ABSTRACT. — The aim of the present paper is to provide a review of the contribution of mineralogical petrographic methodologies to the archaeometric study of pottery in Italy. After a brief history of the archaeometric research of pottery and a summary of the mainly used analytical techniques, the more relevant topics in pottery studies have been reviewed. The topics covered include: the provenance studies, using thin-section petrography and chemical analysis; the reconstruction of the technology used in pottery production, through a combination of bulk (XRD, DTA-TGA, FTIR etc.) and in situ techniques (SEM-EDS, EMPA, Raman etc.). The surface coating technology production have also been reviewed. In particular: permeable slips (engobe), impermeable slips (classic black gloss and red slip) and glassy coatings (glazes, lustre). Some future developments are also emphasized: a wider use of high resolution and spectroscopic techniques (HRTEM; Raman); more studies on the relationships between paste technology and object functionality; investigation of the changes in chemical composition and microstructure occurring as result of use and weathering of pottery during burial.

KEY WORDS: ancient pottery production; archaeometric investigation; provenance studies; ancient technology reconstruction; impermeable slips; glazes; lustre

RIASSUNTO. — Il presente lavoro intende fare il punto della situazione sul contributo delle metodologie mineralogico-petrografiche allo studio archeometrico delle ceramiche in Italia. Dopo una breve storia della ricerca archeometrica sulla ceramica e una sintesi delle principali tecniche analitiche utilizzate, vengono presi in considerazione gli aspetti fondamentali negli studi di questo materiale, in particolare: studi di provenienza sia mediante osservazione di sezioni sottili che mediante analisi chimiche; ricostruzione delle antiche tecnologie produttive attraverso un approccio analitico integrato, comprendente tecniche di “bulk” (XRD, DTA-TGA, FTIR etc.) e in situ (SEM-EDS, EMPA, Raman etc.). È stata presa in esame anche la tecnologia di produzione dei principali rivestimenti ceramici. In particolare: rivestimenti argillosi permeabili (ingobbio) e impermeabili («vernice nera» e «vernice rossa» di epoca classica); rivestimenti vetrosi (vetrine, lustro). Vengono infine messi in evidenza alcuni sviluppi futuri auspicabili: una più diffusa utilizzazione di tecniche ad alta risoluzione e spettroscopiche (HRTEM; Raman); una maggior attenzione alle relazioni fra tecnologia dell’impasto e funzionalità dell’oggetto, così come alle variazioni della composizione chimica e della microstruttura, in conseguenza dell’uso e dei processi di alterazione durante il seppellimento.

KEY WORDS: antichi prodotti in ceramica; indagini archeometriche; studi di provenienza; ricostruzione della tecnologia antica; rivestimenti argillosi impermeabili; rivestimenti vetrosi; lustre.

* E-mail: memmi@unisi.it
INTRODUCTION

This work aims to review the contribution of mineralogical-petrographic methodologies to the archaeometric study of pottery in Italy.

The archaeometric study of pottery purposes to reconstruct wholly or in part the life cycle of pottery, leading to the identification of raw materials and their provenance, and the reconstruction of ancient production technologies, commercial trade routes and post-depositional processes of alteration. This type of study is necessarily interdisciplinary and carried out in close collaboration with archaeologists or art historians, who must select appropriate contexts and define historical-archaeological issues to be solved. Indeed, archaeometric analyses should only be undertaken when the precise definition of chronological and typological characters of the ceramics have been thoroughly investigated (Olcese, 1992, 1999).

The production cycle of pottery is quite complex: it involves the selection and preparation of raw materials, modelling, coating (slip, glaze, decoration), firing, distribution, use and, finally, burial (Maggetti, 1986). Clay products may be considered artificial rocks that recrystallised during heating to high temperatures. The resulting product consists of holes (large pores), a matrix (former clay substance) and non plastic inclusions (either natural and/or intentionally added, that is temper). Just as natural rocks contain records of their evolution, so potsherds record all the steps in their life-cycle.

There is therefore no doubt that earth sciences can play an important role in understanding these processes through the application of analytical methodologies proper to the study of rocks and minerals. Given the complexity of the ceramic production process, it is extremely important that the adopted analytical strategy be suited to the solution of the problem at hand.

This work will only consider studies focussing on the definition of production technologies and the provenance of pottery finds from Italian sites. The absolute dating of finds will not be discussed.

Notwithstanding restrictions, the proposed task is certainly not an easy one. Given the enormous number of works, which are often published in hard-to-find journals, this paper is not likely to be exhaustive. Nevertheless, it will hopefully give an idea of Italian progress in this area of research; such progress has not always been acknowledged internationally because contributions, although undoubtedly valuable, have too often been published in Italian language journals with poor international distribution.

In a recent article in Journal of Archaeological Method and Theory, M. Tite provides a broad and detailed review of the contribution of scientific disciplines to the study of pottery (Tite, 1999). The article, which mainly focuses on the work and experiences of researchers in Anglo-Saxon countries and America, undoubtedly provides an excellent record of the level of international scientific research on this topic; the article and references therein may be consulted for a general introduction.

HISTORY OF ARCHAEOMETRIC RESEARCH APPLIED TO POTTERY

The first archaeometric studies in Italy applied to pottery, in the latter half of the 50s, were undertaken using optical microscopy (De Angelis, 1956-57; De Angelis et al., 1960) and binocular microscopy on freshly broken surfaces (Guerreschi 1964-66). These studies, however, in part due to the scarce collaboration of archaeologists, were not followed by many others. Archaeometry applied to pottery began in 1967 in Genoa thanks to the work of the «Sezione di Mineralogia applicata all’Archeologia» and of T. Mannoni especially, whose research based mainly on the petrographic analysis of thin sections has continued uninterrupted to this day (see Mannoni, 1994, which collects the most significant contributions by Mannoni and co-
workers in 30 years of research). In the ’80s, other than various paper dispersed in many journals very difficult to find, there were two main contributions to the systematic definition of methods for the archaeometric analysis of ceramics: the first one is the volume edited by Ravaglioli e Krajewski (Museo Internazionale delle Ceramiche di Faenza) in 1981; the second one is the volume of Cuomo di Caprio (1985), containing an examination of all major analytical techniques used in the scientific investigation of ceramics, including methods of dating.

Only in the 90’s was there greater diversification of lines of research and increasing interest in this discipline and methodological aspects, with respect to both pottery and archaeometry in general. A great impulse in this direction arose also from the CNR through the establishment of the Progetto Strategico «Beni Culturali - Scienze e Tecnologie Innovative per la Conoscenza, Conservazione e Fruzione dei Beni Culturali», ceased in 1995, and of the Progetto Finalizzato «Beni Culturali» started in 1996.

This increased research activity in Cultural Heritage lead to the institution of «Società Italiana di Archeometria» (AIAR) in 1993, whose first President was Diana.

It is well known, in the same period, the activity of Claudio D’Amico which promoted archaeometry and the role of earth sciences in this field of research, also through the organization of the «Giornate annuali di Scienze della Terra e Archeometria, from 1994 until 2001. In 1999 and 2002 the first national conferences of the AIAR took place, which dedicated much attention to ceramics. In 1991 Burragato and Grubessi organised the first European Workshop on Archaeological Ceramics in Rome. Since 1997, through the initiative of Bruno Fabbri (CNR-ISTEC in Faenza) who has been studying the archaeometry of ceramics for many years, the «Giornate di Archeometria della Ceramica» have been held annually, up today, each focussing on a particular theme. In 1998 and 2003 Bruno Messiga organised the 1st and 2nd Ceramic Archaeometry Week in Pavia. Lastly, International Conferences on Ceramics have been held each year since 1968 at the Ligurian Centre for the History of Ceramics in Albisola. Although these conferences, whose proceedings have been regularly published, deal mostly with archaeological research, invited speakers have occasionally addressed archaeometric topics (with many contributions by Mannoni and co-workers).

Involvement of scientists and of earth scientists in particular in the study of ancient pottery have no doubt increased enormously since the early years; although the level of research has improved, there are still many unresolved issues, especially in relation to collaboration with historians and archaeologists, whose contribution is essential for the correct definition of problems. To conclude this brief historical review, I would like to report an excerpt of a speech presented by Fabbri during the 7th Ceramic Archaeometry Day in 2003, «considering EMAC, Archaeometry, AIAR, Earth Sciences and Archaeometry, and Archaeometry Days alone, a good 119 contributions have been presented. Although some names are a constant while others vary, on average about 100 people study the archaeometry of pottery in Italy. These researchers are divided into about 20 groups from various universities and institutions. A broader project to address archaeological issues is noticeably missing, partly because methods of funding do not allow long-term planning. There is also a need for greater collaboration between scientists and archaeologists». With this aim, a proposal was made by Fabbri to establish a thematic research topic within the AIAR dedicated to ceramics and coordinated by two people: a scientist and an archaeologist.

**Analytical techniques**

The evolution of adopted analytical techniques went hand in hand with increasing interest in this topic and with the growing number of continual studies on the
archaeometry of pottery. Although at the start, only easily accessible instrumentation was used to undertake sporadic collaborations of modest entity, analytical techniques were subsequently selected to suit the problem at hand, ultimately leading to the development of true analytical strategies. Indeed, it became clear that only the integration of various methodologies with different scales of observation would provide global solutions to problems.

As mentioned in the «History of Archaeometric Research» section, the first analytical technique to be used in the study of pottery was transmission optical microscopy and, subordinately, stereomicroscopy. With reference to major contributions reported in this paper, optical microscopy was used only 40% of the time, obviously only for coarse-ware pottery. Chemical analyses alone (X-ray fluorescence, and/or Instrumental Neutron Activation Analyses or Inductively Coupled Plasma Mass Spectrometry) were used in 10% of cases. Integrated analytical strategies (mostly optical microscopy, X-ray diffraction and X-ray fluorescence) were used in 45% of examined cases. In the context of integrated analytical strategies, Scanning Electron Microscopy with Energy Dispersive System was used 38% of the time and Differential Thermal Analyses-Thermo Gravimetric Analyses (DTA-TGA) in 17% of cases. Spectroscopic techniques (Mössbauer, Fourier Transfrom InfraRed, Near InfraRed, Raman) were seldom used (7%). High Resolution Transmission Electron Microscopy (HRTEM) and synchrotron radiation techniques (off the surface X-ray Diffraction and X-ray Absorption Spectroscopy) were used by Gliozzo et al., 2004a to characterise black gloss.

The application of scientific methodologies to the study of ancient pottery, like all studies on ancient artefacts, aims to define the provenance of adopted raw materials and/or of ceramic finds (Where), reconstruct production techniques - from the selection of raw materials, to pre-processing and modelling, to firing conditions (temperature and atmosphere) (How) - and determine when ceramic finds were produced (When), if archaeological evidence or written documents are lacking. Only studies focussing on the provenance of materials and the reconstruction of production technologies are here examined.

Although most works address the problem globally, with the aim of defining the entire productive cycle (i.e. provenance, adopted raw materials and production technology) of a ceramic find, for ease of exposition provenance and production technology issues will be addressed separately, distinguishing between ceramic body and coating.

**PROVENANCE STUDIES**

In order to pursue significant studies on the production and distribution of ancient pottery, it is important to determine where objects were produced and to identify the source of raw materials, taking in mind that, in the past, ceramics were generally produced not far from the source of raw materials.

Although it is relatively easy to determine the source of raw materials when dealing with mechanically processed stones (marbles, different kinds of rocks, chert, obsidian), it is much more difficult to locate sources when dealing with technologically transformed materials such as pottery, even when the production site has been identified.

Clays, indeed, are very rarely used as they are. The potter creates a plastic material by varying the proportions of clay, water and non-plastic material (temper grains). Non plastic grains can be naturally present in the clay or added by the potter when making the paste. If clays contain too much non-plastic particles, the potter decants out the coarse material, thereby concentrating the clay fraction. A more complicated, but quite common practice involves the use of two or more clay sources (characterised by different plasticity) to form a paste. Notwithstanding these difficulties, in the past several decades many provenance studies have been carried out by characterising the
composition of the unknown ceramic object and comparing it with the composition of pottery of known origin or with raw materials.

Two main scientific methodologies were applied: 1) mineralogical-petrographical analysis and 2) chemical analysis.

Petrographic analyses

Mineralogical-petrographical analysis, by optical microscopy (OM) is essentially based on the identification of a aplastic inclusions. These inclusions, intrinsic to the clay or added deliberately, reflect the geology of the region from which the clay or the added temper was obtained. Capelli and Mannoni (1996) proposed a cataloguing sheet aimed at describing thin section and providing a mineralogical-petrographic classification of ceramics. This sheet is very detailed but, probably, slightly flexible and for this reason it was not widespread utilized. In 1997, the same Authors proposed a classification of ceramic pastes based on the mineralogical-petrographical characterisation of temper grains in more than 5,000 thin sections of pottery samples from the Mediterranean basin. Seven petrographic groups and the main source regions in Italy for each group were defined: 1) the Metamorphic Group (central-northern Liguria, northern Tuscany, Sardinia, north-western Sicily and southern Calabria), divided into Acid and Basic (the former is more widespread); 2) the Volcanic Group, divided into Acid and Basic (the latter subgroup is better represented) (Campania-Lazio area); 3) the Ophiolitic Group (central and eastern Liguria, central-western Tuscany); 4) the Intrusive Group divided into Acid Intrusive and Basic Intrusive (the former is most widespread), (southern Calabria, eastern Sardinia); 5) the Aeolian Group, characterised by rounded aeolian quartz (mainly coastal areas near sandy deserts, North Africa, Syria and Palestine); 6) the Sedimentary Group (divided into Calcareous, Terrigenous and Siliceous), which does not yield precise information about provenance due to the widespread diffusion of sedimentary rocks in the Mediterranean basin; 7) the Generic Group, in which the skeleton consists of minerals very common to all kinds of rocks (quartz, plagioclase, micas). These groups are the starting points for more focussed in-depth studies.

Various works have been based on this type of analysis (Alaimo et al., 2000; Capelli et al., 1998, 2001; Capelli, 1998, 1999a, 1999b; Capelli and Di Gangi, 2001; Cuomo di Caprio, 1992; Del Rio et al., 1996; Failla et al., 1992, 1994; Pasquinucci et al., 1997, 1998; see also Mannoni, 1994 and bibliography therein).

Besides OM, Scanning Electron microscopy equipped by Energy Dispersive System (SEM-EDS) has also recently come into use; although the latter technique is mainly used to investigate production technologies (Tite, 1992), it can also be applied to provenance studies. Indeed, not only does it have a higher resolution that enables the observation of fine-scale microstructures associated with traditional clay-based pottery, but it also provides compositional information on single mineral constituents in the non-plastic portion, thereby enriching data provided by optical petrography on rock types and sources. These minerals, especially when the firing T was not extremely high, may have maintained their original chemical characteristics that cannot be defined through OM alone. For instance, Gliozzo and Turbanti Memmi (2001) used OM to identify zoned K-feldspar in Roman kitchenware from Chiusi (Siena); when analysed by SEM-EDS, the feldspar showed compositional zoning with respect to the Ba and Sr content (celsiana-hyalophane series), as reported in the volcanics of the Vulsinian district. Due to the presence of kiln wastes, a hypothesis of importation of raw material can be formulated.

Chemical analyses

Chemical analysis of pottery (major, minor and trace elements) provides a compositional «fingerprint» for grouping together pottery made from the same raw materials and for
distinguishing between groups of pottery made from different raw materials. Due to the variability of chemical composition within individual sources of clay or temper and the possible similar composition of different sources, provenance studies based on chemical compositions involve the analysis of a large number of samples, which are then grouped using statistical methods, and a reference data base formed by kiln wastes and local clays. Chemical compositions can also be used to predict the general area of production on the basis of geochemical considerations. High concentrations of Cr and Co indicate the presence of mafic mineral inclusions, whereas high concentrations of REEs suggest associations with acid igneous rocks (Blackman et al., 1989).

The main adopted analytical techniques are X-ray fluorescence (XRF), Instrumental Neutron Activation Analyses (INAA), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Because the chemical composition of pottery partly depends on cultural practices in clay preparation, obtained compositional data cannot be used to directly search for clay sources exploited by ancient potters. Principal-component analysis and/or cluster analysis (Bishop and Neff, 1989; Baxter, 1994a) is used to search for structure in data from the pottery assemblage at a particular site or cluster of sites. Having defined hypothetical pottery groups, their validity is then evaluated using bivariate and trivariate plots, histograms or statistical methods, such as discriminant analysis (Baxter, 1994b).

Finally, an attempt is made to infer, for each group, whether it was produced locally at the site at which it was found or in the immediate region, or whether it was imported through long-distance exchange or trade. Archaeological criteria are first examined, in particular the relative abundance of different pottery types. Researchers then check whether the chemical composition of pottery is consistent with that of local sources of clay. When production debris (kiln wastes) is available, comparison between the chemical composition of wasters with that of pottery can provide further confirmation of local production.

Many provenance studies have adopted chemical methodologies (XRF or INAA or ICP-MS) alone: Agodi et al. (1996); Battaglia et al. (1995); Bonini and Mello (2000); Costantini et al. (1994); Cuomo di Caprio (1992); Cuomo di Caprio and Picon (1994); Fabbri (1996a); Fabbri et al. (1990, 1995, 1996a); Frontini et al. (1995, 1998); Mello et al. (1980); Mirti et al. (1990); Mirti et al. (1995); Oddone (1998); Olcese (1994a, 1994b, 1998); Olcese and Picon (1998, 2002); Preacco and Ancona (1998).

Which of the two analytical method is better suited to the study of the provenance of pottery has been strongly debated (Maggetti, 1995).

In general, the first methodology (OM) is better suited to the study of coarse-textured pottery, whereas the second (chemical) is best for the study of fine-textured pottery. In actual fact, in the case of coarse-textured pottery without diagnostic inclusions, thin section petrography is of limited value for establishing provenance. However, the results of thin-section petrography are still potentially valuable because they provide information on variations in temper types and temper concentrations, which is crucial for the successful interpretation of chemical data. For this reason, it is now generally accepted that the integration of the two methodologies, irrespective of ceramic texture, undoubtedly yields better results, e.g. see the works of Acquaro et al. (2002), Alaimo et al. (1995, 1997, 1998, 1999, 2002a, 2002b), Amadori and Fabbri (1998), Amadori et al. (2002a, 2002b), Aurisicchio et al. (1994), Barone et al. (1998, 1999, 2002a, 2002b), Bianchin Citton et al. (1999), Borzacconi et al. (2002), Cairo et al. (2002), Capelli and Mariescotti (1999), Cassani et al. (2002), Ciancio et al. (1994), Cuomo di Caprio and Fiorilla (1992), Dell’Anna and Laviano (1994), Dell’Anna and Radina (1994), Eramo et al. (2002), Eramo et al. (in press),...

PRODUCTION TECHNOLOGY

Ceramic body

The technology used to produce pottery is reconstructed by determining first which raw materials were used and how they were prepared, and then how pottery vessels were formed, surface-treated and fired. Various analytical techniques are applied to pottery and to possible production debris (raw clay, kiln wastes, kiln fragments).

It is therefore important that studies specifically focus on mapping and characterisation of clay outcrops, especially in productive sites (e.g. Genova et al., 1999; Muntoni, 1997; Dell’Anna and Laviano, 1991; Laviano, 1995; Fabbri and Maldera, 1990; Amadori et al., 1995; Veniale, 1994). Experimental studies on the transformation of clays during firing (i.e. firing tests) at different temperatures, for different lengths of time, and under variable atmospheric conditions are just as important (Duminuco et al., 1996, 1998; Cairo, 1998; Riccardi et al., 1999). Another aspect that can be investigated in order to assess the production technology is represented by the analysis of wastes and instruments for the glaze processing (Casadio et al., 1997, 1999).

Clays can be used as they are (Amadori et al., 2002a, 2002b, Barone et al., 2002a, 2002b; Cassano et al., 1995, Dell’Anna and Laviano, 1994; Eramo et al., 2002; Morandi et al., 1999), refined to remove excess non-plastic inclusions (Fabbri, 1994; Gualtieri et al., 2002b) or enriched with temper grains (Aurisicchio et al., 1994; Cassano et al., 1994).

Few works (e.g. Casadio et al., 1991; Cassani et al., 1997; Fabbri et al., 1996b; Aldi et al., 1997 and Levi and Sonnino, 1997) focus on the relationship between the type of added temper grains and functional forms. Levi and Sonnino (1997) studied the petrography of 180 specimens of coarse-textured protohistoric pottery and identified a chronological trend in the use of different types of temper for different forms.

On the basis of the lime content in pottery, it is also possible to distinguish between the use of non-calcareous and calcareous clays. In the latter, crystalline calcium and calcium-aluminium (and/or iron) silicates form during firing, producing pottery with different characteristics and functionality.

Fabbri et al. (1997) undertook interesting experimental firing tests on different pastes to investigate the different properties of pottery with chamotte or calcite as temper grains.

Few studies (e.g. Amadori et al., 2002b) have focused on the kind of pottery forming.

As discussed earlier, the nature and composition of mineralogical phases in both the clay matrix and aplastic inclusions are fundamental in provenance studies. This kind of information, together with microstructural observations, can be used to estimate ancient firing temperatures (Fabbri, 1998).

The analytical tools used to determine mineralogical phase compositions and microstructural features are X-ray diffractometer (XRD), optical and electron microscopes (SEM and TEM), and electron microprobes. Spectroscopic techniques such as FTIR, NIR, and Raman can also be used (Artioli et al., 2000). Mössbauer spectroscopy is very useful in the definition of the oxidation state of iron and, consequently, of firing temperature (Stievano et al., 1996) and atmosphere conditions (Bianchin Citton et al., 1999; Maritan, 2002).

Thermal analyses such as DTA or TG can also help define the mineralogy of clay minerals in both raw materials and pottery samples, when the firing temperature was relatively low (Dell’Anna and Laviano, 1994; Dell’Anna and Radina, 1994).
Optical microscopy not only can be used to identify the mineral constituents of temper, but also to determine whether they have a serial or hiatal texture, and therefore if they were naturally present or intentionally added to the clay (Riccardi et al., 1997). The certain identification of chamotte, likely to be confused with argillaceous rock fragments (ARFs, Whitbread, 1986), can provide useful information about the technological choice of the potter (Cuomo di Caprio and Vaughan, 1993; Amadori et al., 1995). It is possible to observe the anisotropy or isotropy of the clay matrix; an anisotropic matrix is non-vitrified and retains its optical properties (chiefly birefringence), suggesting temperatures below the beginning of vitrification (about 850°C; Brisbane, 1981). This temperature could also vary depending on the chemical and mineralogical composition of the matrix, on the firing atmosphere and on the duration of firing process.

SEM has been successfully used to examine the internal morphology of a sherd, that is the extent of vitrification and pore structures (Fabbri, 1996b), and to compare these features with firing tests on raw clays or refired sherds (Tite and Maniatis, 1975). Chemical analysis can be performed on both aplastic inclusions and the matrix. The chemistry of the ceramic body and slip can be compared (Mirti, 2000), and it is possible to detect disequilibrium textures such as compositional zoning and reactions rims developed during firing. For example, albite crystals may be rimmed by K-feldspar due to the K→Na exchange when K is released from the break-down of clay minerals (Riccardi et al., 1999). These textures can provide additional information on the firing temperature, and on the duration and kinetics of the firing process (Dell’Anna and Laviano, 1994; Gualtieri et al., 2002b; Levi et al., 2002).

XRD can be used to define changes that occur in clays upon heating. Indeed, progressive dehydration during heating changes the crystalline structure and d-spacing of clay. Changes obviously depend on the type of clay mineral. If the former clay mineral composition of a ceramic piece is known, the firing temperature can be determined (Maggetti, 1982). In particular, the reaction involving gehlenite (Ca$_2$Al$_2$SiO$_7$), quartz, wollastonite (CaSiO$_3$) and anorthite (CaAl$_2$Si$_2$O$_8$) is generally considered to be diagnostic of the attainment of temperatures higher than 900°C (Peters and Iberg, 1978).

One must bear in mind that all reactions that transform raw materials into finished products generally proceed towards a state of equilibrium; however, true equilibrium is never attained due to relatively low firing temperatures and to the short duration of the process in particular. A detailed SEM or electron microprobe study of microtextural relationships between mineral phases can help define the role of reaction kinetics and evaluate the scale of equilibrium domains, which are generally confined to the reactive interfaces between mineral grains. Riccardi et al. (1999) clearly demonstrated that the composition of phases formed during firing not only depends on temperature but also on the composition of precursor phases and of the different microsites. In this respect the use of bulk analysis alone, such as XRD, to define firing temperatures may yield unreliable results.

**Surface coatings**

The pottery surface may be entirely coated for decoration or to reduce permeability. According to Cuomo di Caprio (1985), there are two main classes of ceramic coatings: 1) clay-rich coatings and 2) glassy coatings.

Depending on their permeability, clay rich coatings can be subdivided into two types: permeable and not permeable slip, which are named «ingobbio» and «vernice» respectively in Italian language (UNI 10739, 1998).

Depending on their transparency, also glassy coatings can be subdivided into two types: transparent and opaque glaze, which are named «vetrina» and «smalto» in Italian language (UNI 10739, 1998).
Clay-rich coatings

Permeable slip. Permeable slip is generally opaque and porous and does not undergo major modifications during firing. In ancient times permeable slip was generally either red or white. Red slip was obtained from a clay rich in iron oxide (up to 15 wt%) and generally fired under oxidising conditions (Serraferlicchio vases, Sicily, Eneolithic age). Permeable white slip was also widely used in the Middle Ages (Capelli and Mannoni, 1998, 1999; Capelli and Marescotti, 1999; Baraldi et al., 1999) on its own or below a transparent glassy layer (Capelli and Di Gangi, 2001; Borzacconi et al., 2002).

White slip generally consists of kaolinite-rich clay or of clays with a very low iron content (Berti et al., 2001). Although permeable slip enhances the beauty of a ceramic piece, it is not very efficient in decreasing permeability.

Impermeable slip. The archaeological names «vernice nera» (black gloss) and «vernice rossa» (red slip) refer to historical classical ceramics. These kind of coatings are intermediate between clay-rich and glassy coatings. In fact, both of these coatings are obtained from fine grained iron-rich clay material, fired in reducing or oxidizing conditions and not completely vitrified. They were applied in a very liquid state to the air-dried ceramic body. Notwithstanding the widespread occurrence of these kinds of ceramics and the large number of previous studies, there is still a large debate about the composition and the firing techniques of these coatings.

Many studies have been performed on black gloss, mainly by foreign researchers (see Gliozzo et al., 2004a for an exhaustive bibliography). Mazzeo Saracino et al. (2000), Mirti and Davit (2001), Acquaro et al. (2002) and Morandi et al. (1998a, 1999) are among the Italian contributors. There is general agreement on the main steps of the technological process: the oxidising-reducing-oxidising firing cycle took place in a single firing which transformed iron oxides and sintered the matrix. In the first phase (oxidising), the clay body turned red and hematite formed. In the second phase (reducing), sintering of the clayey matrix made the gloss layer impermeable to oxygen, whereas the formation of magnetite and/or hercynite produced the black colour. As for firing temperatures, researchers agree that temperatures during reduction were higher than those during oxidation. On the contrary, the significance of the different visual appearances of gloss (shiny, vitreous, silver, metallic, bluish, matt and misfired-black) has not been completely understood. Gliozzo et al. (2004a) investigated «black gloss» samples in order to identify the features and/or technological processes responsible for the different visual appearances and to verify the possible correlation between visual appearance of the gloss and area of production. As black gloss is composed of glassy material and new formed crystals of nanometric size, very powerful techniques such as TEM or those based on synchrotron radiation (µ-XRD, µ-XRF) are necessary to establish the nanotextural relations and compositions of crystals, and mineralogical phases occurring in the gloss. EXAFS spectroscopy is used on the K and L edges of iron in order to establish the oxidation state of existing Fe-compounds (Artioli et al., 2002; Giorgetti et al., 2004; Gliozzo et al., 2004a).

As for the red slip, this coating characterize very widespread ceramic classes, such as the Terra Sigillata Italica and the African Red Slip (Sigillata Africana) wares of Roman and late-Roman age. The majority of papers regarding this kind of wares have been performed by foreign scientists, with few exceptions (Cuomo di Caprio, 1992; Cuomo di Caprio and Picon, 1994, Gualtieri et al., 2002b, Menchelli et al., 2001). The red slip was obtained by a fine-grained iron rich illitic suspension fused to a glass under oxidizing conditions to give a very shiny, red surface which is impermeable.
Glassy coatings (glazes)

Glaze is a term generally used to describe a glassy, silica-rich layer applied onto a ceramic surface. Glazes are usually a silica-based glass; the fusion of silica is produced by the addition of a flux such as lead, alkalis or borates. Depending on the composition (Tite et al., 1998) we can distinguish four glaze types: 1) High lead; 2) Lead-alkali; 3) Low-lead-alkali; 4) Alkali. They can be transparent, charged with colouring agents (for example Cu, Co) or totally opaque, giving a homogeneous colour to the ceramic surface. A tin-lead-silica based opaque glaze is commonly used to create a 30-300 mm-thick opaque white layer on the ceramic clay base (Amadori et al., 2002a; Aurisicchio et al., 1994; Borzacconi et al., 2002; Casadio et al., 1999; Cassani et al., 2002; Gualtieri et al., 2002a; Mannoni and Capelli, 2002).

The analysis of glazes aims to determine raw materials, the technology of application (Fabbri et al., 1999, 2001), temperature and atmosphere during firing, and the presence of colorants. Raman microspectroscopy is useful when samples cannot be manipulated, e.g. for the identification of pigments in slips and glazes (Colomban et al., 2001), and when the chemical composition alone is not sufficient to identify the pigment or a new formed mineralogical phase, such as cristobalite (Fortina et al., submitted).

The study of interactions between glazes and ceramic bodies provides insight into how glazes were applied. Indeed, it is not well understood whether the glaze was applied over the air-dried ceramic body or after a first firing (Tite et al., 1998). The glaze/ceramic body interface can be sharp or rich in new formed mineralogical phases, mainly K-Pb feldspars, largely depending on two-stage or one-stage firing. The new-formed minerals are generally sub-micrometric, and high resolution techniques such as HRTEM (Viti et al., 2003) must be applied for their characterisation.

Lustre decoration

The technique of lustre was developed by the Islamic culture in Mesopotamia, during the IX century AD. It arrived in Europe through the Maritime Republic of Pisa, and developed in central Italy, where it peaked in the 16th century thanks to Master Giorgio Andreoli from Gubbio (Seppilli, 1982; Bojani, 1998). The lustre gave to the pottery gold and copper-coloured metallic reflections and iridescence. These effects was obtained by putting a mixture of copper and silver salts and oxides, together with vinegar, ochre and clay, on the surface of previously-glazed pottery. As revealed by recent SEM and TEM studies of Italian Renaissance pottery from Gubbio and Deruta (Perez-Arantegui et al., 2000; Borgia et al., 2002; Viti et al., 2003), this film is extremely thin and has a microstructure composed of copper and/or silver nanocrystals (20-30 nm in size) homogeneously dispersed in the glassy matrix. The peculiar appearance and colour of lustre depend not only on the chemical composition of metallic crystals but also on the nanotextural features. Further research on mineralogical characterization of enamels and pigments revealed that blue colour is due to a glassy material enriched in Co. In correspondence of yellow decorations, micrometric crystals of Pb₃(SbO₄)₂ have been found. It has been also observed that lustre is successfully applied over the cobalt blue drawings whereas, when yellow coloured decorations are obtained by large lead-antimonate crystals, the formation of lustre nanocrystals is strongly hindered.

Conclusions and future developments

There is no doubt that archaeometric research on pottery is improving in both quantity and quality. Nevertheless, with few exceptions, large research projects regarding complete pottery contexts are still lacking. One reason is that funding does not generally allow for such broad studies. Secondly, there is a
need for integration of different research teams and greater co-operation between archaeologists and scientists. The former must clearly define issues and the latter must devise suitable analytical strategies.

In the future an increasing proportion of ceramic studies involving mineralogical-petrographic sciences should be designed to address real archaeological issues. Issues may require a holistic approach in which the complete life cycle of pottery (from selection, procurement and processing of raw materials to the ultimate disposal of wares) is investigated. Furthermore, samples selected for detailed investigation should be representative of the complete ceramic assemblage. As for the investigative methodology, an analytical strategy that takes into account the problems to be solved must be formulated.

Future developments may stem from the wider use of high resolution techniques such as HRTEM or synchrotron radiation equipment, obviously applied to a selected number of representative samples. Spectroscopic techniques, such as FTIR, Raman or Mössbauer could also be applied more extensively. These techniques can provide unique information that cannot be acquired otherwise, e.g. the oxidation state of iron or «in situ» identification of particularly significant mineralogical phases such as new formed cristobalite in glazes. A further advantage of Raman spectroscopy is that it is a non-destructive analytical technique.

More studies should focus on the relationship between paste technology and object functionality and on modelling techniques. Of general importance is the investigation of the changes in chemical composition and microstructure which occur as a result of use and weathering of pottery during burial and the alteration processes should be taken into account when analytical data are discussed and their significance pointed out. Finally, further research is required into the characterization of animal and plant residues in pottery and into their chemical alteration, occurring both as a result of cooking and subsequent burial.

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