

The Impact of Electron Microscopy on Ceramic Studies

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Summary. Scanning electron microscopy (SEM), in combination with quantitative elemental analysis, provides a powerful technique for studying the microstructure of ancient ceramics. The primary aim of such studies is to elucidate the production technology in terms of the raw materials used, the methods of decoration and the firing procedures. A similar approach can be used to extract information on metal production processes from the associated refractory ceramic debris (e.g., furnace linings, tuyeres, etc.).

To illustrate the power of the SEM, information thus obtained on production technology is presented for Greek Attic red-figure ware, Chinese blue-and-white porcelain and Iznik ware, as well as for glass and other vitreous materials such as faience and Egyptian blue. The role of transmission electron microscopy, which can reveal finer details of ceramic microstructures, is also briefly discussed, and the need to consider ceramic technology in its wider cultural context is emphasised.

1. Introduction

SEM with attached analytical facilities provides an extremely powerful technique for studying the microstructure of ceramics; that is, establishing the composition, identity, shape and distribution of the different crystalline and glassy phases present (Freestone and Middleton 1987).

The fundamental role of both microstructure and macrostructure in investigating ceramic technology derives from the fact that a central paradigm of materials science is that the selection and processing of materials

gives rise to a particular structure which is the source of useful properties (Kingery 1987). Thus by studying the structure of ceramics, one aims to reconstruct what raw materials were used and how the ceramics were produced.

Such microstructural studies have been central to the investigation of metals since the examination of metal sections in reflected light by Sorby more than 100 years ago (Smith 1988, 167). However, the study of the microstructures of ceramics, both ancient and modern, has lagged severely behind that of metals. This is principally because optical microscopy is of limited use in resolving the very complex and fine-scale microstructures associated with ceramics and in particular those associated with traditional clay-based ceramics. Further, unlike the situation for metals the correlation between the microstructure and mechanical properties of ceramics is less clear-cut and therefore there was less motivation for pursuing the investigation of ceramic microstructure. Thus, it was only with the comparatively recent development of the scanning electron microscope (SEM) that it became possible to fully and easily investigate the microstructures of ceramics.

The study of the microstructure, as observed in the SEM, is thus now central to the investigation of the raw materials and their preparation, the methods of surface decoration and the firing procedures employed in the production of ancient ceramics. However, information on the methods used to form the ceramics (e.g., by modelling; from coils or slabs; by wheel throwing or moulding) can still best be obtained by careful visual examination of the macrostructure, supplemented by x-ray radiography.

In addition to providing information on *what* raw materials and production methods were used, the observed microstructure can help in assessing the physical properties both of the raw materials (e.g., plasticity, drying shrinkage, green strength) and of the finished ceramics (e.g., permeability, strength, thermal shock resistance). In turn, a knowledge and understanding of these physical properties can sometimes provide a technological explanation for *why* particular raw materials and production methods were used (Tite 1988a).

Scanning electron microscopy can also make some contribution to provenance studies and usage studies which are the two other main aims of science-based investigations of ancient ceramics. Provenance studies involve characterising and locating the natural sources of the raw materials used to make the ceramics and thus establishing the pattern of trade and exchange. In such studies, quantitative elemental analysis of the individual mineral inclusions (feldspars, pyroxenes, amphiboles) surviving in the fired clay can sharpen the information provided by optical petrography on the type and the source of the rock from which they were derived (Freestone 1982). Usage

studies involve investigating the ways in which the ceramics were used. In this context, the physical properties of the ceramics, which can sometimes be inferred from the observed microstructure, can help in assessing the suitability of the ceramic for its hypothesised use.

However, the prime role of scanning electron microscopy in ceramic studies undoubtedly is the investigation of their production technologies. There is no doubt that the high quality microstructural images and compositional data provided by the analytical SEM has transformed such investigations. As a result, our understanding of ancient ceramic technology has begun to catch up with our understanding of ancient metallurgy and the general pattern of the development of ceramic technology in antiquity is now more-or-less established.

2. Experimental procedures

For the examination of ceramics in a SEM, polished sections from the surface into the body are normally prepared. The SEM is used in the magnification range $\times 10$ to $\times 10,000$ with a range $\times 100$ to $\times 500$ generally being most appropriate. A backscattered electron detector, rather than a secondary electron detector, is normally used. With this detector, the grey level of the image (from black to grey to white) depends on the atomic number of the phase being observed, with black through to white correlating with low to high atomic number. In this way, the different crystalline and glassy phases present can be easily distinguished. Normally, these phases can then be identified by qualitative elemental analysis using the attached x-ray spectrometer and their overall distribution pattern thus established. Fully quantitative analysis of both the bulk material (Table 1) and the individual phases is also possible using the x-ray spectrometer.

3. Case studies

In the overall history of ceramics, it is possible to identify three primary technologies, that is, earthenware, quartz-based ware and stoneware plus porcelain (Kingery and Vandiver 1986). In this paper, the role of SEM examinations in the investigation of each of these three primary technologies will be considered. The developments in earthenware and quartz-based ware technologies resulting from the efforts by Islamic and European potters to imitate Chinese porcelain will then be discussed briefly. In each case, examples will be presented of the reconstruction of the raw materials and production processes from a careful "reading" of the SEM microstructures.

Table 1. Typical bulk chemical compositions for case study ceramics

Ceramic type	Component	Oxide concentrations (per cent weight) ¹										
		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	FeO	CuO	PbO	SnO ₂	
Greek Attic	Body	53.9	20.6	1.0	4.1	5.4	5.0	10.0	—	—	—	
	Slip	47.7	31.6	0.4	3.2	1.8	0.5	14.8	—	—	—	
Faience	Body	96.6	—	1.1	0.5	—	0.5	—	1.3	—	—	
	Glaze	70.0	—	16.2	5.7	0.2	0.2	0.3	7.5	—	—	
Egyptian blue frit	—	70.2	0.5	2.4	0.2	0.6	12.3	—	13.8	—	—	
	—	65.9	0.4	0.4	0.2	0.7	13.2	0.4	18.8	—	—	
Pale blue frit	—	75.1	0.4	5.5	0.8	—	11.3	—	6.9	—	—	
	—	77.5	16.6	0.9	3.2	0.4	0.8	0.6	—	—	—	
Porcelain stone	Body	78.3	15.9	0.8	3.3	0.2	1.0	0.5	—	—	—	
	Glaze	67.0	14.9	0.8	2.5	0.4	13.9	0.5	—	—	—	
Yingqing porcelain	—	72.1	20.6	1.6	4.0	0.2	0.1	1.4	—	—	—	
	—	66.1	16.0	2.2	4.1	0.5	9.3	1.8	—	—	—	
Underglaze blue porcelain	Body	64.7	28.4	0.7	2.0	1.4	2.0	0.8	—	—	—	
	Glaze	69.8	18.7	0.9	2.3	2.7	4.9	0.7	—	—	—	
Ding porcelain	Body	48.0	12.6	2.0	1.0	7.0	21.4	6.7	—	—	—	
	Glaze	68.1	2.4	8.1	5.0	2.4	6.4	0.9	2.0	1.8	—	
Islamic-Abbasid	Body	88.7	2.6	2.2	0.8	1.0	2.1	0.9	—	—	—	
	Slip	91.6	2.2	2.3	0.6	0.6	1.3	—	1.4	—	—	
Isnik ware	Body	49.4	0.5	9.2	0.8	—	1.0	0.4	—	—	—	
	Glaze	—	—	—	—	—	—	—	33.3	5.4	—	

¹ Oxide concentrations normalised to 100 per cent.

3.1 Earthenware

Pottery made from low refractory earthenware clays was first produced on any significant scale in the Near East during the 7th millennium BC. Before the end of the 4th millennium BC, the technological repertoire associated with the production of *unglazed* earthenware (i.e., careful preparation of the clay, throwing on potter's wheel, slip and painted decoration, firing with controlled atmosphere and temperature) was more-or-less complete. Subsequently, various combinations of this overall technological repertoire continued to be used according to local requirements, but with no obvious steady technological progression, through to the Roman period and beyond.

In the investigation of earthenware technologies, the SEM is used to determine the bulk chemical composition of the body clay, to examine the surface decoration and to estimate the firing temperature.

In the context of bulk chemical composition, the alumina content provides a measure of the clay mineral content of the original body clay; the alkali content (potash and soda) determines the refractoriness of the clay; and the iron oxide content in conjunction with the firing atmosphere determines the colour of the body. The distinction between non-calcareous and calcareous clays (i.e., respectively less than or greater than 5 per cent fine textured, well-dispersed lime plus magnesia) is also important since the lime plus magnesia content affects both the firing properties of the clay and the resulting microstructure.

By examining a cross-section through the surface and into the body of the pottery, it is possible to distinguish burnishing from the application of clay slip, both of which can result in a high gloss surface finish. Also any mineral pigments (e.g., iron oxide, manganese oxide) used to decorate the pottery can be identified (Middleton 1987).

The firing temperature employed in the production of pottery can be estimated from the extent of vitrification in the body as revealed by the degree of interconnection between the mineral particles. For low fired pottery, individual mineral particles are readily distinguished and there is only limited grain-to-grain interconnection. With increasing firing temperature, a network of interconnecting glass/relict clay phases is formed between the non-plastic inclusions such as quartz, feldspars and micas (Figure 1). Subsequently, the extent of the glass phase increases and the porosity decreases. The pores then become isolated; trapped gases expand causing the formation of rounded vesicles (Figure 2) and finally at high temperatures, typically in the range 1100–1200°C, the body becomes molten with either slumping or massive bloating.

The temperatures at which these different vitrification stages are reached depends first on the chemical composition of the clay (Maniatis and Tite

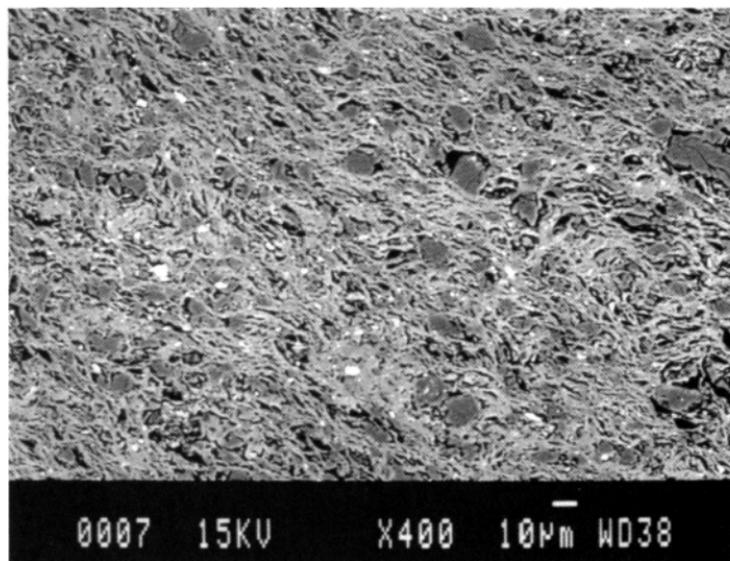


Figure 1. SEM photomicrograph of section through German stoneware sherd showing body which consists of scattered quartz (darker grey) in a fine network of interconnecting glass/relict clay phases.

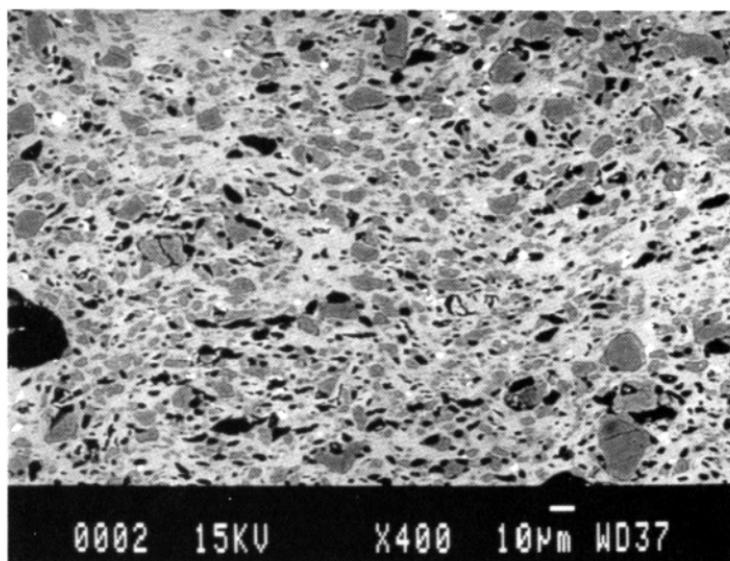


Figure 2. SEM photomicrograph of section through German stoneware sherd showing body which consists of continuous glassy matrix containing fine bloating pores (black) and unreacted quartz (darker grey).

1981). Therefore, in order to estimate firing temperatures, samples of the pottery must be refired in the laboratory at known temperatures until an increase in the extent of vitrification is observed. Further, since firing in a reducing atmosphere, rather than in an oxidising atmosphere, can lower the temperature at which a particular vitrification stage is achieved by between 50–100°C, the refiring atmosphere used in the laboratory should match the original firing atmosphere as closely as possible.

The same approach as that employed in estimating the firing temperatures of earthenwares can be applied to the study of the refractory ceramics (e.g., crucibles, tuyeres, furnace linings etc.) used in metal production and metal working. In this way, information is obtained on the operating conditions (firing temperature, time and atmosphere) used in the associated metallurgical process (Freestone and Tite 1986).

The results of the examination of Greek Attic black-figured and red-figured wares, produced from 7th to 4th centuries BC, provide an example of the information that can be obtained using the SEM (Tite *et al.* 1982). These results show that the bodies which are red in colour were made from iron-rich calcareous clays (approx 10 per cent FeO and 10 per cent CaO plus MgO). The characteristic black high gloss surface finish was produced by applying a fine textured iron-rich non-calcareous clay slip (approximately 15 per cent FeO and less than 3 per cent CaO plus MgO) approximately 10–20 μm in thickness and more-or-less free from non-plastic inclusions. Both the bodies and slips have relatively high potash contents (3–6 per cent K_2O) and therefore the clays used would have been rich in illite. Further, it is possible that both were prepared from a single clay with the unrefined clay being used for the body and the fine fraction for the slip. The bodies exhibit the open network of interconnecting glass/relict clay phases which is characteristic of calcareous clays fired in the temperature range 850–1050°C (Figure 3). In contrast, in the finer textured non-calcareous slip the glass/relict clay phases are essentially continuous with no obvious porosity.

On the basis of these data, it can be inferred that the observed differential oxidation-reduction between the red body and the black slip of Greek Attic ware was produced in a single firing involving an oxidising atmosphere during the heating up of the kiln, then a reducing atmosphere and finally an oxidising atmosphere again. At the end of the reducing phase, both the body and slip would have been black due to the formation of a magnetite-hercynite spinel ($\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$). Then during the final oxidising phase, the porous body would have been re-oxidised with the formation of haematite ($\alpha\text{Fe}_2\text{O}_3$) whereas the impermeable slip would have remained in its black reduced state.

It is apparent that the impermeable slip essential to the production of Greek Attic black-figured and red-figured wares has been achieved by careful selection of the clay. The illitic clay used is non-calcareous and has been

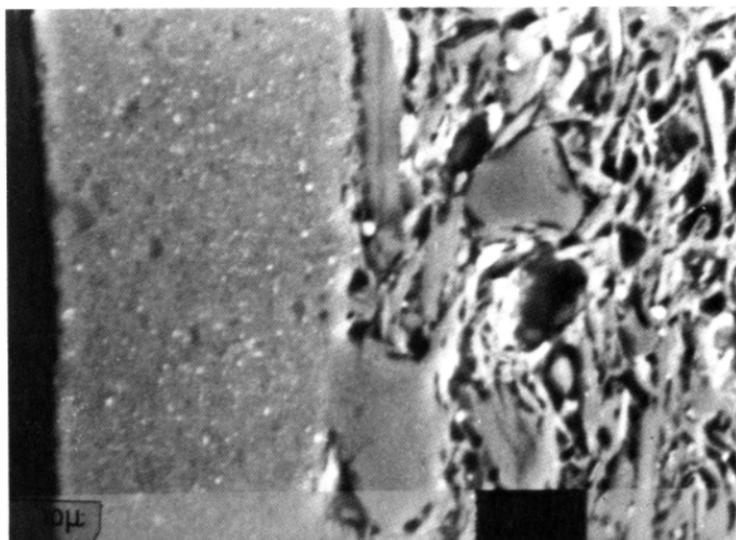


Figure 3. SEM photomicrograph of section through Greek Attic red-figured ware sherd showing high gloss surface slip which is essentially continuous and body which consists of open network of interconnecting glass/relict clay phases.

refined to remove non-plastic inclusions, both features that are necessary to ensure low porosity in the slip. Further, the high iron oxide content increases the extent of vitrification when fired in a reducing atmosphere and thus again tends to reduce the porosity.

3.2 Quartz-based ware

The second ceramic technology to evolve in antiquity was based on the use of a ground quartz or quartz sand body rather than a clay body. The materials first produced within this technology are normally referred to as faience or frit, depending on whether or not they are glazed (Tite 1987). Faience and frit were used in Egypt and the Near East from about the 4th millennium BC onwards to produce small objects such as beads, amulets, seals, figures and vessels. In the first instance, the great majority of faience and frit objects were coloured blue. It seems probable, therefore, that the driving force for the development of these materials was the desire to find a substitute for scarce and highly prized semi-precious stones such as lapis lazuli and turquoise.

The technology associated with faience and frit production is clearly related to that first used in making small objects of glazed stone such as steatite. In turn, the faience and frit technologies themselves provide the basis for the subsequent development of glass production in Egypt and the Near

East during 2nd millennium BC and, ultimately, for the development of the quartz-frit wares produced by Islamic potters from about 12th century AD onwards.

In the investigation of faience and frit technologies, the SEM is used to obtain information on the methods of production employed as well as to establish the technological relationship between the different materials.

In terms of microstructure as seen in the SEM (Figure 4), faience consists of a core of angular quartz grains bonded together by varying amounts of interstitial glass. Normally, the core is covered by a layer of quartz-free alkali-based glaze. Intermediate between the glaze and core, there is an interaction layer which was formed by the reaction between the glazing mixture and the quartz core and which consists of quartz embedded in a continuous matrix of glass. Replication in the laboratory of the three methods proposed for glazing the quartz body (i.e., direct application, cementation, efflorescence) has shown that the thickness of the glaze and interaction layers as well as the amount of interstitial glass in the core depends on which of these methods was used (Tite and Bimson 1986, Vandiver 1983).

When the glaze was applied in the form of a slurry of finely ground prefired glazing mixture (i.e., a mixture of quartz sand, lime, alkali and

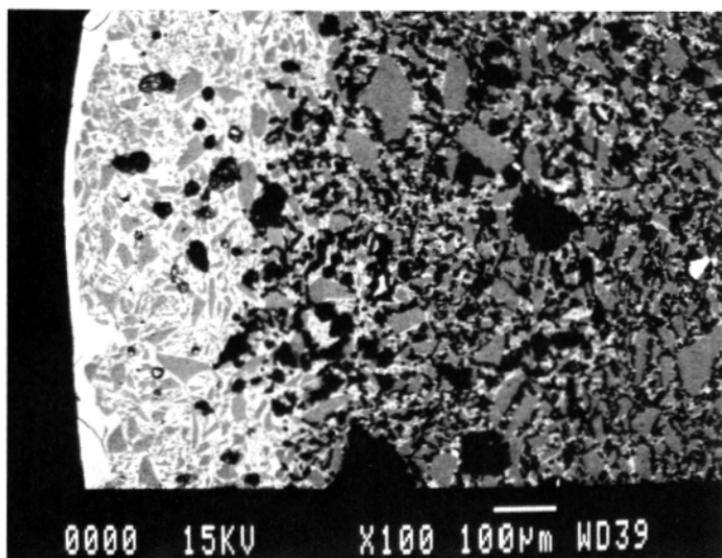


Figure 4. SEM photomicrograph of section through faience produced by efflorescence glazing method showing thin surface glaze layer; glaze-core interaction layer which consists of quartz in a continuous glass matrix; and quartz core which contains fairly extensive interstitial glass.

The glaze and glass appear white compared to the quartz which appears grey.

copper), a thick surface glaze layer was formed during subsequent firing and the quartz core contained minimal interstitial glass. This microstructure reflects the fact that a reaction occurred only at the interface of the glazing mixture and the core and that there was no transport of alkali or copper colorant beyond the glaze-core interaction layer.

With the cementation glazing method, in which the quartz body was fired whilst buried in the glazing mixture, a thin irregular glaze layer was formed and the quartz core contained small amounts of interstitial glass. This microstructure reflects the fact that there was some initial transport of glazing components into the core but that this ceased with the formation of a protective glaze-core interaction layer.

Finally, with the efflorescence glazing method, in which the unfired glazing components were mixed with the moistened quartz body, a reasonably thick glaze layer was formed during subsequent firing and the quartz core contained extensive interstitial glass such that the core tended to merge into and could not always be readily distinguished from the glaze-core interaction layer (Figure 4). This microstructure reflects the fact that the glazing components were only partially carried to the surface during drying and a significant proportion remained in the core to form, on firing, the interstitial glass.

Frits, which by definition are unglazed, differ in bulk chemical composition from faience bodies in that their lime and copper oxide contents are significantly higher (i.e., 6–13 per cent CaO and 2–20 per cent CuO as compared with less than about 1.5 per cent for faience cores). Further, the relative concentrations of lime and copper oxide are of primary importance in determining the microstructure of the frits thus produced, as well as their colour, hardness and texture (Tite 1987).

If the copper oxide content exceeds the lime content, crystals of Egyptian blue (calcium-copper tetrasilicate $\text{CaCuSi}_4\text{O}_{10}$) are formed and the frit exhibits an intense blue colour that is characteristic of this phase. Such Egyptian blue frits consist of an intimate mixture of Egyptian blue crystals and unreacted quartz together with a glass phase (Figure 5), the amount of which increases with increasing bulk alkali content. The glass provides long range interconnection between the crystalline phases and therefore the hardness of the frit also increases with increasing alkali content. Further, the Egyptian blue frit can be classified as coarse- or fine-textured according to the size and degree of aggregation of the Egyptian blue crystals. Coarse-textured frit contains aggregates of large Egyptian blue crystals (Figure 5) which result in a dark blue colour whereas fine-textured frit contains small dispersed crystals (Figure 6) which result in a lighter but still intense blue colour.

On the basis of replication in the laboratory, it has been suggested that the coarse-textured Egyptian blue frit which normally occurs in the form of

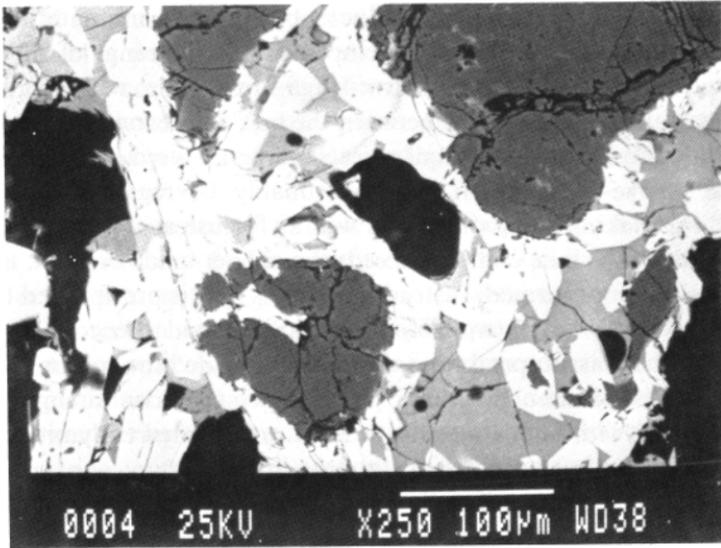


Figure 5. SEM photomicrograph of section through coarse-textured Egyptian blue frit showing aggregates of Egyptian blue crystals (white) and unreacted quartz (dark grey) embedded in glass matrix (light grey).

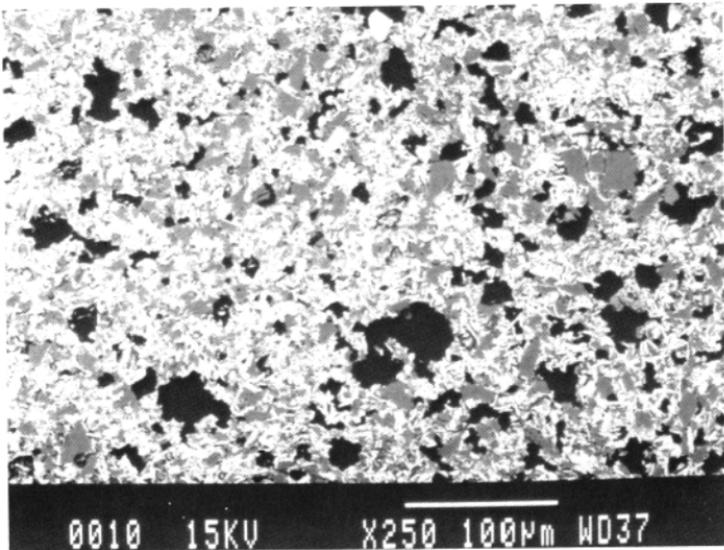


Figure 6. SEM photomicrograph of section through fine-textured Egyptian blue frit showing an intimate mixture of dispersed Egyptian blue crystals (white) and unreacted quartz (grey).

large blocks or small balls was produced by firing an intimate mixture of quartz, lime, copper and alkali at a temperature in the range of 900–1000°C (Tite *et al.* 1984a). In contrast, a two-stage firing cycle, with grinding and moulding to the required shape between the first and second firings, appears to have been used to produce small objects of fine-textured Egyptian blue frit. Thus the coarse-textured frit should probably be regarded as the 'raw material' for making small objects as well as for use as a pigment.

If, however, the lime content exceeds the copper oxide content, Egyptian blue crystals are not formed. Instead, the excess lime is precipitated from the glass as calcium silicate (wollastonite—CaSiO₃) and the copper remains dissolved in the glass to produce a characteristic pale blue colour. Such pale blue frits consist of extended areas of copper-rich glass containing unreacted quartz together with high concentrations of precipitated tridymite/cristobalite and wollastonite.

Thus, it can be seen that for frits, there is a clear inter-relationship between the raw materials (i.e., proportions of lime, copper and alkali), the processing (i.e., one- or two-stage firing cycle), the microstructure and the physical properties (i.e., colour, hardness and texture). Frits, therefore, provide an excellent example of the central materials science paradigm referred to in the introduction.

3.3 Stoneware and porcelain

Stoneware and porcelain production which represents the third primary ceramic technology can be regarded as a development from earthenware production. Stoneware is produced by firing high refractory clays to temperatures of about 1200°C such that well vitrified impermeable bodies are achieved. Stoneware was first produced in China during the 2nd millennium BC (Shang and Zhou dynasties) and associated with its early production was the development of high temperature glazes. Porcelain with its white translucent body requires a somewhat higher firing temperature, typically about 1300°C, and thus represents a development from stoneware. Again porcelain was first produced in China, in this case by about the 9th century AD (Tang dynasty) with large scale production occurring during the subsequent Song dynasty (AD 960–1279).

In the investigation of stoneware and porcelain technologies, the SEM provides information on the raw materials used to make the bodies and glazes as well as providing some indication of the firing temperatures employed.

For example, it has been possible using the SEM to significantly extend our understanding of the different raw materials used in the production of porcelain in southern and northern China. In terms of microstructure as seen

in the SEM (Figure 7), the bodies of yingqing (also known as qingbai) and underglaze blue porcelain produced in Southern China during Song and Yuan dynasties consist typically of a continuous glassy matrix containing rounded partially-reacted quartz grains, ragged lath-shaped aggregates of mullite and glassy pools containing randomly-oriented mullite needles (Tite *et al.* 1984b).

An account of porcelain production at Jingdezhen in southern China, given in a letter written by Père d'Entrecolles in 1712, indicates that, at least by the early 18th century, porcelain bodies were made from a mixture of kaolin and porcelain stone ('petuntse'). Subsequent analyses have established that porcelain stone consists primarily of quartz and a fine-particled muscovite mica of the sericite variety (Wood 1984). In addition, depending on the degree of weathering of the quartz-feldspar rock from which it was formed, porcelain stone contains small amounts of feldspar and kaolinite. With this knowledge, the lath-shaped aggregates of mullite observed in the yingqing and underglaze blue porcelain microstructures can be interpreted as relict mica from the porcelain stone and the glassy pools as pseudomorphs of the feldspar in the porcelain stone. The bulk compositions, and in particular the alumina contents (15–18 per cent Al_2O_3), of Song dynasty yingqing porcelain bodies match those of typical kaolinised porcelain stones. Thus it seems

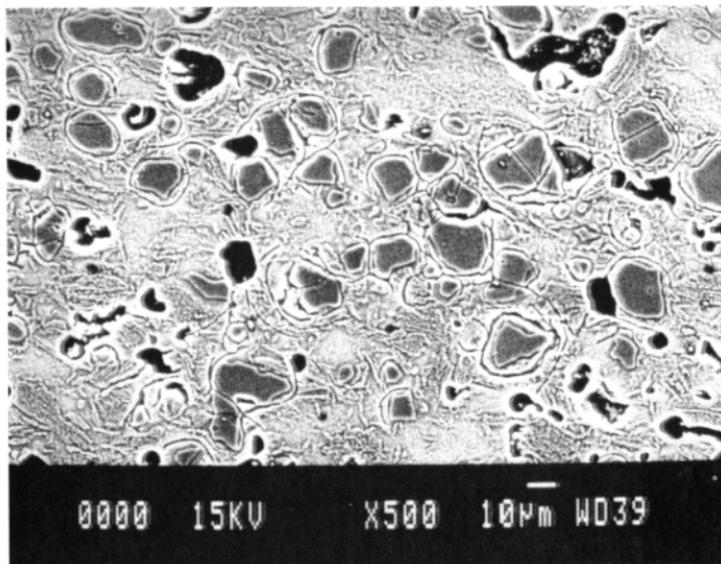


Figure 7. SEM photomicrograph of section through Song dynasty yingqing porcelain sherd showing body which consists of continuous glassy matrix containing partially-reacted quartz (darker grey), ragged lath-shaped aggregates of mullite and glassy pools containing randomly-orientated mullite needles.

probably that kaolinised porcelain stone was used by itself to produce porcelain bodies at this early period, with sericitic mica in the stone not only providing the flux (K_2O) but also, together with the kaolinite, contributing the necessary plasticity to the material. Similarly, the glaze compositions for these porcelains are consistent with their having been prepared by the addition of lime (in the form of glaze ash) to the same kaolinised porcelain stone as used for the bodies. In contrast, the alumina contents of Yuan dynasty underglazed blue porcelain bodies (19–22 per cent Al_2O_3) as well as Ming dynasty porcelain bodies (19–26 per cent Al_2O_3) are noticeably higher than those of both Song dynasty yingqing bodies and known porcelain stones (less than 20 per cent Al_2O_3). It therefore seems probable that these later porcelain bodies were made from a mixture of porcelain stone and kaolin as described in Père d'Entrecolles' letter. The kaolin was probably added in order to provide a finer textured body on which to apply the underglaze decoration. Again, the glaze compositions are consistent with the use of a mixture of lime and the same porcelain stone as used for the bodies but, in the case of the glazes, without the addition of kaolin.

Northern China does not have any deposits of porcelain stone and therefore the microstructure and composition of the associated porcelains differ from those of southern Chinese porcelains (Guo 1987). The bodies of the Ding porcelain produced in northern China during the Song dynasty consist of sparse partially-reacted quartz in a continuous glassy matrix containing a dense mass of fine mullite crystals (Figure 8). Their microstructures are thus more homogeneous than those observed for southern Chinese porcelain bodies. Further, the alumina contents of Ding porcelain bodies (27–33 per cent Al_2O_3) are significantly higher than those of southern Chinese porcelain bodies. Ding porcelain bodies also contain typically 1–2 per cent each of lime and magnesia whereas their concentrations in southern Chinese porcelain bodies are normally less than 0.5 per cent. These observations are consistent with the use of a comparatively pure kaolin to which small amounts of feldspar and dolomitic limestone were probably added as flux. The glazes also seem to have been prepared from a mixture of kaolin, feldspar and dolomitic limestone but with higher proportions of the two fluxing components than in the bodies.

In comparing European hard-paste porcelain with Chinese porcelain, it should be noted that the European porcelain bodies, after some initial experimentation, were made from a mixture of china clay (i.e., kaolin) and potassium feldspar (Kingery 1986). They therefore differ significantly from the southern Chinese porcelain bodies which they were attempting to imitate in that the southern Chinese bodies were micaceous rather than feldspathic. Instead, the European bodies are closer in composition to the Ding porcelain

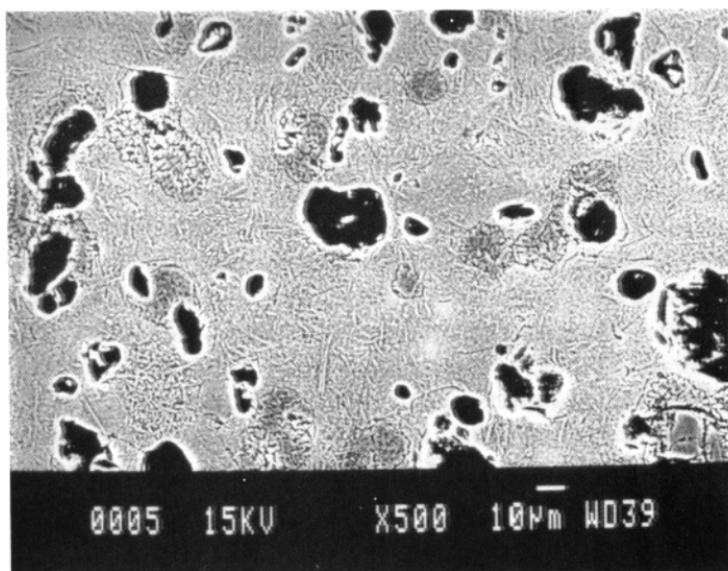


Figure 8. SEM photomicrograph of section through Song dynasty Ding porcelain sherd showing body which consists of sparse partially-reacted quartz (darker grey) in continuous glassy matrix containing dense mass of fine mullite crystals.

bodies although the European bodies contained a higher proportion of feldspar and no limestone.

3.4 Imitations of Chinese porcelains

The import of Chinese porcelains into the Islamic world from the 9th century AD onwards inspired a number of developments in the indigenous ceramic technologies (Watson 1987). These developments resulted from the attempts by the Islamic potters to replicate the hard white Chinese porcelain bodies without having either abundant supplies of the necessary white-firing clay or the associated high temperature technology. Subsequently, from the 15th century AD onwards Chinese porcelain, as well as the Islamic imitations, were imported into Europe where the attempts at replication resulted in the development first of Medici porcelain and ultimately of a wide range of both soft-paste and hard-paste porcelains.

SEM examination of both the Islamic and European imitations again provides information on the raw materials used and thus significantly extends our understanding of the means by which replication of the hard white Chinese porcelain was achieved (Tite 1988b).

During the Abbasid period (9th century AD) in Iraq, the Islamic potters continued to make their bodies from the locally available calcareous earthen-

ware clays (approx. 20 per cent CaO) which were iron rich (approx. 7 per cent FeO) and which fired to a buff colour. Their innovation was to achieve a white surface appearance by opacifying the glaze by the addition of tin oxide which formed clusters of particles up to $10\ \mu\text{m}$ across (Figure 9). The glazes used were of the alkali-lime type containing up to about 2.5 per cent lead oxide. Their whiteness varied according to the tin oxide content which ranged from 1 per cent to 7 per cent. The pottery was decorated using a cobalt-blue pigment which was applied onto the powdery surface of the unfired glaze and which became fused into the glaze during firing. The bodies exhibit the open network of interconnecting glass/relict clay phases which is characteristic of calcareous clays fired in the temperature range $850\text{--}1050^\circ\text{C}$.

This method of decoration onto a tin-opacified glaze subsequently spread through the Near East and along North Africa reaching Europe by the 13th century AD where it was used in the production of Hispano-Moresque lustreware and Italian maiolica. It is interesting to note that calcareous clays were also used for both these European wares, most probably because calcareous clays have a number of technological advantages. First, the high thermal expansion of a calcareous clay body more closely matches that of a typical lead-alkali glaze and this reduces the risk of glaze crazing. Second, the vitrification structure of calcareous clays remains essentially unchanged over

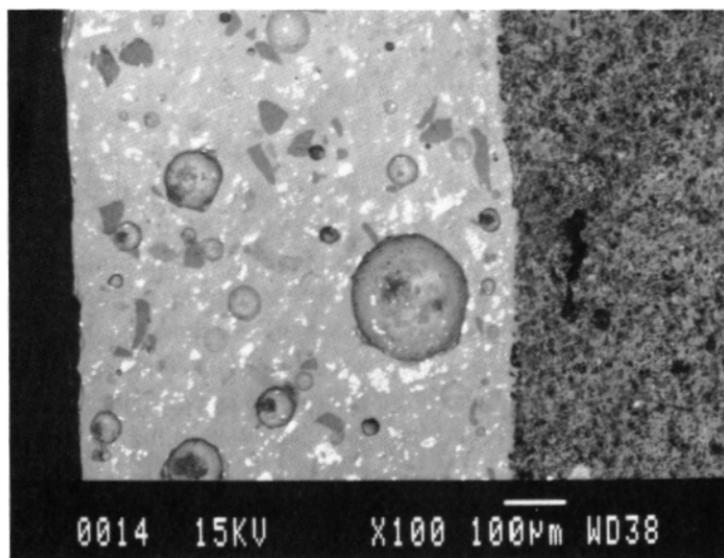


Figure 9. SEM photomicrograph of section through Abbasid blue-decorated sherd from Iraq showing glaze layer which contains tin oxide particles (white) and calcium- magnesium silicate crystals (darker grey) and body which consists of open network of interconnecting glass/relict clay phases.

the 850–1050°C firing temperature range and therefore the temperature control needed to achieve a consistent quality of body is less critical. Finally, even when they contain several per cent of iron oxide, calcareous clay bodies fire to a buff, rather than to a red, colour and this is more easily concealed by the tin-opacified glaze.

A second method of replicating Chinese porcelain which was widely used by Islamic potters from the 12th century AD onwards, involved reviving the quartz-based bodies employed in the Near East in the production of faience from 4th millennium BC through to the Roman period. Since these Islamic bodies were produced by the addition of glass frit to ground quartz or quartz sand, the resulting ceramics are normally referred to as quartz-frit wares.

A late, but technologically sophisticated, example of Islamic quartz-frit wares is Iznik ware which was produced in Ottoman Turkey during the late 15th and 16th centuries AD (Tite 1989). The Iznik ware bodies consist of angular quartz particles bonded together by a fairly extensive glass phase (Figure 10). The glass phase contains some 5–7 per cent each of alumina, alkali (soda plus potash) and lead oxide. On the basis of the composition and microstructure, it can be inferred that the Iznik ware bodies were made from ground quartz to which was added 5–10 per cent each of a white clay and an alkali-lead glass frit. The clay was presumably included in order to provide

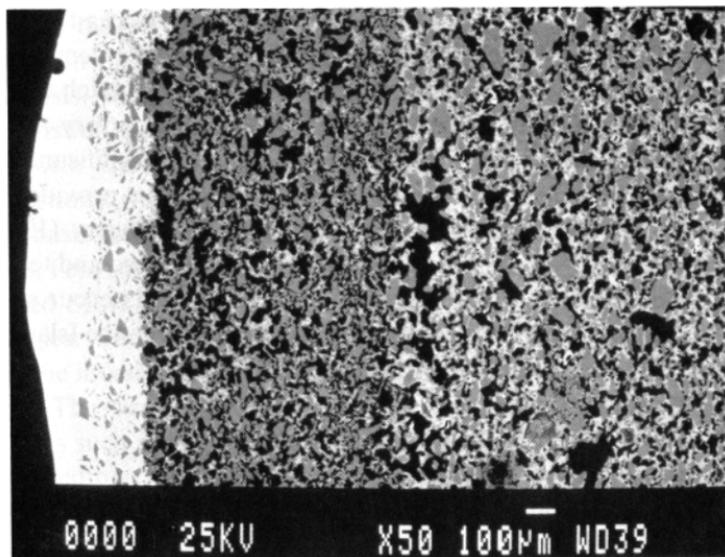


Figure 10. SEM photomicrograph of section through Iznik ware sherd showing glaze layer, fine-textured quartz-frit slip layer and quartz-frit body. The glaze and interstitial glass appear white compared to the quartz which appears grey.

the plasticity and green strength essential during the forming and subsequent handling of the unfired bodies.

The bodies are coated with quartz-frit slip layers which are typically 200–500 μm thick and which have a similar microstructure to those of the bodies. However, the quartz in the slip is finer textured (25 μm across as compared to 25–50 μm in the bodies) and the iron oxide content is lower (less than 0.3 per cent as compared to 1 per cent in the body). The glazes are of the lead-alkali type and contain some 4–7 per cent of tin oxide. However, the majority of the tin oxide is in solution so that it does not act as an opacifier. Therefore, the white surface appearance of Iznik ware is instead due to the very pure quartz-frit slip which coats the body. This fine-textured slip also provided an excellent ground for the mineral pigment decoration (e.g., cobalt, copper and chromium) which was applied under the glaze.

Although Iznik ware clearly falls within the general Islamic quartz-frit ware tradition, it differs technologically from related Islamic ceramics in a number of respects. First, the glass frits used to make both the bodies and slips are unusual in containing lead oxide as well as a alkali. Second, a slip has been applied to a body which itself already has a low iron content and is comparatively white. Third, although the tin oxide content is comparable to that in opaque Islamic lead-alkali glazes, the majority of the tin is in solution so that the glaze is transparent and the reason for adding the tin oxide remains something of a mystery. Thus, there does not appear to be any appropriate immediate antecedent for Iznik ware. Instead it seems possible that the Iznik potters, by careful choice of materials, successfully adapted existing Islamic ceramic technologies in order to meet the demands of the Ottoman court for pottery of a sufficiently high quality to match the Chinese porcelain reaching Turkey towards the end of the 15th century AD.

Thus it is seen that the Chinese imports resulted in significant developments in Islamic ceramic technologies. These developments provide an excellent illustration of the general principle proposed by Kingery (1984) that: "When a market for technology is established and recognised and technological innovations are rewarded, technological developments occur at a rapid rate." In other words, the level of the ceramic technology in the Islamic world rose to meet the market needs.

4. Future research

Having succeeded, I hope, in demonstrating the considerable power of the SEM examination of microstructures in elucidating the raw materials and processes used in the production of ancient ceramics, I now want to consider some of the possible directions for future research.

One important future development will be, I believe, the increasing use of image analysis techniques to obtain quantitative data on ceramic microstructures. In this context, the backscattered electron image is particularly appropriate since the different phases present can be distinguished by means of their grey level which changes progressively with the atomic number of the phase. Thus, it would be possible, for example, to quantify the extent of vitrification in the context of firing temperature estimates or to determine the proportions and particle size distributions of the different phases present in faience and frits.

Second, I expect to see some increase in the use of transmission electron microscopy (TEM). This instrument, with its increased resolution and capacity for crystallographic identification, can significantly extend the data on ceramic microstructure beyond that possible with scanning electron microscopy. For example, TEM examination has shown that the lustre decoration on 13th century Islamic lustre ware is associated with a high concentration of very small metallic silver particles (about 20 nm in diameter) in a thin surface layer in the glaze (Kingery and Vandiver 1986). Again, TEM examination has confirmed that the dichroism of the Lycurgus Cup, an outstanding late Roman cut-glass cage cup which appears wine-red in transmitted and pea-green in reflected light, is due to light scattering by silver-gold-copper colloid particles ranging from 50–100 nm in diameter and with average separation of the order of 10 μm (Barber and Freestone 1990). However, since sample preparation for TEM examination is much more difficult and the time needed to examine each sample at the associated high magnification is much greater, I would not expect the TEM to be used on a routine basis. Instead, transmission electron microscopy will normally be used to answer specific questions which require data beyond the resolution possible with scanning electron microscopy. As with the above examples, such questions will be concerned, typically, with trying to establish the physical basis for the external appearance of ceramics.

Third, I envisage considerable further application of the now more-or-less established SEM-microstructure approach to the study of ancient ceramic technologies. Such applications fall into two main categories. The first involves the investigation of the production technology of specific groups of ceramics. The second involves the investigation of specific technological innovations such as the introduction of glass production and its relationship to the preceding faience and frit technologies or the introduction of stoneware in China and other parts of the Far East and its relationship to the preceding earthenware technologies.

With either category of investigation a prime requirement must be for fully integrated projects involving both archaeologists and scientists in which the technology is studied within its wider social, economic and cultural

context (Tite 1988a). Only in this way will it be possible to extend the answer to the question "Why were particular raw materials and production methods used?" beyond the sometimes rather simplistic technological reasons based on the observed or inferred physical properties of the raw materials and finished ceramics.

Acknowledgements

I wish to express my gratitude to Mavis Bimson and Dr Ian Freestone for the contributions that they have made, in their very different ways, to my understanding of the technology of ancient ceramics. Without the knowledge and insight that I gained from them during our period of collaboration together at the British Museum Research Laboratory, I would not have been in a position to write this review paper.

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