

X-Ray Microanalysis Discloses the Secrets of Ancient Greek and Roman Potters

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Scanning electron microscopy coupled with energy-dispersive detection of emitted x-rays (SEM–EDX) may be useful in the study of ancient ceramic materials coated with glossy sintered slips. Backscattered and secondary electron images of fresh fractured or polished sections may give information on slip thickness and sintering degree and on slip-to-body contact features. EDX analysis of polished sections may disclose compositional features of slips and bodies stemming from a more or less appropriate selection and processing of clays. Insight may then be gained into the technological knowledge and skill of ancient potters. An account is given here of SEM–EDX investigations performed on Greek, late Hellenistic and Roman monochrome black or red gloss pottery. These shed light on the technological achievements of potters from different historical epochs and geographical areas of the ancient world. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Scientific examination of works of art and archaeological objects has gained increasing consideration in recent years. On the one hand, it contributes to widening the knowledge of an object of artistic or historical value by giving information, for example, on its age, authenticity, place and technique of manufacture. On the other hand, it allows a diagnosis of the mechanisms of decay, necessary prior to any conservation treatment, and permits an evaluation of the effectiveness of such treatments.

Investigation techniques have to be chosen with the artistic and historical value of the items under consideration in mind, and non-destructiveness has long been considered a feature of paramount importance for scientific studies in the field of cultural heritage. However, a large number of modern techniques, including x-ray techniques, allow one to obtain data of a high scientific level through the collection of minute samples and may actually be considered micro-destructive. In many cases a more extensive but reasonably limited sampling may be acceptable, if this leads to a significant increase in the understanding of an object or group of objects; this is often the case, for example, with pottery sherds of not particularly high artistic value, which cannot be reassembled into complete vessels. Furthermore, many analytical techniques, even though requiring the removal of a sample, do not destroy it in the course of the analysis. This means that the same sample may be used subsequently for other investigations.

X-ray techniques are widely used in the study of works of art and archaeological objects; x-ray fluorescence

(XRF), particle induced x-ray emission (PIXE), scanning electron microscopy (SEM) coupled with energy-dispersive detection of x-rays emitted by the sample (EDX), x-ray diffraction (XRD) and x-ray radiography are the most relevant for application in this field.

SEM–EDX is an appropriate technique for the examination of limited amounts of samples from objects of artistic or historical interest. In some cases actual non-destructiveness may be achieved if the item under study can withstand high vacuum and its dimensions are such as to allow insertion into the vacuum chamber of the instrument. More frequently, an appropriate sampling is required, and the sample may have to be properly prepared for the analysis, but it is safely recovered afterwards. SEM–EDX is versatile and provides morphological examination and chemical analysis of samples taken from paintings, stone, pottery, glass and metal objects for characterization from an historical and artistic point of view, or for handling decay problems.

An important field of application of SEM–EDX is the study of ancient pottery. Here, morphological details are revealed by microscopic examination, which can be followed by chemical analysis of selected areas by the EDX equipment. A particularly interesting application occurs in the study of ceramic items with surface coatings. In this case, fresh fractured or polished sections may be examined to investigate morphological features of slip and body, while polished sections are preferably used for chemical analysis. In both cases, the sample has to be made conductive by deposition of a thin metal or graphite layer to overcome electron charge accumulation on the surface of the non-conductive pottery fragment.

Various kinds of coatings can be found on ancient pottery.¹ Among these, clayey glossy slips were obtained from a suspension of a very fine clay of suitable composition deposited before firing on the surface of the dry body by brushing or dipping; an appropriate combination of firing conditions (that is time, temperature and atmosphere of firing) with grain size and composition of the used clay

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led to the development of a highly sintered coating on a less sintered body in the course of a single firing.

If a cross-section of a fine ware coated with a highly sintered clayey slip is viewed under an SEM, the degree of sintering of the coating can be evaluated in backscattered (BS) or secondary (SE) electron images, in addition to its homogeneity and thickness, the presence of bubbles and craters and the characteristics of the slip-to-body contact surface. Inclusions of iron-rich phases within the vitrified mass are easily detected, as they appear lighter in BS images. EDX analyses may then be performed on both body and slip to assess the differences in composition which may derive from the use of different clays in their manufacture or, in the case when the same clay was used, from the extent of refinement of the fractions utilized. Owing to residual porosity, body analyses are preferably carried out by allowing the electron beam to scan across a selected area of the section; conversely, point analyses by a more or less defocused beam, or beam scans at very high magnification, are performed to determine the composition of the coating, as its thickness is usually within a few tens of micrometres.

Clayey slips were widely used in antiquity to coat fine ware for both practical (e.g. to reduce permeability) and decorative purposes. Monochrome (typically black or red), bichrome (mostly black and red) and polychrome (prevalently black, red and white) items have been produced in the course of several millennia by use of a variety of techniques.^{1,2} The most widespread of these was based on the chromatic effects derived from the development of compounds of Fe(II) and/or Fe(III) from those naturally present in the clays. Firing in an oxidizing atmosphere led to the formation of haematite, and to the development of a more or less saturated red colour;²⁻⁴ however, if a calcareous clay was used, calcium silicates formed at 900–1000 °C could trap iron ions in their lattice, preventing the growth of haematite crystals with temperature and causing the development of lighter colours.⁵⁻⁷ Conversely, under reducing conditions, the clay turned grey to black as a result of the formation of hercynite and/or magnetite.^{2-4,8-10}

In practice, a sequence of oxidizing and reducing steps during a single firing cycle were carried out to produce black, red or black and red bichrome coatings upon red or grey bodies.^{3,11-13} Typically, an appropriate more or less calcareous clay was refined and used to shape the body of the vase; the same clay, or a more appropriate one, was further refined and suspended in water to form a slurry suitable for surface coating. After a first oxidizing firing step which led to the formation of a red porous slip upon a red porous body, closure of kiln vents and use of wet and/or resinous fuel caused the development of a black slip upon a black body. Skilful control of the firing conditions and an appropriate clay selection and refinement could cause vitrification of the slip in the course of this reducing step while the body remained porous; thus, during a final oxidizing step, and/or during cooling in air, the vitrified slip, now impermeable to the kiln gases, maintained its black colour while the body turned red again leading to a black on red ware. However, if reducing conditions were maintained until cooling was completed, a black on grey ware was obtained, while omitting the reducing step led to the production of a red on red ware. Finally, black and red bichrome decorations could

be obtained if areas on the vase surface were reserved and not coated with the finely divided clay selected for the black slip; in this case, reds are represented by the reserved non-vitrified surface of the body (occasional red); however, use of a clay of appropriate grain size and composition could be exploited to obtain a glossy red surface (intentional red), owing to its vitrification during the final oxidizing step.^{3,4} This technique reached its maximum artistic splendour in the production of black figured and red figured vases in Archaic and Classical Greece.

BLACK AND RED GLOSS POTTERY FROM ITALY: A CASE STUDY

This paper gives an account of the results obtained in the study of monochrome black gloss pottery produced in Greek and late Hellenistic times and of red gloss pottery produced in Roman times, and excavated at Italian archaeological sites.

Greek black gloss ware came from excavations carried out at the site of Locri Epizephiri, founded by colonists from the Greek Locrids at the end of the eighth century BC on the Ionian coast of Calabria, in southern Italy. Chemical data on body composition had been first used to separate local products from imported items.¹⁴ Two imported pieces were subsequently selected for an SEM–EDX study together with eight local products to shed light on the technological achievements of potters working in Locri and abroad.¹⁵

The two imports featured highly vitrified and shining slips; one of them, a piece of very likely Attic production, dated from between the late fifth and the early fourth century BC, while the other, a non-Attic product, could be assigned to the mid-fourth century BC. The local pieces, dating from the fourth and third centuries BC, displayed slips of different quality, from shining, highly vitrified and well preserved (fourth century BC) to less shining and more or less preserved (fourth century to early third century BC), and matt, poorly preserved slips (third century BC).

Late Hellenistic black gloss ware (Campanian pottery) had been excavated at various sites in ancient Calabria. Campanian pottery was produced in the western part of the Mediterranean between the fourth and the first centuries BC, and is known in a variety of productions with different macroscopic features. Type A was produced in the area of Naples from a non-calcareous clay, which led to the development of a red body under the black slip; type B was originally produced in central Italy from highly calcareous clays which caused a creamy paste to form after firing; type C was a typical product of Greek Sicily, characterized by a grey calcareous body. A variant of Campana C featuring a grey slip on the grey body (henceforth g/g ware) was widespread in southern Italy, as well as regional imitations of Campana B.

Previous work has indicated that regional imitations were recognizable by chemical composition among sherds from ancient Calabria, besides original forms of Campana A, B and C.¹⁶ Representative samples were subsequently subjected to a thorough technological study by various techniques of investigation, including SEM–EDX.¹⁷ In this paper, some of the most relevant results obtained

by SEM–EDX are discussed to compare the technological achievements of late Hellenistic potters with those of Greek and Roman artisans. The samples taken into consideration, dating from the second century BC, are three sherds of Campana A, one of Campana B, three of Campana C, three regional imitations of Campana B and three g/g products.

Roman red gloss ware (Terra sigillata) came from excavations carried out at the site of Augusta Praetoria (today Aosta, in north-western Italy), founded in 25 BC. Terra sigillata may be considered the result of a simplified variant of the technology adopted for producing black gloss pottery, with the removal of the reducing step from the firing cycle. The ware was initially produced in central Italy (Arezzo, Pisa) in the first century BC, and later manufactured also in branches established by Italian potters outside Italy; in addition, local imitations were produced by non-Italian potters. Here again, a provenance study had been first performed, which indicated that products from various regions of the Roman Empire were used at Augusta Praetoria.^{18–20} Selected pieces were then subjected to a thorough investigation on the technology of production.²¹ The most relevant results obtained by SEM–EDX are discussed here and compared with those concerning the earlier black gloss products. The sherds had been assigned to workshops situated in Gaul, central Italy, the valley of the river Po and north-western Italy. The Gaulish and central Italian products (henceforth GL and IT, respectively) were coated by a shining, highly vitrified and well preserved red slip; only one IT sample displayed a coating of a more orange shade. Conversely, sherds assigned to north-western Italy and the Po valley (henceforth LC and PV, respectively), displayed less shining and less preserved orange slips.

RESULTS AND DISCUSSION

SEM–EDX data concerning slip and body of the samples considered here are given elsewhere;^{15,17,21} they accord with the general trend observed for black or red gloss fine ware in pointing to a higher content of aluminium and iron, and a lower content of silicon and calcium, in the slips against the bodies.^{4,7,8,10,22} This is the result of the selection and refinement of a proper clay for the coating, with the purpose of obtaining its vitrification at a lower temperature and in a shorter time than those necessary for the body.

Enrichment of alumina and depletion of silica are consistent with the removal of coarse quartz grains and the increase of the relative amount of clay minerals due to the clay refinement; this also leads to a depletion of alkaline earths, as a result of the removal of coarse carbonate grains.^{4,5} Removal of carbonates is considered an important step towards the development of shining and well sintered slips, as they can disrupt the alignment of the clay platelets parallel to the surface of the ware.^{4,5} Furthermore, carbonatic clays form alkaline earth metal silicates at high firing temperatures; these can trap iron ions within their lattice and prevent the growth of iron oxides and the development of a deep red hue in the case of wares fired under oxidizing conditions.^{5–7}

Relatively high levels of potassium are also frequently observed in clayey slips,^{4,8,10,22} and this may principally

stem from the use of naturally K-rich illitic clays; however, addition of wood ash as a deflocculant could also contribute to the potassium enrichment.^{3,13} Low-melting potassium compounds act as fluxes during firing, promoting liquid sintering and vitrification.

High contents of iron in the coatings could result from the selection and refinement of particularly Fe-rich clays, but the use or addition of natural ochres has been suggested in some cases.^{2,11} High levels of iron help in developing a deeper red or black coating; in addition, they favour the vitrification of black slips, due to the fluxing properties of the iron(II) silicates formed under reducing conditions.^{3,4}

Red and black gloss wares were mostly made using highly calcareous clays to shape the body. An exception is given here by the Campanian pottery of type A, which was made from a low calcareous clay; other products with low calcium contents in the body, as the PV and LC Terra sigillata, show rather high contents of MgO, so that their paste has to be considered actually calcareous.

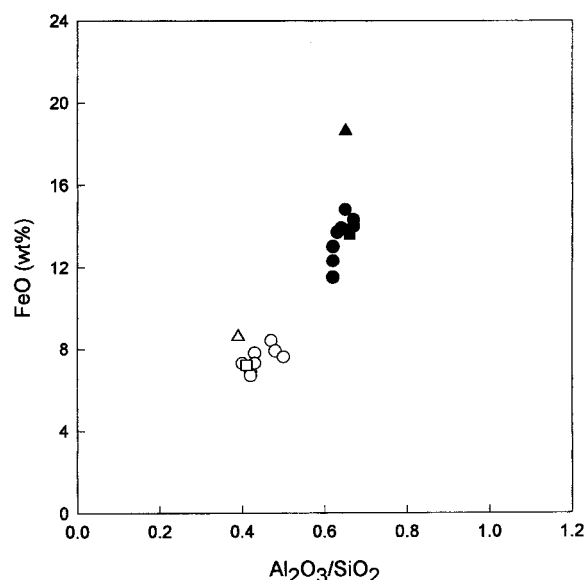


Figure 1. FeO percentage content vs $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in black gloss sherds from Locri. (□) Attic import; (△) non-Attic import; (○) Locrian product. Closed symbols denote slips, open symbols denote bodies.

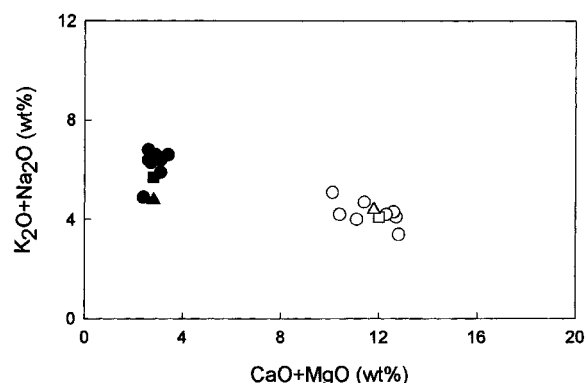


Figure 2. $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ vs $(\text{CaO} + \text{MgO})$ percentage content in black gloss sherds from Locri. (□) Attic import; (△) non-Attic import; (○) Locrian product. Closed symbols denote slips, open symbols denote bodies.

The use of a calcareous clay for the body could diminish the risk of obtaining failed items, as the coefficient of thermal expansion would better match that of the glossy slip.^{2,7} The ancient potters certainly did not know this on scientific grounds, but were fully aware of what happened if they used a clay from one bed rather than another, and if they properly processed it before use.

Greek black gloss ware from Locri

Figures 1 and 2 show that in all cases the clays used for the coating had been properly refined and processed, as indicated by the high proportion of alumina and flux. It is also apparent that most of these coatings share similar compositional features, independently of their place and date of manufacture; however, the non-Attic import is characterized by a slip with a higher iron content than the other products. This similarity of composition accords with the fact that most Locrian products display slips of good quality, in some cases matching that of the two imports. The content of alkali metals, even though fairly high, never reaches the values observed in other kinds of products (see below), but this might not be a particular drawback if a suitably high temperature was reached during the reducing step of firing.

SEM images confirm the generally high technological level of Greek potters (Fig. 3). In fact, highly vitrified slips, with a sharp and regular contact with the body, are evident microscopic features of the imported products, and also of most Locrian pieces; however, a few local products show less regular contact surfaces and/or the presence of craters and voids in the coating. The thickness of the slip is the most evident difference between the Locrian and the imported pieces; in fact, it reaches up to 20–25 μm in the latter, but does not normally exceed 20 μm in the former, where it may even reach down to 10–15 μm . Glossy slips 20–25 μm thick have also been reported for a group of Attic sherds from different archaeological sites,¹⁰ and this could provide a limited, but interesting differentiation between Locrian and Attic products.

Late Hellenistic black gloss ware from ancient Calabria

SEM images of sherds of Campanian pottery indicate substantial differences in the microstructure of the various kinds of products (Fig. 4). In fact, the slips of Campana C are definitely less sintered than those of the other types of Campanian pottery, and characterized by a much more irregular slip-to-body contact surface; furthermore, the thickness is highly variable within a single sherd, ranging from 20 to 50 μm or even more. In contrast, the sherds of Campana A and B display highly vitrified slips with a sharp and regular contact with the body; the thickness is generally between 10 and 15 μm for the products of Campana A, and around 20 μm for the sherd of Campana B. As for the regional products, the imitations of Campana B display coatings with similar features to the original product, but with a lower thickness (generally 10–15 μm); the g/g sherds are coated by well vitrified and thin slips, some 5 μm thick.

The composition of the slips largely accounts for the different microstructures observed in the SEM images. On

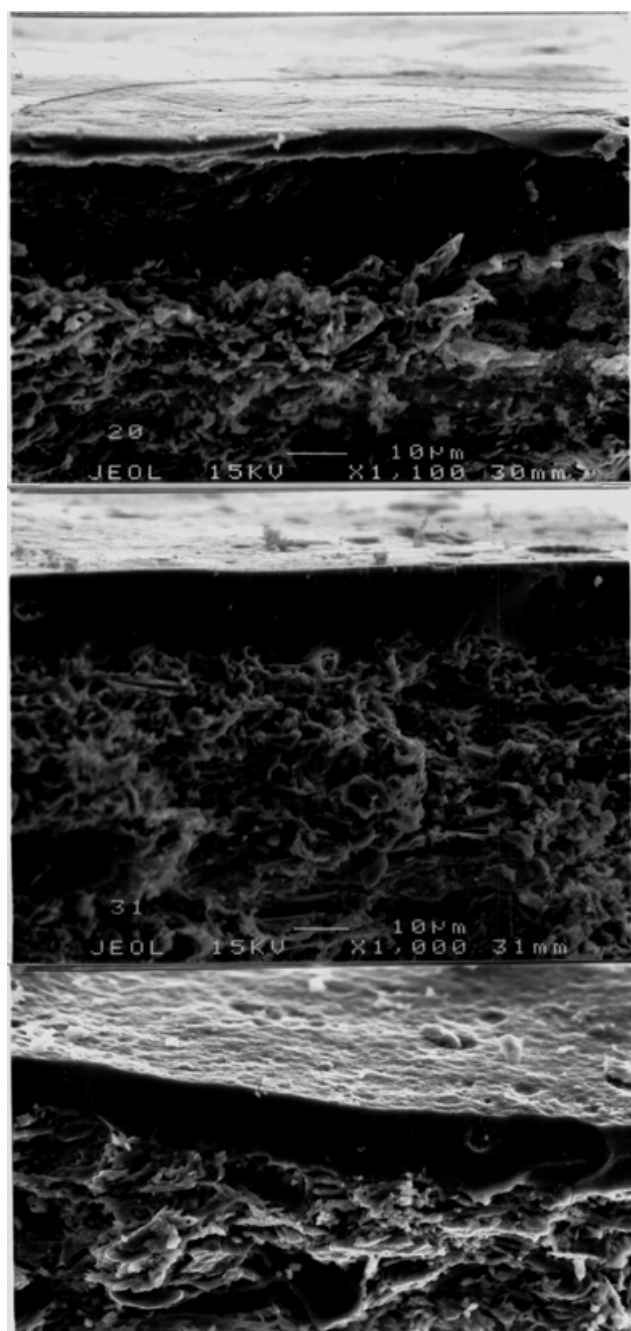


Figure 3. Secondary electron images of fresh fractured sections of black gloss sherds from Locri. Top, Attic import, $\times 1100$; middle, fourth century BC Locrian product, $\times 1000$; bottom, late fourth to early third century BC Locrian product, $\times 1500$.

the one hand, Fig. 5 shows that the coatings of Campana C are characterized by relatively low alumina to silica ratios, while these reach their maxima in the g/g slips. More important, the coatings of Campana C contain the smallest amount of alkali metals, coupled with a relatively high alkaline earth metal content (Fig. 6); as already said, alkaline earth metal carbonates disrupt the regular alignment of the clay particles, while a limited content of alkali metals may prevent extensive sintering, unless suitably high temperatures were reached during firing. Total alkaline earths are relatively high also in the coating of Campana B, but here a higher content of alkali metals could contribute to the development of the well vitrified

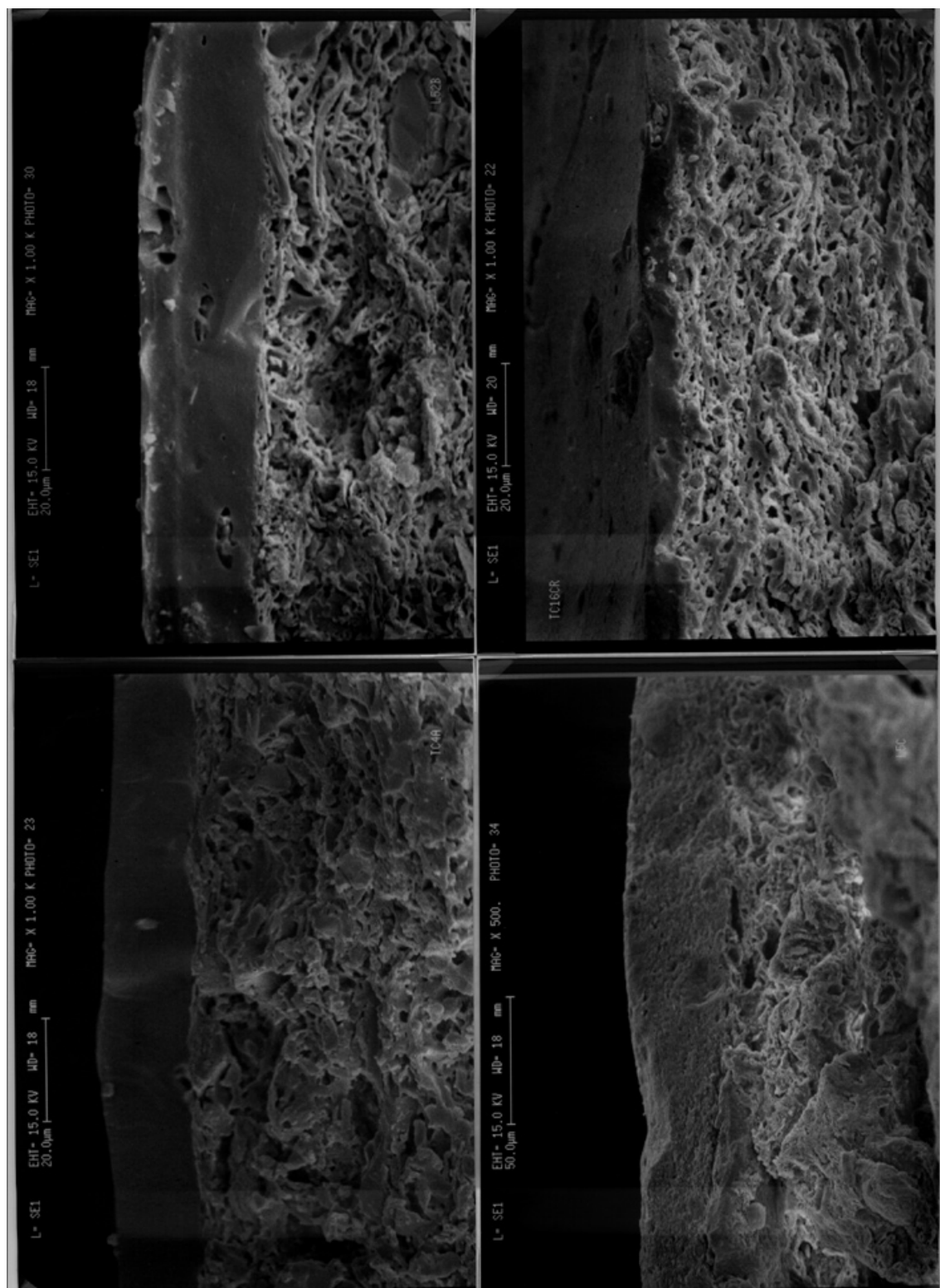


Figure 4. Secondary electron images of fresh fractured sections of Campanian pottery from ancient Calabria. Upper left, Campana A, $\times 1000$; upper right, Campana B, $\times 1000$; lower left, Campana C, $\times 500$; lower right, grey on grey ware, $\times 1000$.

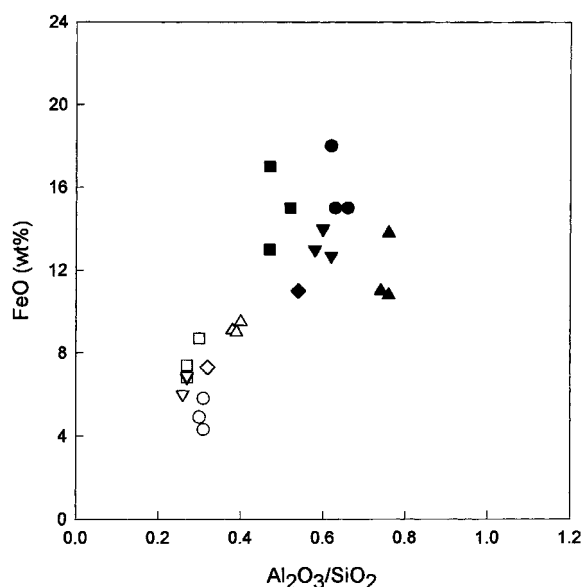


Figure 5. FeO percentage content vs $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in sherds of Campanian pottery from ancient Calabria. (O) Campana A; (\diamond) Campana B; (∇) imitation of Campana B; (\square) Campana C; (\triangle) grey on grey ware. Closed symbols denote slips, open symbols denote bodies.

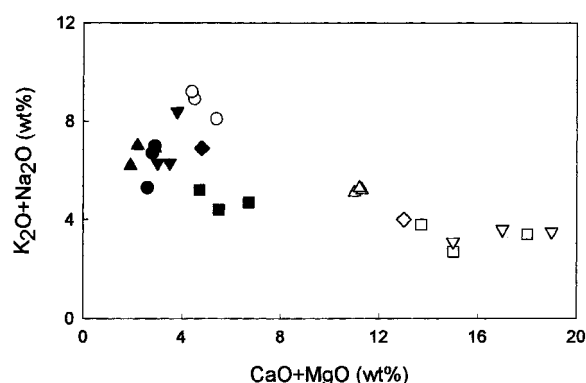


Figure 6. $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ vs $(\text{CaO} + \text{MgO})$ percentage content in sherds of Campanian pottery from ancient Calabria. (O) Campana A; (\diamond) Campana B; (∇) imitation of Campana B; (\square) Campana C; (\triangle) grey on grey ware. Closed symbols denote slips, open symbols denote bodies.

slip. The amount of alkali metals is also suitably high, and coupled with a reasonably low content of alkaline earths, to explain the high sintering observed in both kinds of regional products. Finally, total alkali metals in the coatings of Campana A, even though comparable with the content in most of the other coatings, are lower than in the bodies of Campana A themselves; this stems from the rather large amounts of sodium and potassium found in the latter.^{16,17}

Evaluation of firing temperatures suggested that some sherds of Campana C could actually have been fired at relatively low temperatures, below 800°C , while all the other products would have been fired in excess of 900°C .¹⁷ Thus the combined effect of slip composition and firing temperature contributed to the development of well vitrified slips in the case of Campana A and B and of the regional products, while an inappropriate combination determined the lower degree of sintering in the coatings of Campana C.

Roman red gloss ware

SEM images indicate that microscopic features are also different among the various products of Terra sigillata (Fig. 7). In fact, a high degree of sintering is observed for the Gaulish and the central Italian slips, which are mostly $10\text{--}20\text{ }\mu\text{m}$ thick; thinner (less than $10\text{ }\mu\text{m}$) and less regular coatings are observed in the case of the north-western Italian products, even though the degree of sintering is still fairly high. In contrast, the products from the Po Valley are coated with definitely less sintered slips, $10\text{--}20\text{ }\mu\text{m}$ thick.

Here again, the composition of the coatings largely accounts for their different textural features (Figs 8 and 9). In fact, the slips of the pieces from the Po Valley, even though characterized by the highest alumina to silica ratios, the higher iron contents and the lowest amounts of alkaline earths, show also the lowest contents of alkali metals. In contrast, total alkali metals are particularly high in the Gaulish and central Italian coatings.

Evaluation of firing temperatures suggests that they are fairly high to high, mostly between 800 and 1000°C .²¹ Such conditions would allow the development of well vitrified slips from accurately selected and processed clays; hence it seems that the major factor which caused the development of coatings of different quality was once again an inappropriate combination of firing conditions and clay composition. Potters from Gaul and central Italy would have been capable of choosing and processing adequately their clays, in addition to firing them at high temperatures to produce well sintered and shining slips. In contrast, northern Italian potters would have less properly selected and processed their clays, and would have fired them at temperatures which were not always high enough to overcome the more limited amount of flux present; a higher content of alkali metals allowed the LC slips to reach a higher degree of sintering than the PV coatings, even though they were probably fired up to slightly lower maximum temperatures.²¹

Comparison among Greek, late Hellenistic and Roman products

The bodies of the various products considered here may greatly differ for their alkaline earth metal content, while the coatings may significantly differ for the alkali metal content; this stems from the particular technology required for the production of fine wares coated by glossy slips. In fact, the bodies were most probably shaped from locally available clays subjected to a less extensive refinement than the clays selected for the coatings; this would not remove the finest quartz and carbonate grains. Indeed, $\text{CaO} + \text{MgO}$ contents vary from less than 5 to nearly 20% in the body of the various products; apart from the bodies of Campana A, the less calcareous paste is displayed by the northern Italian Terra sigillata, particularly that produced in the Po Valley. Most of the other wares were made from clays which gave fired bodies containing between 10 and 15% $\text{CaO} + \text{MgO}$, but still higher values are found for two imitations of Campana B, one sherd of Campana C and one IT Terra sigillata. It can also be observed that the Greek and Roman bodies are generally characterized by higher alumina to silica ratios than most

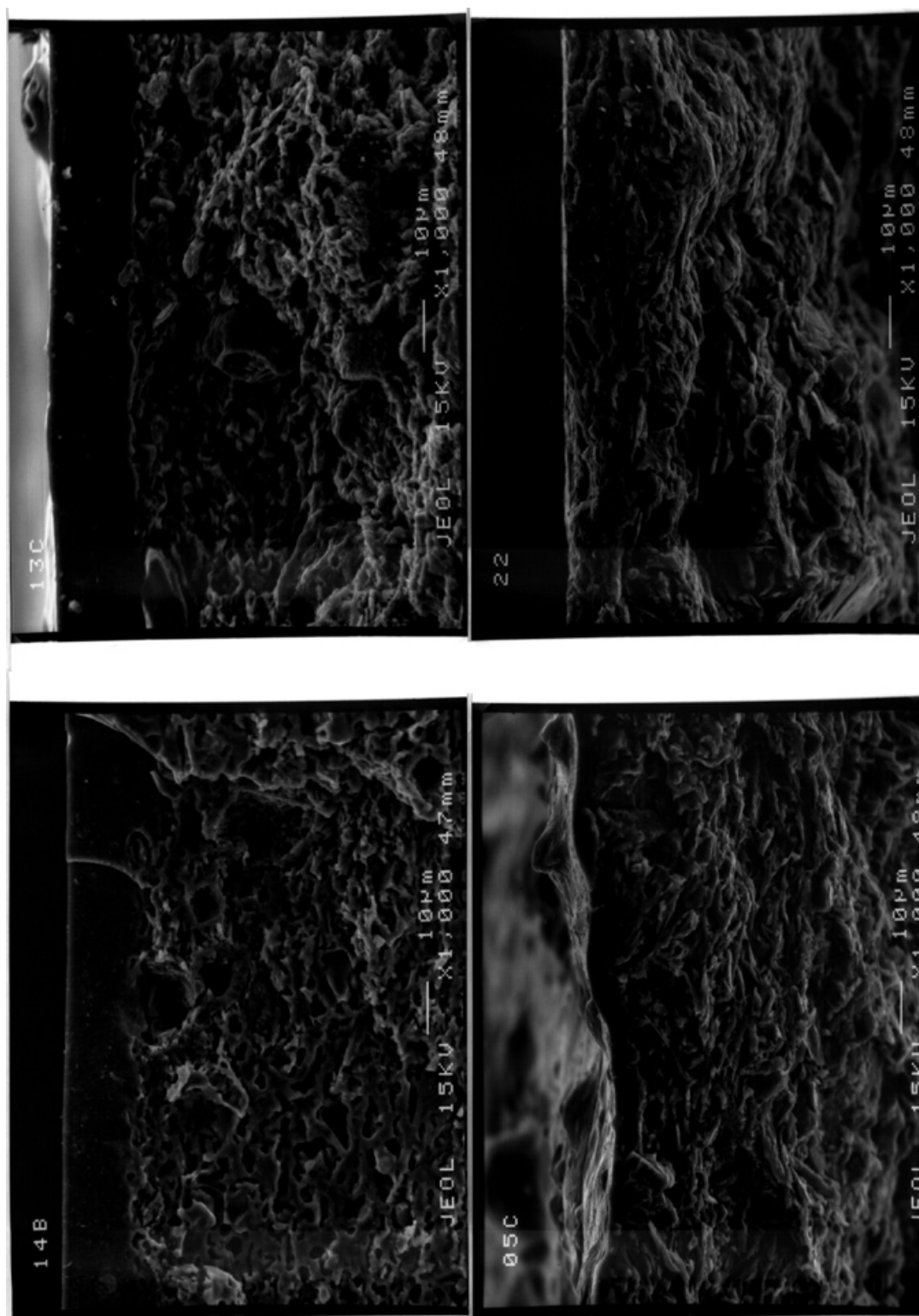


Figure 7. Secondary electron images of fresh fractured sections of Roman Terra sigillata from Aosta. Upper left, Gaulish product; upper right, central Italian product; lower left, north-western Italian product; lower right, product from the Po Valley. $\times 1000$.

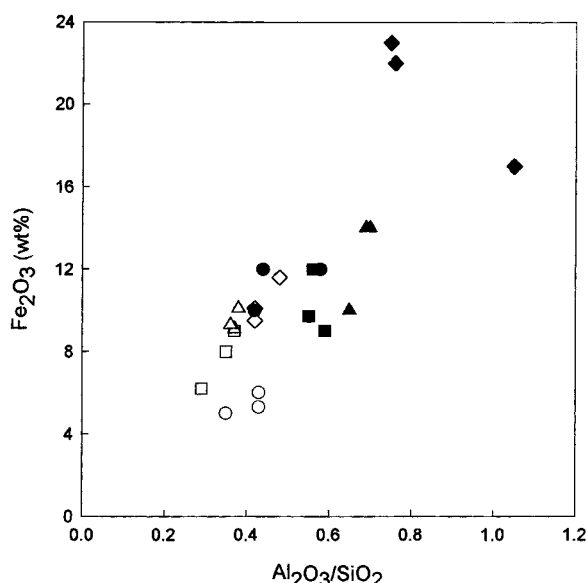


Figure 8. Fe_2O_3 percentage content vs $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio in sherds of Roman Terra sigillata from Aosta. (O) Gaulish product; (□) central Italian product; (△) north-western Italian product; (◇) product from the Po Valley. Closed symbols denote slips, open symbols denote bodies.

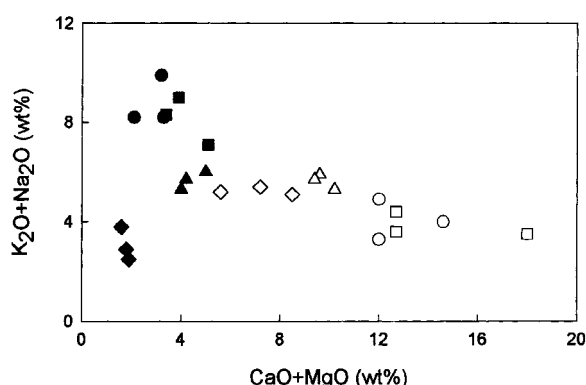


Figure 9. $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ vs $(\text{CaO} + \text{MgO})$ percentage content in sherds of Roman Terra sigillata from Aosta. (O) Gaulish product; (□) central Italian product; (△) north-western Italian product; (◇) product from the Po Valley. Closed symbols denote slips, open symbols denote bodies.

of the late Hellenistic Campanian products and their imitations.

A particular feature of the Campanian products of type A is the fact that their bodies, besides containing only some 5% alkaline earth metal oxides, are characterized by the highest amount of alkali metals among all the wares considered here; furthermore, this content is also higher than that found in the majority of the slips, including those of Campana A themselves. Under these circumstances, only a larger grain size of the clay could prevent these bodies from reaching as high a vitrification stage as their coatings. The alkali metal oxide content in the body of the other wares is generally lower than that found in their coating, and mostly between 3 and 6%. Further exceptions are represented by the northern Italian products of Terra sigillata, whose bodies show about the same (LC sherds) or a higher content (PV sherds) of alkali metals than their slips; these contents, however, remain definitely lower than those present in the bodies of Campana A.

The coatings are mostly characterized by $\text{CaO} + \text{MgO}$ contents below 5%, while the amount of $\text{K}_2\text{O} + \text{Na}_2\text{O}$ may vary from less than 3 to up to 10%. Furthermore, the alumina to silica ratio is generally higher than in the bodies; it mostly ranges from 0.4 to 0.8, but even exceeds unity in one PV Terra sigillata. As already said, this stems from the more careful selection and processing of clays which was required for the production of the glossy slips.

Extensive refinement of the clay to give very fine particles suspended in water and the presence of fluxing agents in suitable amount were necessary for producing slips featuring a high gloss, provided that adequate conditions were then adopted during firing. It is interesting that among the most shiny slips observed here, the black coatings of the Greek Locrian and imported pieces were obtained from clays containing lower amounts of alkali metals than the red coatings of the Terra sigillata produced in Gaul and central Italy four centuries later. This suggests that Greek potters, in both Greece and southern Italy, were more skilful in the control of firing conditions, to allow the development of highly vitrified coatings in the presence of a smaller amount of alkali metal flux. Further credit is due to the Greek potters when one considers that their black slips had to be obtained including a reducing step in the firing cycle, which implies a more careful control of the working conditions than that required of the Roman potters for developing their red coatings; in fact, in this latter case all the operations could be carried out more easily, as oxidizing conditions were maintained during the whole firing cycle. Another differentiation between Greek coatings, on the one hand, and GL and IT Roman slips, on the other, is the slightly higher content of iron which may be found in the former (mostly 12–15% against 8–11%, when both are expressed as FeO), and this may possibly be related to the fact that iron(II) compounds formed under reducing conditions could act as additional fluxes, favouring the development of highly sintered slips. In this respect, it is noteworthy that two Roman slips from the Po Valley, fired under oxidizing conditions, show the highest contents of iron among all the samples under consideration here (21%, expressed as FeO), but did not form a well vitrified layer, owing to the small amount of alkali metals.

An interesting comparison may also be made between the sherds of Campana C and the PV Terra sigillata, that is, the two kinds of products characterized by the lowest degree of sintering of their coatings. On the one hand, the PV coatings developed from clays containing small amounts of both alkali and alkaline earth metals, probably fired at fairly high to high temperatures; in contrast, the coatings of Campana C were obtained from clays with a relatively high content of alkaline earths and still relatively low alkali metal contents (even though higher than in the PV slips), possibly fired at rather low temperatures. Furthermore, the alumina to silica ratios are relatively low in the slips of Campana C, whereas they are high in the PV Terra sigillata. Thus in the case of the Roman products the inadequate amount of flux seems to have been the major cause preventing full vitrification of the slip, whereas in the case of Campana C low temperature of firing, low flux and high alkaline earth metal content could combine in limiting the possibility of achieving a high degree of vitrification. One can further consider that in both cases the scarce degree of sintering could not affect the final

colour of the slip. In fact, on the one hand, Terra sigillata was kept under oxidizing conditions throughout the whole firing cycle; on the other hand, in the case of Campana C, once reducing conditions had first been created, they were maintained during the residual firing and during cooling, as attested by the grey colour of the body; if this were not the case, at least partial re-oxidation of the ill-sintered slip could occur when oxygen had entered the kiln.

CONCLUSIONS

This paper has given an account of the potential of x-ray microanalysis in the study of ancient pottery, with particular emphasis on the characterization of surface coatings. SEM coupled with EDX has been applied to the study of wares produced in Greek, late Hellenistic and Roman times, and coated with black or red monochrome glossy slips. Images obtained from backscattered and secondary electrons allowed considerations on the degree of sintering and the thickness of the coatings, while EDX analyses provided information on the chemical composition of bodies and coatings themselves. It was possible to compare the features of products of different quality and of different dates and to relate them to the use of more or less properly selected and processed clays. Together with an evaluation of firing conditions by appropriate techniques of investigation, this provides a powerful tool for shedding light on the secrets of ancient potters.

EXPERIMENTAL

Sample cross-sections were used to perform the SEM–EDX investigations. Two fractured sections were obtained from each sherd; one of them was used for the morphological examination and the other was impregnated in an epoxy resin and polished for the EDX analysis. Fractured sections were coated with a graphite (Greek and Roman samples) or a gold layer (late Hellenistic samples); all the polished sections were coated with graphite.

The experimental work was carried out by use of a Jeol JSM 6400 scanning electron microscope coupled with a Tracor energy-dispersive system (Greek and Roman samples) or a Cambridge Stereoscan 360 scanning electron microscope coupled with a Link Analytical energy-dispersive system (late Hellenistic samples); images were obtained by collecting either secondary or backscattered electrons.

Both bodies and slips were generally analysed by carrying out 5–7 determinations on different areas of each sample. Body analyses were carried out scanning the electron beam across 350×450 (Greek and Roman samples) or 180×240 μm areas (late Hellenistic pottery). Owing to the limited thickness, the composition of the slips was determined by spot analysis or scanning areas of about 8×10 μm ; their higher homogeneity allowed one to obtain good analytical results from much smaller areas than those selected for the body.

The relative abundance of eight elements (Si, Al, Fe, Ca, Mg, K, Na and Ti) was determined on each sample and a ZAF procedure was used for correcting matrix effects. Pure element oxides and natural minerals were used as standards for the quantitative determinations.

Sample compositions were given as weight percentage of element oxides; the iron concentration was expressed as iron(II) oxide in the case of the black-coated Greek and late Hellenistic pieces and as iron(III) oxide in the case of the red-coated Roman samples. Data concerning each analytical run were normalized to 100% total; this made data obtained on slips and bodies comparable, even though analytical totals were lower for the latter owing to their greater porosity. The results were expressed taking into account the standard deviation calculated for each element from the multiple determinations performed on each sample.

To compare the red gloss with the black gloss products, data concerning the former were recalculated after having expressed the iron content as iron(II) oxide. This implied normalizing again all the element oxides to 100% total and expressing them taking into account the standard deviation of the original measurements.

Full details on operating conditions are given elsewhere.^{15,17,21}

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