Mineralogical applications of the analytical SEM in archaeology

I. C. FREESTONE AND A. P. MIDDLETON

British Museum Research Laboratory, London WC1B 3DG

Abstract

The modern analytical SEM, which can provide high-quality imaging facilities together with quantitative elemental analysis using an energy-dispersive spectrometer, is finding wide application in the investigation of archaeological problems. Many of these investigations involve the study of silicate and carbonate-based artefacts which may be relatively unmodified from their original geological parent raw materials so that mineralogically based interpretations are often appropriate. In this paper we present a series of examples illustrating the role of the analytical SEM in the mineralogical investigation of archaeological problems, including the characterization and provenancing of geological raw materials, the elucidation of the processes used to transform those raw materials into useful objects and the recognition and characterization of changes which archaeological artefacts may have undergone during burial or during storage.

KEYWORDS: analytical scanning electron microscope, archaeology.

Introduction

BEFORE the Industrial Revolution, sophisticated refining and separation techniques were not, in general, available to treat raw materials, with the result that archaeological artefacts are often close or (as in the case of stone) identical in composition to their geological parents. Furthermore, the great bulk of excavated artefactual material is silicate or carbonate-based. A mineralogical input can therefore be critical in their interpretation.

The combination of high-quality imaging and analytical facilities offered by the SEM is particularly valuable in these studies because the materials are often fine-grained. In addition, their paragenesis is such that they may contain associations of phases which are unfamiliar in natural contexts and the analytical facility offered by the SEM allows direct elucidation of these assemblages. The advent of efficient back-scattered electron detectors, which has contributed significantly to the use of the SEM in petrological investigations, for example in the study of fine grained sediments (e.g. Krinsley *et al.*, 1983; White *et al.*, 1984), is of substantial benefit in such work.

The archaeological scientist may be required to answer an array of questions ranging from the mundane to the esoteric; for the present purpose, however, we focus upon those which are particularly amenable to mineralogical solutions. These are (1) the characterization of the material from which an object was made (2) the reconstruction of the technology involved in its manufacture, (3) the inference of the place of manufacture or source of raw materials and (4) the changes that have occurred in the object during burial or storage. Such information can be useful in the evaluation of cultural and economic aspects of past societies. The role of the mineralogist in sourcing artefacts shaped in stone has been thoroughly reviewed by Kempe and Harvey (1983), and in the present paper, we dwell mainly upon synthetic materials, i.e. those in which the chemical and/or phase composition has been modified by Man. There is a very close parallel between such studies and those of mineral and rock paragenesis; in both cases the analysis of an existing assemblage is carried out with a view to the establishment of the processes which gave rise to it.

In the following paragraphs a number of examples are grouped by material or approach to illustrate the range of applications and the benefits conferred by the SEM. The studies summarized are drawn from work carried out by the authors and their colleagues at the British Museum.

Methods

The earlier of our own studies were carried out using a Cambridge S600 SEM fitted with a qualitative energy-dispersive spectrometer. The data so

obtained were supplemented with quantitative analyses obtained using a Cambridge Geoscan microprobe fitted with a Link Systems energy-dispersive spectrometer. In more recent studies we have used a JEOL JSM840 SEM fitted with a Link Systems spectrometer which provides analytical data of comparable quality together with high-quality imaging facilities.

Where possible and appropriate, samples were prepared as polished thin-sections. However, many of the objects we have examined are of high artistic and/or historical value and only the smallest possible sample may be removed; duplicate sampling is in general unacceptable. In such cases small samples are set in blocks of epoxy resin and polished.

The effect of temperature on the microstructure of clay

Clay artefacts are ubiquitous from the Neolithic period and an understanding of the level of clay technology is important to an appreciation of the general technical sophistication of a culture. The temperatures at which ceramics were fired in the pre-industrial world varied over the range 600–1300 °C, depending on the type of clay used and the types of kiln available. The use of clay materials in metallurgical processes extended this range up to 1400 °C. The temperature to which a ceramic has been subjected may be estimated by the examination of its microstructure in the SEM. This approach has been explored particularly by Tite and Maniatis (1975), Maniatis and Tite (1981) and Tite *et al.* (1982*a*).

A photomicrograph of a low-fired (*c.* 800 °C), poorly-refined earthenware clay is shown in Fig. 1*a*. The individual mineral particles are readily distinguished and there is only limited grain-to-grain contact. The source rocks for this particular clay were Precambrian slates, reflected in the quartz and mica-rich assemblage. With increase in temperature localized melting occurs and the ceramic begins to vitrify. The degree of interconnection of the particles increases and the porosity decreases (Fig. 1*b*; $T = c.$ 1000–1050 °C). Finally, the pores are isolated and the trapped gases expand, causing the formation of rounded vesicles (Fig. 1*c*; $T = c.$ 1100–1150 °C), and at higher temperatures (*c.* 1200–1250 °C), macroscopic bloating.

The various stages in the vitrification of a ceramic may be characterized and, by refiring test pieces of the ceramic in the laboratory over a range of temperatures, this sequence of changes can be calibrated for temperature. In order to use such a calibration to determine the temperature at which a ceramic has been fired, it is important to test fire a piece of the same ceramic because the behaviour
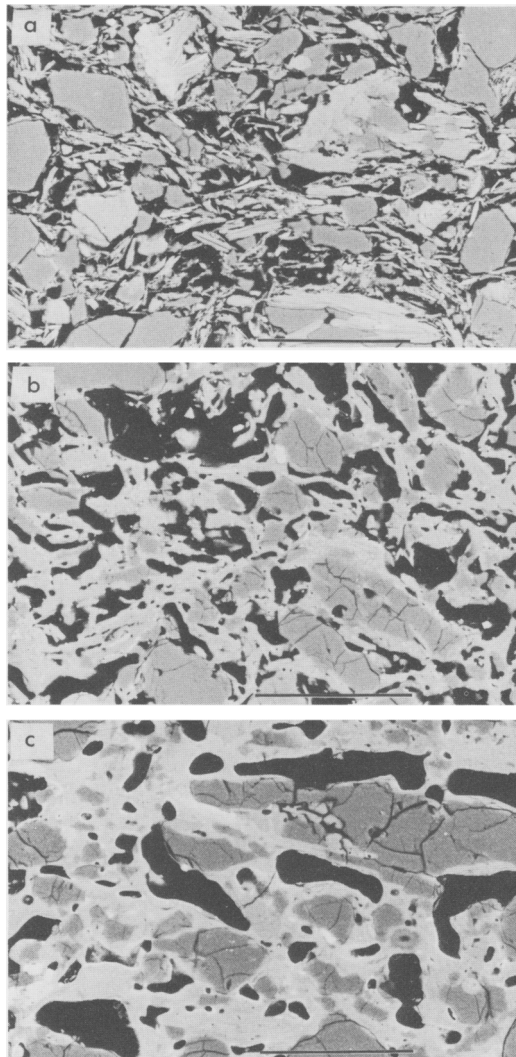

FIG. 1. Micrographs of polished thin-sections showing progressive changes in the degree and texture of vitrification from the cool portion to a position close to the hot surface of a fragment from a zinc distillation furnace at Zawar. (*a*) $T = 800$ °C; (*b*) $T = c.$ 1000–1050 °C; (*c*) $T = c.$ 1100–1150 °C. BSE micrographs; operating voltage 25 kV. The scale bars represent 100 μm.

with temperature is very dependent on composition (Maniatis and Tite, 1981). Analytical data, determined by EDXA, are very useful as they enable the firing behaviour to be matched with that of previously analysed samples of similar composition, allowing the extrapolation of results from refirings at only one, or perhaps two, temperatures. Furthermore, environmental contamination of the ceramic

by fluxes such as sodium chloride may also be recognized and taken into account when interpreting refiring data.

Pottery and porcelain technology

Firing temperatures of pottery can be used to evaluate the sophistication of the firing process; for example, whether in an open bonfire (typically less than 850 °C) or in a simple updraft kiln ($T = 850-1100$ °C). The nature and development of the ceramic microstructure as a function of temperature can be related to the composition of the clay source exploited. For example, calcareous clays (CaO > 5 wt. %) were widely used in the Mediterranean area in antiquity and have a particularly stable microstructure over the temperature range 850–1050 °C. There is thus a considerable margin for error in firing, and such clays would guarantee a consistent product quality relative to the low-refractory, non-calcareous clays which were available as alternatives. Chronological development in clay exploitation and ceramic microstructure has been traced using SEM and EDXA by Noll and his co-workers (e.g. Noll, 1978, 1982; Letsch and Noll, 1983).

The analytical SEM has made possible the detailed examination of the inorganic surface coatings and pigments which were applied to much ancient pottery. Attention has focussed particularly on the fine, glossy coatings on classical fine wares such as Greek Attic, Roman Samian wares and their derivatives and precedents (Noll, 1981; Noll *et al.*, 1974, 1975; Tite *et al.*, 1982b, 1982c; Maggeti and Galetti, 1981). These K-, Fe- and Al-rich coatings (shown in cross-section in Fig. 2) are thought to have been prepared from suspensions of very fine illitic clay particles. The clay platelets oriented flat against the surface of the pots as the slip dried, resulting in a high-quality glossy surface.

A study by Middleton (in press) on applied red coatings on certain Late Bronze Age pottery from Southern England illustrates a number of aspects of such studies. This type of pottery has generally been termed 'hematite-coated ware' because of its distinctive, bright red, often burnished, finish. Detailed examination of the coatings on sherds from about a dozen archaeological sites in southern England has shown that several techniques were used to produce the red finishes. Some sherds showed evidence for the application of crushed hematite or ochre coatings (e.g. Fig. 3 which shows a cross-section through a coated sherd), while the surfaces on others had evidently been produced by the application of various clay slips or even just burnished without the application of any coating material. Variation in the detailed character of both the crushed hematite
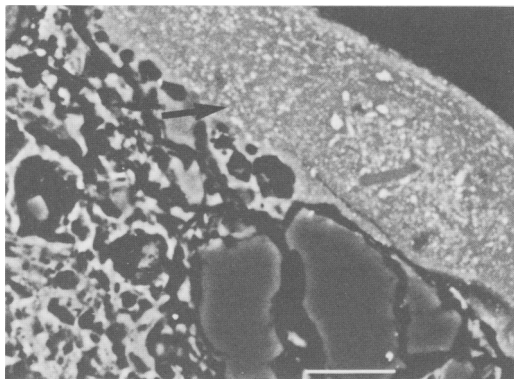

FIG. 2. Red, high-gloss surface finish on a sherd of Roman Samian ware. Note the lack of apalastic inclusions and very fine-grained iron oxide particles (white) in the coating (arrowed). BSE micrograph of a cross-section; operating voltage 15 kV. The scale bar represents 10 μm.

and clay slip coatings was interpreted as reflecting local variation in available raw materials and technique. Thus, in the production of these wares, the potters were trying to imitate a type—they were not sharing techniques. This study showed that the use of the term 'hematite-coated' could be very misleading.

Against the soft, low-fired bodies and coatings of the pottery of Bronze Age Britain we may counterpose the highly vitrified, glazed porcelains of China, which represent a level of technical ability and control that western ceramicists were striving to emulate a millennium after their inception in the East. The availability of appropriate clays and
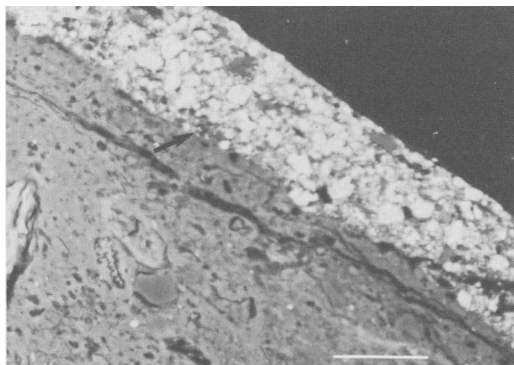

FIG. 3. Sherd of Late Bronze Age 'hematite-coated' ware from Kimmeridge, Dorset showing the use of crushed hematite or ochre to produce a red surface coating (arrowed). BSE micrograph of a cross-section; operating voltage 15 kV. The scale bar represents 40 μm.

fluxes for the production of porcelain was one of the factors accounting for the precociousness of the Chinese ceramic industry, and examination with the SEM gives some insight into the nature of the raw materials. The microstructure of Chinese porcelain may be characterized in terms of four basic morphological units (Tite et al., 1984; Tite and Freestone, 1986): (1) rounded, relict quartz grains, (2) a matrix composed of varying proportions of very fine-grained mullite in glass, (3) ragged, lath-shaped aggregates of mullite and (4) glassy pools containing randomly-oriented mullite needles (Fig. 4). Coupled with morphology, Al_2O_3/SiO_2 ratios suggest that the lath-like aggregates are pseudomorphs of muscovite and that the glassy pools are the result of the melting of feldspar; K/Na ratios are constant throughout due to the mobility of these components.
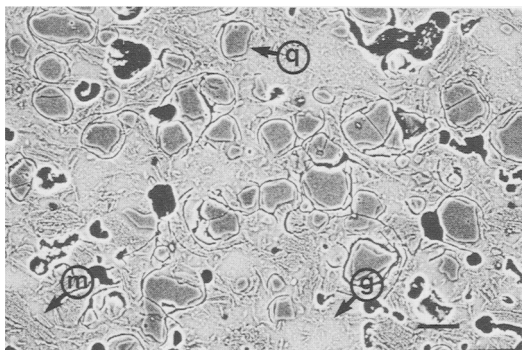

FIG. 4. Etched section of underglaze-blue porcelain showing relict grains of quartz (dark grey, q) in glassy matrix containing ragged, lath-shaped aggregates of mullite and glassy pools containing fine mullite needles (g). BSE micrograph; operating voltage 15 kV. The scale bar represents 20 μm.

Examination of the classic 'yingqing' and blue and white porcelains of Jingdezhen, southern China, dating to the Yuan dynasty (13–14th centuries) suggests that mica was a major component of the bodies and was generally dominant over feldspar. This corresponds well with our understanding of the production of porcelain at Jingdezhen today, when a greisenized 'porcelain stone' or 'petuntse' is mixed with kaolin to produce the ceramic body. In contrast to European hard porcelain, where feldspar is traditionally used as a flux, in China a critical component was sericitic mica which not only provided K_2O as a flux but also contributed to the plasticity of the body, no doubt an important factor in the repertoire of ceramic forms produced.

Indeed, there is evidence that, at one stage, only a single raw material, a kaolinized greisen, was utilized to produce some of the earlier porcelain bodies (Tite et al., 1984). The SEM is also proving extremely useful in the study of Chinese glazes and overlay enamels (Kingery and Vandiver, 1986; Vandiver and Kingery, 1985).

Provenance studies

Thin-section petrography has proved particularly useful in allowing the identification of the sources of raw materials of stone and ceramic artefacts to be established (Kempe and Harvey, 1983). Such information is of value for the insights it provides into the economies of past cultures and the degree of cohesion within them and contact between them.

In such cases the use of the analytical SEM and/or microprobe can sharpen the information provided by optical petrography. As an example we cite the case of a group of ceramic flagons, jars and platters of Roman style found on a number of sites in southeastern Britain dating to the Late Pre-Roman Iron Age (Rigby and Freestone, 1983, 1986). In thin section these wares are found to be relatively fine grained, containing 10–20% poorly-sorted, very fine sand and coarse silt in a matrix of fired clay. The clasts are predominantly feldspar and quartz with common muscovite and biotite, and occasional heavy minerals such as amphibole, clinopyroxene, olivine and sphene. Rock fragments are rare, but in relatively coarse-grained examples of the fabric, occasional fragments of acid plutonic, schistose metamorphic and volcanic rocks are observed. Unfortunately the frequency of occurrence of these rock fragments is so low as to preclude any inferences of the geological source of the clay from their presence. Therefore the mineral fragments in the pottery were analysed to determine their environment of formation.

Using the approach of Trevena and Nash (1979, 1981), feldspars were found to be of at least two types, volcanic and plutonic/metamorphic (Fig. 5). Amphiboles form two clear analytical groups, one tending to kaersutitic compositions and a group of magnesio-hornblendes (Fig. 6). Clinopyroxenes were not very informative, transgressing the boundaries between tectonic groupings (e.g. Nisbet and Pearce, 1977). However, a single olivine had a calcium concentration characteristic of volcanic olivines (Simkin and Smith, 1970). These results were considered to support the limited evidence from the rock fragments that the sand was a mixture of material from at least two sources: volcanic rocks and plutonic/metamorphic rocks. The presence of fresh, volcanic olivine indicates
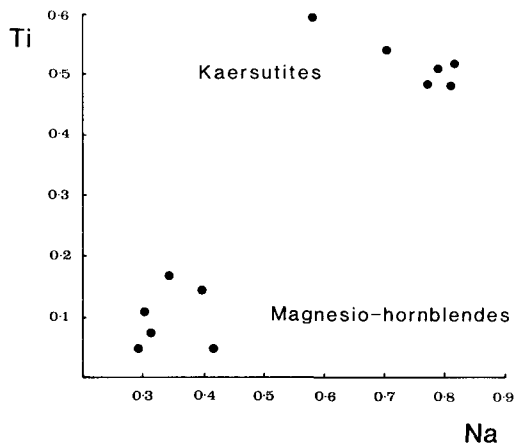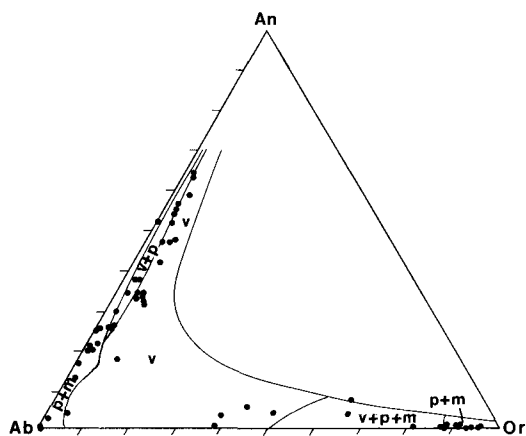
FIGS. 5 and 6. FIG. 5 (*left*). Composition of feldspars from Roman-style pottery of late, pre-Roman, Iron Age date, found in southeastern Britain. The boundaries between the feldspars of different geological origins are drawn after Trevena and Nash (1979, 1981): v = volcanic, p = plutonic, m = metamorphic. FIG. 6 (*right*). Diagram (atoms per 23 oxygens) illustrating the occurrence of two compositional groups of amphiboles in late pre-Roman, Iron Age pottery from southeastern Britain. (See text for discussion.)

that at least the volcanic signature is unlikely to be the result of sedimentary recycling. The Na-, Ti-rich amphibole group (Fig. 6) is suggestive of an alkaline volcanic rock source, and occasional volcanic rock clasts appear to be trachytic in composition. Consideration of the geology of the most likely sources of Roman pottery in Western Europe and the Mediterranean area led to the suggestion that the Massif Central, France, was the most likely source for the pottery (Freestone, 1982; Rigby and Freestone, 1983) and recent examination of the typology of the pottery in that area has confirmed it as the probable source (Rigby and Freestone, 1986).

A second example concerns a small bronze statuette of the Roman goddess Minerva (Fig. 7) which has been in the collections of the British Museum since the last century, but for which there is no record of its origin. Small, black, prismatic crystals found embedded in the corrosion products of the bronze were shown by SEM and EDXA to be salitic pyroxenes with well-preserved crystal morphology (Fig. 8). Melt inclusions in the pyroxenes are of potassic composition. The statuette appears to have been buried in a pyroclastic deposit associated with potassic magmatism. Given the Roman association of the object an Italian origin was clearly indicated, most probably the ashes associated with the catastrophic eruption of Vesuvius in A.D. 79. Examination of the corrosion products on bronzes known to have been excavated from Pompeii or its environs revealed, in some cases, corrosion products and clinopyroxene inclusions similar to those on the Minerva, corro-

borating the inferred source area (Freestone *et al.*, 1984).

Metallurgical by-products

The discarded refractories and slag which may be found in copious quantities on metal extraction and metalworking sites often represent our principal source of information on the metallurgical technologies and it is vital to extract from them the maximum possible information. At the most elementary level it may simply be a matter of identifying the particular metal which was being worked by EDXA analysis of metal inclusions in the slagged surface of a crucible (Tite *et al.*, 1985). More detailed studies involve the determination of parameters such as the temperature, duration and reducing conditions during smelting, the processing of ores and the preparation of refractory materials.

An example which illustrates many of these aspects of investigation is that of zinc and silver-lead smelting at Zawar, Rajasthan. The local ore is a stratabound, sphalerite–galena deposit in an impure dolomitic host. Radiocarbon dating suggests that these deposits have been exploited for lead and silver for at least two thousand years and that the extraction of zinc metal began some time in the Medieval period. This was a major technological advance. Zinc metal boils at 913 °C, which is below the temperature required to reduce the oxide in the presence of carbon. Thus the metal is produced as a gas and it must be distilled rather

than smelted in the normal way. Excavations at Zawar (Craddock *et al.*, 1985) have revealed intact zinc distillation furnaces still containing the retorts in which the zinc was reduced (Fig. 9).

FIG. 9. Excavated zinc smelting furnaces at Zawar showing arrays of inverted ceramic retorts, supported by perforated plates (which divide the hot, upper chamber containing the retorts from the cool, condensation chamber below).

Petrography of the ceramic retort bodies and furnace walls shows that they were made from local clays (Freestone *et al.*, 1985a). Analysis of the ceramic matrices using EDXA in the SEM reveals that they contain around 15 wt. % fluxes (FeO, MgO, CaO, Na_2O, K_2O). Thus the ceramics are closer to house bricks than to modern refractories in composition, a characteristic typical of most metallurgical furnaces up to the end of Medieval times (Freestone and Tite, 1986). Examination of the vitrification textures of the Zawar materials (e.g. Figs. 1a–c) and comparison with refired examples shows that temperatures of *c.* 1200–1250 °C were attained during smelting. These were at the limits of tolerance of the clays and slumped and distorted retorts are common in the field. The furnace walls show a gradient in vitrification structure from the interior (high temperature, highly vitrified) to the exterior (low degree of vitrification). This can be interpreted in terms of a temperature gradient which developed in the furnace wall during smelting and which can be estimated by comparing the micromorphologies at series of points with those of a series of refired examples. The gradient depends

FIGS. 7 and 8. FIG. 7 (*top*). Statuette of Minerva (height 0.10 m). The arrow indicates the area of corrosion containing small pyroxene crystals. FIG. 8 (*bottom*). Pyroxene crystal observed in corrosion products on statuette of Minerva. SE image; operating voltage 25 kV. The scale bar represents 400 μm.

on the duration of the smelt as well as the temperature achieved in the furnace, so that, using a simple heat conduction equation, the time for which a furnace was at high temperature may be estimated (Tite *et al.*, 1982*a*, 1985). For the zinc smelting process at Zawar, durations of around 5 hr are obtained.
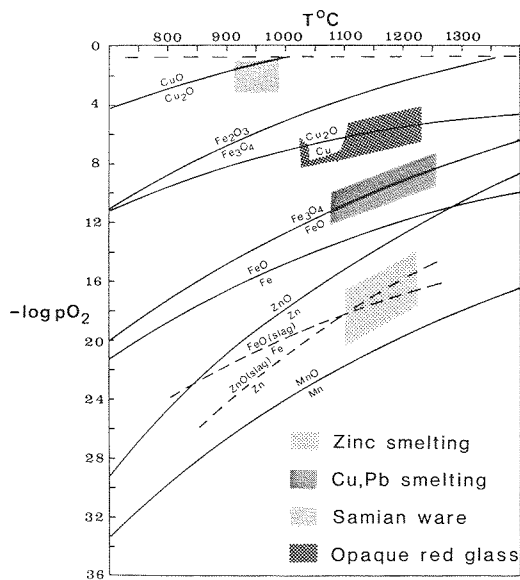

FIG. 10. Temperature/PO_2 relationships for selected reactions of interest (see text for discussion). The probable conditions within the zinc retorts during firing and approximate conditions for some other pyrotechnical processes are indicated.

Analysis of the contents of the zinc smelting retorts reveals that a crushed, siliceous dolomite was used as a carrier material for the roasted sphalerite (Freestone *et al.*, 1985*a*). In some cases this has partially melted to give an assemblage of glass, Zn-bearing diopside and metallic iron. Using the composition of the glass derived from EDXA, and assuming that it was in equilibrium with metallic Fe and Zn, a naive (ideal-mixing) model for the activities of ZnO and FeO in the glass was used to estimate the PO_2 in the retort during smelting. The results for iron and zinc were fairly consistent (see Fig. 10). The conditions attained during zinc smelting were extreme relative to other early pyrotechnologies, emphasizing the sophistication of the process.

Abundant evidence is also found at Zawar for silver–lead smelting, in the form of silicate slags which had been separated from argentiferous lead

as immiscible liquids at high temperatures. These slags can be either earlier or contemporary with the zinc smelting debris. Morphologically the slags can be divided into two groups in the field: glassy slags which are not associated with with zinc distillation debris and crystalline slags which are generally found alongside deposits of discarded zinc retorts. In the SEM it is observed that the crystalline slags contain abundant fayalite and/or iron-rich clinopyroxene, while the glassy slags contain only sparse crystalline phases such as zincian melilite, Mg-rich clinopyroxene and zincian olivine (Fig. 11). This is a reflection of their chemistry; the crystalline (fayalitic) slags have high levels of iron (18–32 wt. % Fe), but low zinc ($< 3\%$ Zn), whereas the glassy slags have low iron contents (8–10%), but higher zinc (7–11%). It is inferred that the glassy slags were a product of the lead smelting activity that preceded the introduction of zinc smelting. At this stage a high value was not attributed to sphalerite and it was not efficiently separated from the galena. With the onset of zinc smelting, however, it became important to maximize the recovery of zinc so that sphalerite was carefully removed from the lead ores; the resulting reduction of the flux context of the slag was compensated by the addition of more iron, possibly as pyrite, which precipitated as fayalite (Freestone *et al.*, 1986).

Vitreous materials

As used here, 'vitreous materials' is a catch-all phrase coined to encompass, in addition to glass itself, a range of ceramics and pigments in which a glassy phase is important, but excluding clay-based ceramics. The SEM has proved invaluable in the characterization and interpretation of these materials.

'Egyptian faience' is a crushed silica body held together by variable amounts of interstitial glass and an alkaline glaze. Beads, figurines and small vessels made from this material were widely used in Egypt and the Near East before the Roman period. At least three methods were used to produce faience, and these can be distinguished by examination of the distribution of glass in the body using the SEM (Tite *et al.*, 1983; Tite and Bimson, 1986).

'Egyptian blue' is a pigment formed by fritting quartz, calcite and a copper salt to produce the mineral cuprorivaite, $CaCuSi_4O_{10}$ which has a vivid blue colour. The pigment was used in paintings, and could be moulded to form small objects such as beads, scarabs and statuettes. Tite *et al.* (1984) examined samples of Egyptian blue dating from the 14th century B.C. to the 3rd century A.D. It was shown that, in addition to cuprorivaite, unreacted quartz and copper silicate glass were also
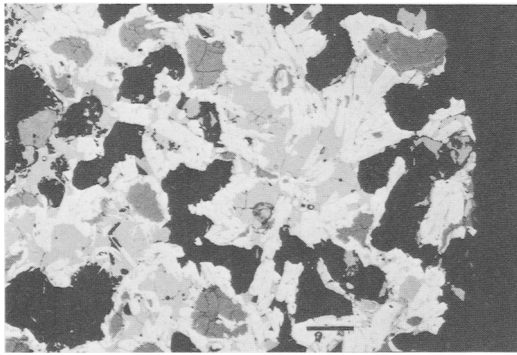
FIGS. 11 and 12. FIG. 11 (*top*). Lead-smelting slag from Zawar, illustrating the development of spinifex zincian olivine (black) and box-like crystals of melilite (dark grey), in a glassy matrix. BSE micrograph; operating voltage 15 kV. The scale bar represents 100 μm. FIG. 12 (*bottom*). 'Egyptian Blue', showing the development of prismatic crystals of the bright-blue mineral cuprorivaite (white). Pools of copper silicate glass (light grey), relict grains of quartz (dark grey) and voids (black) are also visible. BSE image; operating voltage 15 kV. The scale bar represents 100 μm.

(Bimson and Freestone, 1983) and the enamels of the Medieval Royal Gold Cup (Bimson and Freestone, 1985) have been characterized.

Detailed technological studies may involve determination of the relationships between the size and morphology of opacifiers and/or devitrification products, the properties of the glass and its bulk composition. For example, Freestone (1986) has examined a group of opaque, red glasses dating to the first and second millennia B.C. from Egypt and the Near East. The colourant/opacifier in these glasses was cuprite, Cu_2O, and SEM analysis reveals that the range of shades available to the craftsmen depended on the size of the cuprite particles, which in turn depended on the concentration of Cu_2O and PbO in the glass. Thus brilliant red glasses contain extensive dendritic cuprite (Fig. 13), while duller, brownish reds and orange-reds contain very fine blebs of cuprite.
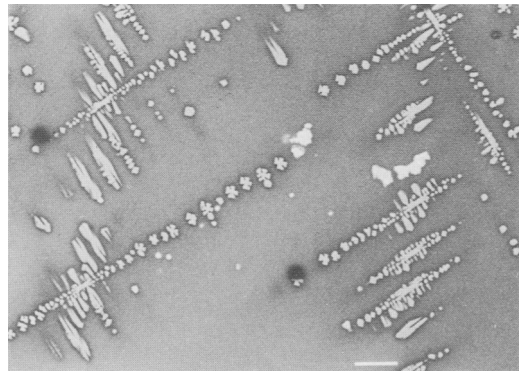

FIG. 13. Opaque red glass from Nimrud, dating to the fourth century B.C. Dendrites of cuprite (light grey) give the glass its bright red colour. The bright white grains are copper. BSE micrograph; operating voltage 15 kV. The scale bar represents 10 μm.

present (Fig. 12). It was possible to relate the colour and hardness of Egyptian blue samples to the grain-size of the cuprorivaite and the amount and distribution of the glass phase, and thus to the bulk composition and manufacturing technique.

Much of the glass of antiquity was opaque and coloured, and was used as a substitute for semi-precious stones such as lapis lazuli, carnelian and turquoise. The aim of the examination of these materials is to identify spatial and chronological variations in composition and technique which may be culturally related. The introduction of the SEM has meant that many previously inaccessible objects may now be sampled, due to the very small sample size required. Thus the glass of unique objects such as the Roman cameo Portland Vase

Weathering

The physical and chemical decomposition of archaeological materials is of considerable importance in that it (1) affects their integrity as unique and permanent records of past cultures and (2) it can affect the results of scientific examination such as dating and sourcing by elemental analysis which require the bulk chemistry of the object to remain constant after it has been discarded.

The decay of limestone in a museum storage environment is very variable in nature and degree: some objects may show only minimal damage with pitting of finished surfaces while others show extensive loss of surface detail and even 'structural

failure' by the flaking off of large fragments of stone. The reasons for these differences are not well understood and a study by Bradley and Middleton (in progress) has sought to understand these for a group of Egyptian limestones. The decayed samples, all considered to require some conservation treatment in order to correct deterioration, fall into three groups on the basis of the nature of their decay and their macroscopic appearance. These groups coincide precisely with those made on the basis of the observation of textural features and identification of non-carbonate phases in the SEM. In particular, the badly decayed sculptures exhibiting flaking contain significant amounts of a palygorskite clay which was not present in those sculptures that showed only decay by localized pitting. In these latter sculptures, by contrast, the non-carbonate fraction was either insignificant (a group of white, chalky limestones) or consisted mainly of lepispheres of opal-CT (Fig. 14; a group of

the range 2-12 wt. % P_2O_5 in the clay matrix, while unmodified clays and soils typically contain less than 0·5 wt. %. Calcium phosphate is added to modern ceramics e.g. 'bone china' to act as a flux and vitrify the body, but ancient ceramics with high P_2O_5 tend to have non-vitrified bodies, indicating that phosphate was not added for this purpose. Determination of compositional variation across the ceramics using EDXA shows that P_2O_5, CaO and FeO have U-shaped profiles in some cases (Fig. 15), indicating that these elements were mobile whilst the pottery was buried and that the high P_2O_5 contents are the result of environmental contamination (Freestone *et al.*, 1985*b*). Furthermore, linear correlations between P_2O_5 and CaO (Fig. 16) suggest that a phosphate compound of relatively fixed stoichiometry is present which is distinct from the more familiar minerals such as
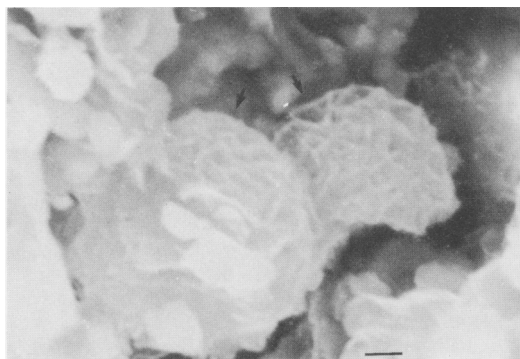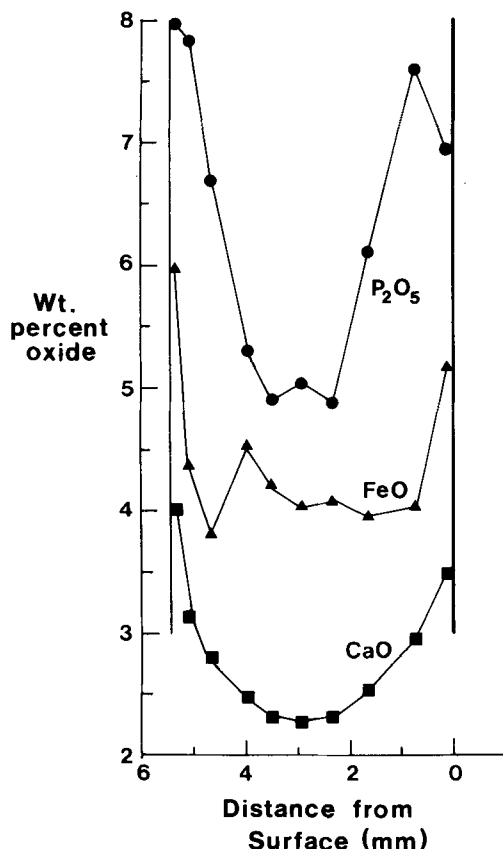

FIG. 14. Fracture surface of a fragment from an Egyptian limestone sculpture from the Cairo area, showing lepispheres of opal-CT (arrowed). SE image; operating voltage 15 kV. The scale bar represents 1 μm.

fine-grained, buff-coloured limestones). The extensive decay of the former group of limestones is possibly the result of the modifications caused to their pore-size distribution by the palygorskite, which grew authigenically, or possibly due to local planes of weakness due to the presence of the clay.

A further point of interest arising from this work is that the groupings defined above correlate well with the ascribed provenance of the objects, probably reflecting the use of locally available stone and also implying the possibility of using observations of this nature to provenance objects of unknown source.

In our studies of ancient pottery we have commonly encountered concentrations of phosphate, in

FIG. 15. Compositional change across a late Iron Age sherd, excavated at St Albans, illustrating the development of U-shaped profiles for P_2O_5, CaO and FeO. The heavy vertical line indicates the 'inner' surface of the sherd, which had a glossy slip coating.

apatite or brushite. Discrete phosphate phases could not be isolated with the SEM, indicating that the very fine-grained phosphate may have been absorbed in the first instance on the fired clay platelets. It is well known that disordered clay minerals such as allophane have a high capacity to retain phosphate; the disorder induced in clays by firing at temperatures below those sufficient to cause vitrification and recrystallization appears to greatly increase this property (Freestone et al., 1985b). In view of the capacity of phosphate minerals to incorporate or adsorb trace elements (Murray et al., 1983; Edward et al., 1984), this may have important implications for provenance studies using trace element data.
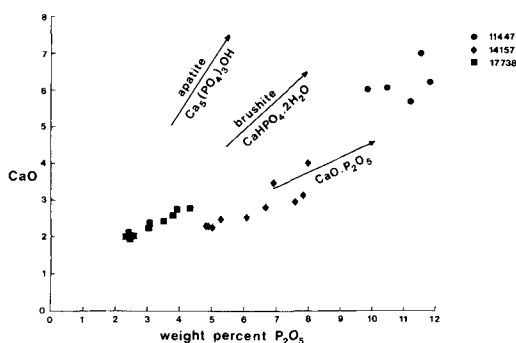

FIG. 16. Relationship between CaO and P_2O_5 for some Late Iron Age potsherds excavated in southern Britain (see text for discussion).

Conclusions

There is a wide range of potential applications for the analytical SEM in the field of archaeological materials. Many of the approaches are directly derivative from mineralogy and petrology and the questions asked of the objects, for example on durations and temperatures of processes, on provenance, weathering, etc. are parallel to those asked of natural materials. The time scales of interest, coupled with the technologies used, results in generally fine-grained materials, so that the SEM has a particularly useful role to play, even in the investigation of relatively simple problems.

This type of study often depends on the availability of suitable geological and mineralogical data and reference materials which can be used to place the archaeological materials in context. A major limitation to a study can be that the required data base, whether it is a phase diagram, the relationship between mineral composition and geological source, or the electron petrography of major

stratigraphic clay groups, is not available. Given that the archaeological requirements do not often precisely match those of the mineralogist in terms of the data required, we can expect the generation of such fundamental information to occur increasingly within the archaeological community.

References

Bimson, M., and Freestone, I. C. (1983) J. Glass Stud. 25, 55–64.

——(1985) In Ann. 9e Congr. Assoc. Int. pour l'histoire du Verre, Nancy 1983, 209–22.

Craddock, P. T., Freestone, I. C., Gurjar, L. K., Hegde, K. T. M., and Sonawane, V. H. (1985) Mineral. Mag. 48, 45–52.

Edward, J., Fossey, J. M., and Yaffe, L. (1984) J. Field Archaeol. 11, 37–46.

Freestone, I. C. (1982) Archaeom. 24, 99–116.

——(1986) In Early Vitreous Materials (M. Bimson and I. C. Freestone, eds.) British Museum Occasional Paper No. 56 (in press).

—— and Tite, M. S. (1986) In Ceramics and Civilisation 3: High-technology ceramics, past, present and future (W. D. Kingery, ed.) American Ceramic Society, Columbus, Ohio (in press).

—— La Niece, S. C., and Meeks, N. D. (1984) MASCA J. 3, 10–2.

—— Craddock, P. T., Hegde, K. T. M., Hughes, M. J., and Paliwal, H. V. (1985a) In Furnaces and Smelting Technology in Antiquity (P. T. Craddock and M. J. Hughes, eds.) British Museum Occasional Paper No. 48, 229–44.

—— Meeks, N. D., and Middleton, A. P. (1985b) Archaeom. 27, 161–77.

—— Craddock, P. T., Gurjar, L. K., Hegde, K. T. M., and Paliwal, H. V. (1986) J. Archaeol. Chem. (Hyderabad) (in press).

Kempe, D. R. C., and Harvey, A. P., eds. (1983) The petrology of archaeological artefacts. Clarendon Press, Oxford.

Kingery, W. D., and Vandiver, P. (1986) In Ceramics and Civilisation 2: Technology and Style (W. D. Kingery, ed.) Am. Ceram. Soc., Columbus, Ohio, 363–74.

Krinsley, D. H., Pye, K., and Kearsley, A. T. (1983) Geol. Mag. 120, 109–14.

Letsch, J., and Noll, W. (1983) Neues Jahrb. Mineral. Abh. 147, 109–46.

Maggetti, M., and Galetti, G. (1981) Archaeom. 23, 199–207.

Maniatis, Y., and Tite, M. S. (1981) J. Archaeol. Sci. 8, 59–76.

Murray, F. M., Brown, J. R., Fyfe, W. S., and Kronberg, B. I. (1983) *Can. Mineral.* **21**, 607–10.

Nisbet, E. G., and Pearce, J. A. (1977) *Contrib. Mineral. Petrol.* **63**, 149–60.

Noll, W. (1978) *Neues Jahrb. Mineral. Abh.* **133**, 227–90.

——(1981) *Neues Jahrb. Mineral. Mh.* 416–32.

——(1982) *Neues Jahrb. Mineral. Abh.* **143**, 150–99.

——Holm, R., and Born, L. (1974) Ibid. **122**, 119–44.

————(1975) *Angew. Chem.* **14**, 602–13.

Rigby, V., and Freestone, I. C. (1983) *Proc. Prehist. Soc.* **49**, 291–3.

————(1986) *J. Roman Pottery Stud.* **1**, 6–21.

Simkin, T., and Smith, J. V. (1970) *J. Geol.* **78**, 304–25.

Tite, M. S., and Bimson, M. (1986) *Archaeom.* **28**, 69–78.

——and Freestone, I. C. (1986) In *Proc. 2nd Int. Conf. on ancient Chinese pottery and porcelain*, Peking 1985 (in press).

——and Maniatis, Y. (1975) *Nature* **257**, 122–3.

——Freestone, I. C., Meeks, N. D., and Bimson, M. (1982a) In *Archaeological Ceramics* (J. Olin and A. D. Franklin, eds.) Smithsonian Institution Press Washington, 109–20.

——Bimson, M., and Freestone, I. C. (1982b) *Archaeom.* **24**, 117–26.

——Maniatis, Y., Meeks, N. D., Bimson, M., Hughes, M. J., and La Niece, S. C. (1982c) In *Early Pyrotechnology* (T. A. Wertime and S. F. Wertime, eds.) Smithsonian Institution Press Washington, 61–71.

——Freestone, I. C., and Bimson, M. (1983) *Archaeom.* **25**, 17–27.

————(1984) Ibid. **27**, 139–54.

————Meeks, N. D., and Craddock, P. T. (1985) In *The archaeologist and the laboratory* (P. Phillips, ed.) Council for British Archaeology Research Report N. 58, 50–5.

Trevena, A. S., and Nash, W. P. (1979) *Geology*, **7**, 475–8.

————(1981) *J. Sediment. Petrol.* **51**, 137–49.

Vandiver, P., and Kingery, W. D. (1985) In *Ceramics and Civilisation* 1: *Ancient technology to modern science* (W. D. Kingery, ed.), American Ceramic Society, Columbus, Ohio, 181–233.

White, S. H., Shaw, H. F., and Huggett, J. M. (1984) *J. Sediment. Petrol.* **54**, 487–94.