in cluster 3 the two Gubbio clay GPA3 and GCP are present. It is worth noting that the samples GPC and GPA3 were characterized by the higher values of the ratio between carbonate and silicate component (see Fig. 2). All the other clays are grouped into two small clusters on the right side of the dendrogram. So, it is possible to conclude that some of the examined clays have a chemical composition which is consistent with that one of the ceramic samples (GPA3 and GPC for Gubbio and DE, C3 and C4 for Deruta) and they could have been used for ceramic production in the two sites. However, due to the difference in calcium content a refinement procedure could have been applied. The other clays show more differences with respect to the samples. It is interesting to note, that all the samples GPA1a, GPA1b, GPA2 and GPA3 came from the site named Ponte d'Assi, but probably this clay bank is not so homogeneous from a compositional point of view.

3.2 Clay firing tests

To better clarify the differences found between the two sites, some of the raw clay materials were submitted to different firing processes in order to understand if it is possible to find further correlations with the mineralogical composition of the examined shards.

The firing tests have been carried out taking into account what reported in the ancient treatises [3]. A furnace able to

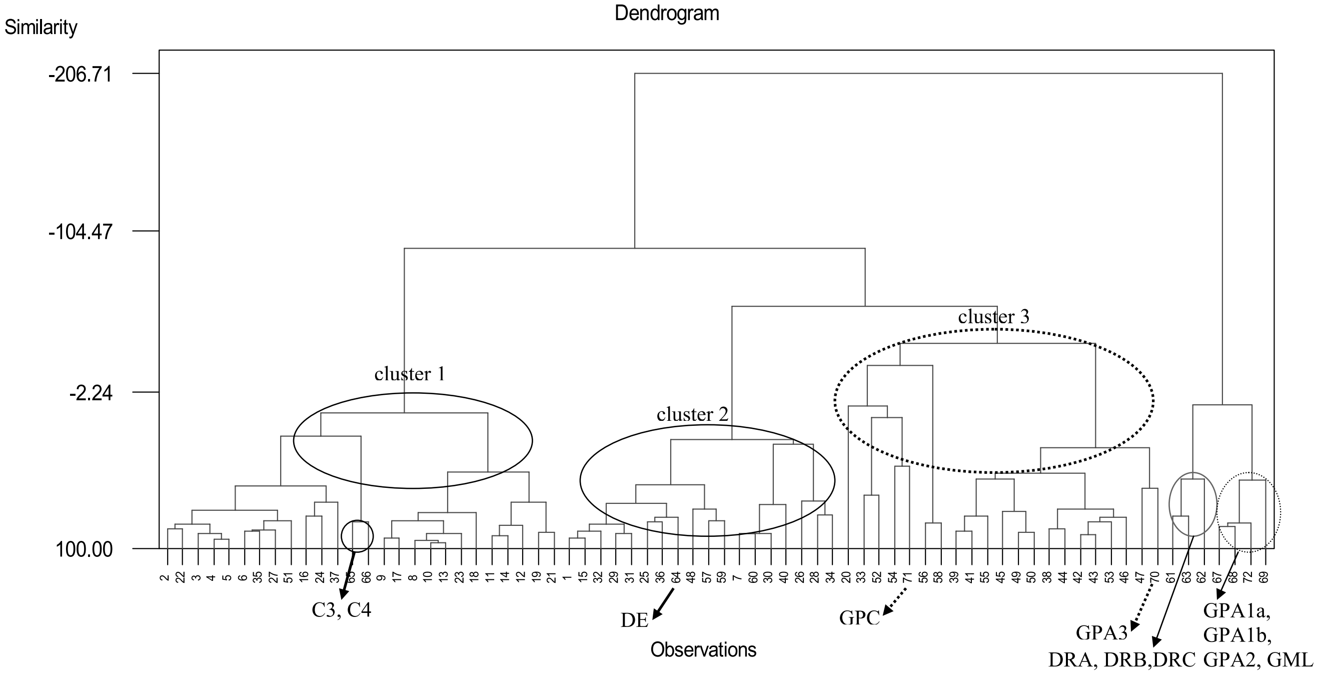


Fig. 6 Hierarchical clustering dendrogram by Ward's method for all the principal components calculated for all the examined samples (shards and clay)

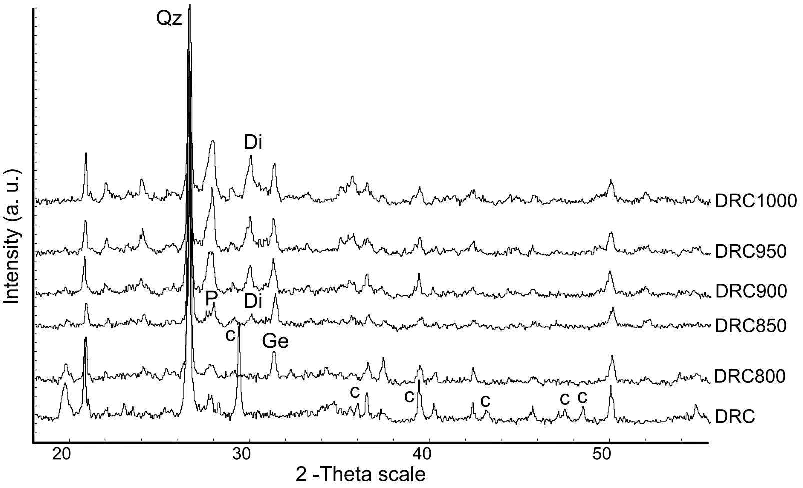


Fig. 7 XRD patterns obtained for DRC Deruta clay submitted for 30 min to different firing temperatures (from 800 to 1000°C); c: calcite, Qz: quartz, Di: diopside, Ge: gehlenite, P: plagioclase

reach high temperatures has been used and the tests have been performed in a temperature range from room temperature to 1000°C. The soaking period at the maximum temperature has been also varied. The soaking period is the duration time in which the maximum temperature is sustained.

Samples DRA, DRB, DRC and GPA3 have been submitted to a firing for 30 min, at 800, 850, 900, 950, 1000 and 1050°C, respectively. During the clay firing, calcite disappears and some typical phases, such as gehlenite, diopside and plagioclase, form.

As concerns Deruta clay, in sample DRB where calcite peak is absent, the formation of the typical firing minerals has not been observed. This is a further confirmation that this clay is not suitable for ceramic production.

Table 4 Experimental firing tests for clay DRC

Sample	*T* max (°C)	Soaking period
DRC800	800	30 min
DRC850	850	30 min
DRC900	900	30 min
DRC950	950	30 min
DRC1000	1000	30 min

Let us consider the different firing tests to which DRC has been submitted (Table 4). From the corresponding XRD

Fig. 8 XRD patterns (*in black*) obtained for PGA Gubbio clay submitted for 30 min to different firing temperatures (from 800 to 1000°C); the sample fired at 950°C (PGA950) has been further on fired at 950°C for 2, 5 and 8 h (patterns *in gray*); c: calcite, Qz: quartz, Di: diopside, Ge: gehlenite, P: plagioclase

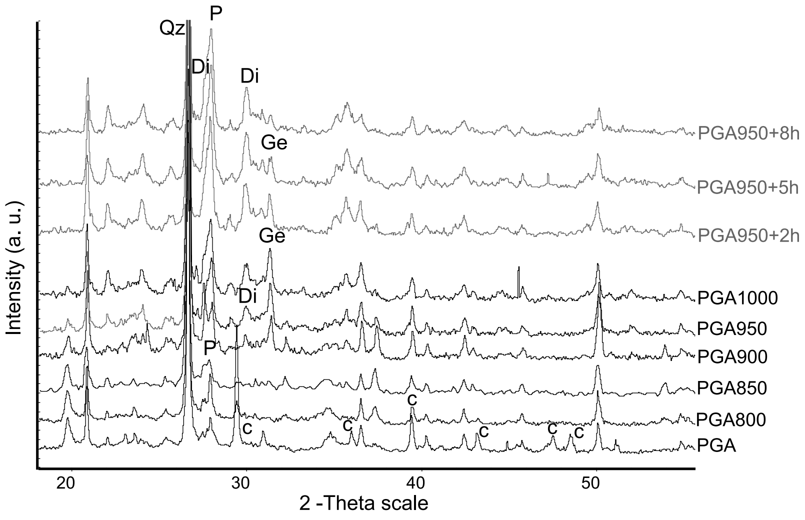


Table 5 Experimental firing tests for clay GPA3

Sample	*T* max (°C)	Soaking period
GPA3 800	800	30 min
GPA3 850	850	30 min
GPA3 900	900	30 min
GPA3 950	950	30 min
GPA3 1000	1000	30 min
GPA3 950 + 2 h	950	30 min + 2 h
GPA3 950 + 5 h	950	30 min + 5 h
GPA3 950 + 8 h	950	30 min + 8 h

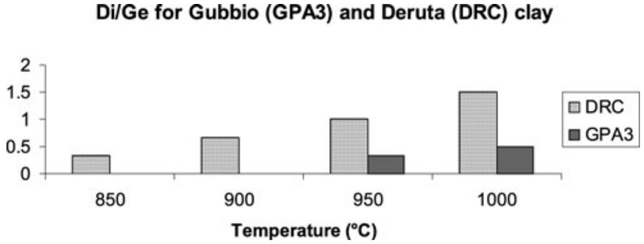


Fig. 9 Di/Ge ratios for two clay: DRC from Deruta and GPA3 from Gubbio submitted to different firing temperature for 30 min

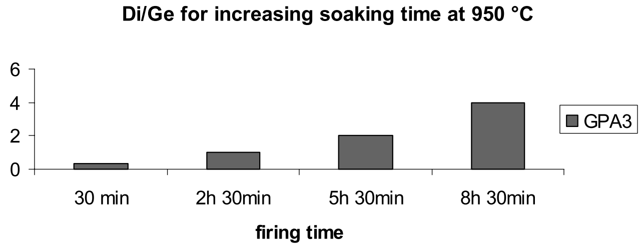


Fig. 10 Di/Ge ratios for the GPA3 Gubbio clay submitted to a firing at 950°C for different soaking times

patterns (Fig. 7), it can be observed that starting from 800°C, gehlenite starts to form and it is still present at 1000°C (at 800°C calcite is already disappeared). Diopside starts to form at 850°C together with plagioclase.

Sample GPA3 has been submitted to the same firing test (Table 5) and from the XRD patterns (Fig. 8) it can be observed that calcite completely disappears at 850°C and a relevant amount of plagioclase is formed. At 900°C, gehlenite starts to form and it persists until 1000°C; at this temperature it is present together with diopside which starts to form at 950°C.

In DRC sample, Ge starts to form at a lower temperature than in GPA3 (800°C with respect to 900°C) but then it transforms quite soon into diopside.

An attempt for GPA3 has been made, increasing the soaking time at 900°C from 30 min to 1 h (diffrattogramm not shown in the figure). It has been observed that diopside starts to form but in minor quantities than gehlenite.

In order to follow the progress of the reaction it is useful to consider some parameters, such as Di/Ge ratio.

For both clay (DRC and GPA3), Di/Ge ratios have been calculated (Fig. 9), and, if we compare the ratios at the same temperature, Di/Ge is higher for DRC confirming that Ge starts to disappear quite soon.

A firing of 30 min represents an indicative time chosen in order to compare the two materials but probably it not reflect the real firing time of a ceramic (the ancient potters fired the objects for longer times). For this reason, sample GPA3, fired at 950°C (PGA950 in Fig. 9), was submitted to increasing soaking times (2, 5 and 8 h). It has been observed a progressive disappearing of gehlenite. This temperature has been chosen since, as previously evidenced, at this temperature diopside clearly starts to form (Fig. 8).

Looking at the trend for the Di/Ge ratios (Fig. 10), it is possible to observe that for GPA3 Di/Ge = 2 after 5 h and 30 min at 950°C, while for DRC the ratio is almost the same after just 30 min at this temperature. So, in the Deruta clay, gehlenite disappears earlier transforming into diopside and this can justify the absence of Ge in the ceramic samples from Deruta.

It is also interesting to observe that Deruta clay are characterized by a higher quartz/calcite ratio (see Fig. 2) and in presence of higher quartz quantities it is known that Ge start to disappear earlier [16]. In fact, considering the Ge decomposition reaction (reaction 3), it can be observed that it is promoted by higher quantities of SiO_2.

We can not exclude that the temperature for Deruta shards was a little higher (or the soaking time longer) than for Gubbio shards. Nevertheless, comparing Gubbio and Deruta clay fired in the same conditions, a different ratio Di/Ge is observed (Fig. 9), and certainly the difference in the chemical composition play an important part.

Since sample PGA3, among Gubbio clay, resulted compatible with the chemical composition of the ceramic shards, the products obtained from the firing of this clay have been compared with the ceramic shards from Gubbio in order to assess the firing conditions applied by the ancient potters. For this purpose, the ratios Di/Ge was calculated for the shards belonging to Gubbio ceramic production and compared with the ratios obtained submitting PGA3 at different soaking time at 950°C (Fig. 11). It is worthy to note that a very good correlation between Di/Ge ratios and the corresponding soaking time at 950°C ($R^2 = 0.9665$), for the fired clay, has been obtained. Therefore, the soaking times at 950°C for the samples have been calculated. In the samples, Di/Ge ratios vary from 0.58 to 1, which correspond to a soaking time varying from 1 h and 30 min and 2 h and 30 min, with an average time of about 2 h.

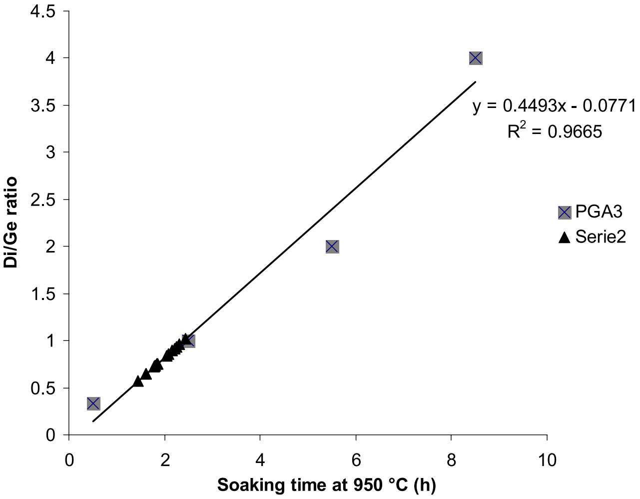


Fig. 11 Di/Ge ratios for Gubbio shards and clay vs the corresponding soaking time (estimated for the shards on the base of the correlation observed for the clay firing products)

This could be in an agreement with the methods used for firing ancient ceramics. In fact, when earthenware were fired in a kiln, it took about an hour or more to reach the maximum temperature, which was maintained for 30 min [5].

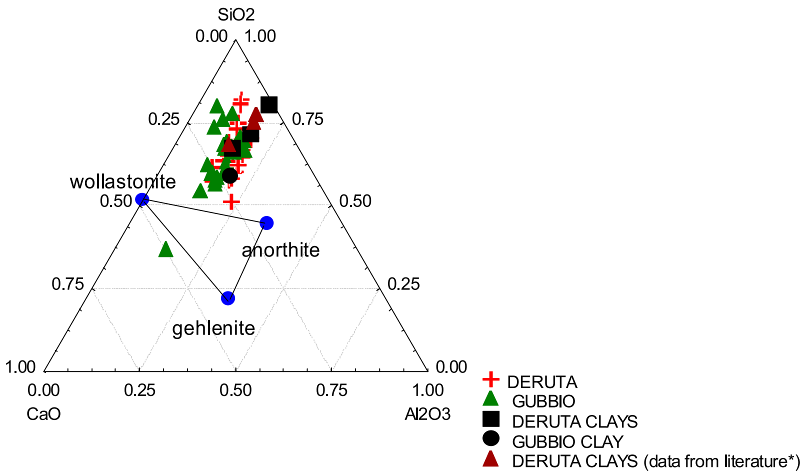
Nevertheless, it is important to underline that these assumptions do not take into account other parameters that can surely influence the final result, such as the heating rate or a slight different chemical composition of the raw clay material. However, it is possible to obtain a quite good assessment of the firing conditions applied by the ancient potters.

It is well known that a kiln such as those used during Renaissance and mentioned by Piccolpasso [3] takes one hour or more to reach the maximum temperature, so, the firing times we have estimated are in agreement with this observation.

If the ceramic samples and the corresponding clay are represented by means of the ACS diagram, i.e. in the ternary oxide system $CaO–Al_2O_3–SiO_2$ [13–15], it can be observed (see Fig. 12) that they lie within the area of pertinence of typical calcareous illitic clays [8, 14]. This kind of representation is commonly used by the archaeologists for earthenware.

This plot allows to predict the composition and the phases with some confidence, even if this approach is based on

Fig. 12 ACS (Al_2O_3–CaO–SiO_2) compositional diagram for the ceramic shards and the clay; compositional data for some Deruta clay have been taken from the literature [8]



the inbuilt assumption that the conditions are of equilibrium, in order to use phases diagrams [13, 14]. Referring to the triangle formed by Ge–Wo–An, our samples lie outside it even if in the XRD patterns gehlenite and anorthite are clearly present. This behaviour, already observed by other authors [8, 14], could be related to the fact that the phase diagrams are referred to equilibrium conditions but in the ceramic shards only micro-equilibrium conditions are present and confined at the reactive interfaces between the mineral grains [14]. For this reason our samples, as already observed in other cases reported in the literature [8, 14] are positioned outside the triangle Ge–Wo–An, in spite of the presence of gehlenite and anorthite in their XRD patterns.

4 Conclusions

In this study, ancient shards of certain origin from Renaissance time and some local raw clay materials have been investigated to define criteria that could be useful for the attribution of works of art of uncertain origin, discriminating pottery production sites in Central Italy, such as Gubbio and Deruta. For this purpose ceramic body micro-structure and mineralogical composition have been investigated.

As concerns the mineralogical composition, XRD analyses evidenced that Gubbio ceramic shards show the presence of gehlenite which is absent in Deruta shards. This behaviour is typical for pottery artefacts produced using calcareous illitic clay. Gehlenite presence in Gubbio samples could be due to a lower firing temperature but also could be ascribed to a different chemical composition of the starting clay. In particular, while Deruta shards show, on average, a lower Ca content (about 15%) Gubbio shards are characterized by a higher Ca content (about 19%). In any case, the presence of gehlenite in Gubbio samples could be a useful marker for the attribution of the provenance of ceramic lustred samples from one of the two sites, through a simple XRD analysis.

The raw clay materials employed were probably refined in order to obtain pastes more suitable for the ceramic production, i.e. richer in carbonate.

In order to carry out a provenance study, the chemical compositional data have been submitted to a multivariate statistical treatment and a good separation between Gubbio and Deruta ceramic shards has been obtained. Furthermore, it has been observed that some of the examined clay has a chemical composition which is consistent with the composition of the ceramic shards.

To acquire information on the firing technology employed by the ancient potters, some of the raw clay materials have been submitted to firing processes similar to those employed during Renaissance. In particular, it turned out to be very useful to follow how Di/Ge ratio varies with temperature. Taking into account this parameter, it was possible to estimate that the soaking time used for the ceramic shards was about 2 h. Nevertheless, it cannot be excluded that the temperature for Deruta shards was a little higher (or the soaking time longer) than for Gubbio shards. In any case, the difference in the chemical composition of the raw clay materials plays an important role.

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