

# Archaeological Ceramics

*Editors*

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Sigalas, I.; Gangas, N. H.; and Danon, J. 1978. Weathering model in paleomagnetic field intensity measurements on ancient fired clays. *Phys. Earth Plan. Int.* 16:15-19.

Simopoulos, A.; Kostikas, A.; Sigalas, I.; Gangas, N. H.; and Moukarika, A. 1975. Mössbauer study of transformations induced in clay by firing. *Clays and Clay Minerals* 23:393-99.

Tite, M. S. 1969. Determination of the firing temperature of ancient ceramics by measurement of thermal expansion: A reassessment. *Archaeometry* 11:131-43.

Tite, M. S., and Maniatis, Y. 1975a. Examination of ancient pottery using the scanning electron microscope. *Nature* 257, No. 5522:122-23.

Tite, M. S., and Maniatis, Y. 1975b. Scanning electron microscopy of fired calcareous clays. *Trans. Brit. Ceram. Soc.* 74:19-22.

Tite, M. S.; Maniatis, Y.; Meeks, N. D.; Bimson, M.; Hughes, M. J.; and Leppard, S. C. 1979. Technological studies of ancient ceramics. In Wertime, T. A., and Wertime, S. F., eds., *Early Pyrotechnology*. Washington, D.C.: Smithsonian Institution Press, forthcoming [1982].

Van der Kraan, A. M. 1973. Mössbauer effect studies of surface ions of ultrafine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. *Phys. Stat. Solidi* 18:215-26.

## 10. The Use of Scanning Electron Microscopy in the Technological Examination of Ancient Ceramics

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### Introduction (section 1)

The primary aim of this paper is to survey the range of technological information that can be obtained from the scanning electron microscope (SEM) examination of ancient ceramics, the technique being supplemented as appropriate by electron microprobe analysis, X-ray diffraction, and thin section optical microscopy.

The data obtained from the SEM examination of fractured and polished sections on the structural and mineralogical changes occurring in ceramics during firing is first summarized (section 2). The use of these data to estimate the effective firing temperatures employed in antiquity is indicated (section 3). This approach to the estimation of firing temperatures is compared with other methods that have been used, and the archaeological significance of a precise estimate of the maximum temperature reached during firing is discussed.

The use of the SEM in the study of the high gloss surface finish applied to ancient ceramics is then considered (section 4) and the results obtained from the examination of the surface finish observed on a selection of pottery from the Aegean area, the Near East, India, and France ranging in date from the Chalcolithic to the Roman period are presented.

### SEM Examination (section 2)

Both fresh fracture surfaces and resin-impregnated polished sections from ceramics can be examined with the SEM. The examination of fresh fracture surfaces — which is the approach previously used by the present authors (Tite and Maniatis 1975; Tite et al. 1979; Maniatis and Tite 1981) and the majority of other workers (Kingery 1974; Noll et al. 1975) — has the advantage that the sample preparation required is minimal. However, in some cases the greater time involved in preparing polished sections is justified by the additional information that can be obtained.

The fracture of ceramics tends to occur through the glass phase when this is present and, therefore, in fresh fracture surfaces, the glass phase is clearly visible under the SEM as smooth-surfaced areas (Fig. 1). The continuity or extent of the glass phase increases with increased firing temperature (Fig. 2), and the firing temperatures employed in the manufacture of the ceramics can therefore be estimated by comparing the vitrification structures observed in their as received state and after refiring in the laboratory at known temperatures for a standard period. In polished sections from ceramics, the degree of continuity and interconnection within the clay matrix (Figs. 3 and 4) provides a measure of the extent to which vitrification has progressed and can similarly be used to obtain an estimate of the firing tempera-

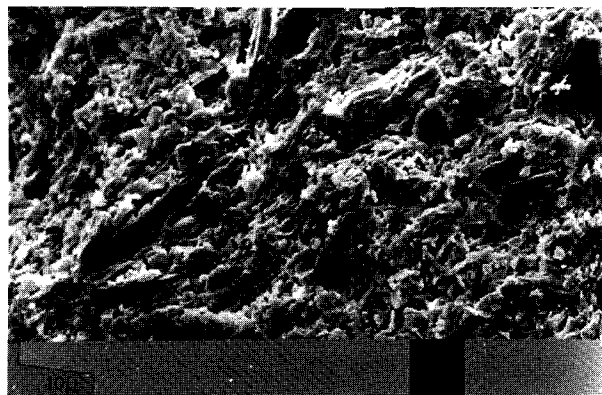


Figure 1. Extensive vitrification structure (fracture section) in TIM 2 (copper smelting tuyere from Timna, Israel).

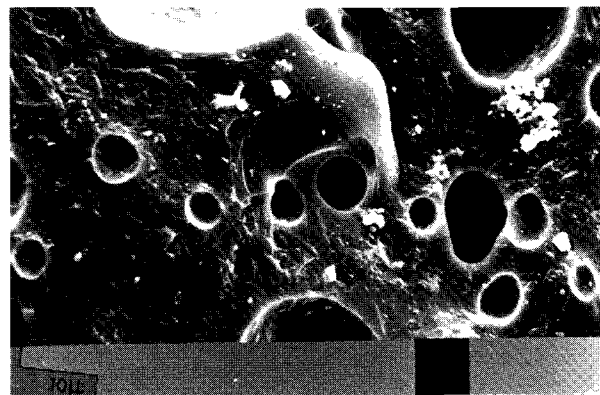


Figure 2. Continuous vitrification structure (fracture section) in TIM 2 (copper smelting tuyere from Timna, Israel).

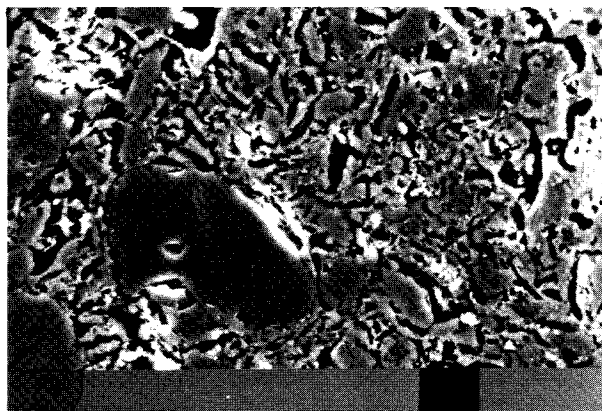


Figure 3. Extensive vitrification structure (polished section) in TIM 2 (copper smelting tuyere from Timna, Israel).

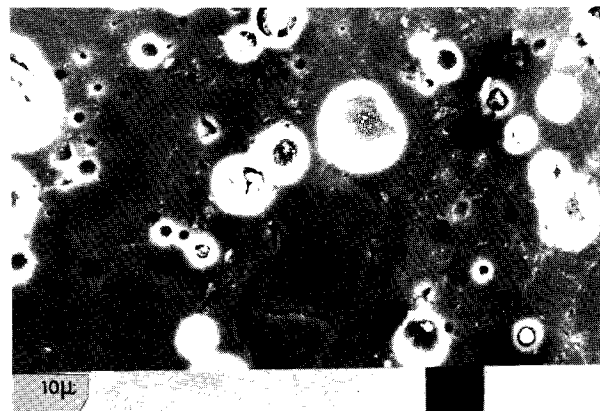


Figure 4. Continuous vitrification structure (polished section) in TIM 2 (copper smelting tuyere from Timna, Israel).

ture employed in antiquity. However, the degree of interconnection also depends on the original texture of the clay and it is therefore sometimes less easy to establish whether or not vitrification has begun from a polished section (Fig. 3) than from a fresh fracture surface in which the smooth-surfaced areas of glass are clearly visible (Fig. 1).

Fresh fracture surfaces, depending as they must on the vagaries of fracture, do not, however, necessarily provide a representative picture of the distribution of inclusions within the clay/glass matrix, nor as a result of the irregularity of the surface are they suitable for quantitative electron microprobe analysis; in these contexts polished sections are preferable. In the SEM, the different phases present can be distinguished on the basis of their atomic number contrast and if polished *thin* sections are prepared, the data obtained with the SEM can be readily supplemented by that from optical microscopy. In addition, polished sections are more suitable for the study of

the surface finish applied to ceramics since it is much easier to control the position of the section through the surface layer, and the surface finish / body interface is more clearly revealed.

#### Microprobe Analysis

A selection of ceramics fired at a range of temperatures has been studied in polished section using the SEM in conjunction with electron microprobe analysis (Table 1).

In the case of the low fired ceramics in which no glass phase or only a limited amount of glass phase had developed, the clay fraction was analyzed using the electron microprobe in an attempt to identify the clay minerals originally present. Using the technique outlined by Courtois and Velde (1981), a series of analyses with a spot 1–2  $\mu\text{m}$  diameter was made of areas in the clay matrix from which nonplastic inclusions such as quartz and feldspar were, on the basis of light optics, apparently absent. Analyses with the

Table 1. Microprobe analyses of pottery body clays and slips

Oxide (% wt)	TIM2	BRH16	IND4		GR4e		GAlc		BRH1	
			Body	Slip	Body	Slip	Body	Slip	Body	Slip
SiO <sub>2</sub>	50.55	53.77	56.43	57.14	57.32	52.79	48.19	43.35	51.00	43.49
TiO <sub>2</sub>	nd	0.94	0.65	0.78	0.38	1.62	0.64	0.51	0.41	0.88
Al <sub>2</sub> O <sub>3</sub>	42.63	36.64	23.77	20.92	17.56	27.10	25.10	30.89	21.01	32.92
FeO	2.18	3.28	7.97	8.94	10.60	9.94	9.81	12.93	5.85	12.38
MgO	0.32	1.45	3.55	3.43	6.14	2.17	6.22	2.28	2.41	0.79
CaO	0.17	0.45	0.86	2.22	2.17	1.67	4.12	0.43	17.17	2.32
Na <sub>2</sub> O	0.54	0.38	1.39	0.84	1.57	0.85	1.12	0.64	0.78	0.34
K <sub>2</sub> O	3.61	3.09	5.38	5.73	4.26	3.86	4.80	3.97	1.37	6.88
Analysis total <sup>a</sup>	91.46	83.11	77.45	91.21	82.67	83.95	81.71	96.88	82.84	98.93

<sup>a</sup> For ease of comparison, the analyses have been normalized to 100%. The analysis totals are also given. The low totals are due to the irregularity of the polished surface formed by the fine grained and porous clay bodies. In general, the totals increase with increasing degree of vitrification; thus, totals for slip analyses are higher than those for the clays of the corresponding body.

highest alumina to silica ratio were readily repeatable and were therefore taken as representative of the clay composition. Evidence in support of this conclusion was the similarity of the peak size and distribution in X-ray spectra of confirmed clay minerals using the semiquantitative X-ray spectrometer attached to the SEM and the spectra of the analyses obtained using the microprobe. However, in using these data, it must be appreciated that a proportion at least of the calcium and iron contents is present as distinct mineral phases which are intimately mixed in with clay minerals. In Figure 5, the analytical data for the four ceramics examined is plotted on a ternary diagram together with fields defined by corresponding analytical data for standard clay minerals and theoretical clay formulae (Deer et al. 1962). The results indicate that the clay fraction in TIM2 (copper smelting tuyere: Timna, Israel) and BRH16 (Roman mortarium: Hartshill, England) contained a high proportion of the two-layer kaolinite mineral whereas the clay fraction in IND4 (black slip ware: Kausambhi, India) and GR4e (Early Bronze Age: Servia, Greece) consisted predominantly of the three-layer illitic or montmorillonitic clay minerals. This conclusion is consistent with data obtained previously (Tite et al. 1979) which established that the former two ceramics were high refractory in that the development of a glass phase did not begin until the ceramics were fired to about 1000°C in an oxidizing atmosphere whereas the latter two were low refrac-

tory with a glass phase beginning to be formed after firing at 800°–850°C.

In the case of the high fired ceramics in which an essentially continuous glass phase was visible in the polished section, the crystalline and amorphous phases present within the glass were investigated either in the section as prepared or after etching in dilute hydrofluoric acid. For the ceramics made from both low and high refractory noncalcareous clays (i.e., clays containing less than about 5% CaO) and fired or refired to temperatures in the range 1150°–1200°C, etching revealed that the apparently continuous glass phase (Fig. 4) consisted of partially dissolved quartz grains embedded in a matrix made up of both a glass phase and a high alumina phase (Figs. 6 and 7). The high alumina phase generally has the form of shapeless, interconnected grains, and in the case of the tuyere, TIM2, the proportion of this high alumina phase decreases with the increasing effective firing temperature towards the surface of the tuyere, which suggests that this phase consists mainly of unreacted relict but almost certainly amorphous clay minerals. However, the X-ray diffraction data, together with the presence of at least a proportion of acicular crystals in the glass phase, suggest that the high temperature phase, mullite, is also present in TIM2 as well as in BRH16 (Roman mortarium: Hartshill, England) and T3b (Middle Bronze Age: Thessaly, Greece). Conversely, no acicular mullite crystals were visible in the glass phase in a low refrac-

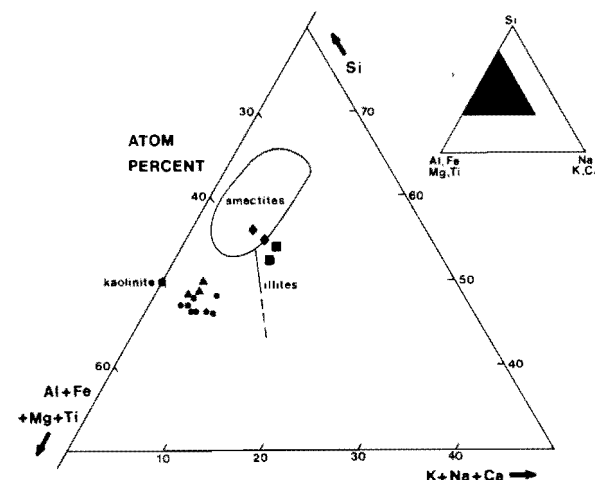


Figure 5. Compositions of clays from ceramics compared with those of major clay mineral types. The field of smectites is based on analyzed montmorillonites from Deer *et al.* (1962) and the point for kaolinite and the line defining illites are based on theoretical formulae for those minerals. Each point represents a single spot analysis on the clay (TIM 2—circles; BRH 16—triangles; GR4e—diamonds; IND 4—squares).



Figure 6. Continuous vitrification structure after etching (polished section) in TIM 2 (copper smelting tuyere from Timna, Israel). The high alumina phase, the partially dissolved quartz grain, and the glass phase are visible as increasingly dark areas.

tory London clay sample fired at 1160°C and this is again consistent with only a very weak mullite line at 5.39 Å being detected by X-ray diffraction.

For ceramics made from calcareous clays containing more than about 15% calcium oxide and again fired or refired in the range 1150°–1200°C, a calcium-rich phase was normally clearly visible within the glass phase prior to etching (Fig. 8). However, in some cases, this phase could be more easily seen after etching. On the basis of analysis using the energy dispersive X-ray spectrometer attached to the SEM

and the X-ray diffraction data, the calcium-rich phase was identified as wollastonite with some diopside (Fig. 9) in AH5 ('Ubaid ware: 'Ubaid, Iraq) and as a mixture of wollastonite with some diopside and anorthite in IR3b (Halaf ware: Arpachiyah, Iraq). In the case of JR2a (Pottery Neolithic B: Jericho, Jordan), two distinct calcium-rich phases were detected in different areas of the ceramic. The first (which predominated) was probably a mixture of gehlenite and wollastonite and the second was wollastonite by itself.

### Firing Temperature Determinations (section 3)

The determination of the extent of vitrification observed with the SEM is only one of many methods that have been used to estimate the firing temperatures employed in the manufacture of ancient ceramics. These other methods are normally based either on the measurement of macroscopic properties such as porosity (Sanders 1973), hardness (Fabre and Perinet 1973), and thermal expansion (Tite 1969; Heimann 1978), which are again dependent on the extent of vitrification or on the use of a mineralogical temperature scale. In the latter case, differential thermal analysis, X-ray diffraction or thin section optical microscopy are used to identify the mineral phases present in the ceramics, and the presence or absence of certain diagnostic minerals (e.g., hydrated clay minerals, calcite, mica, calcium silicates) then provides a basis for establishing the maximum or minimum values for the firing temperature. Alternatively, the state of the iron oxides present in the ceramics as revealed by Mössbauer spectroscopy (Chevalier *et al.* 1976) or color (Matson 1971) can provide an estimate of both the firing temperature and the atmosphere.

The precision with which the firing temperature can be determined with the above methods, including that of SEM examination, is typically 50°–100°C. The estimation of the firing temperature with the SEM is, however, less precise in those cases where the extent of vitrification is either essentially stable such as in the 850°–1050°C firing temperature range for ceramics made from calcareous clays (Tite *et al.* 1979) or changing only slowly with increasing temperature such as in the firing temperature range below 800°–850°C prior to the appearance of a definite glass phase. Although other methods such as thermal expansion (Maniatis and Tite 1978; Heimann 1978) and Mössbauer spectroscopy in principle provide a more precise estimate of the firing temperature in these circumstances, uncertainty regarding the firing atmosphere and firing time employed in antiquity tends to limit the precision irrespective of the inherent accuracy of the method.

Also, the question that must be asked is, What, if

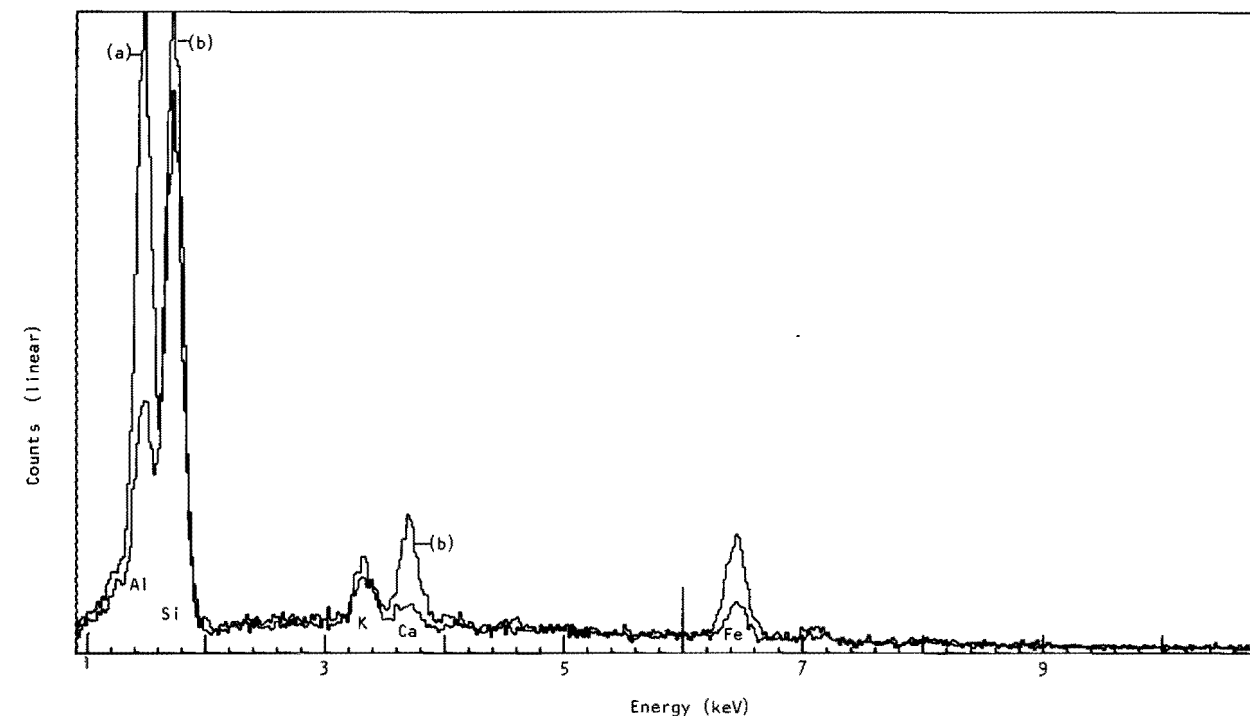


Figure 7. Energy dispersive X-ray spectra for (a) the high alumina phase and (b) the glass phase observed in the continuous vitrification structure of TIM 2 after etching (see Fig. 6).

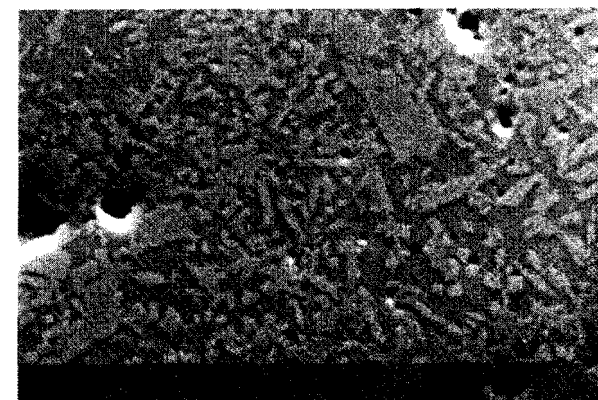


Figure 8. Continuous vitrification structure (polished section) in AH 5 ('Ubaid ware from 'Ubaid, Iraq). The calcium-rich phase (wollastonite with some diopside) is visible as light-colored areas within the darker glass matrix.

any, is the archaeological significance of attempting to determine the firing temperature employed in antiquity with a high precision? In this context, it should be noted that experimental firings of Roman and medieval kilns (Mayes 1961, 1962; Bryant 1970, 1978) have indicated that the temperatures reached in different parts of a kiln can vary by more than 100°C. We would therefore argue that it is normally adequate to provide a rough estimate of the firing temperature sufficient merely to distinguish between

the different primary pyrotechnologies: that is, firing in a bonfire or clamp to temperatures less than 800°–850°C, a normal kiln firing to temperatures in the range 800°–1000°C, or a high temperature kiln firing to temperatures in excess of 1000°C. Experimental firings have clearly demonstrated that temperatures up to about 1000°C can be achieved in kilns without any great difficulty. Also for firing temperatures up to 1000°C, careful selection of the clay used is not necessary although the examination of a wide range of ancient ceramics has suggested that for pottery fired in the 800°–1000°C range, calcareous clays were preferred (Tite *et al.* 1979). Controlled firing to above 1000°C obviously required greater technological expertise and, with the exception of the occasional kiln "waster" and Early Bronze Age pottery of 'Ubaid type from Iraq (Tite and Maniatis 1975), these high firing temperatures do not appear to have been employed in Europe or the Near East during the prehistoric periods.

We would further suggest that, in future, much greater emphasis should be placed on establishing the effect of the different types of clay and firing conditions on those physical properties of the resulting ceramics which are relevant to their suitability for the various uses to which they would have been put in antiquity (Shepard 1956). Such a project would involve the measurement of the strength, toughness, permeability, porosity, and thermal shock resistance of a



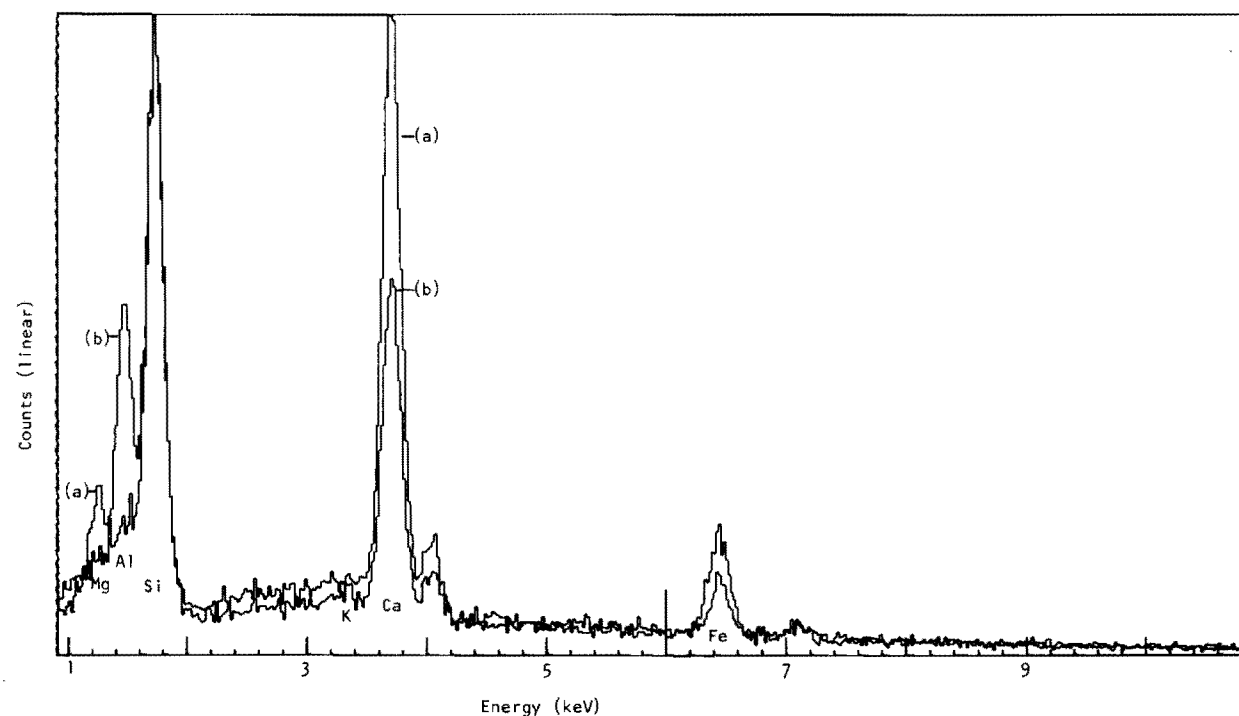


Figure 9. Energy dispersive X-ray spectra for (a) the calcium-rich phase (wollastonite with some diopside) and (b) the glass phase observed in the continuous vitrification structure of AH5 (see Fig. 8).

range of ceramics, and the investigation of the relationship between these properties and the microstructures of ceramics. The data would then need to be assessed in the context of the properties required for the different uses to which the ceramics would have been put, the extent to which the observed properties match these requirements, and the production methods employed to achieve the different properties. In interpreting these data, one would, of course, have to be very careful to avoid assuming a greater degree of technological sophistication on the part of the ancient potters than is justified in the context of what is essentially a craft tradition.

#### High Gloss Surface Finish (section 4)

High gloss surface finishes have been a feature of pottery essentially from its earliest production through to the Greek Attic black and red figure ware and Roman Samian ware (terra sigillata). The reasons for applying these surface finishes were both practical, in that they provide a more impermeable surface layer, and decorative.

A selection of pottery from the Aegean area, the Near East, India, and France ranging in date from the Chalcolithic to the Roman period were examined in order to characterize the burnishing techniques and the different types of slip used to achieve a high gloss surface finish. No attempt has, however, been made to establish the chronological development or

Table 2. Provenance and chronological data for pottery with high gloss surface finish

Sherd No.	Provenance	Period/type
H3a	Toszeg, Hungary	Early Bronze Age
GR4e	Servia, Greece	Early Bronze Age
IND1	Kausambhi, India	Black slip ware c500 B.C.
IND4	Kausambhi, India	Black slip ware c500 B.C.
IND2	Rajghat, India	Black slip ware c500 B.C.
IND3	Kausambhi, India	c500 B.C.
AN1a	Hacilar, Anatolia	Chalcolithic
G3b	Korakou, Greece	Early Bronze Age
GAlb	Attica, Greece	Greek black or red figure ware
GAlc	Attica, Greece	Greek black or red figure ware
BRH1	Central Gaul	Roman Samian ware
BMI	Central Gaul	Roman Samian ware

Table 3. Results for pottery with high gloss surface finish

Sherd no.	Body			Surface finish		
	Clay type <sup>a</sup>	Vitrification stage <sup>b</sup>	Firing temperature	Color	Thickness (μm)	Composition (compared to body)
H3a	NC	NV	<750°C	Black	—	—
GR4e	NC	NV	<750°C	Black	30–40	High Al
IND1	NC	IV	750–800°C	Black	~15	High Al
IND4	NC	IV	750–800°C	Black	~10	High Al
IND2	NC	IV/V	~800°C	Black	5–10	High Al
IND3	NC	NV	<800°C	Red	15–20	High Al
AN1a	C	NV	<800°C	Red	10–30	Low Ca, Fe, K
				White	~100	High Ca
G3b	C	V	850–1050°C	Red	20–30	High Al — Low Ca, K
GAlb	C	V	850–1050°C	Black	~15	High Al — Low Ca
GAlc	C	V	850–1050°C	Black	20–25	High Al — Low Ca
BRH1	C	V(+)	1000–1100°C	Red	5–10	High Al, Fe, K — Low Ca
BMI	C	V	850–1050°C	Red	~20	High Al, Fe, K — Low Ca

<sup>a</sup> NC, noncalcareous clay; C, calcareous clay.

<sup>b</sup> NV, no vitrification; IV, initial vitrification; V, extensive vitrification; CV, continuous vitrification.

the geographical distribution of the different techniques that have been identified.

Fresh fracture surfaces and resin impregnated polished sections through the pottery were examined with the SEM. The former were used to determine the extent of vitrification in the pottery body and hence estimate the effective firing temperature employed in manufacture. The latter, however, provided a clearer picture of the surface finish / body interface and, in some cases, further information was obtained by reexamining these sections after etching in dilute hydrofluoric acid. The compositions of the surface finish and body were compared in terms of the peak heights of the X-ray spectra obtained by analyzing areas approximately 10 μm and 1 mm diameter respectively in the polished sections using the energy dispersive X-ray spectrometer attached to the SEM. The ratio of the peak heights for aluminum and silicon in the surface finish and body respectively were taken as a measure of the relative amounts of clay and quartz, and the aluminum peak heights were used as normalizing factors when comparing the peak heights for the other elements detected (K, Ca, Fe). In addition, spot analyses (1–2 μm diameter) of the clay phase in the surface finish and body were undertaken for some sherds using an electron microprobe (Table 1). The polished sections were also examined in reflected light and, when polished thin sections were available, in transmitted light under a

polarizing microscope. Details of the provenance, chronology, and pottery type are given in Table 2 and the information obtained on the surface finish and body is given in Table 3 for a representative selection of the sherds examined.

Sherd H3a is an example of direct burnishing without the prior application of a surface slip. In general, the appearance of this surface, both visually and under the SEM, was very similar to that of a clay sample which had been burnished and fired in the laboratory. No surface layer was visible in polished section in the SEM (Fig. 10), although there tended to be fewer quartz inclusions at the surface, presumably as a result of their having been pushed back by the burnishing action.

Sherds GR4e, IND1, IND4, IND2, and IND3 are examples of burnishing after the application of a noncalcareous surface slip to a body which was also made from a noncalcareous clay. In each case, a clearly defined, fine textured surface layer which contained a lower concentration of quartz inclusions than the body was visible in polished section in the SEM (Fig. 11). In the fresh fracture surfaces through the slips, the flaky structure of the clay particles was still visible and the absence of vitrification was further confirmed by the birefringence observed in thin section under the polarizing microscope. Except for their higher clay contents (i.e., higher aluminum), the compositions of the surface slips were similar, on the

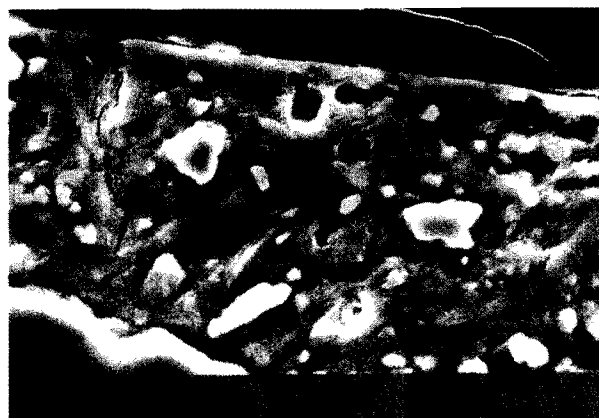


Figure 10. Burnished surface (polished section) on H3A (Early Bronze Age sherd from Toszeg, Hungary).

basis of X-ray peak heights measured in the SEM, to those of the bodies. Electron microprobe analyses (Table 1) showed that the compositions of the clay phase in the slip and body of IND4 were essentially the same, which suggests that the fine-particle fraction from the body clay was used for this slip. In contrast, the compositions of the slip and body clays were different for GR4e but this fact does not necessarily exclude the possibility that the fine-particle fraction from the body clay was again used for the slip. Although the slip of IND4 contains a slightly higher concentration of iron oxide than the body, these results do not really confirm the suggestion made by Hegde (1979) that the slip for the black slip ware from India (IND1, IND4, and IND2) was prepared from a mixture of clay and red ochre. However, the slip on the black slip ware was clearly different from that used for the northern black polished ware from India which, on the basis of analyses and electron microscopy, was shown by Hegde (1979) to have been prepared using a mixture of clay, red ochre, and *sajjimatti* (a natural efflorescence rich in sodium carbonate) and fired to a sufficiently high temperature to produce vitrification.

The remaining sherds are examples of a slip prepared from a noncalcareous clay which was applied to a body made from a calcareous clay. In the case of sherd AN1a, the surface finish was produced by applying a double layer of slip which was then burnished. These two slip layers were clearly visible in terms of color differences in polished section under the optical microscope and were detected in the SEM by their compositional differences (Fig. 12), although no clear textural difference between the slips and the body was visible. It appears that a thick layer of white slip ( $\sim 100\mu\text{m}$ ) which contained a much higher concentration of calcium than the body was first

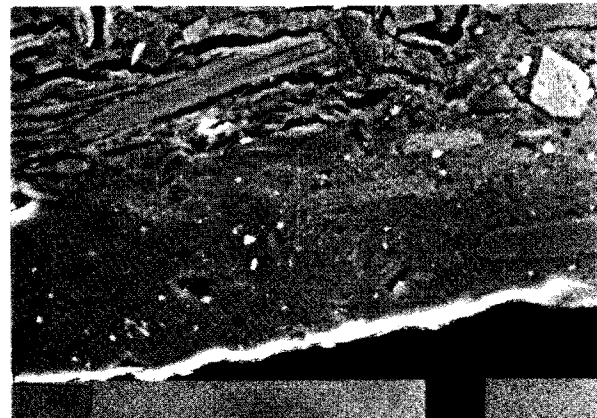


Figure 11. Slip / body interface (polished section) in GR4e (Early Bronze Age sherd from Servia, Greece).

applied. This was then covered with a thinner layer of a second slip ( $10\text{--}30\mu\text{m}$ ) which contained a negligible amount of calcium and which fired to a definite red color. Burnishing of the slipped surface produced the high gloss mottled red and white finish. In the case of sherd G3b, the slip layer, which was clearly visible in polished section in the SEM, consisted of fine textured noncalcareous clay containing some quartz inclusions and its structure contrasted with the more open structure of the calcareous clay body.

The high gloss black slip on the Greek Attic black and red figure ware (GA1b, GA1c) consists of a very fine textured noncalcareous clay (Fig. 13) in which the flaky structure of the clay particles is not visible even in the fresh fracture section. However, the examination of thin sections under the polarizing microscope revealed birefringent clay minerals set in an isotropic glassy matrix. Furthermore, some texture associated with clay particles was visible in the SEM after etching polished sections with dilute hydrofluoric acid (Fig. 14) and in addition, etching resulted in a large increase in the relative concentrations, as measured with the electron microprobe, of aluminum and silicon (0.6 to 1.4 for GA1c) as well as a decrease in the potassium concentration. These observations therefore suggest that the slip layer is partially vitrified and that the etching has preferentially dissolved the glass phase. In contrast to the slips, the bodies exhibit the characteristic open structure associated with calcareous clays which have been fired to a sufficiently high temperature ( $850^\circ\text{--}1050^\circ\text{C}$ ) to produce extensive vitrification. Apart from their significantly lower calcium contents and their higher clay contents (i.e., higher aluminum), the compositions of the slips were, on the basis of the X-ray peak heights measured in the SEM, similar to those of the bodies. Electron microprobe analyses (Table 1)

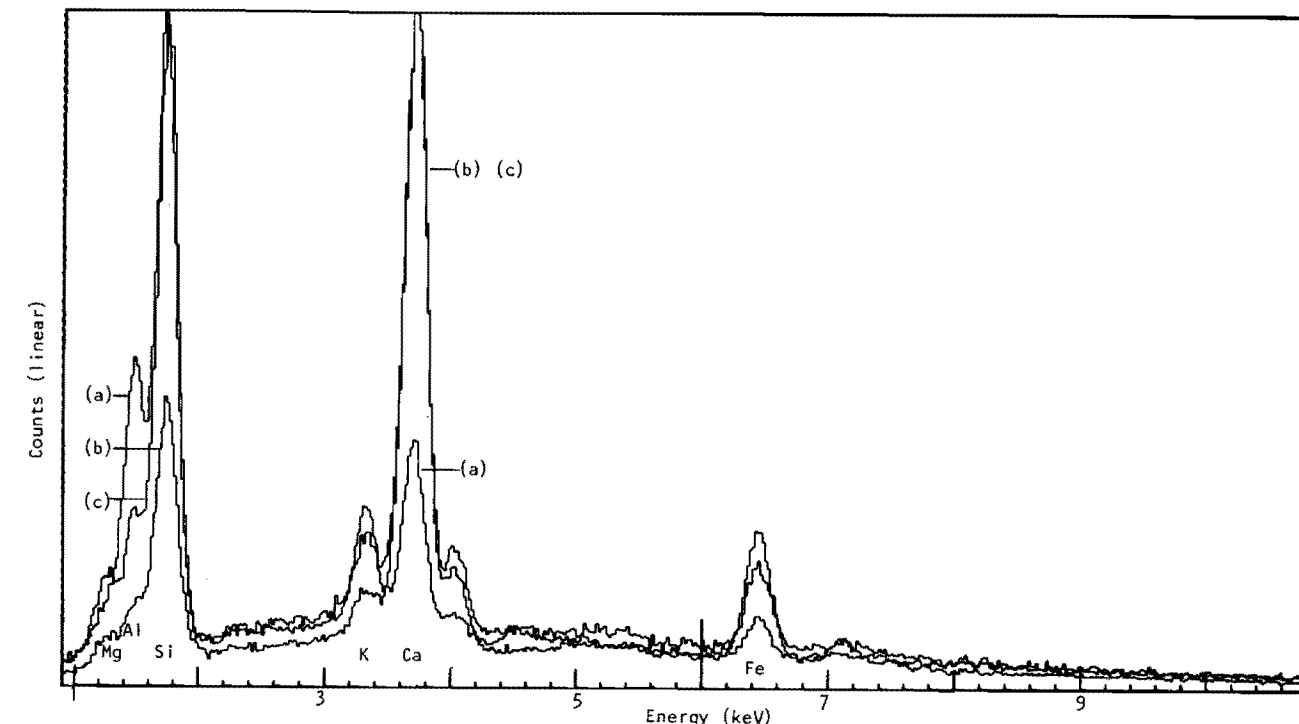


Figure 12. Energy dispersive X-ray spectra for (a) red slip, (b) white slip and (c) body of AN1a (Chalcolithic sherd from Hacilar, Anatolia).

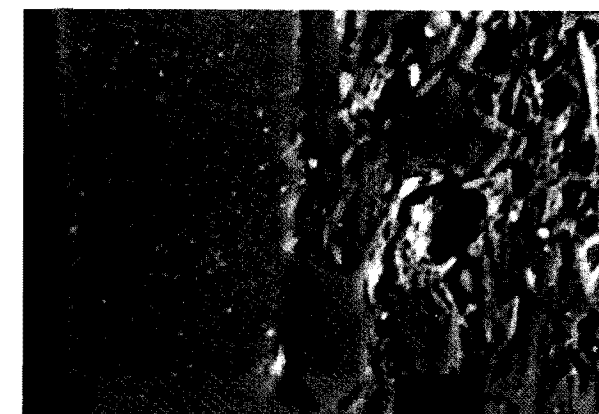


Figure 13. Slip / body interface (polished section) in GA1c (Greek Attic black or red figure ware).



Figure 14. Slip / body interface after etching (polished section) in GA1c (Greek Attic black or red figure ware).

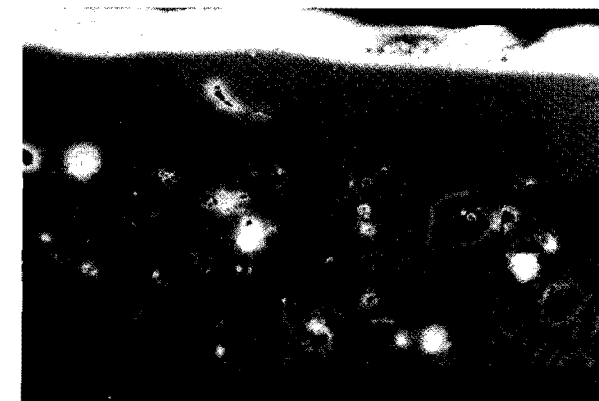


Figure 15. Slip / body interface (polished section) in BM1 (Roman Samian ware).

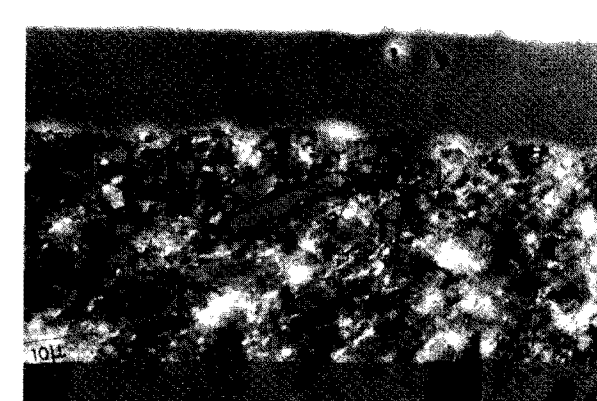


Figure 16. Slip / body interface after etching (polished section) in BM1 (Roman Samian ware).



showed that the slip clay of GA1c contained lower magnesium and calcium contents but a higher iron content than the body clay. However, since the aluminum to silicon ratio was only slightly higher in the slip (0.64 as compared to 0.52 in the body) and there was no significant difference in the potassium content, the clay used for the slip did not contain a significantly higher proportion of illitic clay minerals than that used for the body. Further, and in spite of these differences in composition, it is possible that the fine-particle fraction from the body clay was used for the slip (Harbottle 1980).

The high gloss red slip on the Roman Samian ware (BRH1 and BM1) again consists of a very fine textured noncalcareous clay (Fig. 15) with no clay structure visible even in the fresh fracture section. In the case of BRH1, the slip appeared isotropic in thin section under the polarizing microscope and only slight birefringence was observed for other Samian slips examined. Furthermore, no texture associated with clay particles was visible in the SEM after etching in dilute hydrofluoric acid (Fig. 16) and the increase in the relative concentrations, as measured with the electron microprobe, of aluminum to silicon (0.8 to 1.0 for BRH1) and the decrease in the potassium concentrations were less pronounced after etching than in the case of the Greek Attic slip. Therefore, on the basis of the examples examined, the Roman Samian slip appears to be more fully vitrified and homogeneous than the Greek Attic slip. The bodies of the Roman Samian ware again exhibit the characteristic open structure associated with calcareous clays. Etching of the bodies in dilute hydrofluoric acid resulted in some increase in the relative concentration of aluminum to silicon and a significant increase in the calcium content. Hence the etching appears to have preferentially removed the glass phase to leave the relict clay minerals as well as the calcium aluminosilicates (e.g., anorthite) which were formed during firing and which were detected by X-ray diffraction. Electron microprobe analyses (Table 1) showed that the compositions of the clay phase in the slip and the body of BRH1 were very different. In addition to the significantly lower calcium content and higher iron content in the slip, the aluminum to silicon ratio (0.76 as compared to 0.41) and the potassium content were also much higher in the slip. Hence the clay used for the slip contained a significantly higher proportion of illitic clay minerals than that used for the body. However, it is again possible that the fine-particle fraction from the body clay was used for the slip (Heimann 1980).

The techniques used in the production of the Greek Attic and Roman Samian wares have been the subject of extensive investigations (Binns and Frazer 1929;

Schumann 1942; Bimson 1956; Hofmann 1962, 1966). On the basis of this work it is now generally accepted that an illitic clay was selected for the slips and that a reducing-oxidizing firing cycle was used to produce the Greek Attic black and red figure ware, while an oxidizing atmosphere was maintained throughout the firing in the case of the Roman Samian ware. The current analytical data confirm the use of illitic clays for the slip although in the case of Greek Attic sherds examined, the proportion of illitic clay minerals was not significantly greater in the slip than in the body. Similarly, the open structure of the calcareous clay body of the Greek Attic ware is consistent with its being more readily oxidized than the impermeable slip during the oxidizing phase of the firing cycle. However, Bimson (1956) has pointed out that this purely physical explanation is inadequate since, after slight exposure to a reducing atmosphere, the Roman Samian red gloss is reduced to a black color while reoxidation even to a reddish-brown color was correspondingly difficult. The differential oxidation of the slip and body in the case of the Greek Attic ware must therefore be due, at least in part, to the different stabilities of the associated ferrous iron phases and not merely to the lower porosity of the partially vitrified slip layer. Mössbauer spectroscopy (Longworth and Warren 1975; Longworth and Tite 1979) has confirmed that, in the black slip, the iron is present as a spinel (i.e., a member of the  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  series), and this phase may be less readily oxidized than the calcium iron silicates in which the iron exists in the calcareous clay body.

#### General Discussion

The results presented above establish that the slips used to produce high gloss surface finishes were prepared almost exclusively from noncalcareous clays. This observation is consistent with the fact that a noncalcareous clay is necessary in order to produce an impermeable slip without firing to very high temperatures since calcareous clays exhibit an open, porous structure when fired in the 850°–1050°C temperature range. This open structure is most probably due to the disruption of the clay particles when carbon dioxide is released in association with the decomposition of the calcite. In addition, when fired in an oxidizing atmosphere, a noncalcareous clay is likely to produce a more attractive red color than a calcareous clay since the iron will remain as haematite rather than forming calcium iron silicates. Also, when a noncalcareous clay slip is used with a calcareous clay body, a more definite color contrast between the slip and the lighter colored body will be achieved.

A further question that needs to be considered is why, other than for reasons of color contrast, were

calcareous clay bodies used in conjunction with noncalcareous clay slips? As discussed above, this combination of clays is probably necessary for the Greek Attic ware in order to achieve the differential oxidation of slip and body during the oxidizing phase of the firing cycle. However, the benefits of a calcareous clay body are less obvious in the case of Samian ware. Picon et al. (1971) have shown that calcareous clays were used almost exclusively for Samian ware from both Gaul and Arezzo even when other pottery types from the same manufacturing center were being made from noncalcareous clays. There is, therefore, no doubt that calcareous clays were being deliberately selected for the production of Samian ware. Picon and Vichy (1974) have further suggested that it is possible that calcareous clays were selected for historical reasons and that the Roman potters were continuing a long-established tradition for the production of pottery with a slipped surface even though the original reasons (e.g., color contrast, permeable body) were no longer relevant.

There are, however, a number of technological advantages to be gained from the use of calcareous clays for the body. First, a calcareous clay body will tend to have a higher thermal expansion coefficient ( $4.5$ – $7.0 \times 10^{-6}/^\circ\text{C}$ ) than that of comparable noncalcareous clay bodies ( $2$ – $3.5 \times 10^{-6}/^\circ\text{C}$ ). Its thermal expansion coefficient will therefore more closely match that of the partially vitrified slip which is likely to be in the range  $5$ – $10 \times 10^{-6}/^\circ\text{C}$  and consequently there will be less risk of the slip crazing during cooling. Second, as a result of the formation of crystalline phases, calcareous clays produce bodies which have a higher rigidity and compressive strength than those produced from comparable noncalcareous clays (Peters and Iberg 1978). The resulting pottery is therefore more practical when used as domestic tableware as was the case with Samian ware. A further advantage of calcareous clays is that their vitrification structure remains essentially unchanged over the 850°–1050°C firing temperature range and therefore the control of the firing temperature needed to produce pottery of a consistent quality is less critical than would be the case for a comparable noncalcareous clay.

#### Conclusions (section 5)

The above examples indicate that the SEM examination of fresh fracture and polished sections through ceramics when used in conjunction with hydrofluoric acid etching, electron microprobe analysis, optical microscopy, and X-ray diffraction provides a powerful technique for elucidating the structural and mineralogical changes occurring when ceramics are fired and hence for obtaining information on the raw

materials and procedures used in the production of ancient ceramics. For example, the clay type used for the body and slip can be identified and the effective firing temperature employed can be estimated. In addition, the detailed information obtained on microstructure would be relevant to an understanding of the physical properties of ceramics (e.g., strength, toughness, permeability, porosity, thermal shock resistance) determined by direct measurement.

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#### 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. The genesis of the Greek black glaze. *American Journal of Archaeology* 33:1–10.
- Bryant, G. F. 1970. Two experimental Romano-British kiln firings at Barton-on-Humber, Lincolnshire. *Journal of the Scunthorpe Museum Society* 3:1–16.
- \_\_\_\_\_. 1978. Romano-British experimental kiln firings at Barton-on-Humber, England, 1968–75. *Acta Praehistorica et Archaeologica* 9/10:13–22.
- Chevalier, R.; Coey, J.M.D.; and Bouchez, R. 1976. A study of iron in fired clay: Mössbauer effect and magnetic measurements. *Journal de Physique* 37, C6:861–65.
- Courtois, L., and Velde, B. 1981. Petrographic and electron microprobe studies of Cypriot white slip ware. *Revue d'Archéométrie Supplément*: 37–43.
- Deer, W. A.; Howie, R. A.; and Zussman, J. 1962. *Rock-forming minerals*. Vol. 3, *Sheet Silicates*. London: Longmans.
- Fabre, M., and Perinet, G. 1973. Mesure de la dureté de pâtes céramiques calcaires. *Bulletin de la Société Française de Céramique* 99:39–49.
- Harbottle, G. 1980. Private communication.
- Hegde, K.T.M. 1979. Analysis of ancient Indian deluxe wares. *Archaeo-physika* 10:141–55.
- Heimann, R. B. 1978. Mineralogische Vorgänge beim Brennen von Keramik und Archaeothermometrie. *Acta Praehistorica et Archaeologica* 9/10: 79–102.
- \_\_\_\_\_. 1980. Private communication.
- Hofmann, U. 1962. The chemical basis of ancient Greek vase painting. *Angewandte Chemie* 1: 341–50.

\_\_\_\_\_. 1966. Die Chemie der Antiken Keramik. *Naturwissenschaften* 53: 218-23.

Kingery, W. D. 1974. A technical characterization of two Cypriot ceramics. In Bishey, A., ed., *Recent Advances in Science and Technology of Materials*, Vol. 3, pp. 169-86. New York: Plenum Publishing Corporation.

Longworth, G., and Warren, S. E. 1975. Mössbauer spectroscopy of Greek "Etruscan" pottery. *Nature* 255: 625-27.

Longworth, G., and Tite, M. S. 1979. Mössbauer studies on the nature of red or black glazes on Greek and Indian painted ware. *Journal de Physique* 40, C2:460-61.

Maniatis, Y., and Tite, M. S. 1978. Examination of Roman and Medieval pottery using the scanning electron microscope. *Acta Praehistorica et Archaeologica* 9/10: 125-30.

Maniatis, Y., and Tite, M. S. 1981. Technological examination of Neolithic-Bronze Age pottery from Central and Southeast Europe and from the Near East. *J. Archaeological Science* 8: 59-76.

Matson, F. R. 1971. A study of temperatures used in firing ancient Mesopotamian pottery. In Brill, R. H., ed., *Science and Archaeology*, pp. 65-79. Cambridge: M.I.T. Press.

Mayes, P. 1961. The firing of a pottery kiln of a Romano-British type at Boston, Lincolnshire. *Archaeometry* 4: 4-30.

\_\_\_\_\_. 1962. The firing of a second pottery kiln of a Romano-British type at Boston, Lincolnshire. *Archaeometry* 5: 80-92.

Noll, W.; Holm, R.; and Born, L. 1975. Painting of ancient ceramics. *Angewandte Chemie* 14: 602-613.

Peters, T., and Iberg, R. 1978. Mineralogical changes during firing of calcium-rich brick clays. *American Ceramic Society Bulletin* 57: 503-509.

Picon, M.; Vichy, M.; and Meille, E. 1971. Composition of Lezoux, Lyon and Arezzo Samian ware. *Archaeometry* 13: 191-208.

Picon, M., and Vichy, M. 1974. Recherches sur la composition des céramiques de Lyon. *Revue Archeologique de l'Est et du Centre-Est* 25: 37-59.

Sanders, H. P. 1973. Pore size determinations in Neolithic, Iron Age, Roman, and other pottery. *Archaeometry* 15: 159-61.

Schumann, T. 1942. Oberflächenverzierung in der antiken Töpferei, Terra Sigillata und Griechische Schwarzrotmalerei. *Berichte Deutscher Keramischen Gesellschaft* 23: 408-426.

Shepard, O. A. 1956. *Ceramics for the archaeologist*, pp. 113-36. Washington, D.C.: Carnegie Institution of Washington.

Tite, M. S. 1969. Determination of the firing temperature of ancient ceramics by measurement of thermal expansion: a reassessment. *Archaeometry* 11: 132-43.

Tite, M. S., and Maniatis, Y. 1975. Examination of ancient pottery using the scanning electron microscope. *Nature* 257: 122-23.

Tite, M. S.; Maniatis, Y.; Meeks, N. D.; Bimson, M.; Hughes, M. J.; and Leppard, S. C. 1979. Technological studies of ancient ceramics. In Wertime, T. A., and Wertime, S. F., eds., *Early Pyrotechnology*. Washington, D.C.: Smithsonian Institution Press, forthcoming [1982].

## 11. Phase Analysis and Its Significance for Technology and Origin

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### Abstract

This paper presents the results of investigations on temper, paste, and porosity of ancient ceramics by application of optical microscopy, X-ray diffractometry, and measurement of porosity. Porosity data must be interpreted carefully; the results of controlled firing and refiring of illitic calcareous and kaolinitic noncalcareous clays show how difficult their interpretation in terms of ancient firing temperatures and initial granulometry can be. The effect of reducing atmosphere is also discussed. Much more research work is needed, however, before porosity data can be interpreted correctly. The mineralogical changes during firing of the paste are very useful for an estimation of the ancient firing temperature, the nature of the raw material, the technology of the processing and firing atmosphere. Firing experiments on kaolinitic noncalcareous and illitic calcareous clays are discussed. There is a great need for more detailed research, especially with respect to reducing firing conditions. A review of the mineralogical changes during burial leading to secondary products as calcite, montmorillonite, mixed-layers, and zeolites is presented. Finally, the application of temper analysis for identification of local or foreign production of coarse ware is discussed and arguments for identifying artificially added temper are presented.

### Introduction

If an archaeologist gives a sherd to an archaeoceramist for analysis, then the sherd has reached the fifth step of its long life (Fig. 1). These steps are: (1) extraction of the clay from a clay pit ("origin"); (2) manufacture of the ceramic object (processing, firing); (3) use with subsequent breakdown; (4) burial stage; and (5) analysis. From the first four steps the sherd has stored information and it possesses a memory which can be activated by the analysis (step 5) gaining the "sleeping" information about the steps 1 to 4. This can be done by a lot of physicochemical methods based on the analysis of the chemistry, mineralogy, and other physical parameters as magnetism, thermoluminescence, etc., of the sherd. Considering the *chemical composition*, it is obvious that the chemistry is a function of the composition of the original clay, of its processing (the extraction of coarse particles or addition of temper fragments can change the chemistry), of the use (the chemistry of a cooking pot can be affected by reaction processes between the pot itself and the food), of the burial stage (infiltration of foreign matter in the sherd body, extraction of sherd matter due to solvents from invading solutions) and of the archaeological treatment (cleaning with acids can lead to dissolution of carbonates). Therefore, the chemical analysis *alone* can-