CAMPANIAN POTTERY; THE NATURE OF THE BLACK COATING

M. MAGGETTI, G. GALETTI

Min. Petr. Institut der Universität, Pérolles, CH-1700 Fribourg, Switzerland

H. SCHWANDER

Min. Petr. Institut der Universität, Bernoullistr. 30, CH-4056 Basel, Switzerland

M. PICON

Laboratoire de Céramologie, 1 rue Raulin, F-69365 Lyon, Cédex 2, France

and R. WESSICKEN

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

1. *Introduction*

Campanian pottery is generally defined as being a black-coated ware which was produced from the fourth to the first centuries B.C. in the western area of the Mediterranean basin (Morel 1980). During the second and the first centuries B.C. three productions can be clearly distinguished by their extensive distribution and by their particular typological characteristics. The type A has a red paste, the type B a creamy-yellow paste and the type C a grey paste (Lamboglia 1952). In all three cases we are dealing with ceramics produced in Italy which were very widely exported in the western and even the eastern Mediterranean. The type B includes several varieties which correspond to productions coming from different regions of Italy. This is not the case for the type A which originates in the Naples region and the type C which originates in Sicily. A variety of Campanian B, of very high quality, seems to have been produced in Etruria where it is well represented in the excavated material from Cosa (Taylor 1977). Another variety, very prevalent amongst the exports, would have been produced in the Calès region, a site already known for its relief productions of the second half of the third century and the beginning of the second century B.C. (Pagenstecher 1909).

The characteristics of the paste's colour of the Campanian types A and B are due to differences in the percentages of CaO (Picon 1977), the type A having a non calcareous or moderately calcareous paste (3–5 wt% CaO), the type B being very calcareous (8–11 wt% CaO) according to the nomenclature of Maniatis and Tite (1978, 1978/79).

At Calès itself, two types of paste are found. One is very calcareous (13.6 wt% CaO, as mean for 8 analysed specimens) and appears at a later period on the site and concerns above all the so-called pre-sigillata pottery. The other paste, less calcareous (9.0 wt% CaO, as mean for 25 analysed specimens), corresponds to the vast majority of black-coated wares from this site. More recent analyses carried out on twenty specimens (from the collection of M. Picon) of the most frequently found type of paste at Calès confirm these characteristics (table 1).

The present study deals with the characteristic black coating of these twenty objects; all

Table 1   Chemical analysis by X-ray fluorescence of Campanian sherds, all without gloss

wt.%	3 individual sherds from Min. Petr. Institut, Fribourg			20 sherds from Min. Petr. Institut, Fribourg			25 sherds from M. Picon		
	KP 1	KP 5	KP 10	x	s	$s_{rel}(\%)$	x	s	$s_{rel}(\%)$
SiO_2	59.97	58.07	58.37	58.94	1.07	1.8	59.5	1.2	2.0
TiO_2	0.75	0.77	0.81	0.77	0.02	2.6	0.79	0.05	6.3
Al_2O_3	16.78	17.42	17.90	17.08	0.42	2.4	17.4	0.56	3.2
Fe_2O_3	5.89	4.94	6.35	6.27	0.22	3.5	6.60	0.28	4.2
FeO	0.25	0.97	0.33	0.18	0.25	138.9	n.d.	n.d.	–
MnO	0.10	0.10	0.10	0.11	0.01	9.1	0.11	0.01	9.1
MgO	3.13	2.74	2.99	3.06	0.25	8.2	3.37	0.34	10.1
CaO	9.66	10.53	8.60	9.11	1.34	14.5	9.0	1.36	15.1
Na_2O	0.99	0.98	1.01	0.95	0.08	8.4	n.d.	n.d.	–
K_2O	2.95	2.98	3.25	3.03	0.09	2.9	2.96	0.14	4.7
P_2O_5	0.28	0.69	0.67	0.52	0.24	46.1			
	100.75	100.19	100.38						
loss	2.06	1.98	2.13						
ppm									
Ba	395	405	453	418	62	14.8			
Zr	177	167	170	169	9	5.3			
Sr	315	319	312	300	45	15.0			
Rb	141	140	143	143	8	5.6			
Zn	95	93	108	99	9	9.1			
Cu	33	41	45	42	14	33.3			
Ni	64	59	65	64	5	7.8			
Cr	103	99	102	104	6	5.8			

s = standard deviation, s_{rel} = relative standard deviation, x = mean value, n.d. = not determined.

sherds were analysed by X-ray diffraction technique, X-ray fluorescence, five studied by scanning electron microscopy (nos. 1, 4, 6, 11, 17), three by microprobe (1, 5, 10) and eleven by direct X-ray diffraction of the surface (1–7, 10, 11, 14, 17, 19).

Similar glossy clay coatings have been widely used in antiquity for pottery production (e.g. Attic black vases, red Terra Sigillata). However, only a few authors presented *complete chemical analyses* of these coatings. Our results are therefore compared with the conclusions of Pavicevic (1974), Tite *et al.* (1981) on the black coatings and of Willgallis and Heyer (1976), Tite *et al.* (1981) on the red coatings.

2. Experimental

X-ray fluorescence   The sherds were analysed without the coating. *Glassy pill*: 900 mg of the heated powder (1 hour at 1100°C) were mixed with 4.5 g of a Li-tetraborate-, Li-carbonate-, La-Oxide-mixture, and fused in a PtAu crucible during 10 min at 1050°C. *Powder pill*: 4.5 g of the dried powder (110°C for 24 h) were mixed with 8 drops of a 2.5% Mowiol-solution and pressed under vacuum at 2.5 tons pressure. For precision and accuracy of the method see Kuepfer and Maggetti (1978).

Electron microprobe Microprobe: SEMQ-ARL combined with EDS TN 2000, PDP 11-04. WDS: Ca Kα, Fe Kα, K Kα, Na Kα. EDS: Mg Kα, Al Kα, Si Kα, Ti Kα, Mn Kα. 15KV, 30nASC, $\emptyset \pm 3\mu$, BC-Integration. Pointanalysis, coating: C $\sim$ 200 Å.

Electron microscope A scanning electron microscope Cambridge Stereoscan MK II A, fitted with an energy-dispersive X-ray analyser EDAX 707 was used to produce secondary electron images of the fragments and to obtain a qualitative chemical analysis.

X-ray diffraction The samples were analysed with a Siemens powder X-ray diffractometer (Cu Kα). The cell parameter a_0 of coexisting spinels was calculated from the lattice spacings (110); the (220) and (440) lattice spacings were used for confirmation.

3. Morphology

The contact between the black coating and the sherd body is sharp (plate 1). The coating is 15–30 μm thick, isotropic and contains some small frequently elongated irregular pores. Its surface is rough and shows small rounded particles (plate 2). Some open craters and closed bulbs can be noticed. The whole aspect is characteristic of a coating of the 'glossy clay layer' type and our samples are identical in the macroscopic aspect to those of the Greek black painting (e.g. Noll *et al.* 1973, Noll 1976/77, 1979, Tite *et al.* 1981). By comparison, a glaze has a very smooth surface and would be rich in gas bubbles.

In contrast to the coating, the sherd matrix is very porous and no relict mineral grains can be identified.

4. Chemical composition

An initial survey by EDX (energy dispersive X-ray analysis) revealed the presence of Al, Si, K, Fe, with minor Ti (figure 1). In the nomenclature of Noll (1975–1979) the glossy clay layer therefore belongs to the iron reduction or iron-black type of black painting. Quantitative microprobe analysis gave the compositions listed in table 2. The black coating is rich in SiO_2, Al_2O_3, FeO, K_2O and contains moderate amounts of MgO. In its composition it resembles the classic Attic black coating, of which semiquantitative analyses were published by Brongniart (1844), Hofmann and co-workers (1962–1966) and Noll and co-workers (e.g. 1973). Comparing our results with the complete analysis of Pavicevic (1974) and Tite *et al.* (1981), the higher MgO and K_2O contents of our sherds become apparent.

The contrast in chemical composition between the gloss and the sherd matrix is pronounced and corresponds to the findings of the authors cited above; the matrix differs markedly in its major elemental chemistry, especially for CaO which is virtually absent in the gloss but high in the sherd.

Some variations between the three coatings analyzed can be noticed for MgO, FeO, CaO and K_2O. The standard deviations for the oxide contents in a single specimen (very high for MnO and CaO, moderately high for FeO, MgO, Na_2O and TiO_2) show the heterogeneous nature of these coatings. This would be expected in the case of a glossy clay layer.

5. Mineralogical analysis

The colouring agent of the Attic black pottery has been the object of many studies, and differing pigments have been postulated: *magnetite* and/or *hercynite* (Farnsworth and Wisely 1958,
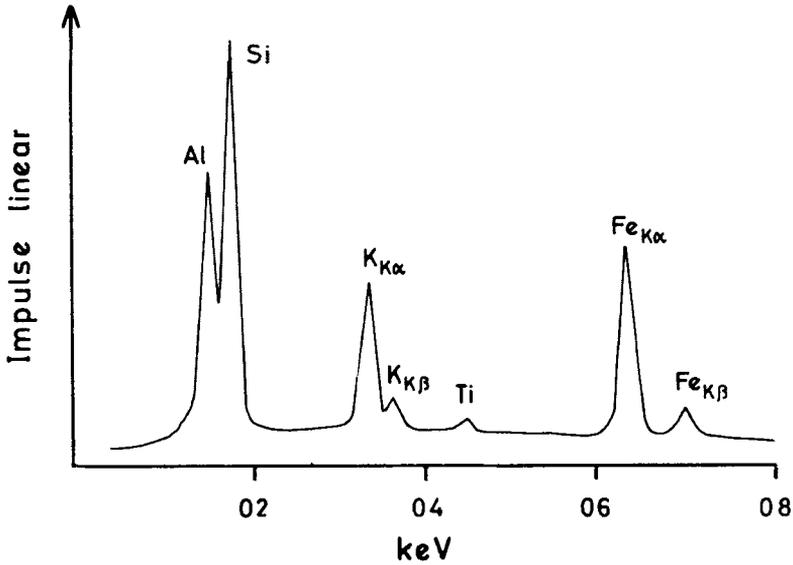
Figure 1   Semi-quantitative analysis of a black coating by EDX.

Table 2   Chemical composition of the black coating (mean and standard deviation) of the Campanian pottery and the Athenian black (Pavicevic 1974). Analysis by electron microprobe.

| | KP 1 (n = 7) | | | KP 5 (n = 3) | | | KP 10 (n = 9) | | | |
	x	s	s%	x	s	s%	x	s	s%	Athenian black
SiO$_2$	45.89	0.64	1.4	45.06	0.30	0.7	45.02	0.27	0.6	43.12
TiO$_2$	0.41	0.09	23.6	0.32	0.02	6.2	0.48	0.02	5.2	0.43
Al$_2$O$_3$	29.12	0.44	1.5	28.86	0.07	0.2	28.80	0.28	0.9	29.00
FeO*	15.64	0.88	5.7	14.09	0.75	5.3	14.40	0.69	4.8	14.15
MnO	0.09	0.07	75.6	0.11	0.02	18.2	0.12	0.07	57.5	0.02
MgO	3.17	0.21	6.7	2.21	0.13	5.9	2.35	0.18	7.6	1.69
CaO	0.17	0.03	17.5	0.65	0.08	12.3	0.76	0.19	25.6	0.35
Na$_2$O	0.83	0.05	6.8	0.88	0.08	9.1	0.94	0.08	8.3	n.d.
K$_2$O	4.89	0.20	4.1	6.98	0.17	2.4	6.74	0.25	3.7	3.69

* total Fe as FeO, x = mean value, s = standard deviation, n.d. = not determined.

Hofmann and Russow 1963, Hofmann and Theisen 1965a, 1965b, Hofmann 1966, Hofmann et al. 1966, Noble 1960, Noll 1979, Oberlies and Koeppen 1953, 1962), wuestite (Bimson 1956), hypersthene (Pavicevic 1974).

The surface of 11 objects was studied by X-ray diffractometry. Two phase associations have been identified:

(a) hercynite + magnetite + hematite + quartz + sanidine (figure 2)
(b) hercynite + magnetite + quartz + sanidine.

An amorphous phase is to be expected. Cristobalite could not be detected. The relative amounts

Plate 1   *Contact zone between the black coating and the porous sherd matrix. Sherd no. KP* 1.6-3259/11.
Bar = 40 μm.
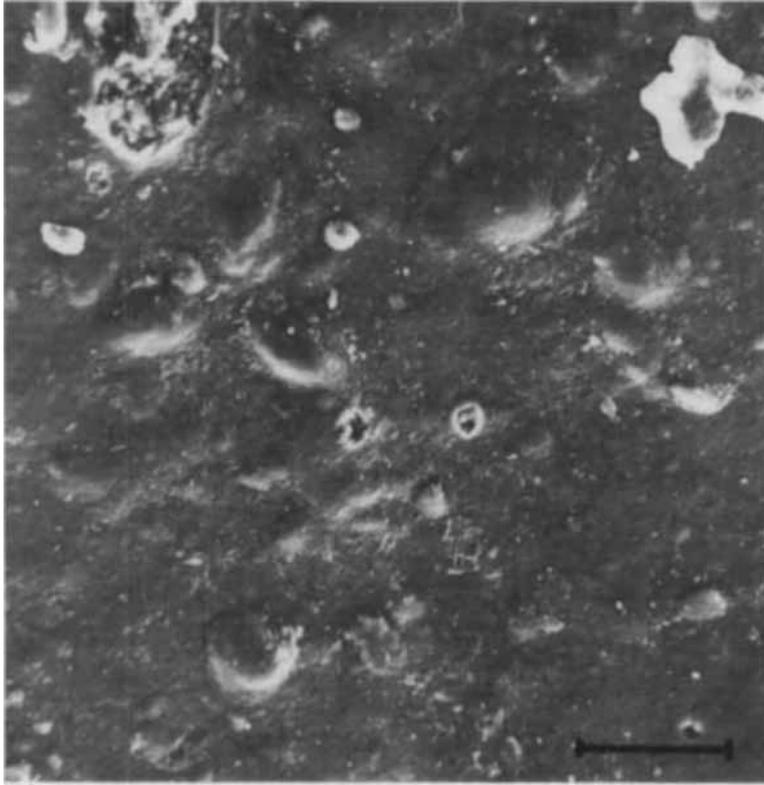
Plate 2   *Surface of a black coating. Specimen no. KP* 1.6-3268/2.*Bar* = 20 μm.
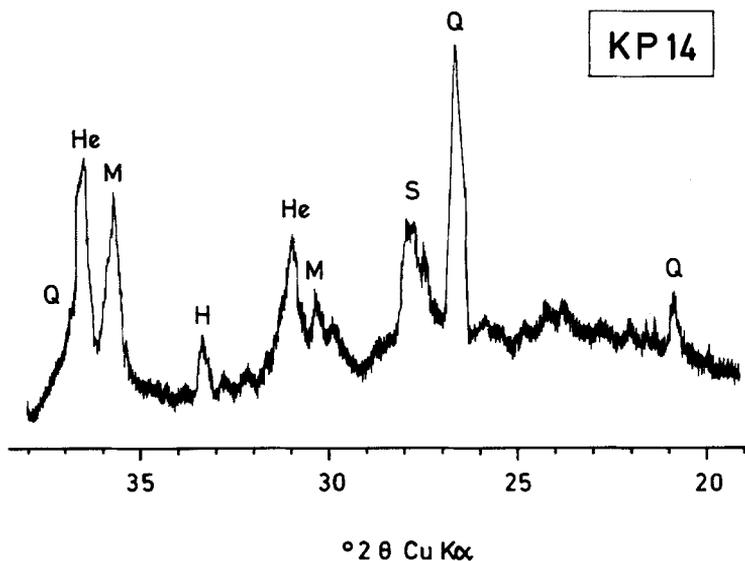
Figure 2   *X-ray diffractogram of a black coating (surface X-rayed) composed of hercynite (He), hematite (H), magnetite (M), quartz (Q) and sanidine (S). Sample KP 14.*

Table 3   *Cell parameter a_0 of coexisting spinel phases in the black coating and chemical composition after Turnock and Eugster* (1962, figure 4)

specimen	a_0 (Å) hercynite	magnetite	% hercynite in magnetite	% magnetite in hercynite
KP 1	8.172	8.390	—	8
KP 5	8.164	8.364	12	3
KP 6	8.163	8.341	21	3
KP 10	8.169	8.362	14	6
KP 14	8.162	8.328	30	4

of these minerals vary greatly, especially the magnetite/hercynite ratio. The measurements of the cell parameter a_0 for the coexisting spinel phases are given in table 3. They are in close agreement with those of Hofmann *et al.* (1966) and Noll (1979).

A rough approximation of the composition of these coexisting spinels can be made on the basis of the experimental data of Turnock and Eugster (1962). According to these authors a certain amount of MgO, TiO_2 and Fe_2O_3 must be expected. However, the particles considered here are too small for an exact determination of their chemical composition by microprobe.

6. Technology

The firing technique of the Attic potters used for the production of the famous Attic black pottery was elucidated among others by Bimson 1956, Oberlies and Koeppen 1953, Schumann 1942, Winter 1978. The pottery was produced in a single firing during which a first oxidizing
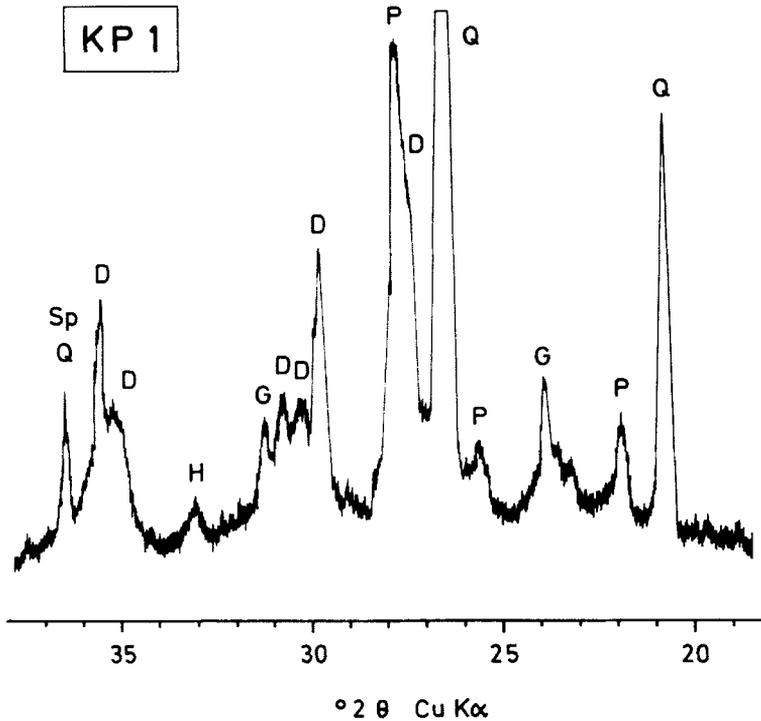
Figure 3   *X-ray diffractogram of the powdered sherd matrix from sample KP 1.* D = *diopside*, G = *gehlenite,*
H = *hematite,* P = *plagioclase,* Q = *quartz,* Sp = *spinel.*

phase up to 800°C was followed by a reducing one (maximum at 900–950°C) with a final cooling process under oxidizing conditions.

The *firing temperature* of our samples can be estimated by the mineralogy of the sherd bodies, assuming that the phase association present in the sherds reflects the one formed at high temperature and that no important changes occurred during cooling or during burial. The analysed samples KP 1, 5 and 10 have the same phase assemblage:

diopside/wollastonite + gehlenite + quartz + plagioclase + hematite + spinel (figure 3).

The problem of gehlenite in ceramic bodies has been treated by Heimann and Maggetti (1980) and Maggetti and Heimann (1979), who showed that the presence of gehlenite depends primarily upon the grain-size of the initial clay. Illite could be detected in some of the other 17 sherds from the same locality, indicating therefore that a calcareous illitic clay was used for this pottery. Based on the refiring experiments of Kuepfer and Maggetti (1978), Maggetti (1980a, 1980b) and Peters and Jenni (1973) a firing temperature of at least 900°C must be assumed. The absence of illite in some specimens may indicate that the upper limit was slightly higher (950–1000°C). This is in good agreement with the assumptions made for the Athenian black ware (800–950°C: Binns and Frazer 1929, 800–950°C: Farnsworth and Wisely 1958, 825–950/975°C: Noble 1960, 850–1050°C: Tite *et al.* 1981, 830–850°C: Winter 1959/1978).

Some assumptions about the *reducing conditions* can be made by the coexistence of two Fe-spinels (magnetite$_{ss}$ + hercynite$_{ss}$) in the black coatings. Turnock and Eugster (1962)
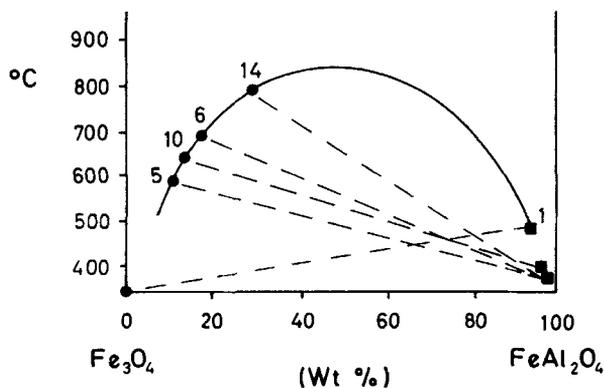
Figure 4   *Solvus relations of the X-rayed spinels in the diagram of Turnock and Eugster (1962). Dots =*
magnetite$_{ss}$(Fe$_3$O$_4$), squares = hercynite$_{ss}$(FeAl$_2$O$_4$). Numbers = specimen.

showed that both spinels are separated from the complete solid solution spinel phase stable at
higher temperatures by a solvus with a convolute temperature of $860 \pm 15°C$ for 48 wt.%
FeAl$_2$O$_4$. The presence of two spinel phases is therefore due to a unmixing process on cooling
involving a homogeneous spinel formed at the assumed firing temperatures of $900-950°C$
during the reduction firing phase. By plotting the composition of the coexisting spinels on the
solvus of Turnock and Eugster (1962) the equilibration temperature of both phases could in
principle be established. However, our specimens give contrasting temperatures, i.e. $600-800°C$
for the magnetite$_{ss}$, $350-500°C$ for the hercynite$_{ss}$ (see figure 4) indicating that both spinels
are not in equilibrium. This is probably connected with the fact that the exact chemical com-
position of both spinels could not be determined. Alternatively, the rapid cooling did not allow
equilibration.

   According to Turnock and Eugster (1962, figure 12a), the absence of wuestite and corundum
in the black coating points to oxygen fugacities in the range of -12 to -21 $\log_{10}$ fO$_2$ for the
magnetite$_{ss}$; the 'equilibration temperature' of the hercynite$_{ss}$ is too low for a correct inter-
polation.

   An indication that the reoxidation phase also affected the black layer is given by the
presence of hematite in some specimens which certainly formed on the outer parts of the gloss.

   The *mineralogical nature* of the unfired glossy clay layer used for the production of the
Attic black vases and the Roman terra sigillata remains a matter of debate. Some authors assume
that special additions i.e. borax or potassium carbonate were made to a fine grained clay
suspension (Neumann 1932, Schumann 1942); more recent authors however tend to assume
that a natural illitic clay suspension was used without additions (Bimson 1956, Farnsworth and
Simmons 1963, Farnsworth and Wisely 1958, Hofmann 1962–1966, Noble 1960, Noll 1973–
1979, Oberlies and Koeppen 1953, Pavicevic 1974, Tite *et al.* 1981, Willgallis and Heyer 1976,
Winter 1959, 1978).

   The comparison of our analyses with the published illite compositions shows agreement for
all elements with the exception of SiO$_2$ which is lower and FeO which is higher. The high
FeO-content is characteristic of the Attic black and the terra sigillata red and it indicates the
presence of an iron-oxide or -hydrate in the slip, present naturally or added artificially. The
coatings of Rheinzabern are similar to our samples with respect to the low SiO$_2$-content. By
comparison with the results of Willgallis and Heyer (1976) as well as Tite *et al.* (1981) it can be

assumed with some certainty that our coatings too were initially a highly ferrous, illitic clay suspension. A test on boron by emission spectroscopy was negative, so that at least the addition of borax is excluded.

Another question is the *origin* of the gloss; was it made locally from the same calcareous clay used for the production of the sherd bodies or did the ancient potters use another, imported low calcareous clay? The contrasting chemical nature between gloss and matrix, especially in CaO content, points to differences in the initial clays; however a local calcareous illitic clay with coarse calcite grains subjected to decantation could also result in a CaO-free slip. If this assumption is correct, the very high FeO-content of the slip, which was either present naturally in the initial calcareous clay or was added in the form of Fe-oxides or -hydrates, must be explained. Without a definite knowledge of the possible clay sources of the Calès region where this pottery was found no attempt can be made to solve this problem.

REFERENCES

Bimson, M., 1956, The technique of Greek Black and Terra Sigillata red, *Antiquaries Journal* 36, 200–204.
Binns, C. F. and Frazer, A. D., 1929, Genesis of the Greek Black Glaze, *Am. J. of Archaeology* 33, 1–9.
Brongniart, A., 1844, Traité des Arts Céramiques, Paris.
Farnsworth, M. and Wisely, H., 1958, Fifth Century International Red Glaze, *Ann. Journ. of Archaeology* 62, 165–173.
Farnsworth, M. and Simmons, I., 1963, Coloring Agents for Greek Glazes, *Ann. Journ. of Archaeology* 67, 389–396.
Heimann, R. and Maggetti, M., 1980, Experiments on simulated burial of calcareous terra sigillata (mineralogical changes), *British Museum Occ. Paper*, in press.
Hofmann, U., 1962, The Chemical Basis of Ancient Greek Vase Painting, *Angewandte Chemie* (International) Vol. 1, No. 7/5, 341–350.
Hofmann, U. and Russow, J., 1963, Untersuchung antiker Keramik mit der Röntgenfluoreszenzanalyse, *Keram. Z.* 11, 676–678.
Hofmann, U. and Theisen, R., 1965, Elektronenmikrosonde und antike Vasenmalerei, *Z. anorgan. u. allgem. Chemie* 341, 207–216.
Hofmann, U. and Theisen, R., 1965, Untersuchung antiker Vasenmalerei mit der Mikrosonde, *Archäologischer Anzeiger* 2, 165–168.
Hofmann, U., Theisen, R. and Yetmen, Y., 1966, Die Anwendung der Elektronenmikrosonde und Röntgenanalyse zur Aufklärung der Chemie der antiken Keramik, *Ber. Dt. Keram. Ges.* 43, 607–614.
Hofmann, U., 1966, Die Chemie der antiken Keramik, *Die Naturwissenschaften* 53, 218–223.
Küpfer, T. and Maggetti, M., 1978, Die Terra Sigillata von La Péniche (Vidy/Lausanne), *Schweiz. mineral. petrogr. Mitt.* 58, 189–212.
Lamboglia, N., 1952, Per una classificazione preliminare della ceramica campana, Istituto Internazionale di Studi Liguri, Bordighera, 139–206.
Maggetti, M., 1980a, Composition of roman pottery from Lousanna (Switzerland), *British Museum Occ. Paper*, in press.
Maggetti, M., 1980b, Recherches minéralogiques, chimiques et technologiques sur la terre sigillée de l'atelier de la Péniche (Vidy/Lausanne), *Cahiers romands d'archéologie*, 20, 81–95.
Maggetti, M. and Heimann, R., 1979, Bildung und Stabilität von Gehlenit in römischer Feinkeramik, *Schweiz. mineral. petrogr. Mitt.*, 59 (3), 413–417.

Maniatis, Y. and Tite, M. S., 1978, Ceramic technology in the Aegean World during the bronze age, Thera and the Aegean world I, London, 483–492.

Maniatis, Y. and Tite, M. S., 1978/79, Examination of Roman Pottery using the Scanning Electron Microscope, *Acta Praehistorica et Archaeologica* 9/10, 125–130.

Morel, J. P., 1980, La Céramique campanienne: Acquis et Problèmes, Dialogues d'Histoire ancienne, Besançon, in press.

Neumann, B., 1932, Die Glasur der Terra Sigillata, *Sprechsaal* 65, 253–254, 273–275, 291–292.

Noble, J. V., 1960, The technique of Attic Vase-Painting, *Am. Journ. of Archaeology* 64, 307–313.

Noll, W., Holm, R. and Born, L., 1973, Material und Techniken antiker Vasenmalerei, *Jahrbuch der Staatlichen Kunstsammlungen in Baden-Württemberg*, Band X, 103–126.

Noll, W., Holm, R. and Born, L., 1975, Bemalung antiker Keramik, *Angewandte Chemie* 87 (18), 639–651.

Noll, W., 1976/77, Neolithische und chalkolithische bemalte Keramik des Vorderen Orients: Material, Rohstoffe und Herstellungstechnik, *Acta Praehistorica et Archaeologica* 7/8, 15–47.

Noll, W., 1979, Anorganische Pigmente in Vorgeschichte und Antike, *Fortschr. Miner.* 57 (2), 203–263.

Oberlies, F. and Köppen, N., 1953, Untersuchungen an Terra Sigillata und griechischen Vasen, *Ber. Dt. Keram. Ges.* 30, 102–110.

Oberlies, F. and Köppen, N., 1962, Untersuchungen an griechischen Gefässfragmenten aus verschiedenen Jahrhunderten v. Chr., *Ber. Dt. Keram. Ges.* 39, 19–31.

Pagenstecher, R., 1909, Die calenische Reliefkeramik, *Jahrbuch des Kaiserlich Deutschen Archäeologischen Instituts, Ergänzungsheft* **VII**, Berlin.

Pavicevic, M., 1974, Untersuchungen der schwarzen Malschicht attischer Vasen mit der Elektronenmikrosonde, *Ber. Dt. Keram. Ges.* 51, 61–63.

Peters, T. and Jenni, J. P., 1973, Mineralogische Untersuchungen über das Brennverhalten von Ziegeltonen, *Beitr. zur Geologie der Schweiz, Geotechn. Serie* 50, 1–59.

Picon, M., Vichy, M. and Chapotat, G., 1971, Note sur la composition des céramiques campaniennes de type A et B, Rei cretariae romanae fautores, *Acta* **XIII**, 82–88.

Schumann, T., 1942, Oberflächenverzierung in der antiken Töpferkunst, Terra Sigillata und griechische Schwarzrotmalerei, *Ber. Dt. Keram. Ges.* 23, 408–426.

Taylor, D. M., 1977, Cosa: black-glaze pottery, *Memoirs of the American Academy in Rome*, 25, 65–193.

Tite, M. S., Freestone, I. C., Meeks, N. D., Bimson, M., 1981, The Use of Scanning Electron Microscopy in the Technological Examination of Ancient Ceramics, Washington: Smithsonian Institution Press. In press.

Turnock, A. C. and Eugster, H. P., 1962, Fe-Al Oxides: Phase relationship below 1000°C, *J. Petrol.* 3 (3), 533–565.

Willgallis, A. and Heyer, H., 1976, Die Glanztonschicht römischer Terra Sigillata: Untersuchungen mit der Elektronenstrahlmikrosonde, *Ber. Dt. Keram. Ges.* 53 (9), 239–276.

Winter, A., 1959, Die Technik des griechischen Töpfers in ihren Grundlagen, *Techn. Beiträge zur Archäologie* I, Röm. germanisches Zentralmuseum zu Mainz.

Winter, A., 1978, Die antike Glanztonkeramik, Ph. von Zabern, Mainz, 58p.