

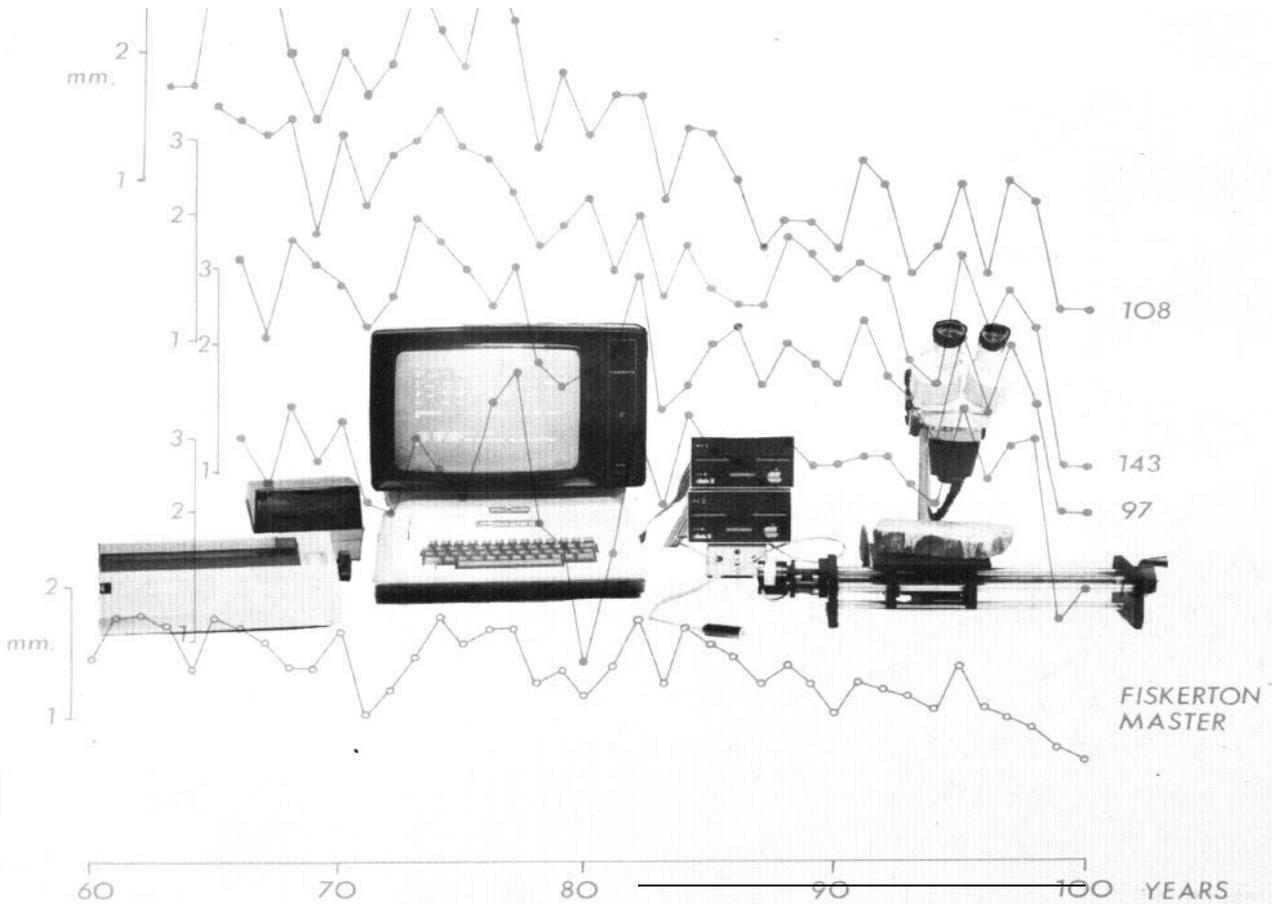
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edited by
Patricia Phillips



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The archaeologist
and
the laboratory

edited by Patricia Phillips

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This volume contains papers delivered at a conference entitled *The Archaeologist and the Laboratory*, held in Oxford on 18–20 November 1983. The impulse for the conference came from the Council for British Archaeology's Archaeological Science Committee (*chairman* Dr Paul Mellars) and the organization was in the hands of the Oxford University Department of External Studies. The conference sought to publicize developments in archaeological science (excluding environmental archaeology) to a wider archaeological audience. In the event it attracted about 100 participants. The conference involved an opening session in the form of an archaeological science forum, an evening of videos and films on archaeological science subjects, and four sessions of lectures. Dr Michael Tite chaired the forum, and the chairmen for the four lecture sessions were Dr Paul Mellars, Dr Elizabeth Slater, Mr Arnold Aspinall, and Miss Kate Foley.

Each of the speakers at the conference took a particular raw material or group of raw materials and explained the

analytical techniques which could be applied to them, with the limitations and successes of those techniques. Their papers are reproduced in this volume. It emerged during the conference that several speakers had made use of scanning electron microscopy (SEM) in their analyses, and, as this technique is still unfamiliar in detail to many archaeologists, Dr Ian Freestone kindly agreed to produce a short paper describing the use of both SEM and the electron microprobe. This forms the final paper in the volume.

The editor is grateful to Dr Michael Tite and Dr Michael Cowell for editorial advice on papers written by non-scientists, and to Dr Christine Williams for her work as sub-editor. The contributors to the volume are warmly thanked for their lively presentations at the conference, and for producing the written versions with a minimum of editorial pressure. Any errors that remain are, of course, the responsibility of the editor.

April 1984

The archaeological science forum consisted of Dr Michael Tite, *Chairman* (Director, Research Laboratory, The British Museum), Dr Martin Aitken (Deputy Director, Laboratory for Archaeology and the History of Art, Oxford), Ms Justine Bayley (Ancient Monuments Laboratory), and Mr Stanley Warren (Department of Archaeological Sciences, University of Bradford).

The purpose of the forum was to explain to a mainly non-scientific audience the range of dating and fingerprinting techniques and services now available, and to give examples of the work of some archaeological science laboratories.

The forum opened with each member of the panel outlining the resources and equipment of his or her laboratory. The second half of the forum consisted of questions and general discussion on scientific techniques and services.

Dr Aitken outlined the history of the Oxford Laboratory for Archaeology and the History of Art. Following a discussion between Professor Christopher Hawkes and Lord Cherwell, the Laboratory was founded in 1955, funded by the Nuffield Foundation and Wenner-Gren. In January 1958, they began work on a proton magnetometer, utilizing a principle developed only three years before in pure physics. The magnetometer was used successfully in March of that year at Water Newton, near Peterborough, to locate kilns. In 1958 the journal *Archaeometry* was also founded. The laboratory's first research degree was granted in 1959, covering neutron activation analysis and back-scattering work on Greek silver coins. In the 1960s attention turned to the thermoluminescence (TL) dating technique, and, more recently, work has been in progress on the radiocarbon accelerator. The laboratory's aim was principally to develop techniques and to demonstrate their application to archaeology, rather than to pursue routine applications (except in the case of the authenticity testing facility). Initially, the laboratory had envisaged that there would be rapid assimilation and usage of the techniques they had developed by other archaeological institutions. This had not generally been the case, and the need to have substantial involvement in application has been realized, and has been seen to be advantageous in the stimulation of new research.

Ms Bayley said that the Ancient Monuments Laboratory existed to answer archaeologists' questions. Its brief was to work on material from excavations funded by the Department of the Environment, and no charges were made for this work. The laboratory covered a wide range of disciplines: conservation, environmental studies, geophysical prospection, dating, and technology. 'In-house' facilities were supplemented where necessary by arrangements with other laboratories and consultants. The work of the technology section was most relevant to the subject area of the conference, and included the examination and

analysis of both finished artefacts and industrial residues. No new analytical techniques had been developed in the course of this work, but new applications of existing techniques were routine.

Mr Warren described the growing involvement in archaeological science by members of the Department of Physics at Bradford in the late 1960s. In 1972-73 a post-graduate course in scientific methods in archaeology was established, and in 1974 the first students were enrolled for a BSc programme in archaeological sciences. At present, twenty students per year are enrolled as undergraduates, plus postgraduate students and research assistants. Senior academic staff have heavy teaching commitments, so the basic labour force for archaeological science are third-year students, postgraduate students, and a number of students on SERC research and case awards. The three technicians also have a very high workload, as sample preparation is very time-consuming. With two neutron activation counting lines, three X-ray fluorescence (XRF) spectrometer systems, one atomic absorption system, and a neutron activation facility in the laboratory, there is spare capacity in the equipment. Mr Warren highlighted the importance of sample suitability and its research potential for student programmes. Other strengths of the Department are in geophysical survey and linear plotting of aerial photographs by computer programme.

Dr Tite stated that the British Museum Research Laboratory contained eighteen scientists. Work in the laboratory was project-orientated and undertaken in collaboration with the Museum's various departments. Neutron activation analysis and petrology were among the provenance techniques used. The Laboratory has undertaken studies of ancient technology, especially in the fields of metal, ceramics, and glass, on a world-wide basis; only 30% of its work concerns Great Britain. Coins have also been studied in detail. The Laboratory also carries out radiocarbon dating, and uses thermoluminescence for the dating of pottery and burnt flint, and for authenticity.

During the discussion period, a range of techniques and services for the archaeologist were mentioned. Two representatives of service facilities indicated the availability and cost of their analytical processing (Dr Peter Northover, of the Department of Metallurgy, University of Oxford, and Ian Watson, of the Thermoluminescence Dating Service at the University of Durham). Other services mentioned included the microcounter for radiocarbon dating at Harwell, which unfortunately has a long waiting list of samples. The British Museum, Harwell, and Belfast were noted as the main radiocarbon laboratories working on archaeological materials. Other radiocarbon laboratories less involved with archaeological samples included those at East

Kilbride, Glasgow, Cardiff, Cambridge, and Birmingham. It was stated that access to the Oxford accelerator for the dating of very small samples is available to archaeologists if their proposals are accepted by the Programme Advisory Panel.

With regard to the TL dating technique, the point was made that the dates derived are not always as reproducible as those obtained by radiocarbon dating. However, TL dating is probably a more accurate technique for the very recent period, where problems arise with the calibration of radiocarbon dates. The method has the added advantage of dating the artefact itself, rather than the associated material, as is usually the case with radiocarbon dating.

Magnetic dating of hearths, silts, and sediments was discussed. It was pointed out that this technique is effective only for certain periods, and that, in respect of silts and sediments, the work is still only in an investigatory phase. The Ancient Monuments Laboratory carries out such analyses for sites funded by the Department of the Environment, and a centre also exists at Newcastle.

Another subject of discussion involved timbers. Excavators of large quantities of timber were worried about sampling problems and conservation. Present techniques of analysis included species identification and dating by dendrochronology, but excavators questioned how to ensure that sufficient samples were being retained for new types of scientific analysis in the future. Some of these questions were addressed by Jennifer Hillam in her paper.

The first petrological analyses of medieval pottery were carried out at Bonn in the 1930s, as a direct result of Buttler and Obenauer's success in their pioneering work on the Neolithic *Bandkeramik* of Kõln-Lindenthal (Schmitt 1937). The work thus initiated has continued and petrological examination has been attempted in other countries, such as Britain, France, Scandinavia, Italy, and Poland, resulting in a substantial body of data upon which the potential and limitations of the method can be assessed. The object of this paper is to evaluate the scope of petrological techniques in medieval archaeology by reviewing some of the achievements to date. Work of this type is often published as short specialist appendices or comments included in more general works, thus not receiving the attention it deserves: this paper should in some measure rectify the balance.

The underlying principles of the two fundamental techniques of ceramic petrology, examination in thin-section and heavy mineral analysis, have been discussed elsewhere and details need not be reiterated here (eg Schmitt 1937; Peacock 1967; 1970a). Their value in medieval pottery falls within four partially overlapping areas of study. They are of obvious value in assessing questions of ceramic technology, or in assigning pots to their geological source on the basis of exotic rock and mineral inclusions. However, when the majority of inclusions are non-distinctive it can be possible to detect differences in texture, which may indicate the number of production centres involved in making a particular type. Finally, petrological methods may be of value in identifying the types or forms to which small non-distinctive body sherds belong: a process that can be crucial in dating or in assessing questions of economic importance.

Technology

Examination in thin section is of particular value in assessing the way in which raw materials were prepared and fired. In Poland, Kociszewski and Kruppe (1968), following the pioneering work of Reyman (1959) and Wirska (1967), have suggested that granulometric studies can be used to differentiate natural inclusions from artificial admixture of temper, and their work includes reference to medieval pottery from Tarnõw. A similar approach was adopted by Beckmann, Strunk-Lichtenberg, and Heide (1971) in their study of the development of the Siegburg potteries throughout the medieval and early Renaissance periods. They were able to demonstrate the way in which the local Pleistocene Rhine sand was used to temper the clay, sometimes being sieved to give an even size grade. With the introduction of stoneware in the 15th century no temper was used and any quartz grains are natural impurities of the local Tertiary clay. Using other techniques it was possible to

demonstrate that there was also a progressive decrease in porosity and increase in hardness.

Some time ago Obenauer (1939) made a technological study of 9th century AD stonewares and porcelain from Samarra near Bagdad. Examination in thin section enabled him to suggest the deliberate selection of pure rock crystals or quartz pebbles which were crushed to provide an essential additive for the clay. This is presumably the *Hajar-i Maha* or 'crystal stone' referred to in Abu'l Qasim's treatise on ceramics (Allan 1973).

Petrological techniques have a number of other applications in the study of ceramic technology. Frierman (1970) has drawn attention to the value of mineralogy in studying early glazing methods, particularly those of the Palestinian Crusader period where undissolved relicts of quartz plagioclase felspar can be seen. Another interesting approach is that used by Sabine on 13th century sherds from Beere in Devon. He attempted to assess firing temperatures on the basis of the structure and optics of black mica, which is known to change its properties on heating (in Jope & Threlfall 1958). Potentially this could be a very useful tool for studying firing and it is unfortunate that the idea has never been seriously followed up.

Medieval brickwork has also been the subject of technological investigation. Firman and Firman (1967) adopted a specifically geological approach, treating bricks as sedimentary rocks metamorphosed by the movement of the potter's hand and by heat. Their study carried out over wide areas of England has produced a wealth of technological detail about the nature of the raw materials and the way in which they were mixed, moulded, dried, and fired; information which serves to amplify and confirm data from historical sources. Mineralogical investigations have also been used in studying the technology of late Gothic and early Renaissance tiles from Dubieko Castle in Poland (Wirska-Parachoniak 1970) and of building materials used in the mausoleum of Khodzi Akhmed Yasevi (Kvatbaev & Takibaeva-Beloborodova 1970).

Origins: diagnosis and differentiation

Pioneering work in the Rhineland must take pride of place in discussion of the use of petrology to assess pottery origins. Over the last forty years a considerable body of data has been accumulated, principally by Frechen, and it is now possible to recognize petrologically the products of the main pottery centres operating during the Frankish and later periods. The characteristics of the potteries operating in the Cologne region have been defined and they can be readily distinguished from material produced in more distant sources such as Mayen

in the Middle Rhineland or the lower Rhenish region (eg Lung 1956; 1959; Steeger 1948). Also noteworthy is Frechen's contribution to the study of late Roman and early medieval pottery of Frankfurt (in Stamm 1962), later expanded to include an extensive study of over 200 Merovingian vessels from wide areas of southern Germany (in Hübener 1969). He was able to characterize the pottery of the Munich, Strasbourg, Worms, and Wiesbaden areas and could recognize imports from the Mayen district. Unfortunately the lower Rhineland presents problems, as wide areas of northern Germany, Holland, and southern Scandinavia are covered with glacial moraine, and pottery from the whole of this area tends to be characterized by inclusions of gneissic or granitic origin (Böhner 1950; Steeger 1948; Sundius 1955). It is not yet possible to pinpoint sources in this zone, but at Duisburg, for example, it has proved feasible to distinguish local imitations of products from the potteries further south (Tischler 1950; 1952; Stampfuss 1939). More precise differentiation may prove possible in the future, and one thinks in particular of a group or groups of Frankish wares of probably lower Rhenish origin which contain fragments of sandstone (Steeger 1948; Böhner 1950).

Of particular note are vessels made in the Mayen region, which can be recognized by their exotic assemblage of volcanic materials, such as pumice, sanidine, plagioclase, hauyne, aegerine augite, and brown hornblende, together with fragments of greywacke sandstone and weakly metamorphosed argillaceous rocks. Petrology is essential for the correct identification of this ware, as it was imitated in other places (eg Tischler 1952; Hübener 1953). The ware has a broad distribution, even extending southwards against the strong Rhine current, doubtless a reflection of its technological strength, and hence value. There is undoubtedly continuity between the late Roman production of the 4th century and that of the post-Roman period (Böhner 1949) and it seems probable that some of the wide markets established under the Romans may have continued in existence (cf Nierhaus 1940; Fulford & Bird 1975).

Frechen's detailed work in the Rhineland permits exports to be recognized with confidence, even when fragments are small and without typological features, as with Rhenish imports to the settlements of Kaupang and Haithabu (Hougen 1969; Hübener 1959). It has also provided material for useful ceramic synthesis within the Rhineland. Thus, Lung (1959), drawing on petrological as well as archaeological evidence, was able to give a clear picture of the main sources of ceramics used in medieval Cologne. It is interesting to note the way in which early supplies from distant sources at Mayen and in the lower Rhine area were gradually replaced with pottery from kilns situated within a 10-20km radius of the city. Lung's synthesis illustrates the great potential of petrology in providing information of direct interest to the economic historian.

One of the most extensively sectioned medieval pottery types is Tating ware, the fine black pottery with characteristic tinfoil ornament, current in the 8th and 9th centuries, and it has now become the subject of a petrologically based controversy. This pottery was

studied at length by Selling (1955), who argued for a source in the Archbishopric of Mainz on archaeological analogies for the cross decorative motif used on many of the vessels. Sherds from Birka and Kunsta were studied under the microscope by Sundius (1955) but, as the published section shows the fabric contained fine- or medium-grained quartz with no minerals diagnostic of source. Schindler (1959) had further sherds from Hamburg and Süderende-Föhr analysed with similar results. Frechen (in Hübener 1959) reported further inconclusive results on material from Haithabu, while examination of the Norwegian Kaupang material suggested that some vessels might have origins in the morainic areas of southern Scandinavia, northern Germany, or Holland. This led Hougen (1969) to reject Selling's Rhenish hypothesis, to which she responded by having further material examined in Stockholm by Hulthén (Selling 1972). The three sherds from Birka each contained inclusions of trachyte, a volcanic rock of restricted geological occurrence. The only outcrops within the area of Tating ware distribution are in the Middle Rhineland between Koblenz and Bonn. The area indicated is not the Mainz region as Selling supposed, nor can the comparison with brick and clay samples from the Abbey of Lorsch, near Mainz, be used to support her argument, for no details of mineral inclusions are recorded.

Tating ware provides an interesting case of petrologists coming to different conclusions. The reason must surely be that pottery of this type was made at a number of centres, of which at least three seem to be indicated on available published evidence. This is a very surprising conclusion, for one might expect the exotic technique of tinfoil decoration to be the monopoly of a single production region.

Thin-section examination has also been used effectively in Britain. Analysis of a 12th century grass-marked sherd from Southampton revealed large crystals of plagioclase feldspar and pale green or colourless amphibole, minerals which are characteristic of the altered basic igneous rocks of south-western Britain. The material compares closely in petrology with sherds of grass-marked ware from Cornwall, and it is possible to find a very precise mineralogical match for all the pottery in the clays overlying the gabbro of the Lizard Peninsula (Peacock 1975). This implies a centre of manufacture in that region and provides an argument against Thomas's (1968) hypothesis of localized home production.

Rix and Dunning (1955) have published a vessel from a late 13th century wardrobe in Snargate Street, Dover, which Sabine attributed to the Launceston region of Cornwall on the presence of considerable quantities of talc. However, this must now be questioned, as Giot (1971) has published a group of talc-rich medieval pottery from western Brittany, and it now seems certain that the Dover dish was transported from Finistère, some 350 miles to the west. Mannoni (1969; 1971; 1972; 1982) employed thin sections extensively in his study of the medieval and later pottery of Liguria. He has revealed criteria for discriminating the local products of towns such as Savona and Genoa, as well as recognizing imports from more distant places such as Africa and Spain.

More recently, large-scale investigations have been undertaken in Britain by workers such as Hodges (1977; 1981), and these have amply demonstrated the value of thin sections in provenancing pottery containing distinctive rock and mineral inclusions. Furthermore, Streeten (1983) has developed methods of textural analysis which have greatly expanded the range of inferences that can be drawn from simple quartz-tempered wares. An up-to-date review of the current state of the art will be found in the volume edited by Freestone *et al* (1982). However, it cannot be claimed that the results of petrological examination are always clear-cut. Thus Barton's report on the petrology of 12th-13th century pottery from Alton Barnes (Wilts) is inconclusive (Thompson & Ross 1973). Long ago Schmitt examined certain sherds of hard sub Roman pottery from Lagore Crannog in Ireland, but was unable to suggest a source (Hencken 1950). This ware, a characteristic import of the 6th-8th centuries in western Britain, was later christened Class E ware by Thomas (1959). Further thin sectioning by Nisbet, and later by the writer, again failed to produce evidence diagnostic of the origin (Peacock & Thomas 1966). In view of the difficulties, heavy mineral analysis was attempted and resulted in a measure of success. The assemblage obtained ruled out any likelihood of the previously suggested Rhenish source and pointed to an origin in an area of geologically young sedimentary rocks. Comparison with later pottery from the Saintonge region of France suggested the Aquitaine basin, centred on Bordeaux, as a likely source. As Alcock (1971) has pointed out, the suggested source cannot be regarded as proven until comparative material of the correct date comes to light, but at least the scientific analysis gives a good indication of where research might profitably be directed.

The non-distinctive nature of sand inclusions was a problem that also confronted Biddle and Barclay (1974) in their study of the Saxo-Norman glazed Winchester ware. However, a preliminary programme of heavy mineral analysis served to differentiate Winchester ware from analogous Stamford products and suggested the possibility of two production centres in the Winchester region.

During the late 5th and early 6th centuries, amphorae were imported into western Britain from unknown sources in the eastern Mediterranean (Thomas 1959). Two of the more important types, Thomas's Class Bi and Bii, have been the subject of thin-section examination (Peacock 1970b). This work has demonstrated that Class Bi amphorae contain fragments of limestone, indicating an origin in an area of sedimentary rocks, while Bii are characterized by grains of limestone and pyroxene, indicating a source area dominated by basic igneous as well as sedimentary rocks. It is impossible to predict sources on these data, but the analysis does indicate distinct and geographically separate origins for the two types. Thus, Thomas's (1959) suggestion that the two forms originated in the same area and were containers for different commodities is now untenable. The petrology also provides grounds for discounting the source on the Black Sea coast of Romania suggested by Alcock (1971). Amphorae of both classes were found in the debris of a brick kiln at Oltina (Irimia 1968). This discovery is

relevant because there is evidence to suggest that amphorae were sometimes produced alongside bricks in the Roman period (eg Leite de Vasconcelas 1898; Ponsich 1974; Peacock 1977a). However, the petrological evidence indicates that one of these categories (probably Bii) could not have been made at Oltina, and if imported amphorae were in use at the brick kiln there is no reason why both types could not have been made elsewhere.

Sherd identification

The use of petrological techniques to identify the forms or types to which small featureless body sherds belong is an approach that has been little explored. However, on several occasions the writer has been able to discount claims of Bi and Bii amphorae from the late Roman towns of lowland Britain, on the basis of petrology. For example, the supposed Bi amphora sherd from late 4th or early 5th century London (Alcock 1971, 208) could be shown on petrological grounds to belong to the very different form, Almagro 54, which Riley (1975) suggests originated in the Gaza region. Furthermore, petrological study of amphora sherds from the very latest contexts of Roman Britain has permitted the identification of cylindrical types from the Byzacena region of North Africa (Peacock 1977b). This material has escaped attention to date as it usually occurs as small unfeathered sherds. Not only does the recognition of this type add a new facet to the study of the economics of this period, but it provides for the first time a ceramic fossil that may be of value in recognizing deposits of the most elusive of all periods, the early 5th century.

Conclusions

It will be evident from the examples cited above that petrological analysis has a considerable role in medieval ceramic research. Thin-section or heavy-mineral analysis does not replace the traditional archaeological approach, but when used alongside provides a very powerful combination. Petrology has certain advantages over other scientific techniques in that postdepositional changes in mineral composition are usually evident, and it can be possible to predict sources on the internal evidence of a single sherd. No other technique can normally offer such precision. However, petrology is most effectively applied to sherds with exotic mineralogy, and other methods can be as good or better when dealing with fine-grained untempered wares or those with fine quartz sand.

This paper has concentrated on thin-section and heavy-mineral analysis. Other geological approaches such as the palaeontological identification of organic inclusions have considerable potential. Swinnerton was able to suggest that Saxo-Norman Stamford ware was made from the local Jurassic Estuarine Clays on the basis of plant remains in the clay, though this is somewhat dubious as it was inconclusive whether the ceramic inclusions were fossil or recent (Dunning 1956). Schindler's (1959) report on the 8th-9th century *Muschelgruskeramik* of the Hamburg region shows more promise. The shell fragments could be referred to the cockle *Cardium* while the presence of brackish water diatoms suggested the use of marsh clay. Such approaches are in need of further application and development.

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Why neutron activation analysis?

In the scientific sense we may define 'analysis' as the measurement of significant physical and chemical properties of matter. The significant properties we are concerned with are those which would elucidate some archaeological problems associated with ceramics; the properties may be classified loosely as structural and elemental. 'Structure' in the form of particulate components within a ceramic may be used as a means of identification. However, unambiguous identification of a ceramic is a considerable scientific as well as archaeological problem and may require more than one approach in order to achieve it. Rather than examine structure, a distinctive approach is that of measurement of elemental composition. It is presumed that the relative concentrations of chemical elements present in artefacts may vary, depending on source of raw materials, technique of manufacture, environment of deposition, and so on, so that an artefact (or group of artefacts) may carry a unique 'fingerprint'. In the main, the more complete the element analysis, the more likely it is that success in characterization will be achieved. Thus, spectroscopic techniques, which yield simultaneous analyses of several chemical elements at trace concentrations, have been employed extensively for ceramic studies (Wilson 1978).

As distinct from atomic spectroscopy, neutron activation analysis (NAA) is concerned with the study of elements through the distinctive properties of their nuclei, and these may be readily energized, to reveal their identity, by neutron bombardment. In order to examine the elemental composition of ceramics, an intense source of neutrons, 10^{10} - 10^{12} neutron/mm²/s, is required; therefore a nuclear reactor is a prerequisite for ceramic analyses. The sensitivity of the method for an element in particular concentration depends fundamentally on the neutron cross-section—effectively the nuclear target area for neutron absorption by a particular nucleus. It also depends on the half-life for radioactive decay of the unstable nucleus which is created by neutron absorption. The radioactivity we are concerned with is that of γ -rays, the penetrating electromagnetic radiation emitted by a particular unstable nucleus with precisely defined energies. Modern electronic detection techniques enable us to receive and measure the energies and intensities of these γ -rays so that we can identify an unstable element through its γ -ray energies and its concentration by the intensity, or amount, of this radiation emitted in a definite time. Many elements may be assessed simultaneously by this approach.

Practical considerations

Element concentrations are not determined through the use of the fundamental physical equations governing the nuclear reactions involved. Instead, a direct comparison

is made between the 'unknown' specimens and made-up standards of known composition. Indeed, the standards are frequently powdered pottery with element concentrations comparable with most ceramics (Perlman & Asaro 1969).

The unstable nuclei produced in the reactor have a wide range of half-lives. By selective timing of irradiation period and analysis after irradiation, it is possible to optimize conditions for 'best' sensitivity. To this end the sought elements may be divided into three coarse groups depending on half-life: 1. very short (up to lh), 2. short (up to several days), and 3. long (up to several years). This is a very arbitrary grouping and, for ceramics, most information appears to be obtained from short and long half-life radioactive nuclei, which entail irradiations in the nuclear reactor of up to 24h, depending on the flux of neutrons available. Thus potassium (12h) and sodium (15h) are typical examples of short half-life elements, as is the rare earth element lanthanum (42h). These are best examined no more than a few days after irradiation. Chromium (28 days), iron (45 days), and cobalt (5.3 years), as well as several rare earths, have long half-lives and are seen at their best several weeks after irradiation, when short-lived activity has virtually disappeared. Obviously some value judgement has to be placed on these analysis timings. At each stage of analysis, however, the standard and unknown samples may be compared directly for elements present and intensity of radiation. These comparisons are translated to concentrations present in the unknowns using well established computer programmes (Korthoven & de Bruin 1977). In this overall analysis some thirty elements may be identified as being present in a typical ceramic, many of them at trace (ie parts per million) level. Problems of extraction of evidence from 'noise' and mutual interference of spectral peaks preclude some of these from quantitative assessment and, in practice, up to twenty elements are usually measured. However, 'presence' or 'absence' of an element, relative to the limits of detectability in a particular experiment, may also be diagnostic evidence.

As indicated above, experimental constraints limit the number of elements quantifiable, but which elements may be measured and what is their value to ceramic 'fingerprinting'? By fortunate circumstances, involving low cross-sections for neutron absorption and very short half-lives, the dominant elements, silicon and aluminium, do not appear in the γ -ray spectra measured. Thus NAA has the very great advantage that little or no pre-analysis chemical preparation is required for minor and trace element assessment of ceramic or other aluminium silicates. Of particular potential value for sample characterization are the rare earth elements, present at trace level in ceramics. The varying patterns of concentrations of the rare earths in lithic materials are well

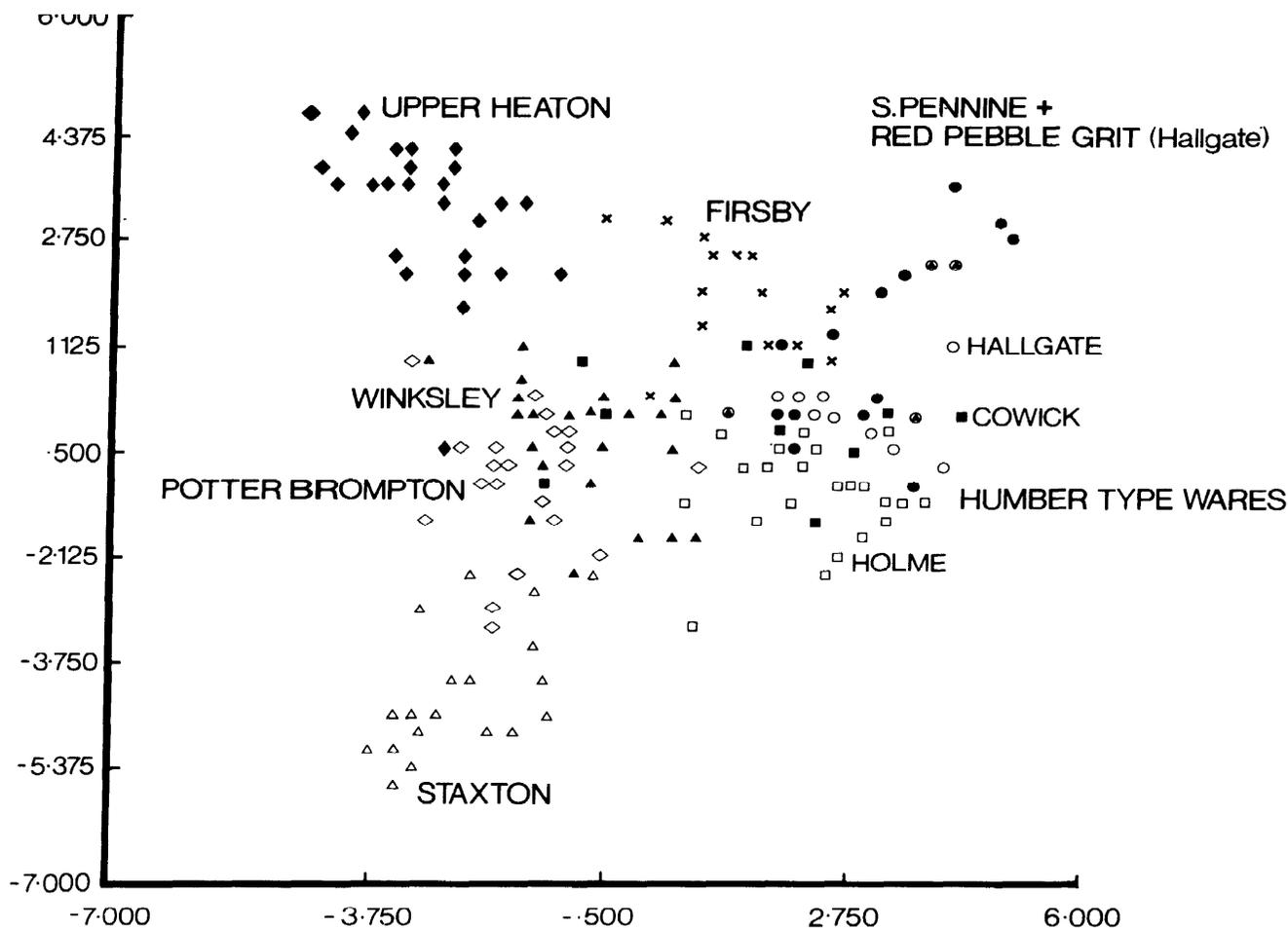


Fig 1 Yorkshire medieval kilns: discriminant analysis (Ipson & Walker)

known to geologists and are used for diagnostic purposes (Allen & Pennell 1978). Metals such as cobalt, chromium, and particularly iron also show useful variations between clay deposits.

Although in general NAA has value as a non-destructive method of analysis, it is usual practice, for ceramic studies, to extract powdered samples of about 100mg mass. These are often pelletized under pressure in order to produce a standard shape for presentation to the detector system. The introduction of possible systematic errors during this sampling and subsequent analysis have been recognized (Wilson 1978). Thus the presence of inclusions as temper and gritting, the take-up of ground water, and the deposition and leaching of elements during the period when sherds lie in the ground must be considered. During irradiation, some check or correction must be made for possible non-uniformity of neutron flux through a batch of specimens. During analysis, the siting of the sample relative to the detector must be defined. The use of an internal 'standard' (a particular element which is common to all specimens examined) within each

sample may be utilized to eliminate systematic errors; scandium, an element present in readily measurable quantities, has been used as such a reference (Aspinall 1977). However, the possible influence of such rationalization on subsequent statistical data treatment has been pointed out by several authors (eg Leach & Manly 1982).

Ceramic studies using NAA

In the main the enormous numbers of analyses undertaken on ceramics of all archaeological periods from all parts of the world have been associated with provenance studies. If sherds are available in statistically adequate numbers from known sources then, ideally, fingerprints of such sources may be produced through element concentration patterns. Practice, however, may be very different. Even though the large number of elements measured creates a series of fingerprints amenable to statistical interpretation, the heterogeneity of samples from a single source, often complex in itself in terms of period of use, change of resources, etc, may provide the

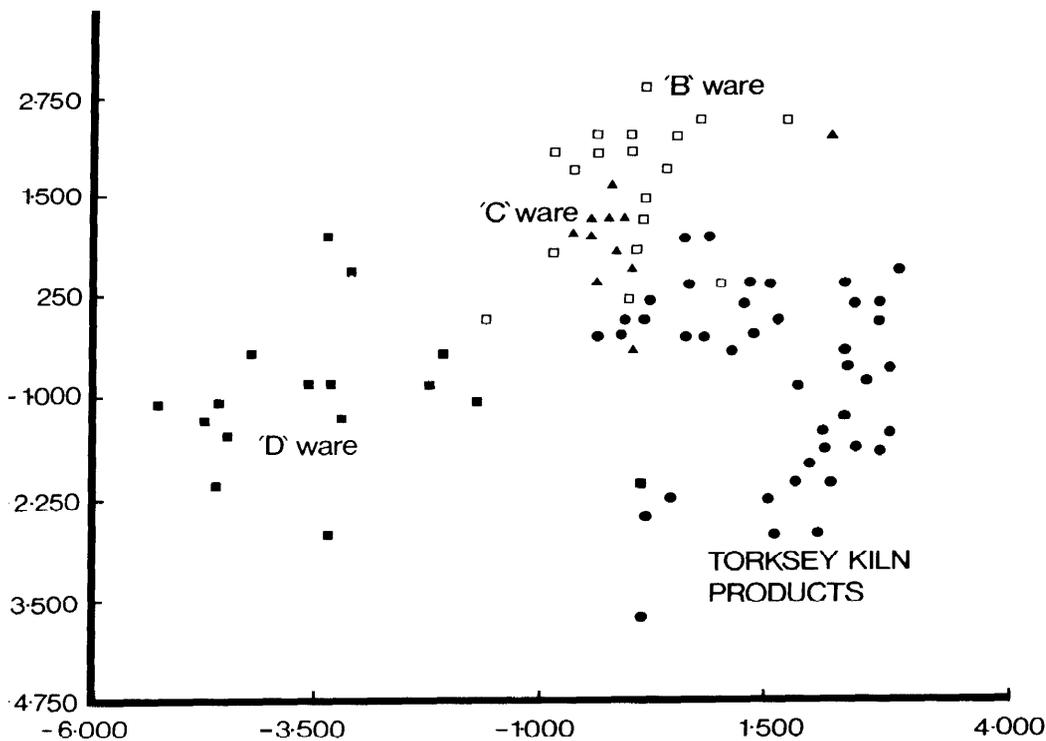


Fig 2 Torksey kiln products and Torksey-type wares: discriminant analysis (Ipson)

limit to successful discrimination. Often no true source identity is available and the problem to be solved is purely that of group discrimination, for example between 'local' and 'imported' wares, the implication here often arising from archaeological evidence alone. The lack of basic information on actual sources in such cases often leaves the results in an increased state of uncertainty with the postulation of subgroups present within the main groupings.

Case studies

Taking examples from our own experience, we can very readily see the problems of kiln characterization on a large scale. We have undertaken a characterization programme for the medieval kilns of (mainly) Yorkshire and some East Midland counties and have used standard statistical methods (Wilson 1978) in an attempt to distinguish them from one another. In Fig 1, the two prime functions, following stepwise discriminant analysis for ten such industries, are plotted so as to obtain a two-dimensional representation. The general overlap of data is evident, although there is clear discrimination of some individual groups such as Upper Heaton. If a less ambitious goal is accepted, however, and fewer variables (sources) are entered, more satisfactory results are obtained. Excavations at Torksey (Lines) revealed the presence of an extensive late Saxon pottery industry represented by five kilns producing similar wares (Barley

1964). Torksey-type pottery has been found in excavations at habitation centres remote from Torksey itself, including Lincoln and York. It was of interest to examine this apparent distribution through NAA, and Mrs F Ipson undertook the study at Bradford. Samples from the five kilns were analysed as a group and compared with sherds from occupation sites in the vicinity of the kilns, from Lincoln, and from York. The data were subjected to discriminant analysis as before and it was found that 'non-Torksey' sherds from Lincoln formed a distinctive group. Although 'Torksey-types' associated better with the kiln samples, the assignment was only fair. However, when the kiln products were compared with three 'Torksey-type' fabrics (B, C, D) from York (Fig 2), significant differences were seen. The D wares formed a distinctive group whilst B and C came together with rather less discrimination from the source assembly. The ready conclusion from this study is that the York 'Torksey-type' sherds do not originate from Torksey, but it may be better to state merely that these sherds are unlikely to have originated from the five kilns excavated at Torksey. As is often the case, a 'not proven' answer is the most appropriate one here.

As an example of group differences in the absence of kilns, the 'Torksey-ware' investigation was extended to cover other ceramic samples excavated in York, covering a period from Roman to high medieval times. It could be that local resources were in use for the whole or part of

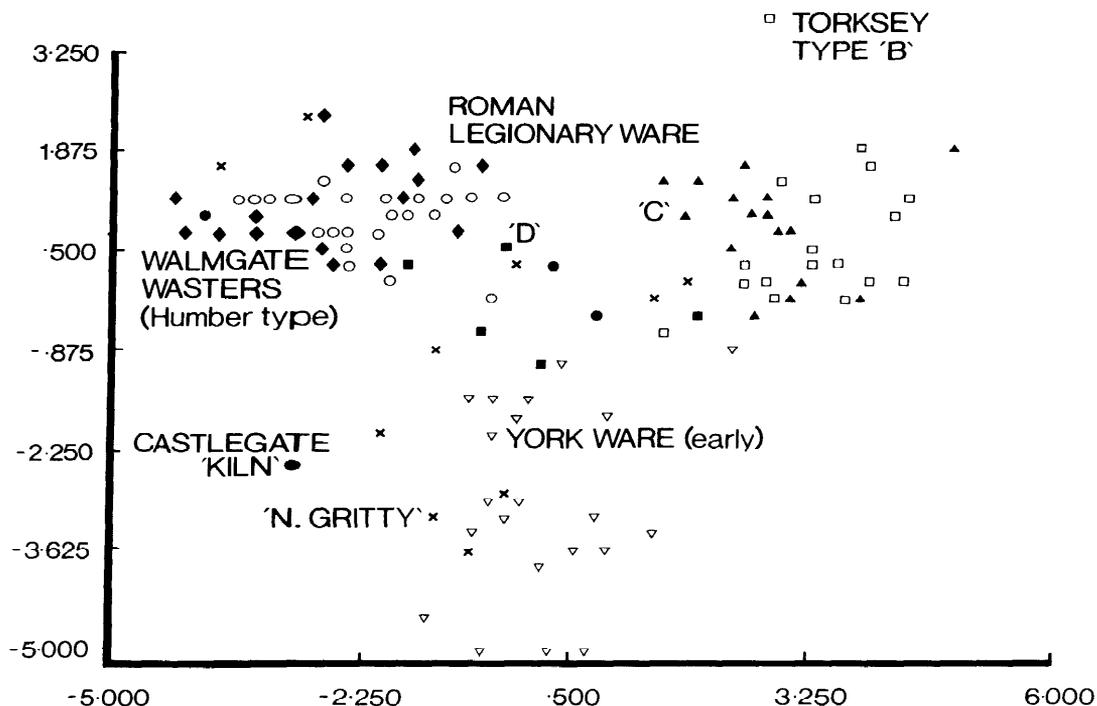


Fig 3 Wares from York sites: discriminant analysis (Ipson)

this period, and there is evidence for the existence of a medieval kiln in York. The three 'Torksey-type' wares were compared with five other defined fabrics from York, as shown in Fig 3. If we take into account the limitations of the plotting of data from eight groups in this way, it does appear that the Roman and Walmgate sherds form a good grouping, with other fabrics rather ill-defined. The 'Torksey-type' groups, particularly B and C, are distinctive, so that it is tempting to assign a distinct source to them. Clearly we still have the question of the actual origins of these 'Torksey-type' groups. The evidence points to a non-Torksey and non-York source. Our uncertainty arises from our inevitable lack of knowledge of other pottery sources, either lost or unexcavated, in either of the source areas or, indeed, in a third undefined industry.

Concluding remarks

The application of neutron activation analysis to ceramic provenance studies has greatly strengthened the data base on which such studies are mounted. Multivariate statistics are applicable to the element concentration patterns relating to specific sources, and reliable criteria for discrimination can be established. However, the success of NAA, or indeed any other method of ceramic characterization, is limited by the nature of the material under examination. As the data base of ceramic analysis, even within a particular temporal or archaeological context, increases it becomes evident that we are attempting to rationalize, through minor differences, products of complex natural resources which are typified by the early

ceramic industries. It may well be that the strength of such analysis will be in its ability to produce a 'negative' answer for a particular sherd of unknown origin in that sources where the specimen was *not* manufactured may be reliably defined.

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A wide range of analytical techniques have been applied to the study of building materials and some of, these, eg thin-section petrology and neutron activation analysis, are well described in other contributions to this volume. Since most of the emphasis in previous studies has been to establish the geological sources of the materials used in building construction—the stone and the clay for bricks and tile—this paper adopts a rather different approach by considering in some detail the technical examination of plaster surfaces before mentioning briefly some recent and current work on stone, brick, and tile.

Pigments in Roman painted plaster

Although it is possible to identify the nature of surface pigments without destructive sampling, it is more usual to scrape a small amount of pigment from the surface (c 1mg will suffice) and to analyse this separately by *X-ray diffraction* (XRD) (Klug & Alexander 1954). In this technique any crystalline structure in the pigment causes scattering (diffraction) of incident X-rays into well defined directions characteristic of the structure and results in a pattern of lines on X-ray sensitive film. Interpretation in terms of the interplanar spacings of atoms in the structure (so-called 'd-values) provides identification of the structure(s) (Powder Diffraction File 1981) in the pigment. The pigment is usually contaminated by the plaster, which sets as calcite, a mineral form of calcium carbonate. This can be removed chemically or can be disregarded in the analysis. In our examination of Romano-British plasters (Wetzel & Warren 1979) only a limited range of pigments were found:

White

This is the background calcium carbonate (CaCO_3) in the form of calcite. The harder-setting gypsum plaster ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has not been observed in our studies.

Black

This is a finely dispersed carbon which did not produce a diffraction pattern. Carbon is outside the range of elements detectable by our *energy-dispersive X-ray fluorescence* (EDXRF) equipment, but we were able to establish that it was not bone or ivory black. Dr D Robins (pers comm), using *electron spin resonance* (ESR), was able to confirm that the carbon had been formed by combustion and it is hoped that more detailed study in conjunction with the ESR group at Queen Mary College will

distinguish between different types of carbon black.

Yellow

This is attributed to the hydrated iron oxides, limonite or goethite $\text{FeO}(\text{OH})$, and is often found and applied as an ochre, ie as an iron oxide in a clay base. Apart from lines on the XRD film attributed to the iron oxide, the dominant lines are those of quartz. The colours range from yellow to brown, and the span from brown to red/purple is obtained from the red ochres in which the colour is attributed to the iron oxide, hematite (Fe_2O_3). As with the yellow ochre, the other dominant lines for red ochres are those of quartz.

Green

This is almost invariably green earth—a mixture of glauconite and celadonite minerals ($\text{K}(\text{MgFeAl})_2(\text{SiAl})_4\text{O}_{12}(\text{OH})_2$).

Red

Apart from hematite/red ochre the other red pigment is vermilion or cinnabar (HgS). According to Pliny (a) the principal source was at Sisapo in the Almadén region of Spain from where it was delivered to Rome for purification. Some confusion arises over the use of the term *minium* for cinnabar since this is now restricted to red lead (Pb_3O_4). In spite of this it is clear from Pliny's writing that the high cost of cinnabar encouraged its adulteration with red lead and that quality testing was necessary to ensure its purity. Cinnabar was used at three sites in Roman York (Wetzel 1980), but in no case was there any evidence of adulteration. More care was usually taken in smoothing the surface prior to painting with cinnabar, and the resulting glossy appearance can give the impression of wax, which was sometimes applied (Augusti 1967) to prevent transformation to the black form of mercury sulphide (Gettens *et al* 1972) by the action of sunlight and moonlight (Pliny a), or to enhance the colour (Gettens *et al* 1972). No wax was detected on any of the cinnabar samples from York, although the *organic mass*

spectrometer used for the purpose had sufficient sensitivity to detect contamination from the Polythene bags used for storage.

Blue

This is Egyptian blue (Chase 1971), a man-made copper calcium silicate ($\text{CaCuSi}_4\text{O}_{10}$) (Tite *et al* 1982). The mineral is translucent and some control over the shade of blue is achieved by controlling the grain size. It is usually applied in a coarse-grained form readily seen under a x10 or x20 hand lens.

With the possible exception of cinnabar, very little can be said about possible sources of the pigments. They would have been prepared from naturally occurring and relatively common mineral deposits or, in the case of Egyptian blue, from a simple recipe (not that given by Vitruvius (Vitruvius a) unless a calcareous sand was being used). Of more interest is the use by the artist of combinations of pigments: to extend the more expensive one as in the case of cinnabar on goethite, to give greater optical density as with Egyptian blue on carbon, to modify the colour as with Egyptian blue on hematite (to produce purple) or, more rarely, to effect a different colour (green) with Egyptian blue and goethite, a technique observed in other contexts (Wilkinson 1878; Cameron *et al* 1977). A summary of analyses of pigments found in British contexts is provided by Biek (1982). As discussed by Ling (1976), the pigments were probably applied while the plaster was still damp, the bond being provided by the setting of the slaked lime adhering to the pigment. The pigment is usually restricted to a thin surface coat (Cameron *et al* 1977; Wetzel 1980) and close examination of the plaster surface often indicates that the smoothing marks of the brush or the trowel have set sufficiently hard to be unaffected by the subsequent painting.

The plaster

While it is natural for attention to be focused on the painted surface, the plaster rendering offers much more scope for the analyst, and it is desirable that the full thickness of the plaster (*stucco*) is sent to the laboratory. The plaster is built up in two or three layers, the surface (*intonaco*) being, essentially, a pure lime plaster applied by brush or trowel as a thin skim coat on a much thicker base (*arriccio*) to which filler has been added prior to application. It is the base layer which may have been built up in stages not always readily apparent when the plaster is fragmented. The filler used in plaster and mortar can be examined once the calcium carbonate has been dissolved in dilute acetic or hydrochloric acid. While this also removes any carbonate present in the original filler, the residue provides information on the type of deposit from which it was extracted. At York these fillers are typical of local riverine deposits (Wetzel 1980) and it is not unexpected that the use of local gravels has been confirmed in other studies (Hall 1977; Langley 1979). Measurement of mass and volume before and after acid attack allows us to assess the filler/lime ratio and to compare it with those quoted in the classical texts. A

mean value of 1.6:1 volume ratio found at York was rather lower than that 'expected'.

Apart from identification of gross features, it is common practice to establish the particle size distribution of the filler by standard sieve techniques. While this does add a further descriptive parameter, some caution has to be exercised in the use of particle size distributions. Reference to washing and sieving of sands used as fillers (Vitruvius b), a practice persisting in the medieval period (Salzman 1952), and of the selectivity and testing of sands for sharpness and particle size would make it inadvisable to compare the particle size distributions of filler and natural deposits as a guide to provenance. More confidence can be placed in comparisons of distributions between samples in the one structure where differences in phases of construction are suspected, or between sites. Differences in cumulative frequency distributions can be checked for significance using a *Kolmogorov-Smirnov test* (Miller & Khan 1962) or, when several samples are being compared, *duster* or *principal components techniques* (Wishart 1978) can be applied to the actual distributions, preferably after elimination of one of the grain-size categories.

The actual sources of the limestone used by the plasterer are also difficult to establish because the burning (calcination) to calcium oxide at temperatures of c 800°C, followed by transformation to hydroxide during slaking, destroys any fossil evidence in the original limestone. Trace and minor element variability in carbonates and sulphates is usually too large to permit sourcing by chemical composition, but at York the closest sources are magnesian limestones with, farther west, older carboniferous limestones and to the east, younger chalks. *Atomic absorption spectroscopy* was applied to a number of Romano-British plasters excavated by the York Minster Archaeology Unit and gave a low but significant percentage of magnesium, consistent with the exploitation of magnesian limestone. Although not as yet undertaken, confirmation of the geological age of the limestone could almost certainly be provided by strontium isotope ratio determinations using a *mass spectrometer*.

On the geological time scale the decay of the naturally occurring radio isotope rubidium-87 to strontium-87 has resulted in systematic trends in strontium-87 to strontium-86 ratios (Fauré 1977). The variation in the 87/86 ratio has been determined for marine carbonates (Peterman *et al* 1970), and it is likely that a systematic study of strontium isotope ratios for limestone/chalk outcrops in the York region could establish the geological period of the limestone being exploited. The method relies on the substitution as an impurity of strontium for calcium during formation of the carbonate, the isotope ratio for strontium being dependent on that in the water at the time of formation and on this isotope ratio remaining constant during firing and reconstitution.

On the archaeological time scale considerable interest has been aroused in the possibility of dating lime plaster and mortar by the *carbon-14* method (Folk & Valastro 1976). In principle calcination would drive out all carbon dioxide from the carbonate and carbonation would take in carbon dioxide from the atmosphere. While the former

is depleted in carbon-14 the latter would be expected to have a carbon-14 activity consistent with the atmospheric level at the time of construction of the building. Assuming no subsequent exchange or contamination, the present-day activity should provide a date for construction or repair. The method is not wholly reliable, but successful dating has been achieved by restricting dating to a finer fraction extracted from a mortar—a precaution against incomplete calcination which would result in dates systematically older than the construction. A useful first check, provided by mass spectrometry, is a measurement of the carbon-13 to carbon-12 ratio which, when expressed as a ^{13}C value, should be close to the value of c -10% for atmospheric carbon dioxide. Such values have been reported in a consistent set of dates for mortar from a medieval church at Dijon (Malone *et al* 1980), but more variable results are being experienced in initial studies of mortar from Brixworth (J Ambers, pers comm).

Analysis of medieval mortars from Northampton (Barlow 1979) indicates that the process of carbonation is not yet complete. Similar observations have been noted by Evans (pers comm), and it is clear that samples of mortar submitted for radiocarbon dating should be examined first by *X-ray diffraction* and *differential thermogravimetry* (DTA). Incomplete initial carbonation followed by a slow take-up of CO_2 from the atmosphere is likely to produce dates systematically younger than the construction.

The use of crushed brick and tile as fillers in the backing layers is obvious on visual inspection and, apart from interest in the comparison of particle size distributions with those of sand/gravel fillers, dissolving the lime plaster would indicate whether or not these fillers are mutually exclusive, as at York, or used in combination, as suggested by Faventini. The Romans were well aware of the improved setting (hydraulic) properties under wet conditions produced by pozzolana (Pliny b), and that mortars incorporating this pyroclastic material hardened progressively with time. When suitable volcanic deposits were not available they recommended the use of crushed brick and tile for building foundations and for waterproofing the lower levels of plastered walls (Vitruvius c). A possible functional reason should therefore be considered when ceramic fillers are noted in excavated material. Davey (1961) discusses the hydraulic properties of different types of limestone and comments on the reversion to the use of non-hydraulic limes from the immediate post-Roman period up to the 16th-17th century when Dutch trass (volcanic tuff) was imported. Malquori (1967), in an opening session of a symposium on pozzolanas, describes the origin, chemical composition, and exploitation of natural Italian pozzolanas and, in a subsequent technical paper on the reactions in trass-lime and pozzolana-lime systems, Ludwig and Schwiete (1967) refer to the re-exploitation of Eifel tuff in Germany in the late 17th century after a lapse of over 1000 years. This post-Roman lapse may well apply only to the exploitation of naturally occurring and highly reactive volcanic materials because Cennini, probably drawing on earlier texts, describes the use of crushed ceramics in a method of waterproofing walls.

Analysis of brick, tile, and stone

Laboratory techniques applicable to the study of pottery are equally applicable to the study of brick and tile. However, the production of brick and tile (Drury 1981) requires less preparation and working of the raw materials, and the analyst has to consider more critically just how large a sample must be taken before it is sufficiently representative of the whole. The influence of sample size on variability of results has been considered for *neutron activation analysis* (Hancock 1983) and for *thin-section petrology* (Betts 1982). Imperfect mixing of different clays can sometimes be seen in thin section or in a freshly fractured cross-section. It presents more of a problem for physico-chemical analysis where sampling is frequently carried out by core drilling or grinding after removal of the immediate surface layer. As a rough working guide for ceramic analysis, if the fabric contains numerous inclusions of 1-2mm size, take a sample of about 1g and, if of 10mm size, take at least 10g for homogenization in the laboratory. The analytical sample is usually less than 100mg. Techniques may be used singly, as in the neutron activation analysis of medieval decorated floor tiles from Bistrup (Hansen *et al* 1976), or in combination, as in the neutron activation and petrological analysis of floor tiles from the Midlands (Hughes *et al* 1982). Most analytical techniques require extensive sample preparation time, whether it be to put the sample into solution for atomic absorption or plasma emission spectroscopy, into powder for neutron activation or X-ray diffraction, or as a fused disc or compressed pellet for X-ray fluorescence (XRF) analysis (Dow-1982). *The energy-dispersive version of XRF* (EDXRF) is better suited than the wavelength-dispersive equipment to the handling of small, irregularly shaped specimens, although it lacks the precision and sensitivity of the latter method. If the fabric to be examined is sufficiently fine-grained, EDXRF can be used directly on a freshly buffed and flattened surface of a sherd and may well provide sufficient evidence to resolve the archaeological problem. Smith (1984) adopted this approach in an attempt to answer a question posed by Everson (Everson & Parsons 1978) on the origin of tile incorporated into the structure of Brixworth church. Measurement of the tiles strongly suggested re-use of Roman tile, perhaps from Leicester. Smith, in a preliminary assessment of his intensity data, found significant differences between the two fabrics. However, his data also revealed significant differences between the church samples and those from other sites nearby. The suggestion that the Brixworth tiles could have come from Leicester, some 35km to the north, has to be considered in the context of the remarkable variation in stone used in the construction of the church. Sutherland, working in association with the Brixworth Archaeological Research Committee, has just completed a detailed survey of the fabric in which every stone has been drawn and, in nearly every case, identified. A preliminary account (Sutherland 1980) indicates that, in what is probably the oldest part of the building (the north-west end of the nave and lower part of the tower), the fabric consists of a range of igneous rocks, including granites and banded grey volcanic ashes. The type of stone changes in horizontal bands as one moves progressively up the tower, with first a phase of construc-

tion incorporating pale grey limestone, then a mixture of 'Northampton Stone' and limestone, and above that a phase with tufa. Similar phasing is observed in the upper part of the tower and in the adjoining stair turret, and is strongly suggestive of contemporary construction. It is, however, her more detailed study (Sutherland, pers comm) which has revealed more than 30 different types of stone used in the construction, with the Great Oolite Limestone being similar in texture to that of southern Northamptonshire, and with the geological source of the reddish granite at Mountsorrel and of the volcanic ash at Charnwood Forest, both to the north of Leicester. Distances for direct transportation of the igneous rocks are about 50km and this, with the possibility of glacial drift discounted, puts into proper perspective the suggestion by Everson and Parsons (1978) that the tile/brick at Brixworth derives from earlier Roman building in the Leicester area.

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Colour microfiche illustrations

- A1 Fragment illustrating brush marks from intonaco application
 A2 Section showing brush marks from intonaco application
 A3 Fragment with skim coat and intonaco layer over an original painted surface
 A4 Section showing two intonaco layers over an original painted surface
 A5 Variation in hardness of painted plaster. Compare the soft, chalky surface on the right (marked with an incised line) with the harder surface on the left
 A6 Fragment showing design over a solid cinnabar background
 A7 Section through design, showing layering of Egyptian blue, cinnabar, and goethite
 A8 Fragment with coarse Egyptian blue applied over gray
 A9 Photomicrograph of surface painted with a mixture of goethite and Egyptian blue
 A10 Photomicrograph of surface painted with a mixture of haematite and Egyptian Blue

Thanks are due to Rebecca E Wetzel, from whose MA dissertation, *Technical examination of painted Roman plaster excavated in the City of York* (Univ Bradford, 1980), these photographs are taken.

Wood has always been an important natural resource (Coles *et al* 1978) in the British Isles. Timbers, usually of oak (*Quercus*), were the main building material, whilst brushwood from many species was used for wattling and firewood. Only a very small proportion of this has been preserved, usually in waterlogged conditions, so it is important that the maximum amount of information is extracted from the wood that is found. The aim of this paper is to review the sort of information that the examination of wood or timber can produce; sampling and laboratory techniques are then discussed, and finally, the analysis of wood from a single site is described to illustrate the results that can be obtained, as well as some of the problems and limitations of the method that may be encountered.

Information from wood

Dendrochronology has become a well known and accepted technique amongst archaeologists so that, when wooden remains are uncovered, most excavators think first of tree-ring dating; a comprehensive survey of the method is given in Baillie (1982). To obtain an absolute or calendar date of when a timber was felled is obviously of prime importance to the archaeologist, especially when dating from pottery or coins is vague or absent. Even if absolute dating is not possible, relative dating can yield important results, particularly for complex wooden structures or for the prehistoric period, for which few reference chronologies are available. Various species-for example, ash (*Fraxinus excelsior*) and hazel (*Corylus avellana*)-can be used for relative dating, whereas absolute dating in Britain is so far confined to oak, since this is the only species found in sufficient quantities to construct long reference chronologies.

Even if the wood is not suitable for dating purposes, sampling can yield further information, as tree-ring analysis of the Somerset Levels wood has demonstrated (eg Morgan 1982). Identification of each piece reveals the range of trees and shrubs available at a particular time, and for what function they were used. Analysis of the size and age of the samples from each species may indicate some form of woodland management, such as coppicing, or give some insight into the woodland ecology. Choice of timber and methods of conversion can also be studied. These may in turn indicate the size of trees available: for example, radially split planks require trees with double the diameter of those used to produce tangentially cut planks.

Finally, dendrochronology is possible because climate, more than any other factor, determines the wide and narrow ring patterns. This 'climatic signal', if extracted, would provide information on the prevailing climate (see

Fritts 1976; Hughes *et al* 1982). Dendroclimatology is a complex study, however, and it will be some time before dendrochronologists can provide climatic information as well as the date of a timber (Pilcher & Hughes 1982).

sampling

On finding wooden remains, the excavator should notify a dendrochronologist, who will be able to advise on whether the material is suitable for dating and what sort of results might be obtained. Archaeologists may be able to distinguish oak from other species on site, since oak is the only species which has distinct growth rings plus wide rays running from pith to bark (Morgan 1975).

As many timbers as possible should be sampled; one sample per structure is not normally enough for dating purposes. If several samples are taken, a site master curve may be constructed which facilitates cross-dating by eliminating much of the 'background noise' present in an individual timber. Furthermore, the interpretation of tree-ring dates and the estimation of felling dates are made easier and more accurate if several samples can be dated. Ideally all timbers should be sampled and any sub-sampling left to the dendrochronologist.

Each timber should be sampled at its widest part, and a 50-150mm slice extracted (samples thicker than this cannot be handled in the laboratory). Care should be taken if sapwood is present. This is the outer part of the tree which, when waterlogged, is very soft and fragile. As will be seen below, it is important in the interpretation of tree-ring dates.

Each sample must be washed, any excess water being shaken off, and then stored in a sealed Polythene bag. A Dymo label inside the bag, plus some form of labelling on the outside, has proved the most durable and convenient method of labelling waterlogged wood samples. Duplicate samples of brushwood should be taken: one for tree-ring analysis and one for identification, since the two processes may be carried out at different centres. Some of the identification of tree-ring samples sent to the Sheffield Dendrochronology Laboratory, for example, is done at the Ancient Monuments Laboratory in London. The samples should be sent to the dendrochronologist with information about the site and the context of the wood or timbers.

At this stage there may be a conflict between dendrochronology and conservation, but it is not unresolvable (Morgan *et al* 1981). Dendrochronology is not a destructive technique, but it does require a complete cross-section (cores are not suitable because of the difficulty of extracting them from waterlogged wood, and because their ring widths are often difficult to measure

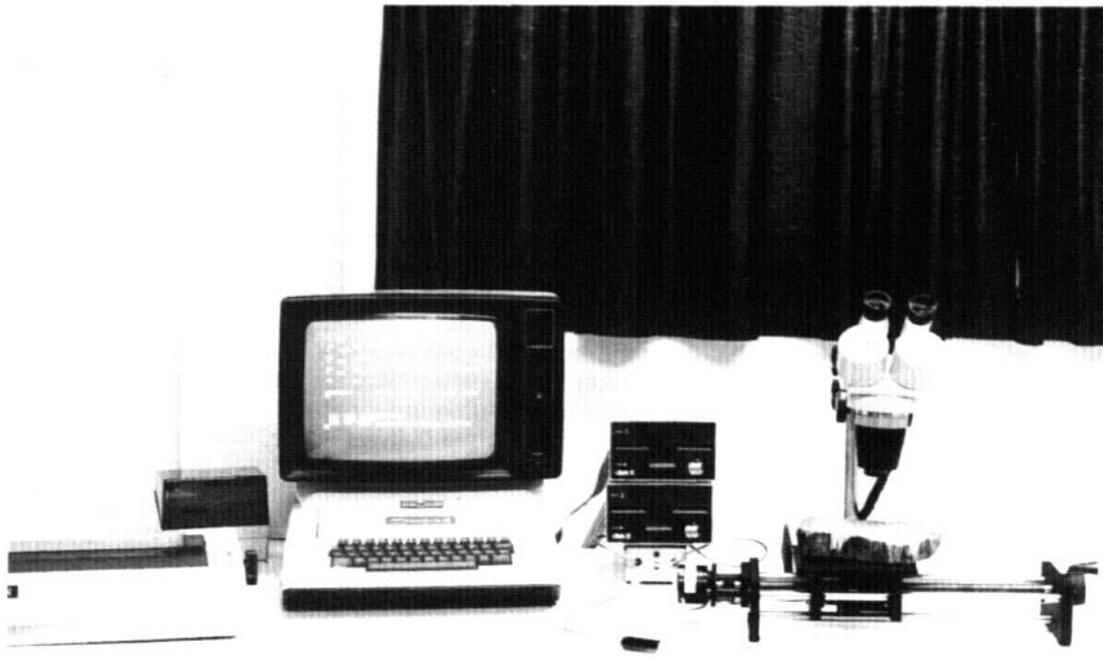


Fig 4 Tree-ring measuring equipment. From right to left: travelling stage and microscope, disc drives (back), button for signalling end of ring measurement, microcomputer, and printer

with reliability). It is sometimes possible to remove the top of a timber, where it is weathered or broken, or a slice can be removed, examined by the dendrochronologist, and then returned to be slotted back into the timber (eg Morgan *et al* 1981, plate XVIIIa).

Laboratory techniques

Dry samples (ie those from standing buildings) are sanded with several grades of emery paper. Waterlogged samples are deep-frozen for about 48h and then planed with a Surform file whilst still frozen. This produces a cross-section on which each annual growth ring is easily distinguishable. If the wood has dried out at all, either prior to or during excavation, the cross-section may need touching up with a sharp Stanley knife. This method of preparation is also suitable for samples which are to be conserved, since only a minute sliver of wood needs to be removed. Timbers which have already been conserved are treated differently, and with varying degrees of success, depending on the method used for conservation (Morgan *et al* 1981). Frozen samples are left to thaw out before their ring widths are measured.

The equipment used for the measurement of the annual rings (Fig 4) consists of a Bannister travelling stage linked to an Apple II microcomputer. The wood sample is placed on the stage and viewed through a binocular microscope at x10 magnification. As each ring is traversed, a button is fired, and the ring width, in units of 0.02mm, is stored in the Apple's memory. When measurement is complete, the ring record is transferred to a floppy disc. A listing of the data can then be obtained from the Epson printer. The software (written by Dr J R Pilcher of the Belfast tree-ring centre) contains a series of tree-ring programs. As well as the measure option, plots

of the ring record can be obtained (although at present the ring widths are still plotted by hand on transparent semi-logarithmic paper to facilitate visual comparison). There is also a cross-dating program, and master curves can be constructed. The introduction of this computer-linked equipment to the Sheffield laboratory has greatly speeded up the measurement and dating of samples.

Once the ring widths are represented as graphs, or tree-ring curves, the ring sequences can be superimposed and moved past one another until a match is found (Fig 5). An objective measure of the degree of correlation is given by a computer program (Baillie & Pilcher 1973), but it is the quality of the visual match which is decisive in the acceptance of a match.

How a site is tackled depends on the number of samples. If there are only a few samples—say fewer than 30—the samples are measured and cross-matched and a site master curve is produced. The master is then dated by comparison with dated reference chronologies from different regions. If there is a large number of samples, however, and there are reference chronologies for the period in question, each sample may be measured, and compared directly with the reference curves. The 180 Roman timbers from Pudding Lane in the City of London are currently being analysed in this way. The important factor in dendrochronology is replication (Baillie *et al* 1983): it is not sufficient to date the site master or the individual sample against one reference curve; for complete reliability, it must be dated against two or more.

The tree-ring results are represented by a bar diagram (Fig 6). This enables the felling date of the timbers to be estimated. The date of the outer ring is only equal to the felling date if the bark or waney (outermost) edge is

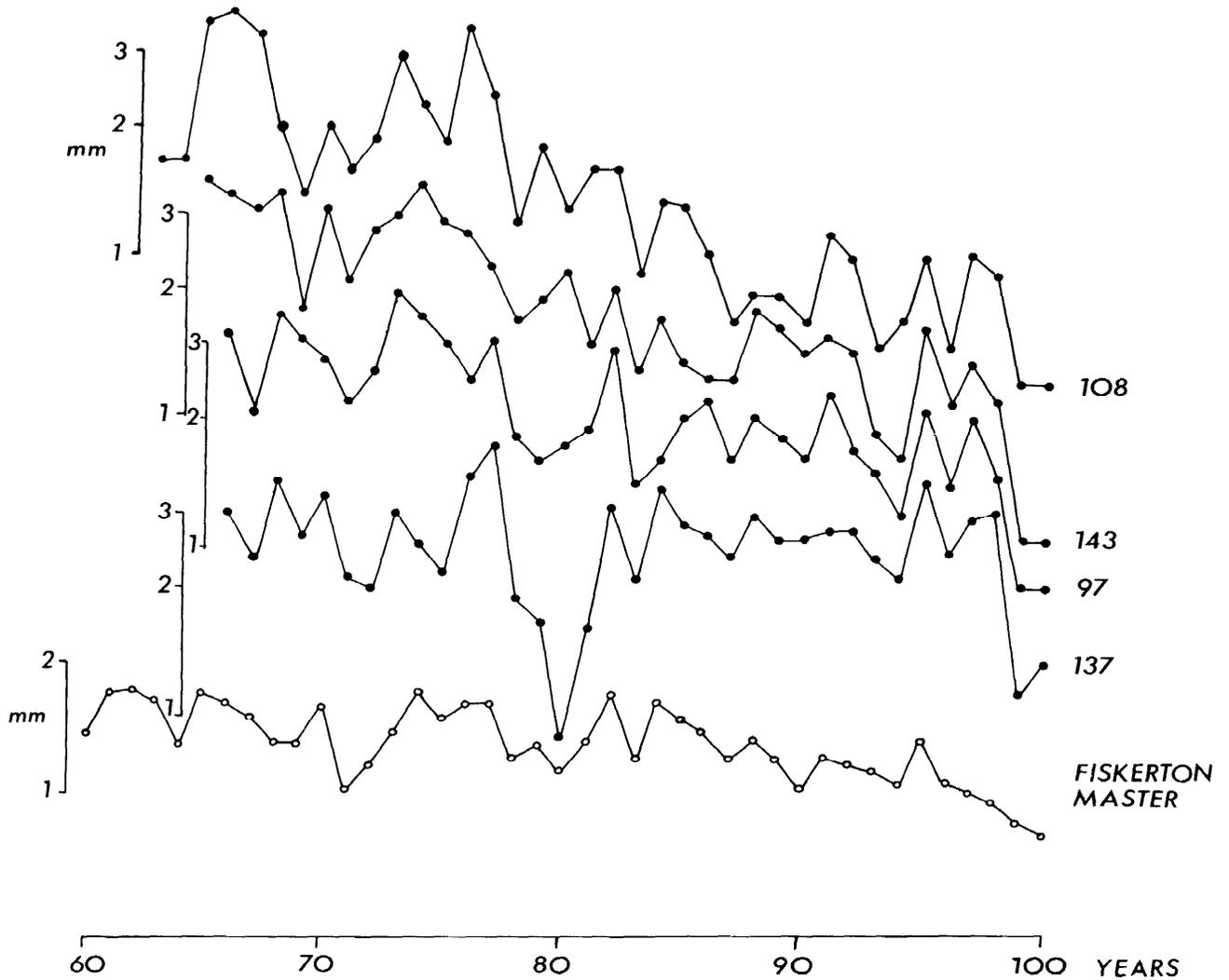


Fig 5 Matching tree-ring curves. Four short ring patterns from separate timbers with the corresponding section of the Fiskerton master curve

present. Usually wood was removed when the timber was converted into a plank or beam. If some of the sapwood is preserved, the felling date can be estimated with some accuracy, since the number of sapwood rings in oak is relatively constant (for further details see Hughes *et al* 1981). In the absence of sapwood, a *terminus post quem* is calculated for the felling date. In this situation, examination of the bar diagram may help: if several samples end within a few years of each other, it can be assumed that only the sapwood, less strong than the heartwood, has been removed, and therefore the felling date can be estimated more accurately (eg Baillie 1982, fig 2.2). The bar diagram also indicates which timbers have been re-used, or where a structure has been repaired.

A site example: Fiskerton

Fiskerton in Lincolnshire (NGR TF 050 716) was excavated in 1981 by Naomi Field of the North Lincolnshire Archaeology Unit (Field 1983). A double row of vertical posts (Fig 7) was found running perpendicular to the River Witham. The structure is thought to be the remains of a causeway leading to a jetty or bridge, or part of the jetty/bridge itself. The site was in use during the Iron Age and Roman periods, and two of the posts were dated to 510 ± 70 bc (HAR 4472) and 330 ± 70 bc (HAR 4471). There were about 180 vertical posts in the 20m length of structure excavated, of which 170 were sampled for tree-ring analysis. There were also some horizontal timbers but these were not *in situ* and so were not sampled. Many of the vertical timbers were untrimmed

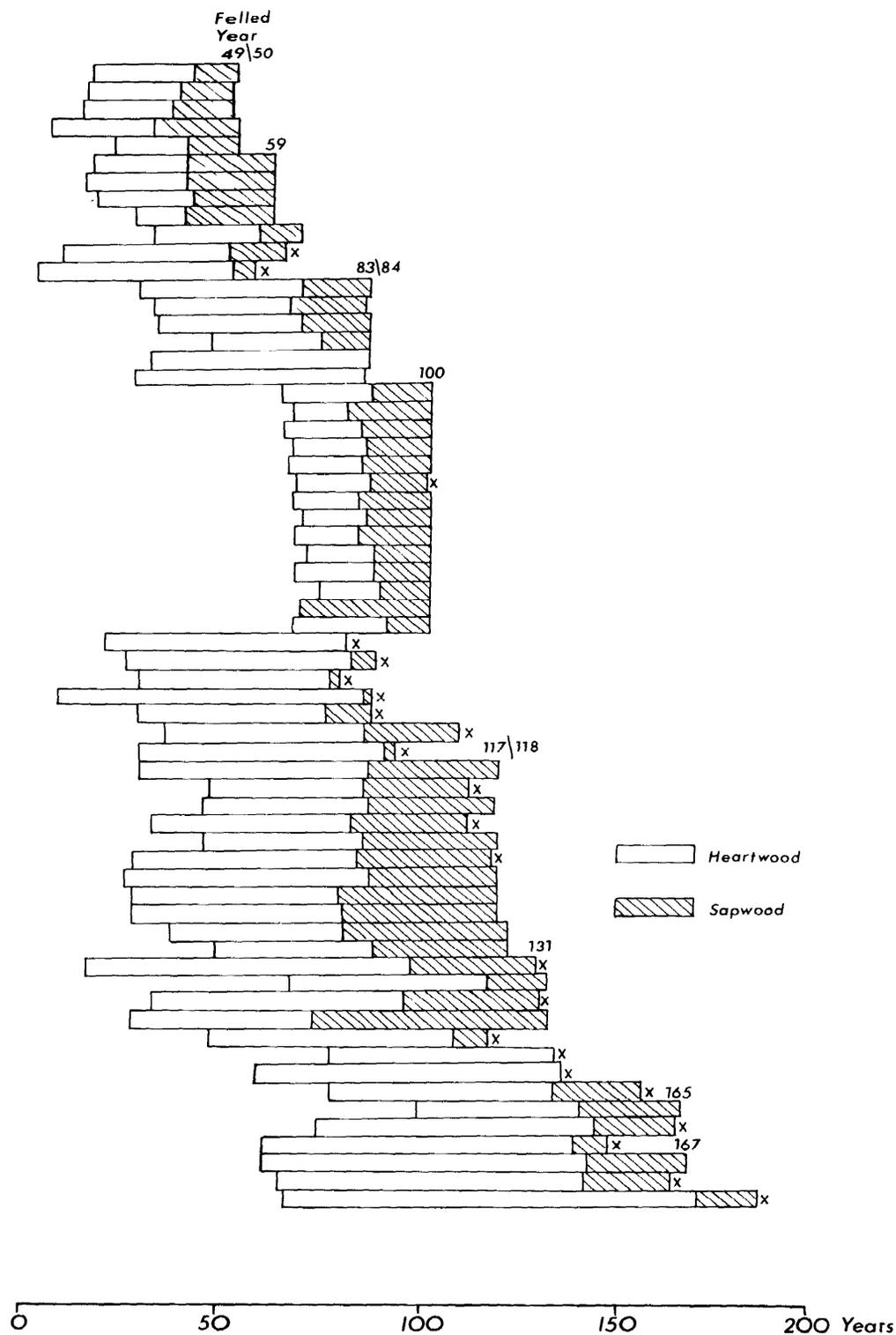


Fig 6 Fiskerton bar diagram: each bar represents years spanned by a single timber. Crosses = exact felling date not known

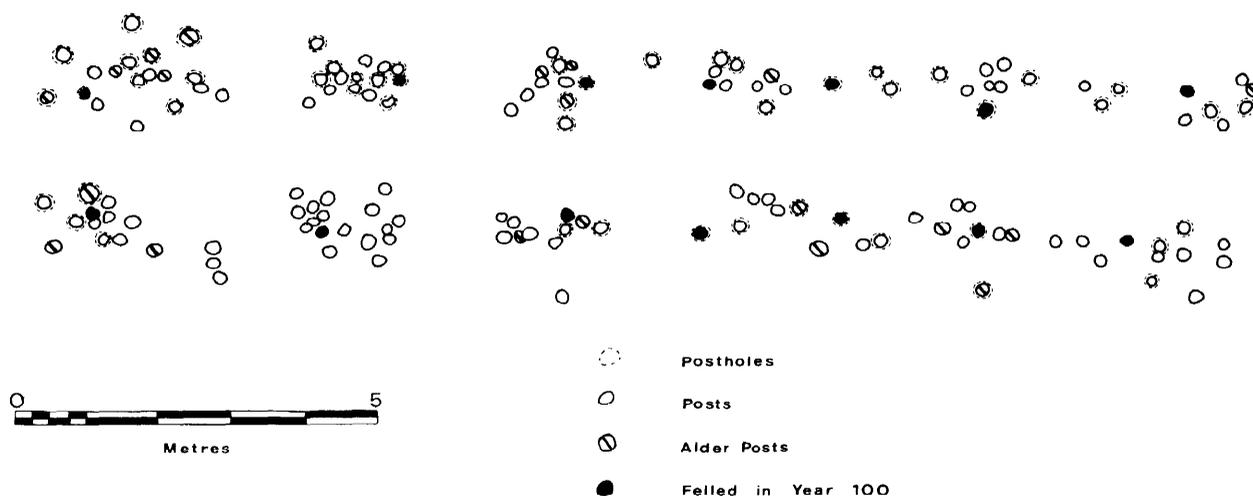


Fig 7 Fiskerton causeway

roundwood, often with bark still attached; others were slightly trimmed, perhaps on one side only; whilst a few were worked pieces, sometimes split from larger trees. Some of the posts were surrounded by a posthole, but the remainder had been rammed into the ground without any holes. One of the aims of the tree-ring analysis was to look at the relationship between the posts with postholes and those without. The other objectives were absolute and relative dating, examination of the size and age of the timbers, and the calculation of an average sapwood number for the site.

When the samples were identified, 142 were oak, 27 were alder (*Alnus glutinosa*), and one was a small piece of willow or poplar (*Salix* or *Populus*). Alder is not used for relative dating because, unlike oak, its rings are indistinct and do not seem to be formed annually. The size and age of the alder samples were recorded: the age was very variable but the diameter was relatively constant at between 110 and 190mm. This indicates that the timbers were being selected for size from an uncoppiced woodland (compare Morgan 1982, fig 1). The same results were obtained when the oak roundwood was examined. The diameters were mostly between 110 and 200mm whilst the age varied considerably.

Normally samples with fewer than 50 rings are not used for dating purposes since such ring patterns tend not to be unique, and indeed it cannot be denied that samples with over 100 rings have a much higher chance of being dated than those with fewer rings. Unfortunately, English archaeological sites tend to yield timbers with less than 100 rings: the majority at Fiskerton had 15-60 rings. It was therefore decided to investigate whether those samples with 30-50 rings could be dated with reliability.

The ring widths of 109 oak samples were measured, and of these 64 cross-matched to give a tree-ring sequence of

167 years. This sequence has not yet been dated absolutely. It was found that samples with 30-50 rings could be dated but great care was needed: a match was only accepted if the sample matched with at least three other ring sequences, as well as with the master curve, and provided it did not appear to match in more than one position. The curves illustrated (Fig 5) are four from a group of fourteen, all of which match each other and all from timbers felled in the same year.

The bar diagram (Fig 6) shows that the Fiskerton 'causeway' has a rather complicated history of construction and/or repairs. Using the arbitrary time scale which corresponds to that of the master curve, the first five timbers were felled in year 50, three in summer and two in winter. Others were felled at intervals, always in winter, during the next 150 years: a group in year 59, some in year 83/84, the group of fourteen (Fig 7) in year 100, and a group in year 117/118. After this, the picture becomes more complicated, although there appears to be a group with felling dates in year 131. Most of the worked pieces were felled after this date, but it is often difficult to tell their exact felling date as they did not have complete sapwood. Those with known felling dates often belong to pairs of timbers: the group of fourteen, felled in year 100, represent pairs of posts distributed evenly throughout the excavated structure (Fig 7). There was no difference between the dates of the timbers with postholes and those without.

Clearly, tree-ring analysis does not give the whole story of the 'causeway', since it is not known where the alder or the undated oak fit in, nor is it easy to decide to which group those without complete sapwood belong. There does, however, appear to be a regular pattern of repairs throughout the excavated structure about every seventeen years.

Fiskerton provided an added bonus in that it was possible

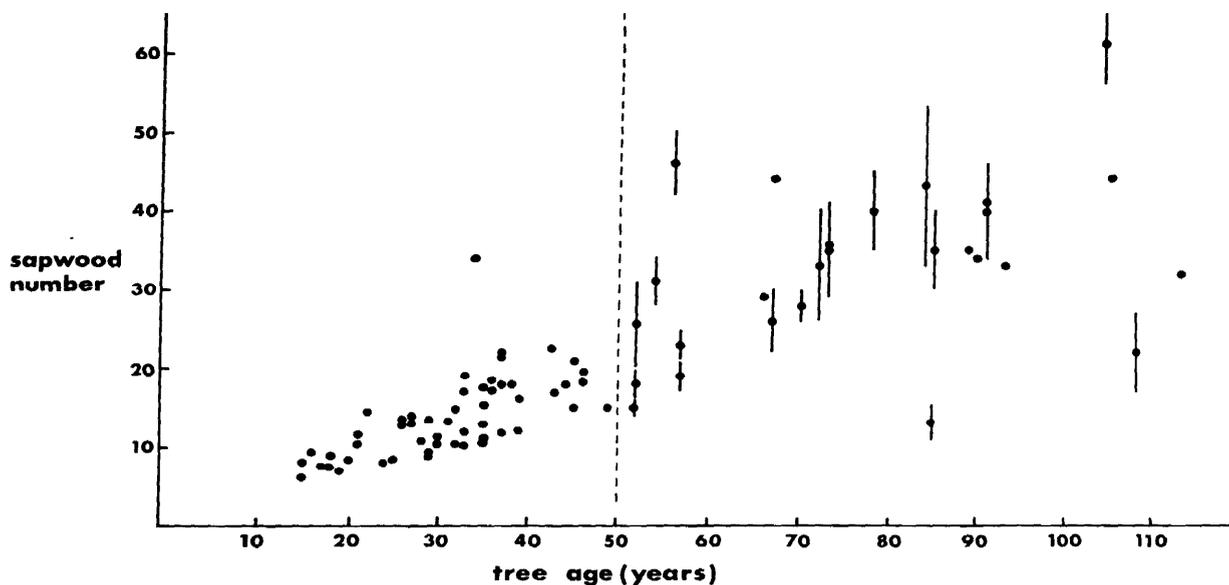


Fig 8 Sapwood data from 81 Fiskerton timbers. Vertical bars on samples over 50 years old represent variation in sapwood number within each sample

to look at the number of sapwood rings in the oak roundwood samples. Most studies on sapwood number are based on modern oak trees (Hughes *et al* 1981), since the sapwood is frequently removed from archaeological timbers, and it is rare to find a site producing many timbers with complete sapwood. At Fiskerton the amount of sapwood varies considerably, not only between different samples, but also within the same sample (Fig 8). The most extreme sample had a variation of ± 10 rings. The average sapwood number for the 27 samples from trees older than 50 years of age is 33 rings, while trees younger than 50 years tend to have fewer sapwood rings. Of the 27 samples, the minimum number was 15, and maximum over 60. The results will be published in detail elsewhere but they do show that, in the absence of bark, the felling date can be estimated, but only approximately.

Conclusion

Out of the 170 timbers sampled at Fiskerton, 64 have so far been relatively dated. This confirms the need for total sampling. If only ten to twenty samples had been taken, the results would have been meaningless. Even with 170 samples, the history of the causeway's construction is not fully explained. This is not to say that sites with only a few timbers should not be sampled for dendrochronology; the structure may not be as complicated as the one at Fiskerton.

The Fiskerton tree-ring results provide some interesting facts about 150 years of the site's history, even though it is not the complete history. The first five timbers were felled in year 50 (arbitrary scale), followed by four in year 59. A group of six timbers were cut in years 83/84, fourteen in year 100 (Fig 7), and twelve in years 117/118. These were added in pairs, and are spread evenly

throughout the structure. They seem to represent a regular repair of the causeway. After years 117/118, the northern end of the excavated structure was strengthened by the addition at irregular intervals of at least sixteen timbers, including the worked pieces. The last timber in the tree-ring record was felled in about year 200.

It is possible that techniques will be developed in the future which allow timbers with short ring patterns to be dated. The number of samples dated from any one site might then be improved. What Fiskerton does show is that it is unlikely that an exact value will ever exist for the number of sapwood rings in oak. The variation within and between samples is too great for that. However, the estimated felling date will still be more accurate than that given by other dating methods.

Even if the wood or timbers cannot be dated, they will produce some information, and the data will be there for future reference (when perhaps new techniques will have been developed). Considering how much wood and timber was used in the past, it is important to make the most of that which is preserved.

Acknowledgements

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The recognition and identification of traces of organic materials in association with metal artefacts

J Cronyn, E Pye, and J Watson

The archaeological record from most excavations is biased in that it does not reveal the once abundant use of organic material; such bias is brought home clearly when a waterlogged site is excavated, and many wood, skin, and fibre artefacts are retrieved. The conditions prevailing on sites can be crudely subdivided into aerobic (oxygen-rich) which allow organic materials to decay and *anaerobic* ones in which it is primarily the absence of oxygen (as in waterlogged sites) which prevents the activity of destructive microorganisms and thus preserves organics. In general, therefore, organic artefacts of any size are not found in aerobic deposits, although improved methods of examination have shown that parts or traces of organic artefacts can be found in micro-environments in these otherwise destructive conditions. In many cases the organics have been preserved in close association with corroding metal artefacts and are often termed *mineral-preserved*.

Most of the organics considered here have characteristic structures which can be identified by visual examination if they are well preserved. By their nature, however, these traces are often small, and may be hidden under soil attached to the metal artefacts. They may be superficially altered in appearance and difficult to recognize. It is obvious that minute examination and delicate investigative cleaning are essential; thus the retrieval of these traces and their identification becomes one of the tasks of the archaeological conservator.

Mineral-preservation of organic materials

There are several ways in which organic material may survive in exceptional circumstances. It may become sequestered and an anaerobic or even desiccated micro-environment may result; thus a thread lodged inside a bead may be preserved. Another type of preservation involves charring, which converts the organic into an inert substance (carbon). In some cases, as with charred wood, the structure may be well preserved; in other cases the original structure must be inferred from the material retrieved. For example, an ancient adhesive from charred plywood may be retrieved as a froth-like charcoal adjacent to wood charcoal (Corfeld 1972).

It is preservation in association with metal artefacts which is the subject of this paper, and here the organic material may be preserved relatively unchanged or it may be preserved as a pseudomorph. In the first case, decay of the organic material by microorganisms has been prevented by the presence of a substance which is toxic to these organisms. On a large scale the effect of common salt or of tannin on skins is probably familiar, but on a small scale the salts derived from corroding copper alloy artefacts are also preservative. Thus, for example, shroud

cloths may be preserved solely underneath the coins placed in the eye sockets, the copper salts migrating only a short distance before their effect is diluted excessively. Many of the materials preserved in this way are more or less heavily stained by the salts, although occasionally original colour may be seen. They may also be shrunken and warped.

Pseudomorphic preservation is found when the structure of an organic material is recorded by the corrosion products from a deteriorating metal. The phenomenon is commonly seen in association with iron artefacts, though it could occur to some extent with other metals, and it has also been noted with calcium salts (Girling 1979). In the case of iron, the corrosion products coat the organic material and may fill the voids in the structure. In some cases the organic substance remains inside this coating, although it may be partially deteriorated; in other cases the organic decays completely leaving a cast of its structure in the corrosion products (a pseudomorph). The process is sometimes termed 'replacement' (Keepax 1975).

It appears that true pseudomorph formation is restricted to fibres and plant materials such as wood, whereas denser materials like bone and ivory are impregnated with the salts. Organic components of artefacts such as the handles of knives and traces of shield-board attached to a shield boss are often found to be preserved in these ways.

Archaeological contexts

There are three main contexts in which the necessary micro-environments are likely to develop. The first is where natural non-artefactual organics are associated by accident with corroding metal artefacts and so become preserved. Both vegetable matter, such as grasses, and animals can be affected; an example of the latter is the preservation of nematodes on an Anglo-Saxon brooch (Platt 1980). Whilst such information may tell us something about the immediate deposit in which the artefact lay, it is unlikely to be of any significance in the study of the wider environment of the site.

Probably the best example of the second type of context is a cemetery where shrouds, garments, leather, skin, and hair have been deliberately associated with metal artefacts such as brooches, pins, and weapons. It is not surprising that some of the richest sources of mineral-preserved organic material are the metal artefacts from pagan Saxon cemeteries (Gingell 1978; Bojko 1982). A similar example is that of a metal object containing organic matter; thus the copper-alloy early medieval reliquary from Winchester (Hinton *et al* 1981) contains preserved fragments of untanned skin. A textile or leather

purse containing coins would be a reversal of this situation.

The third major category is that of composite artefacts made of both organic material and metal; it is from this group that perhaps the most significant evidence has been derived. Previously, when all that was recognized and retrieved of such artefacts was the metal element, the information yielded from their study was inevitably limited. Recently, however, work on this type of material has produced some interesting details. The structure of Anglo-Saxon shields is a case in point, and has been discussed by Brown (1980). Comparatively frequently both the iron shield boss and the iron handle brace have been found in association with traces of the wood, leather, and cloth of the shield board and grip (Bruce-Mitford *et al* 1978; Corfield 1972; Stansfeld 1979). From these fragments details of the structure of the whole shield can be built up. Another example is that of a Roman chest from the villa at Bradwell (Keepax & Robson 1978). Here the totally corroded iron fittings were retrieved, and from the traces of wood preserved upon them, not only could the thickness of the planks be calculated, but so could details of Roman methods of jointing, which are rare in the British archaeological record.

Recognition

For the archaeologist it is important to be able to recognize mineral-preserved organic material and to know how to deal with it; notes on this have been produced by the Ancient Monuments Laboratory (1983). The presence of the material may be inferred from the type of site, the archaeological context, and the nature of the artefact under study. Although the material is often preserved as relatively small traces, sometimes it may occupy three or four times the volume of the metal artefact; it is most likely to be found under layers of sand, gravel, or chalk, which may be coloured by the corrosion products. With experience, the presence of the material can be recognized before initial cleaning; on close examination the corrosion products may appear to be regularly patterned or to contain discrete amorphous areas, perhaps of different colour or texture: for example, an orange-brown mass representing the remains of a scabbard on an iron knife.

Field treatment

In the field certain precautions should be adopted. If the object is large or remarkable, such as a sword, a conservator should be called to the site to lift the item using specialist techniques. Thus, for example, the Bradwell Roman chest was lifted as a block by the staff of the Ancient Monuments Laboratory (Keepax & Robson 1978). For a smaller, less outstanding object, lifting must ensure that as much of the neighbouring soil remains attached to the object as possible. No synthetic consolidants such as polyvinyl acetate emulsion should be used, as these make subsequent examination extremely difficult. Objects must not be cleaned in any way on site, but should be carefully packed using correctly chosen storage conditions (Archaeology Section UKIC 1983), and dispatched to the conservation laboratory as speedily as possible.

Laboratory examination and treatment

In the laboratory, preliminary examination, including radiography, is essential, and can sometimes reveal associated organic material. With the aid of a binocular microscope and small hand tools the soil and corrosion products are investigated and the presence of organic traces is established. A decision can then be made about whether it is feasible to take a sample for closer identification.

Once the material has been located and identified it is recorded and becomes part of the basic data available for research. To ensure that the data are usable, it is important that the conservator works closely with those carrying out research on the site as a whole or on particular artefacts; the part of the conservation record concerning identification of materials and technology of artefacts should be considered alongside other sources when the site is being prepared for publication.

The second aspect of conservation, namely treatment, seeks to prevent any further deterioration of the archaeological evidence. There may be some demand to remove preserved organic material from a metallic artefact, especially when it does not constitute part of the object. This should be resisted, however, since the evidence may be important in the future, and it is, moreover, difficult to remove the material without severe damage or loss. Traces therefore are left *in situ* wherever possible and may at this stage undergo consolidation.

Long-term stabilization of the whole artefact is unfortunately complicated by the presence of mineral-preserved organic material. It is particularly difficult to stabilize traces which retain their organic nature, for they have very different demands to the corroded metal below. Where the traces are in fact pseudomorphs and are therefore similar to the other corrosion products present on the artefact, it may be possible to stabilize the object in the normal way without loss of evidence. However, many treatments are potentially damaging to the preserved organic material because they aim to remove or modify the corrosion products in order to stabilize the object. In addition, protective surface coatings of synthetic polymers or waxes obscure detail and make subsequent identification difficult, if not impossible. This means that the treatment of each individual object must be particularly carefully considered; in important cases storage or display in a rigorously controlled environment may be preferable to any active stabilization.

Identification

Where material has been preserved in association with copper salts, it is often possible to remove the superficial salts using a complexing agent and then to examine the samples in the same way as fresh materials. For example, a wood sample, after removal of the salts, can be waterlogged; sectioned, and examined under transmitted light in the normal way. However, where the sample is severely infiltrated with salts, or badly decayed, or preserved as a pseudomorph, the use of transmitted light is not possible, and much higher magnifications and a greater depth of field than are available with incident light microscopy are needed. Thus resort is made to the

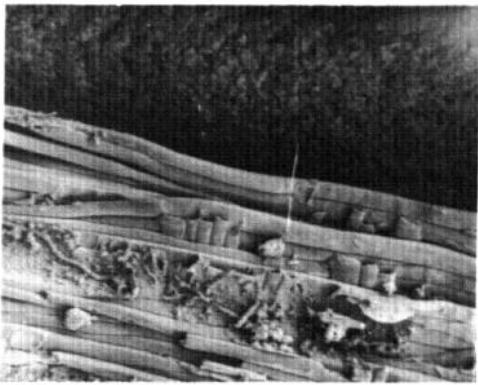


Fig 9 Wood from a sword scabbard from Ozengell (Kent). Vessels and rays exhibiting the phenomenon of replacement can be clearly seen. Identified as *Salix* or *Populus*
x 100

scanning electron microscope (SEM), where an electron beam is used to visualize the surface of material in place of a light beam. Normally a sample of *c* 2mm³ is taken, coated with an electrically conducting substance such as gold/palladium, and placed inside the SEM for inspection

The SEM was used (by JW) in the identification of the materials associated with the Anglo-Saxon sword from Ozengell cemetery in Kent (Youngs & Clark 1982). Here traces of the scabbard were found to consist of several layers, one of the main elements of which was wood, a material which has been extensively examined in this way. The scabbard wood was found to be either *Salix* or *Populus* and, from examination of the micrographs (Figs 9 and 10), details of the mechanism of preservation become apparent. This wood exhibits the phenomenon of replacement first described by Keepax (1975). The iron corrosion products have penetrated into the voids in the cell-structure of the deteriorating wood and solidified whilst the organic material gradually decomposed completely. What is left then is a cast of the inside of the wood cells with all the features of fresh wood seen in reverse. This reversal makes identification a skill which must be developed over time.

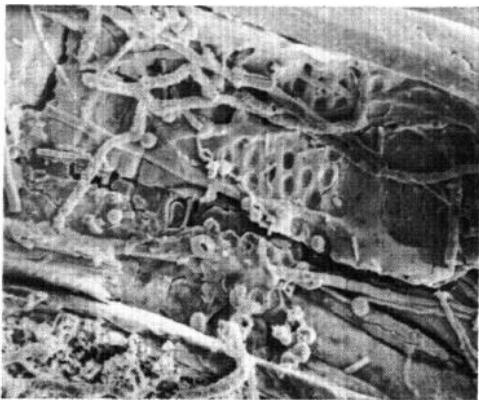


Fig 10 View of specimen in Fig 9 showing pits in the vessel wall and hyphae of a fungus which had attacked and partially degraded the wood in the early stages of burial
x 300

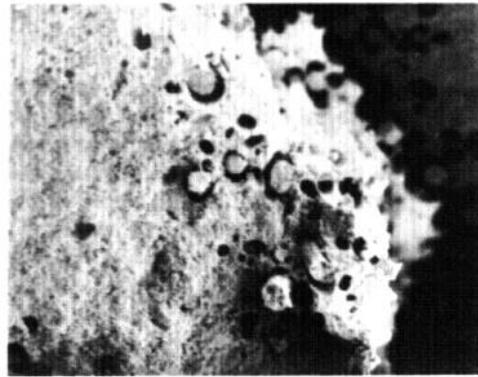


Fig 11 Cross-section of the sheepskin lining of the same scabbard from Ozengell shown in Figs 9 and 10: the wool fibres can be seen projecting from the coating of iron salts
x 100

The innermost layer of the scabbard consists of a sheepskin complete with hair, seen as a dense mass from which wool fibres emerge (Fig 11). Here the micrograph shows that corrosion products have solidified over the hairs, thus producing a mould of the outside of the fibre on the inside of the corrosion layer (Fig 12). In this situation identification can in fact be hampered by the remains of the decayed hair within the corrosion product.

The identification of wood and fibres has been well developed. Robert Janaway, then of University College, Cardiff, has looked at textile fibres (Janaway 1983), whilst more recently, projects have been instigated by the Ancient Monuments Laboratory to study other materials. Anita Moraitou, a student of the Institute of Archaeology, London, has worked on the identification of horn, bone, and ivory (Moraitou 1983). Through her studies she has established that many handles of medieval knives previously thought to be of wood are in fact horn; it is now hoped that a further project will cover bone and antler. There remains the problem of identifying leather, and current work by Annie Maclane of the University of Durham may help to resolve this.

By means of this type of examination it is possible to add

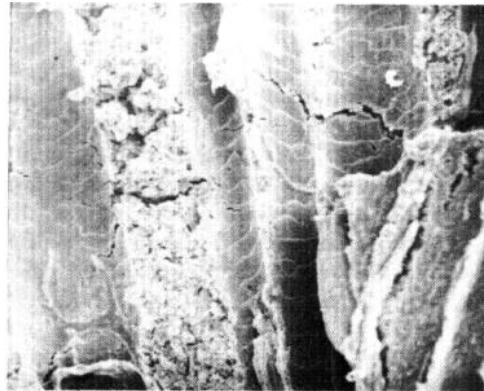


Fig 12 Longitudinal view of the moulds formed round the wool fibres by the coating of iron salts; surface details of the fibres are clearly visible
x 300

significant details to our knowledge of the ways in which organic material was used in antiquity, or to contribute to the understanding of archaeological contexts where both metallic and organic materials are associated. However, to gain as much information as possible, it is essential that archaeologist, finds researcher, and conservator work together from the very earliest moment. A current example of this type of coordinated work is the detailed study being made at the Lincoln Archaeological Trust (now part of the Trust for Lincolnshire Archaeology) of material from the grave of an Anglo-Saxon metalworker. Iron and copper-alloy tools and metal scraps are all badly corroded and embedded in a mass of soil. Careful work has revealed a quantity of preserved organic material which probably represents amongst other things the boxes in which the smith kept his belongings and even the remains of the smith himself.

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'The-formation of an archaeological site can be viewed as rather similar to breaking up the lead type of Hamlet; both processes are associated with reduction to a ground-state of disorder or randomness . . . Nevertheless, the ground-state is not completely attained, and the analysis of residual patterns can reveal some of the original messages in Hamlet' (Leach 1978).

The 'residual patterns' of an archaeological site comprise structures and artefacts in a variety of raw materials, plus 'ecofacts', or remains relating to the environment or subsistence history of the site (Schiffer 1976). This paper focuses on the stone elements of these residual patterns.

Stone forms a large proportion of excavated finds on quarry sites, workshops, and sites with stone-walled buildings and other structures (eg Saville 1981; Shackley 1977). Early prehistoric assemblages may consist almost entirely of stone artefacts and debris. Archaeologists seek to determine the role of stone artefacts and features in the activities carried out at each site, and in the framework of human exploitation of the contemporary landscape. Many different types of analysis are employed to achieve these goals (Table I).

As far as large stone artefacts are concerned, analysis can involve the determination of quarry sources, the methods of distribution of the raw and semi-finished materials, the technology of finishing off stone blocks to form walling or large-scale sculpture, and the study of building sequences, repair, and alterations. A recent argument in *Archaeometry* concerned the cutting of the giant polygonal stone blocks used in Peruvian Inca building: were they cut by a heat-expanding material, by the use of wedges, or by pouring water into cracks, sealing the cracks with clay, and relying on the freezing temperatures of the Andes (Frank 1980; Arnold 1983)? This question remains to be resolved, perhaps by close examination of the cut surfaces. With regard to the determination of raw material sources, the quarry for quartzites used for the Colossi of Memnon in Egypt and the sources of marbles used in Greek inscriptions and sculpture have been established by neutron activation analysis and by stable carbon and oxygen isotope analysis respectively (Heizer *et al* 1973 and Herz *et al* 1977, quoted in Rapp and Gifford 1982). Thermoluminescence has identified sources for limestones used in Spanish medieval sculptures by looking at the geological TL spectra (Carriveau *et al* 1976). Macroscopic and thin-section studies of stones found at the palace of Fishbourne have identified British limestones and sandstones used for walling and gutters, Mediterranean white limestone columns, and decorative stones from as far afield as Turkey and Greece (Shackley 1977, fig 13; Cunliffe 1971,2, 141).

Stones worked into smaller sizes form a large proportion of British assemblages from the earliest settlement of man

in western Europe until well into the Bronze Age. We may divide this material into site furniture, artefacts, and debitage (the by-products of stone knapping). Site furniture is a term applied to items such as hearthstones, querns, mortars, hammers, anvils, and weights by ethnographers and ethnoarchaeologists working in Australia and the Arctic (eg Peterson 1968; Binford 1979). The mobile societies in these areas regard such items as immovable, and they tend to remain at one camp-site. Among the more settled societies of western Europe from the Late Neolithic onwards, items of site furniture like querns were distributed over considerable distances. Geological determination of provenance of querns from such sites has mainly been by macroscopic means, but in some cases thin sections have been examined (eg Courtin 1976). Peacock (1980) has identified many of the sources of querns used in the Roman world. Microscopic analysis and chemical tests can also resolve questions about the food items or raw materials hammered or ground on to them.

Small stone artefacts and debitage are among the most numerous remains collected and excavated by archaeologists. Many techniques of analysis are employed to determine their role in the activities carried out on site (Table I).

Schiffer (1983) has outlined some cautious present-day approaches to site interpretation, a long way from the initial euphoria in the 1960s and early 1970s about the possibility of identifying past activities directly from horizontal exposures of stone and other debris. Ammerman and Feldman (1974) were among the first to draw attention to potential errors when they produced a mathematical model of 'dropping rates' of tools used in particular activities on a site during a single occupation. Their study indicated that horizontal surfaces, even just after abandonment by their users, only partially reflected the activities undertaken there. Since many sites would

Table I Analysis of stone from archaeological sites

- | | |
|---|--|
| a | Architectural and technological analysis of stone structures; technological and typological studies and conjoining of tools and debitage from quarries, workshops, occupation floors, activity areas and surface collections |
| b | Investigation of extent of heating of stone structures (eg by thermoremanent magnetism, thermoluminescence) |
| c | Dating (eg by thermoluminescence, fission track, obsidian hydration) |
| c | Raw material characterization (eg macroscopic, thin section, trace element, stable isotope analysis) |
| e | Microwear analysis of stone tool edges (eg optical microscopy, scanning electron microscopy) |

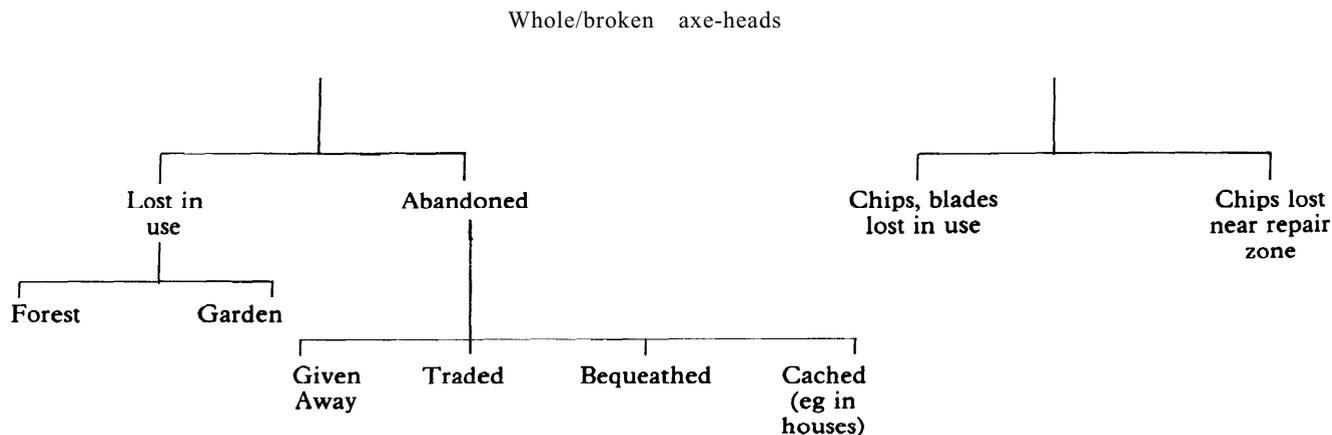


Fig 13 The disposal of axe-heads among the Duna of New Guinea (after White & Modjeska 1978)

have been occupied more than once, the pattern of refuse was likely to be much more complex than in the model.

Illustrations from ethnographic reports bore these theoretical points out. Akerman (1974) planned a western Australian desert spear-making site during its period of use. Returning to the site after a wet and windy interval, he reported that many transformations had taken place, including a reduction in the number of shavings, displacement of the forked shaft straightening sticks, and slumping of the mounds of earth. Another ethnoarchaeologist, Hayden (1977) visited two western desert sites with aborigines who had inhabited them 30 years before, and who could remember the individuals who had been there and the activities that had taken place there. Hayden's excavations were used to produce a table of production of debris per person per week. This varied widely between the two camps: according to his informants, the low usage of stone at the second site was accounted for by its being a wood-working site, so some tools were discarded near trees at some distance. The first site's apparently higher usage of stone may owe something to its having been used on subsequent visits (Hayden 1977, 166).

Research amongst other present-day (or at least recent) users of stone tools has confirmed the vagaries of stone tool deposition. A study by White and Modjeska (1978) of how axe-heads of the New Guinea Duna were disposed of (many away from the workplace) provides a practical example of the possible biases in 'dropping rates' which might occur with one artefact type amongst people inhabiting settled villages (Fig 13). It should be noted that some of the Duna axes 'lost in use', often because of falling out of their bindings in the damp conditions, may be recovered and put back to use later. As Schiffer (1983, 679) has noted, the smaller chips are more likely to remain lost near their 'use-zones'.

Experimentation has illustrated how various natural and cultural events could have altered a site after abandonment. Trampling experiments have shown how fragments of stone and pot might have become dissociated in the past, and frost-action experiments have quantified the disruptive effect of freezing and defrosting on soils and

their contents (eg Barton & Bergman 1982; Bowers *et al* 1983).

Despite the difficulties of establishing significance in stone tool and debris patterning, theoretical and scientific approaches exist which can resolve many of the problems. As indicated above, Schiffer (1983) has assembled a programme for assessing the range of likely post-depositional changes, while models derived by Binford (1979) have provided means of assessing even disturbed assemblages and surface collections. From his ethnoarchaeological studies of the Nunamiut Eskimo, Binford (1977; 1979) identifies 'curated' and 'expedient' technologies (tools prepared in advance, for specific purposes, possibly of special raw materials and with special styling, as opposed to those made on the spot, for an immediate task, probably of local raw materials). The two technologies will be recognizable by the variation in the association of mint condition and broken tools, by-products, and remains of the food resources of raw material being exploited (Binford 1977, 35). This study and others suggest that, perhaps to an even greater extent than with large stone structures and site furniture, the archaeologist's interpretation of site assemblages is dependent on accurate identification of the raw materials used to make stone artefacts.

As will be seen from Table I, raw material characterization is one of the main activities of the archaeological scientist working with stone. Kempe and Harvey (1983) have edited a detailed book on this subject, and studies in this volume by Davis and by Cowell and Bowman cover respectively the techniques and results of thin sectioning and of trace element and stable isotope analysis.

Other scientific techniques can add significantly to archaeological interpretations (Table I). These include the investigation of the extent of heating of stone structures (eg Aspinall *et al* 1983), microwear analysis of the edges of stone tools (eg Anderson 1980), and various methods of absolute dating (eg Tite 1972). Of the latter, thermoluminescence has the potential to date not only early man sites such as Pontnewydd, Wales (Green *et al* 1981) but also burnt flint from later prehistoric sites.

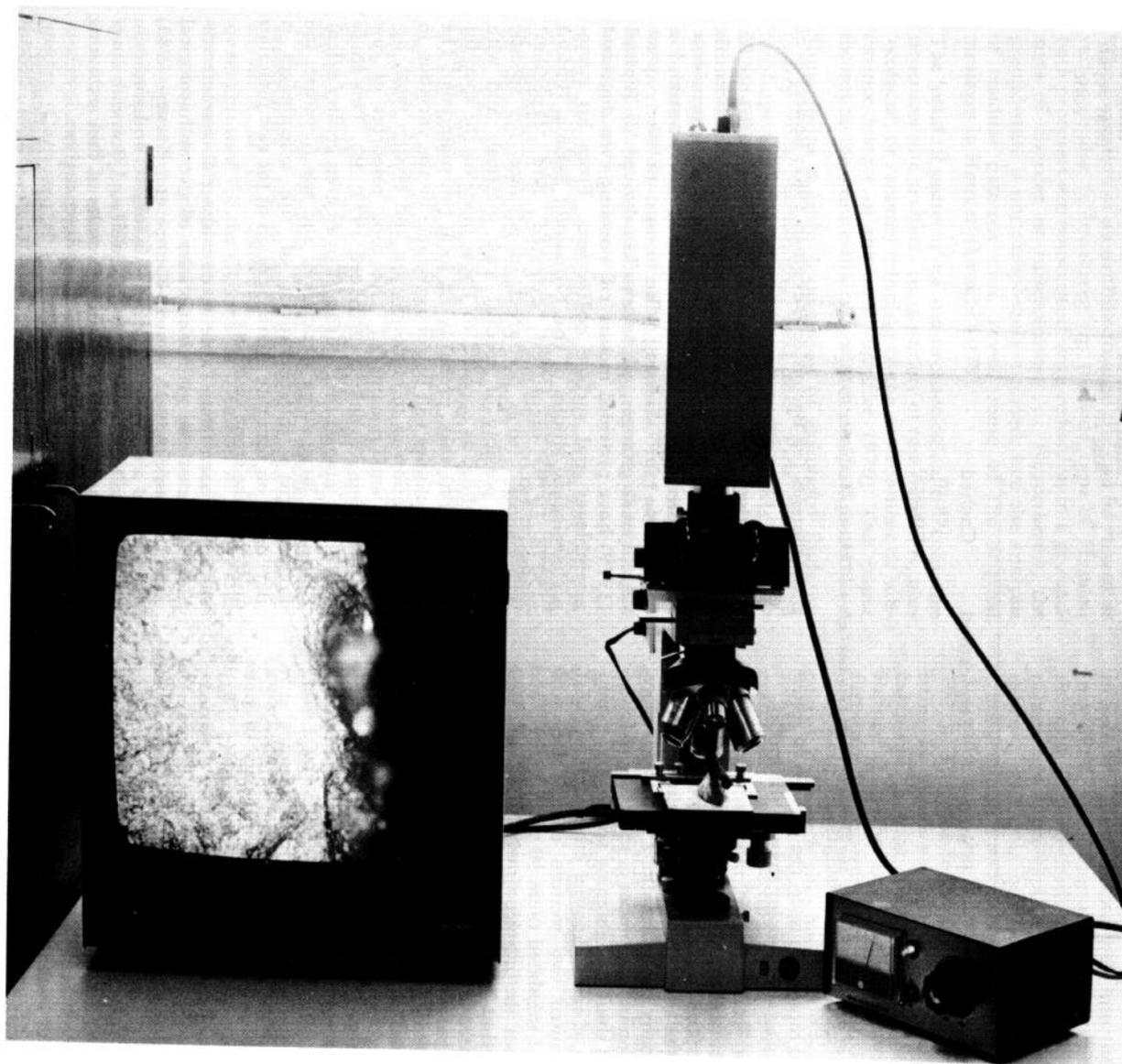


Fig 14 Metallux-2 microscope, University of Sheffield, Department of Prehistory and Archaeology. The microscope is focused on the edge of a flint artefact used on bone at $\times 250$ magnification. The TV screen demonstrates both damage to the edge and bone 'polish' on the surface of the artefact

Unfortunately flint, one of the most common materials in use in British prehistory, does not 'decay' by patination, or secondary cortication, in a uniform manner unlike obsidian, on which the hydration rim grows at an essentially constant rate (Meighan 1983).

A relatively new technique, microwear analysis, represents a major breakthrough for archaeologists working on stone tool sites. Both high-power microscopy (up to x400 natural size) and the use of the scanning electron microscope (up to x 10 000 natural size) have revolutionized interpretations of stone tool uses. Microwear analysis has been used to confirm meat-eating by early hominids (*c* 1.5 Myr ago at Koobi Fora (Keeley and Toth 1981) and *c* 1.79 Myr ago at Olduvai Gorge (Potts & Shipman 1981)). In artefacts from sites ranging in date from Middle Palaeolithic to Mesolithic, work in progress and in print has clearly identified wood-working, bone-working, cutting of meat, and scraping of skins, where all organic remains had disappeared from the site itself. Anderson has identified not only wear polishes but also fragments of woody and non-woody plants, bone, and hair captured in the silica on the edges of prehistoric tools, using scanning electron microscopy (1980). These and other residues are perhaps even clearer on the edges of obsidian tools (eg Loy 1982). Keeley, the American initiator of microwear analysis at Oxford (following the lead of the Russian S A Semenov), has recently emphasized the importance of looking for traces of hafting on stone tools, in addition to use-wear, since hafting, rather like curation, is a feature of more carefully protected artefacts (Keeley 1982). Microwear analysis cannot always be carried out, because of damage to the surface of the implement during the period of deposition, but where it is successful the results represent totally new, independent, data, identifying unequivocally at least some of the activities carried out on site.

At present microwear analysis is mainly undertaken by research students in university laboratories with access to metallurgical microscopes (Fig 14) and scanning electron microscopes. The service often costs nothing to the few archaeologists who benefit from it, but usually no routine work can be accepted, and no samples which do not fit into the research programme. However, recently money has been advanced for microwear analysis of stone tools found on several DoE excavations. This exciting new research tool, now well established in its methodology and results, needs to be opened up to a wider clientele to herald a new era in British stone tool studies. The founding of a small research unit in one of the universities, with access to the necessary microscopes and staffed by two or three experienced microwear analysts, would be an excellent investment; the founding of the thermoluminescence dating service at Durham (mentioned in the Archaeological Science Forum) could perhaps provide a model.

Archaeologists need to work closely with analysts in all fields of stone tool studies. Collaboration is necessary in treatment of stone materials during and after excavation, and in sampling suitable pieces for the various analyses. Only in this way can we hope to obtain the full potential of archaeological science techniques as they affect stone

raw materials, and to be able to incorporate the results in an overall interpretation of site activities and landscape exploitation.

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Introduction

Stone tools form an important part of the archaeological record, and implement petrology studies attempt to provide information about their manufacture, use, and dispersal in prehistory. The exact intentions and expectations of the artisans, and the precise significance of their products, remain unknown. However, through accumulating knowledge by careful observation and experiment, archaeologists are gradually increasing their sensitivity to and understanding of stone tools in prehistory. Implement petrologists are regarded as valuable contributors to archaeological enquiry, particularly in connection with stone axes; as Grimes (1979) states, 'The thanks of archaeologists must go to the petrologists.'

As an ideal, implement petrology may be defined as a study of rocks utilized by prehistoric artisans for stone tool manufacture. After macroscopic inspection, it is usual for the implement petrologist (IP) to examine the implement rock in thin-section under a polarizing microscope. This reveals the main textural elements of the rock: the degree of crystallinity, grain size, crystal shapes, and the geometrical relationship between particles and any amorphous materials present. Each thin-section slide is examined in both plane-polarized light and cross-polarized light to determine details of its mineralogical characteristics. The IP produces petrographic descriptions for each thin-section slide, seeking to discover unique or distinctive characteristics which will allow the matching and grouping of like specimens. It follows, therefore, that the ultimate validity of grouped material depends on the recognition of any unique features in the rocks at source, and in the implements themselves (Clough & Cummins 1979). The archaeologist expects the petrologist to provide scientifically accurate and reliable evidence from which to produce accurate distribution maps (see, for example, Cummins's (1974; 1979) studies of the Neolithic stone axe trade, which document changes in interpretation arising from accumulating implement petrology data). However, many archaeologists appear to be unaware or unappreciative of the constraints facing the IP, and of the strict limitations placed on archaeological enquiry by petrological evidence.

Problems of implement petrology data

The first and most serious problem concerns the level of scientific sensitivity required to obtain the level of valid data expected by archaeologists seeking to use stone tools as cultural markers (Wright 1977). It is unfortunate that so many British stone axes lack provenance. A majority of these implements were manufactured from igneous rocks which can sometimes be identified macroscopically, but,

unfortunately for the IP, very few igneous textures have been reproduced in the laboratory, and the origins of even fewer are adequately understood. Indeed, it has been recently stressed by Mackenzie *et al* (1982) that many textures are open to more than one interpretation - a point well illustrated in atlases of rock-forming minerals in thin-section (Mackenzie & Guildford 1980). Six rock textures used for the manufacture of prehistoric stone tools are illustrated in microfiche frames **B1-B6**.

IPs have always been greatly concerned that the allocation of an artefact to a particular rock source should depend on its own elemental analysis not only falling within the limits of variation of the same elements in that source, but also clearly failing to do so in the case of other analysed sources. Until every possible source has been located and analysed, there exists the possibility of a new one being discovered with the same pattern of trace elements, or of two or more already known having inseparable patterns (Shotton & Hendry 1979). Many archaeologists will probably not realize that the traditional and widespread practice of examining rocks in thin-section under a polarizing microscope does not provide this level of elemental analysis, and that more sophisticated geochemical techniques are necessary: X-ray diffraction, X-ray fluorescence, and microprobe analysis. These additional techniques are, however, expensive to apply, the hardware is seldom accessible to most IPs who work mainly on a voluntary basis, and, in addition, the results are not easily interpreted. Thus, in the general absence of more sophisticated geochemical investigations, the bulk of available implement petrology information only provides indications and helpful suggestions to complement evidence from other sources, except, of course, where the data concern highly individualized rocks - Group 9, porcellanite, for example (Clough & Cummins 1979). The problem arising from this lack of predictability becomes more acute when dealing with the numerous, relatively featureless rocks which outcrop in widely different geographical localities; Group 6, 'Langdale', is a good example of this, and is discussed by Morey (1950), Ritchie (1953), and Fell (1954). For a general discussion of the problems of the Great Langdale axe factory, see Piggott (1954), Mayoh (1977), Houlder (1979), and Davis (1983). The recent discovery that rocks matching the published petrological descriptions for Groups 8, 'South-west Wales', and 20, 'Charnwood Forest' outcrop in the north-west England highland zone (Davis 1984) does not prove that *all* implements originate from this source. There is considerable difficulty in differentiating between similar rocks from sources in south Wales, the Midlands, and north-west England, especially when the whole range of petrological variation of rocks suitable for implement manufacture from each

region and elsewhere in Britain is unknown. (For further discussion of the relationships between Groups 6, 8, and 11 see Stone & Wallis 1951.) These similarities led Piggott (1954,293) to report that two flakes found on the Great Langdale screes may have an origin in Pembrokeshire, an earlier idea which Ritchie (1953) had regarded as 'manifest absurdity'. A similar and equally important example concerns the Group 1, 'Cornish', products, especially since the recent discovery of a source of similar rock in the north-west England highland zone (Davis 1984).

The IP faces many other problems, some of which are briefly identified below in two related groups. The first problem area is archaeological, and includes both the lack of provenance for the great majority of British stone axes (Moore 1979), and the indiscriminate and widespread removal of archaeological material from sites, for instance from the Great Langdale factory sites. IPs are also concerned about the lack of standardization of implement classes represented in product distribution maps, ie the occasional use of one or more categories (completed tools, rough-outs, fragmentary tools, and waste flakes), which makes it difficult to compare data published since Keiller *et al* 1941. In addition, some archaeologists appear not to question appealing theories sufficiently deeply—for example, that the popularity of Group 6 rock can be readily explained by its similarity to flint, when rocks which respond equally well to napping occur much more widely than on the restricted outcrops adjacent to the Great Langdale axe factory sites (Davis 1984).

The second group of difficulties concerns the availability and communication of data. The former practice for IPs to circulate duplicate material, especially type specimens of new groups, now seems to have lapsed. Consequently, what was already a difficult task is made even harder. The present practice of thin-section slide collections being held regionally rather than being centralized nationally should continue, but communications between implement petrologists and archeologists should be improved. Particular attention needs to be given to: 1) a constant updating and revision of material in implement petrology collections; 2) validation of existing petrological groups and the establishment of new ones, but with constant reference to type material and with an awareness of the petrological boundaries for groups defined by their originators; and 3) a periodic revision of all grouped material in the National Collection which is essential in order to sustain many current archaeological beliefs founded on important pioneer work which involved only small numbers of specimens and which is now more than 50 years old.

Another problem is that differences of data interpretation, although seldom discussed in the literature, have always existed throughout the history of the Implement Petrology Survey.

Possibilities of implement petrology data

In spite of these difficulties, IPs value their tradition in helping to solve archaeological problems, catalogued by articles and notes which have appeared regularly in the

literature for about 50 years. Ever aware of the limitations placed on their work by a shortage of time and the need for more discriminating evidence, IPs are combining macroscopic, optical microscope, and geochemical techniques, mainly X-ray diffraction and X-ray fluorescence, in their investigations. Microprobe analysis is an additional technique available for solving particularly difficult or controversial issues. The recent additional use of back-scatter scanning electron microscopy (SEM) has definite advantages: rapid identification of elemental composition; clear visual imagery across a broad magnification range; visual and printed elemental traces; and the facility for placing complete flakes (subject to size) in the SEM, thus not disfiguring the artefact. Although not as powerful as the microprobe, SEM can be used in a defocused mode to scan fine-grained homogeneous rocks (eg Group 6 and its variants), and in a focused mode is suitable for coarse-grained rocks (eg Group 1 and its variants). For best results a highly polished surface is required, but useful information can still be obtained by scanning a freshly fractured or weathered surface. The SEM is particularly suited to the study of opaque minerals, and it can identify trace elements for subsequent microprobe analysis. SEM data were used in the investigation of implements of supposed Cornish origin found in the north-west England highland zone, which proved to match rocks from local sources (Davis 1984).

Implement petrology offers many other exciting possibilities for contributing data for archaeological interpretation, including the analysis of macro/micro fracture patterns in perforated and unperforated tools; for example, indicating whether large axe-hammers were manufactured from naturally occurring, suitably sized detached blocks (Roe 1979). Implement petrology data can help clarify the relationship between implement style and function, and provide a control for experimental archaeology; for example, providing a petrological basis for assessing the durability of implements in use, and the testing of facsimile tools to destruction. Another important role for implement petrology is providing a basis for international stone axe studies, particularly where these involve a substantial ethnographical element (Davis 1982). Finally, it must be stressed that the examination of rocks in thin-section under a polarizing microscope still remains the most important and widespread implement petrological technique, although increasingly sensitive techniques are now being used to investigate new material and re-examine old material in an attempt to improve our level of understanding about prehistoric stone implements. However, implement petrologists and archaeologists alike must avoid the obvious temptation to generalize beyond the limits of the available implement petrological data.

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Colour microfiche illustrations

Photomicrographs of rocks in thin-section by cross-polarized light (magnification x 20)

- B1 Group 1, uraltized gabbro, epidiorite (greenstone); source near Mount's Ray, Penzance, Cornwall
- B2 Group 4a, sheared picrite; possible source near Callington, Cornwall
- B3 Group 6, epidotized intermediate tuff; source Great Langdale, Cumbria
- B4 Group 9, porcellanite, source Tievebullagh and Rathlin Island, County Antrim, Ireland
- B5 Group 14, camptonite; source near Nuneaton, Warwickshire
- B6 Group 24, calc-silicate hornfels; source near Killin, Perthshire, Scotland

Introduction

Flint- and related materials have been used for the manufacture of tools far longer than almost any other material. Their importance is enhanced by their survival rate over periods when they may represent man's only visible remains and form an invaluable record of his development and movement. The chemical and structural properties of flint are such that they can be exploited by scientific examination in order to produce information potentially useful to the archaeologist. Provenance studies and thermoluminescence dating are just two areas where this potential has been tapped.

Provenancing

A significant amount of analytical research into archaeological flint has been directed towards provenance studies. Except for the validation of techniques, the interest here is not in the composition of flint as such but rather the relationship between artefacts and sources. There are, of course, no technological questions which can be answered by analysis of lithic material as there are for metals, except studies of the heat treatment of flint, where electron spin resonance spectroscopy (ESR) has been applied (eg Robins *et al* 1978; 1981; Jones *et al* 1979).

An essential prerequisite to the provenancing of artefacts is the characterization of sources. The difficulty with flint, in common with other geological raw materials, is that there are virtually unlimited numbers of sources, particularly, the abundant nodular surface flint in soils and gravels. Provenancing artefacts made from such random material would seem to be an insoluble problem, since these are secondary deposits some distance from the parent rock which are derived from a range of widely stratified layers of flint. Only where individual flint layers still within the chalk have been systematically exploited is true provenancing likely to be possible.

The ability to distinguish one source of flint from another is dependent on its geochemistry. In geological terminology, flint is a specific type of chert which occurs as bands of nodules in the Cretaceous Chalk. The structure and formation of flint and other types of chert have been extensively studied. The structure is known in some detail (Micheelson 1966), but there is still some debate about the precise mechanism of formation. Nevertheless, there is a general consensus on the overall mechanism for nodular flint formation (Pettijohn 1975, 402). Thus it is certain that flint was not formed concurrently with the chalk sediment but formed later, probably by a replacement process. On a strictly localized scale, chemical conditions were such that silica was able to replace some of the calcium carbonate structures and matrix of the chalk, eventually producing a nodule by accretion. Either directly, or more likely by re-arrangement, the silica in

the nodule formed as microcrystalline quartz which is the dominant constituent of flint. During this process some of the non-carbonate minerals in the chalk, contained in clays for example, became enclosed and preserved by the flint *in situ*. Therefore, although flint typically consists of over 96% silica, there are in addition substantial amounts of unreplaced chalk (up to 3%) and small amounts of many other components (Cowell 1979).

The composition of flint is thus dictated by that of the sediment in which it has formed. Since chalk is a relatively pure form of limestone the flint which has formed within it is likewise a relatively pure form of chert. When characterizing flint we are in effect characterizing different layers in chalk. There are good reasons for expecting trace-element differences between and along chalk strata, and actual measurements have shown this to be the case (Hancock 1975). One would therefore expect marked compositional changes through a vertical sequence of flint layers and even horizontally over long distances. This is the key to the use of flint as a provenancing tool. There are potential problems, however. First, the closer sources become which exploit the same band of flint the more difficult they are to separate chemically. Secondly, flint is not an homogeneous material, which is why relatively large samples must be removed in order to get representative results. Hence, it is desirable in the characterization of sources to analyse as many individual items as possible which are representative of that site's production. Thus discarded workshop material is to be preferred for characterization since this is more likely to be representative of the material being exploited at the source.

It is unfortunate that petrology is of little general help in flint provenancing, although it has been useful in a few restricted instances (Wray 1948; Deflandre 1966). The main reason for this is the lack of observable distinctive mineral components. With the exception of calcium and iron minerals, the trace elements used in chemical characterization are at too low a concentration to be visible in thin section as discrete minerals. Trace fossils are often the commonest observable feature, but these do not normally appear to be specific enough to characterize a particular source.

In common with most other exploited stone materials, there is in principle a direct relationship between flint artefact and source composition because the material is normally not chemically altered by man through use. Certainly there are not the difficulties inherent in the use of mixtures of component raw materials from potentially different sources or, for example, the technological influence of smelting on metal ores. However, flint is not completely stable and the natural alteration or patination which develops on worked surfaces may place limitations on the type of artefact which can be studied or the

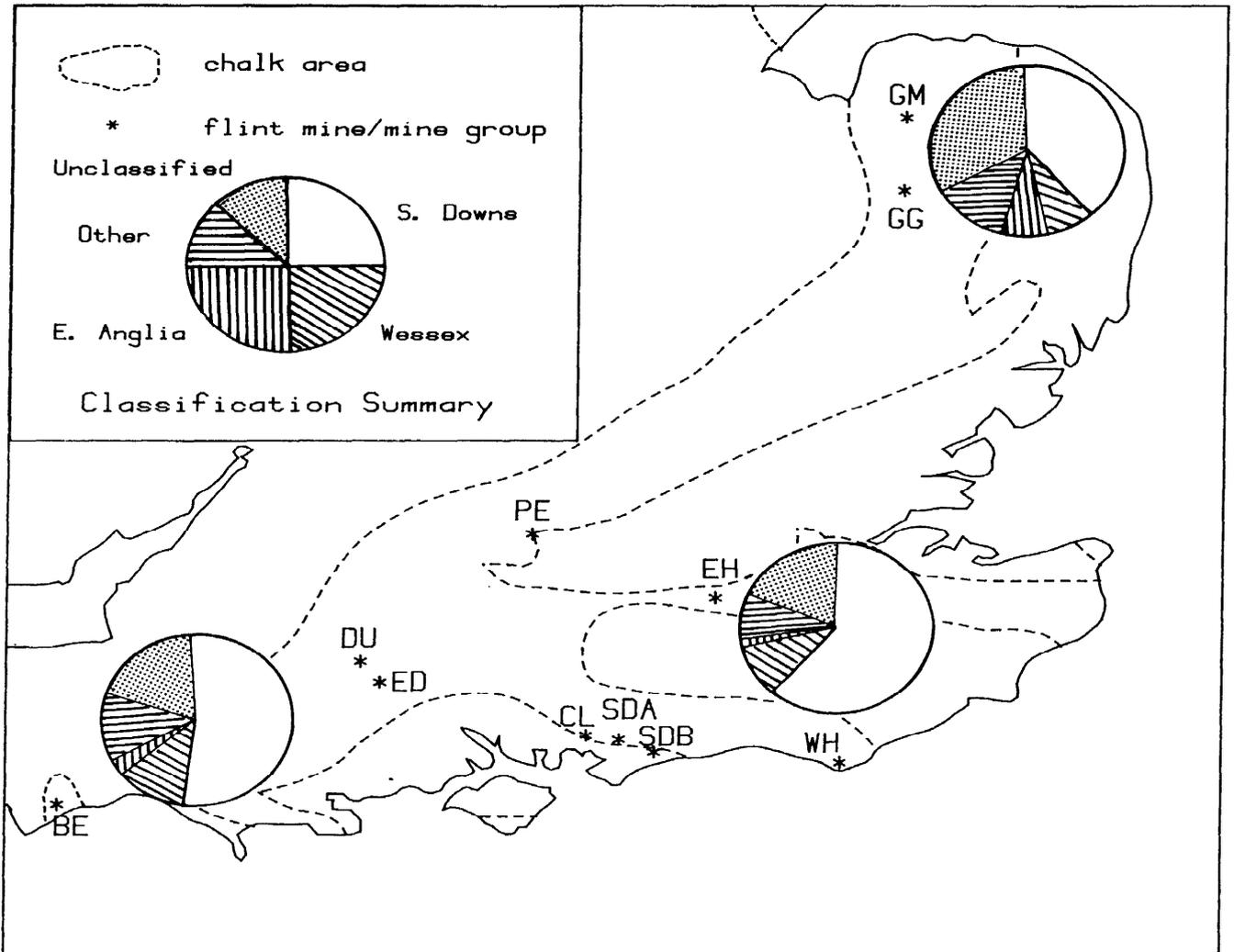


Fig 15 Classification summary. Each pie-chart shows the proportion of axes classified to mines in the South Downs area, Wessex, East Anglia, and other mines, and also the proportion unclassified. The three charts correspond to flints found in south-eastern England, Wessex, and East Anglia. Code letters indicate flint mines or mine groups as follows: GG, Grimes Graves; GM, Great Massingham; PE, Peppard; EH, East Horsley; DU, Durrington; ED, Easton Down; CL, Clanfield; SDA, South Downs Group A; SDB, South Downs Group B; WH, Windover Hill; BE, Beer (after Craddock *et al* 1983)

method of sampling used. This weathered layer, which may be several millimetres thick, is so altered by leaching and absorption of ground water that for purposes of trace-element characterization it is undesirable and must be avoided in sampling. What is required is a representative sample from the unaltered interior of the artefact. Since flint is a very hard material sampling is difficult without introducing contamination. Perhaps the most convenient method has been that used by Sieveking *et al* (1972) where a solid core, measuring approximately 5mm in diameter and 15mm in length, was removed using a hollow diamond-impregnated drill. This causes the minimum amount of damage to the artefact and the undesirable patinated layer can be easily removed and discarded from the top of the core. However, heavily

patinated thin flakes may have insufficient unaltered internal material for a reliable sample to be taken.

There have been a number of provenance studies on flint. These have included material from Holland (de Bruin *et al* 1972), France (Phillips *et al* 1977; Aspinall *et al* 1979; Mundy & Aspinall 1982), Belgium (Stockmans *et al* 1979), Eastern Europe (Kunchev 1975), and North America (Luedtke 1978; 1979). Studies of British material have concentrated on the Neolithic flint mine sources with the intention of provenancing their polished flint axe products. A pilot survey using emission spectrometry on raw material from the major sources gave encouraging results (Sieveking *et al* 1970), and this was later extended to include further sources after

switching to atomic absorption spectrophotometry (AAS) as the analytical technique (Sieveking *et al* 1972). Some of the same material was also analysed by neutron activation (NAA), although this did not lead to improved separation of sources (Aspinall & Feather 1972). Recently, archaeological material comprising over 300 flint axes from southern Britain has been provenanced (Craddock *et al* 1983). However, because of the incomplete separation of sources, individual artefacts could not be reliably assigned to a particular source, although general conclusions based on assignments over a region provided useful information. In particular, this showed that the South Downs group of mines were responsible for the production of the majority of the axes analysed (Fig 15), a conclusion which is in accordance with recent research on British flint mining, such as their periods of operation.

In addition to AAS and NAA, inductively coupled plasma spectrophotometry (ICP) has been recently applied to British flint (Bush & Thompson, forthcoming), so far only on source material, with promising results. Relatively sensitive techniques and comparatively large samples (weighing 0.5g or more) are required for flint analysis because of the low concentration of most of the elements of interest, but this also ensures that the sample is representative. The precision of the analytical technique is less critical because of the natural variability of the material. The relative standard deviation of most elements in a single nodule normally exceeds 7%, for example.

An important part of the process of provenancing is the statistical treatment of the data. In most cases, because of the size and structure of the data, rigorous multivariate methods are necessary. Variants of discriminant analysis have usually been applied and seem to be the most appropriate in this application (de Bruin *et al* 1972). An advantage over simpler methods is that there is an objective measurement of the strength to which an unknown is assigned to a source.

Provenance studies on flint have met with varying degrees of success. However, the lack of success in some cases can perhaps be put down to selection of material and inappropriate sampling techniques as much as to difficulties with flint itself: for example, using too few samples, geological material remote from the ancient exploitation for characterizing sources, and sampling procedures which do not adequately exclude patina. Nevertheless, the major problem in all these investigations has been the fundamental stage of obtaining a complete characterization of all the relevant sources. In some cases, where a satisfactory separation was obtained in a preliminary survey of a limited number of sources, the subsequent addition of further sources produced a much less distinct characterization (eg Mundy & Aspinall 1982). Sources close geographically which exploit the same flint layer are particularly difficult to separate. However, by grouping these and treating them as regional sources, as was resorted to by Craddock *et al* (1983) for the South Downs mines, meaningful archaeological interpretations are still possible, though not on the refined scale originally envisaged. More precise separation of sources would only be possible if a suitable

combination of elements was found with the right properties. This might be achieved by extending the range of elements determined or possibly by pooling the data from several techniques.

Thermoluminescence dating

There are two techniques applicable to the dating of burnt flint: thermoluminescence (TL) and electron spin resonance (ESR). The two have certain basic similarities, particularly in the requirements for evaluation of an age. Only the former will be discussed since TL has been in use over a longer period of time and there are few ESR dates available yet. The potential ESR dating signals for flint are discussed in Griffiths *et al* (1983). Flint, however, is not the only stone that can be dated when burnt; examples of other stones dated by TL include sandstone (Huxtable *et al* 1976; Valladas 1981) and a biotite microgranite (Schvoerer *et al* 1977).

The application of thermoluminescence (TL) to the dating and authenticity testing of ceramics has been reviewed by a number of authors (eg Aitken 1977; Seeley 1975). TL dating of non-pottery materials has been reviewed by Wintle (1980) and has applications both in archaeology and geology. In archaeology such applications, which include dating of burnt flint and other stone, have particular importance beyond the range of radiocarbon dating or where suitable material for dating by other methods is not available.

Thermoluminescence is the light given out on heating by nonconducting crystalline materials that have previously been exposed to ionizing radiation. This light is in addition to the incandescence. The TL measured in the first laboratory heating of a portion of the burnt flint is referred to as the natural TL. In simple terms, this is proportional to three factors: the time elapsed since the flint was last heated to a temperature of about 500°C, the effective TL sensitivity of the flint to radiation, and the rate at which radiation has been received (the dosimetry). If the natural TL and the last two of these factors can be measured, then in principle the date when the flint was burnt can be determined. One important fact which must be noted is that the radiation received by the sample derives from minute quantities of radioactive elements both internal to the flint itself and in the burial environment. The latter can provide more than half of the received radiation, and to facilitate dating it is consequently essential that measurements be made on the burial soil. This is best achieved by leaving an encapsulated TL phosphor for a period of about a year in the context to be dated (Aitken 1974).

The initial work on TL dating of burnt flint was hampered by the observation of light signals, referred to as spurious and regeneration TL, that were not related to the radiation history of the sample (Göksu & Fremlin 1972). These were overcome by using samples which, rather than being powdered, were prepared as polished slices approximately 300µm thick. The first dates published using such samples (Göksu *et al* 1974) were for Carigüela, a site in Spain, where the environmental radiation was dominant. Although in general such a situation is far from desirable, the slices made the evalua-

tion of the TL age more straightforward. When the internal radioactivity is significant, the dosimetry is complex and involves measurement of the optical absorption characteristics of the flint. The general age equation for slices has been derived by Aitken and Wintle (1977) and used to obtain two dates averaging to $230\,000 \pm 40\,000$ years BP for the Lower Palaeolithic site of Terra Amata in the south of France (Wintle & Aitken 1977).

Preparing slices is, however, rather time-consuming and, owing to the sample size required, can severely limit the number of burnt flints that can be dated. Furthermore, the TL properties of a series of slices from the same flint can be very variable (Bowman & Seeley 1978).

Valladas (1978) showed that not all crushed samples of flint exhibited the interfering effects observed by Göksu and Fremlin (see above), and that, where observed, such effects could sometimes be reduced to an acceptable level by treatment with hydrochloric acid, which removes unconverted calcium carbonate, a well known cause of spurious TL. Valladas used grains of about $100\mu\text{m}$ diameter; other workers (eg Danon *et al* 1982) have also had success with similar grain sizes. Crushing of flint and deposition of samples as fine grains (approximately $1\text{--}8\mu\text{m}$) on aluminium discs, as frequently used in pottery dating (Zimmerman 1971), greatly simplifies the internal dosimetry, and dating programmes employing this sample preparation technique are now being reported (eg Bowman *et al* 1982; Huxtable 1982).

In addition to the examples cited in the above discussion, there are now dates for burnt flint from a number of sites. Joan Huxtable's published work includes dates for the following British sites: the Mesolithic site of Longmoor Inclosure, East Hampshire (Huxtable & Jacobi 1982); two sites, one Upper Palaeolithic and one Mesolithic, at Hengistbury Head, Dorset; and a Lower Palaeolithic level at Pontnewydd Cave, North Wales (Green *et al* 1981). Sequences of dates for different levels of the same site are rare, but one such sequence is that for the site of Combe Grenal in the Dordogne, France (Bowman & Sieveking 1983). The dates separate into three groups corresponding to the three depositional periods at the site and span an age range of about 45 000 to 110 000 years.

A general age range cannot be given for the applicability of TL dating to burnt flint since this depends on the TL characteristics of the flint and on the radioactivity levels in the flint and in the burial soil. The papers cited above, however, altogether contain dates spanning from about 5 000 to 230 000 years. Typically the error on an individual result is $\pm 15\%$ at the 68% confidence level. Where a group of flints from the same level can be dated, the error on the average age is likely to be about $\pm 10\%$ (see, for example, Barton & Huxtable 1983).

Although many of the early difficulties encountered in the dating of burnt flint have been overcome, a number still remain. In the dating of Combe Grenal (see above), for example, a large number of pieces of flint were available for dating. Approximately 50 pieces that showed signs of heating and were of a sufficient size for dating were selected for TL examination. Of these only six had a measurable natural TL, were sufficiently well heated, and had satisfactory TL characteristics. Although in the

collection of samples for dating it is not possible to select material that will necessarily be datable, there are a number of factors which must be taken into account, some of which have already been indicated. Aitken (1974, 109) provides a set of notes for the collection of pottery samples intended for TL dating. In general the criteria for collection of flint are the same. The main features are: a minimum sample size is required, a number of flints from each context to be dated is desirable, and access to the burial environment is needed. The need for a minimum size arises because the outer 2mm of the flint is removed and ideally about 10g of material should remain on which the measurements can be made. In addition to the three main requirements given, there is a further one for flint collection that is not quite so critical for pottery: that is to avoid exposure to light, whether natural or artificial. Huxtable (1981) showed that such exposure can bleach the natural TL and consequently could lead to an underestimate of the age. Although it is unlikely that light would have penetrated the outer 2mm of the flint which are not used for TL measurements (Bowman & Sieveking 1983), nevertheless it is highly advisable that any unnecessary exposure to light be avoided.

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The primary archaeological question posed by any technological finds is 'what process or processes produced them?' This is a deceptively simple question and one to which it is often difficult to get a sensible answer as each specialist will recognize his own class of material but may not be able to identify others. The best solution is for all archaeologists to learn enough about ancient technology and the processes involved in it so they can roughly recognize their finds and so approach the right specialist with them, as they would do with pottery or small finds of different periods. A point worth stressing here is that for industrial remains it is the process rather than the period which is important, as techniques changed little over long periods of time.

As the title suggests, this paper will not deal with the whole range of ancient crafts and industries, but only with those which required high temperatures. By this is meant temperatures above those used for cooking food, roughly speaking over 300°C. This means that the working of organic materials such as bone or leather is not covered, as at high temperatures they would only burn or char. The only relevant organic materials are those used as fuels, wood and charcoal.

The end products of high-temperature processes include metals, glass, ceramics of all sorts, and lime plasters and mortars; for any particular end-product there are normally several processes involved in its production from natural raw materials. For example, to make a bronze object both copper and tin ores have to be smelted, the metals refined, and then alloyed with each other in the required proportions before being cast (in a mould that has been made), and then probably worked further by a smith. Each process in this chain requires its own tools and produces its own range of by-products. It is because of this variety that individual industries or processes can be identified. If the wastes produced are recognized and correctly identified, the process that gave rise to them will be known.

In practice it is not quite as simple as this because some processes produce almost no wastes (or none with a good survival potential), some processes produce wastes that are easily confused with those of other processes, and some natural materials can look very like industrial wastes. For these reasons any preliminary identifications of industrial wastes should be confirmed by a specialist.

In identifying industrial wastes the most important features are gross morphology (ie size, shape, and texture), together with colour and weight or density. Qualitative analyses can be useful to confirm identifications, but qualitative analysis is not generally helpful in identifying processes, though it can contribute other

information about the skill of the craftsman, the efficiency of his process, or the origin of his raw materials.

The high temperatures necessary for the industrial processes being discussed were produced by containing a fire of wood, or often charcoal, in a structure which is variously described as a hearth, oven, kiln, or furnace.

Conventionally, structures used for firing ceramics, either pottery or tiles, are known as kilns unless they are very primitive and/or impermanent, when they are known as clamps. Bricks are also fired in either kilns or clamps, and lime is 'burnt' in a kiln before being slaked and used for building or agriculturally. Metals are smelted from their ores in furnaces, but most other metal-working operations involve hearths. Ovens are normally used at lower temperatures and for organic materials such as bread or malt.

All these structures were necessarily made of non-combustible materials such as earth, clay, stone, or ceramics, which usually contain silicates of one sort or another. These materials will melt (fuse) if they are heated to sufficiently high temperatures, but these extremes were not generally obtainable in antiquity even when a good draught was provided for the fire—either naturally because of its situation or a chimney, or artificially by bellows whose air-blast entered the fire through tuyeres (perforations in the containing structure). However, even somewhat lower temperatures, around 1 000°C, do affect silicate materials. The ash in a fire, which is rich in alkalis, reacts with silicates (it is said to 'flux' them) producing glassy (vitreous) materials, which are usually called slags. These alkali silicate slags are often known as fuel-ash slags and are not of themselves evidence for any specific industrial process; they simply indicate a fire at high temperatures.

Alkali silicates

A great variety of alkali fluxed silicate slags are found, some more commonly than others. The clay surface of a structure that has become vitrified from contact with the fire is known as hearth (or furnace) lining. It shows a gradation from ordinary fired clay furthest from the fire to a fully vitreous surface (see microfiche frame **B10**). Discrete pieces of silicate materials that have been in a fire can acquire a surface 'glaze' (see **B11**) or can be completely vitrified, the classic fuel ash slag (**B12** and **C1**). Alkali silicate slags are found in a very wide range of colours, from off white through greys and browns to black. The thin glazes are often pale bluish-green. Most of the colours are due to the presence of small though variable amounts of iron, which were present in the

original silicate material- Alkali silicates are quite light in weight; the heaviest are no denser than ceramics and many appear lighter, as they are very porous (vesicular).

A second group of alkali silicates are deliberate glasses which were made by reacting iron-free sand (silica) and an alkali (see Hunter, this volume, 63-6). The raw materials were first heated together in a fritting furnace, where they partly reacted but did not fuse. The resulting frit was then broken up and placed, together with scrap glass known as cullet, in crucibles in the main furnace, where it was heated more strongly to complete the reaction and melted ready for use. If too high a temperature was reached during the fritting stage, glass containing a lot of part-reacted material was produced (C2), which was discarded as it was not possible to refine it sufficiently during the second stage of the process with the furnace temperatures that were obtainable in antiquity. Evidence for glass re-melting is commoner than for glass making and includes crucibles containing glass (see C3), dribbles of glass (C4), and lumps of cullet (C5).

The third group of alkali silicates are ceramics that have been overheated. This can happen accidentally when a pottery kiln gets too hot, and the result is a lot of wasters-vessels that are distorted or have glazed or vesicular surfaces (C6). Crucibles, on the other hand, are deliberately placed in a fire and heated strongly to melt the metal they contain. Their surfaces become fluxed and traces of the metal they contained are often trapped in this vitreous layer. Copper gives a bright red colour (C7), quite different from the liverish, purplish-red that iron can produce (C5). However, a red colour is no guarantee that it was copper or one of its alloys that was being melted, as ancient gold and silver usually contained enough copper to produce this coloration, even if the metal had not been deliberately debased. Silver-melting crucibles can be positively identified from droplets of the metal trapped in the vitreous surface. The metal normally corrodes to a soft brownish-black lump which has a lilac-coloured powdery surface, unless very thoroughly scrubbed in the pot shed, when the lilac layer disappears (C9)! Gold is even easier to spot as it does not corrode, although the droplets tend to be very small; a good size is 0.1mm (C10).

Crucibles are not the only evidence for non-ferrous metal-working. Once the metal is molten, it is cast, either directly into an object or into an ingot that can then be smithed to produce rods, wires, or sheet metal, which can in turn be made into a variety of objects. Moulds for casting objects directly are either one-piece clay moulds for investment (lost wax or *cire perdue*) castings, which has to be broken to remove the object (C11), or else piece moulds, which may be made of a variety of materials and can be taken apart and re-assembled a number of times (C12 and D1). Ingot moulds are usually made of stone and often have hollows for casting more than one ingot (D2). Rough castings that have not been cleaned up are also evidence for metal-working (D3).

Iron silicates

The second major group of slags are iron silicates, which are also known as fayalitic slags as they contain considerable quantities of the mineral fayalite, $2\text{FeO}\cdot\text{SiO}_2$, some

of it in a glassy form. These are produced during iron smelting and smithing operations, and also when other metals such as copper are smelted from their ores. Iron ores are often first roasted as it makes them easier to break up and converts all the iron in them to oxides. In the smelting furnace these oxides are then reduced to metallic iron. The problem is that the roasted ores are never pure metal oxides but also contain rock or earthy material, which is silicate-rich. In order to separate this gangue from the iron it has to be fluxed and turned into a liquid slag which can flow down to the bottom of the furnace, allowing the metal to collect together into a coherent mass known as a bloom. There is insufficient ash in the furnace for alkali silicate slags to form, so some of the iron oxides in the ore react with the gangue to produce an iron silicate slag. Though wasteful of iron, fayalite slags have the advantage of being liquid at the temperatures at which early smelting furnaces operated. Sometimes the slag was allowed to solidify in the furnace, but a more developed technique involved tapping the furnace and letting the liquid slag run out into a hollow. The advantage of this was that the furnace could be kept running for longer and a larger iron bloom produced.

In order to convert the bloom into usable iron it had to be smithed to compact the metal and squeeze out any trapped slag. The slag from this stage of iron-making has a similar composition to that of the corresponding smelting slags but its form is quite different. Smithing is carried out at lower temperatures than smelting so the slag is less liquid and does not flow into a pool. The individual droplets squeezed from the bloom collect at the bottom of the smith's hearth, where they stick together and form a more open, porous iron silicate slag (D4 and D5). By comparison smelting slags are denser (D6), they tend to have fewer, larger gas bubbles, and if they have been tapped from the furnace they often have flow lines visible on their surface (D7 and D8), which is smooth rather than rough and lumpy, as those of smithing slags are. All fayalitic slags are dark grey in fracture, although they often show rust colours on weathered surfaces.

A further stage of iron working is the manufacture of objects from the raw metal, This also produces smithing slags, but in smaller quantities than the primary smithing. These slags tend to be less homogeneous and often have patches which are really just fuel-ash slags. They can also be weakly magnetic, either because an offcut of metallic iron fell into the hearth and got trapped in the slag or, more usually, because they contain quantities of hammer scale. Hammer scale is the magnetic oxide film that forms on the surface of iron when it is heated in a forge or smithy. When the iron is hammered this brittle surface skin flakes off as the metal is deformed. It can collect in considerable quantities round the anvil and some usually gets into the smith's hearth. The flakes are never more than a millimetre or two across and can be easily identified with the help of a magnet.

One final type of iron-working slag is that formed in blast furnaces, which were late medieval introductions. These could reach far higher temperatures than earlier furnaces, so it was possible to use slags that had higher melting points than iron silicate slags. Limestone was added to the furnace with the iron ore and a calcium

silicate slag formed. The advantage to the smelter was that almost all the iron in the ore was converted into metal. Blast-furnace slags are always glassy in appearance and range in colour from blue and green through grey to brown. They are far less dense than fayalite slags as they only contain a small percentage of iron, which also gives them their colour (D9).

Lead silicates

Lead is another element that forms glassy silicates. When lead is smelted from its ores the slag that forms is black and glassy and feels very heavy, as it contains considerable quantities of lead, which is a very dense metal (D10). The main evidence for lead working, however, is not smelting slags, which are restricted to the few parts of the country where lead ores are found, but lead melting dross (D11). When lead is melted the surface oxidizes, so before the metal is poured the oxides are skimmed off. They and the small amount of metal removed with them make up the dross, which is powdery and usually looks pale grey, though the individual oxides are white, yellow, and red.

Lead oxides were sometimes produced deliberately so they could be used as a raw material in the manufacture of lead silicate glasses and glazes (D12). These vitreous materials are usually translucent pale yellow, but different colours can be produced by adding small amounts of other elements, as with ordinary alkali glass. High-lead glass was not used for making vessels but for trinkets, like beads and gaming pieces. Some lead glasses are opaque and these were used for beads and also as enamels; finds of crucibles containing the glass are evidence for its working (E1). If the glass is opaque red, confusion can arise between red enamel and red-coloured fuel-ash slags on a metal-melting crucible, but they are not difficult to separate visually, as deliberately made glasses are found inside the crucible and usually in a far thicker layer than accidentally produced red 'glazes' (compare E2 and C7).

Lead-rich wastes are also produced in metal refining processes. Precious metals, silver and gold, can be separated from base metals by cupellation; the mixed metal is heated with an excess of lead, which is then oxidized by a strong air blast. The base metals such as copper and tin dissolve in the lead oxide which is removed, leaving the precious metals behind. The same process is called assaying when it is carried out on a small scale to test the purity of gold or silver. Bone ash is used both to make cupels, which are shallow dishes in which the assaying is carried out, and as a lining for hearths for larger-scale refining, as it absorbs the lead oxide. The earliest known English cupels date to around AD 1600 (E3), though in late Saxon times small ceramic dishes known as heating trays were used for metallurgical operations involving lead and precious metals, probably some sort of refining. As heating trays are made of silicates they react with the lead oxide, producing a thick vitreous upper surface, often coloured red by traces of copper and containing droplets of silver (E4).

Not all lead silicates are by-products of industrial processes; they sometimes form accidentally when, for instance, a building is destroyed by fire. Any lead in the

building-roof flashings, plumbing, or window comes-melts and can oxidize, and then reacts with silicate materials such as brick or tiles. The result is a mass of lead-rich, vitrified ceramic (E5). When leaded windows are burnt some of the metal reacts with the glass and some stays as discrete metal droplets, dispersed through the mass of molten glass (E6).

Some naturally occurring materials can be confused with the man-made slags described above. Most of the imposters are usually thought to be iron slags. High on this list must come ironstone masquerading as tap slag (E7) or smithing slag (E8) and pyrites nodules which also look like smithing slag (E9). Pieces of puddlingstone, a ferruginous conglomerate (E10), bog iron ore (E11), and Niedermendig lava, which has the right porous texture, though its grey colour and light weight identify it (E12), can also be confused with smithing slags. Objects which have decayed in unfamiliar ways can be wrongly identified, too, so one must think twice before labelling any unidentifiable lump as 'slag'.

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The above articles and books cover various parts of the subject matter of this paper. Those given below are useful mainly for their descriptions of the industrial features where slags etc were produced. For metal-working residues see also articles in the journal *Historical Metallurgy*.

- Crossley, D W (ed), 1981 *Medieval industry*, CBA Res Rep, 40
 Frank, S, 1982 *Glass and archaeology*
 Tylecote, R F, 1962 *Metallurgy in archaeology*
 —, 1980 Furnaces, crucibles and slags, in *The coming of the age of iron* (eds T A Wertime & J D Muhly), 183-228

Colour microfiche illustrations (all photos: English Heritage Photographic Section)

- B10 Hearth lining
 B11 Stone with a fuel ash 'glaze'
 B12 Pale fuel ash slag
 C1 Fuel ash slag coloured by iron
 C2 Part-made glass with much unreacted silica (sand)
 C3 Base of a crucible containing glass
 C4 Dribbles of glass dropped during working
 C5 Cullet (pieces of scrap glass)
 C6 Waster from a pottery kiln
 C7 Red (copper-coloured) fuel ash 'glaze' on a crucible
 C8 Fluxed clay showing the liverish, purplish red colour due to iron

- C9 Corroded silver droplets on a crucible base
- C10 Gold droplets in a crucible
- C11 Clay mould for investment (lost wax) casting
- C12 One valve of a clay piece mould
- D1 One valve of a stone piece mould with holes to take locating pegs
- D2 Stone ingot mould
- D3 Casting of buckles that has not been cleaned up
- D4 Section through a 'bun' of smithing slag that collected at the bottom of a hearth
- D5 Smithing slag showing a variety of textures and colours
- D6 Section through a block of non-tapped smelting slag
- D7 A run of tap slag
- D8 A typical fragment of tap slag
- D9 Blast furnace slag
- D10 Lead smelting slag
- D11 Lead melting dross
- D12 Lead oxides and the pot in which they were produced
- E1 Translucent yellow lead glass in a crucible
- E2 Opaque red glass (enamel) in a crucible
- E3 Bone ash cupels
- E4 Heating tray with lead-rich vitreous surface
- ES Accidentally lead-fluxed tiles
- E6 Droplets of corroded lead trapped in melted glass from a window
- E7 Porous ironstone
- E8 Dense ironstone
- E9 Pyrites nodule—exterior and section
- E10 Section through a puddingstone boulder
- E11 Bog iron ore
- E12 Niedermendig lava

The underlying theme of this publication, and the conference on which it is based, is the need for a close liaison between the laboratory and the archaeologist. This is no less vital when the products and processes of metalworking are involved, but close collaboration is normally only apparent during the initial selection of samples for scientific investigation and the final discussion of the results. However, contact is probably even more important during the intervening period when key decisions are taken during the analysis or metallographic examination of the material. Since a complete description of a sample is impossible, choices must be made about the parameters worth investigation, the analysis method, the element concentrations to be measured, the size and location of the metallographic sample etc, and these decisions should be as much influenced by the archaeological perception of the material as by the material itself. Without the necessary liaison, archaeology may be reduced to a mere collection of objects, each with a different level of description, rather than acting as an integrated discipline that uses the material evidence as one factor in the overall assessment of a site or period. Additionally, the metallurgist is often left to make wider interpretations without being informed that the sample is unrepresentative or that any comments of the nature of contemporary industry are belied by other archaeological evidence.

If the ultimate aim of the laboratory work is an investigation of technological development or the control and manipulation of material resources, the increasing trend towards specialization and the separation of those working on different aspects of a technological complex may be equally damaging. The evidence surviving for one process is usually incomplete and further insight might be gained by looking at related industries. It has long been recognized that the elevated temperatures and atmospheric control involved in ceramic production can be paralleled in the conditions needed to smelt metal ores, but other similarities may be less obvious. For instance, the heat treatment of chert to produce changes in the mechanical properties of the solid (Bleed & Meier 1980) finds a degree of equivalence in the annealing of metals and, when the origins and development of metallurgy are considered, evidence for a knowledge of suitable raw materials also becomes of interest. This is particularly important for the Bronze Age because most metals would have been produced from mineral ores but few samples of the actual raw materials used have been recovered. Many brightly coloured metal ores can serve as pigments (Warren, this volume, 13-16), and there are isolated examples of the use of azurite, malachite, chrysocola, orpiment, realgar, cinnabar etc in the Bronze Age of southern Europe, Egypt, and the Near East. This at least indicates that these minerals were available, although they were rarely used as pigments because the natural

earths and manufactured varieties seem to have been preferred. Unfortunately, this means that the absence or demise of an ore pigment cannot be attributed to a restriction in supply, with a contemporary usage in metallurgy being demonstrated through any simultaneous change in the products of that industry. The preparation of synthetic pigments and the coloration of glasses, glazes, and faience also involves the use of minerals containing copper, tin, lead, zinc, cobalt, manganese, iron, arsenic, and antimony but, whilst the manufacturing processes are of interest, it is often difficult to determine the actual starting materials. Only when the producers of, say, copper-base metal, Egyptian blue pigments, and blue faience might have been drawing on the same raw materials can a combined study help to pinpoint their sources. For a situation like the Bronze Age in Britain, the metal industry itself has to provide most of the evidence about the resources being used. However, since industries might have been interrelated in some areas but not in others, any comments on the role and organization of metal-working must be restricted to the specific context.

As with any work involving provenance, the study of resource exploitation in early metallurgy centres on four main elements: the possible raw materials, the production processes, the products, and the scale of the industries. Cold, silver, platinum, copper, arsenic, and, to a lesser extent, lead, tin, zinc, and antimony all occur in the native form, but only the more noble metals of gold, silver, and platinum are found in sufficient quantities for this to be considered a major resource. Most metals have to be produced from ores (Table II). The main ores of lead are galena, anglesite, and cerusite; tin is usually found as the oxide cassiterite, and zinc today would normally be produced from sphalerite, although smithsonite (calamine) may have been more important in the past. For arsenic, antimony, and copper, the picture is more complex. The main ores of arsenic are often given as the sulphides--orpiment, realgar, and arsenopyrite--but arsenic is a constituent of around 130 minerals, or 12% of all known species. The small quantities of arsenic found in much Bronze Age material may have come from a variety of sources and not necessarily only from those that are clearly recognizable as arsenic-bearing. Antimony, too, is most easily identified in the form of the oxide or sulphide, but it is widely distributed as a minor or trace component of many other ores, as well as being a constituent of some of the more complex varieties. Chemical formulae, such as those given in Table II, can be misleading because they only give the composition of the pure compound. Few native minerals are pure, but the impurity elements are at such low concentrations that they are not reflected in the formulae. An extreme example is provided by the mixed ores of tetrahedrite/tennantite, where the chemical formula itself is imprecise

Table II Some common metalliferous minerals

Mineral	Chemical formula	Colour
<i>Copper ores</i>		
melaconite	CuO	black
cuprite	Cu ₂ O	red
azurite	(CuCO ₃) ₂ Cu(OH) ₂	blue
malachite	CuCO ₃ Cu(OH) ₂	green
chalcocite	Cu ₂ S	black
covellite	CuS	dark blue
chalcopyrite	CuFeS ₂	metallic yellow
bornite	Cu ₃ FeS ₃	iridescent
chrysocolla	CuSiO ₃ ·2H ₂ O	turquoise
chalcantithite	CuSO ₄ ·5H ₂ O	blue
atacamite	Cu ₂ (OH) ₃ Cl	green
pseudomalachite	6CuOP ₂ O ₅ ·3H ₂ O	green
<i>Arsenic ores</i>		
realgar	AsS	red
orpiment	As ₂ S ₃	yellow
arsenopyrite	FeAsS	silver grey
<i>Antimony ores</i>		
senarmontite	Sb ₂ O ₃	grey
stibnite	Sb ₂ S ₃	grey
<i>Lead ores</i>		
galena	PbS	metallic grey
cerusite	PbCO ₃	white
anglesite	PbSO ₄	white
pyromorphite	Pb ₄ (PO ₄) ₃ PbCl	green
<i>Tin ores</i>		
cassiterite	SnO ₂	grey
<i>Zinc ores</i>		
sphalerite	ZnFeS	yellow/black
calamine/smithsonite	ZnCO ₃	white
<i>Complex ores</i>		
enargite	3Cu ₂ S ₂ As ₂ S ₃	black
famatinite	3Cu ₂ S ₂ Sb ₂ S ₃	grey
tetrahedrite/tennantite	(Cu, Fe, Zn, Ag) ₁₂ (Sb, As) ₄ S ₁₃	dark grey
stannite	Cu ₂ FeSnS ₄	metallic grey
bournonite	CuPbSbS ₃	dark grey

because the concentrations of the major constituents can be very variable. These compositional variations within an ore body, which can extend to minor changes even within a single nodule, are a product of the processes that the minerals encounter during formation and weathering, and this can be illustrated by considering the evolution of a typical copper-bearing deposit.

The ultimate sources of rocks and minerals are molten magmas that solidify within the Earth's crust. They consolidate to yield agglomerations of minerals (igneous rocks) but, if the magma composition is favourable, localized concentrations of metalliferous minerals may also form. The solidification process is extremely complex, but three main stages may be recognized. The

high-melting-point rock-forming minerals separate first to leave a less viscous, metal-rich liquid. As the temperature falls further, part of this liquid solidifies to yield pegmatitic deposits that may include cassiterite, copper sulphides, and other sulphurous pyrites ores. The hot gases, representing the volatile constituents of the magma, and any residual aqueous solutions, penetrate into the surrounding rock and yield hydrothermal ore concentrations that are rich in common metals like tin, lead, gold, copper, antimony, and silver. The copper-tin ore complex of south-west England is an example of this type of deposit. These primary lodes may then be subject to metamorphic processes within the Earth's crust, but for the economically important deposits near to the surface the main agent of alteration is weathering. Any

sulphides exposed to the atmosphere tend to become oxidized and, therefore, a vein of galena and sphalerite might appear at the surface as a mixture of cerussite, anglesite, and smithsonite. The less noble metals oxidize most readily, and they can be leached out of mixed deposits, leading to a breakdown of complex minerals. Thus, a ferruginous copper-bearing lode might be capped with a gossan of iron and manganese oxides that intermingle with, or even conceal, the secondary copper minerals of malachite and azurite. Water also plays an important part in the weathering process. It can leach metals out of the upper layers of an ore body, only to redeposit them at the base of the water table to form an enriched zone between the primary ores and the oxidized surface layers. Sections through a typical ore deposit are therefore likely to reveal considerable horizontal and vertical variation in the minerals present, their relative concentrations, and the overall chemical composition (eg Constantinou & Govett 1972).

In all provenance work it is useful to be able to define potential source areas or, at least, eliminate those in which fieldwork would be less fruitful. The colours of the various minerals are given in Table II because their visual characteristics, which also include lustre and morphology, are their most diagnostic feature. Outcrops of coloured minerals would have attracted attention but, as Table II indicates, azurite and malachite are only two of a series of green and blue copper-bearing minerals. Many of these, including chalcantinite and pseudo-malachite, can hardly be classed as ores because they are difficult to smelt and give a very low yield. Therefore, source location cannot just be based on colour. It must involve identification of the minerals and some measure of the relative proportions of the species present because zones of mineralization are extremely complex and rarely contain an appreciable concentration of only one compound. There is no universal association between igneous rocks and ores comparable to that between obsidian and areas of recent volcanic activity, but the original composition of the magma determines the minerals produced and, thus, there can be some correlation between the host rock and any ore deposits that it might contain. The Cornish ore field provides a good example of the relationship between cassiterite and granite, and there is a similar association between gold and quartz veins. However, these minerals are seldom recovered from primary lodes. Their main sources are the secondary placer deposits that are formed after the breakdown of the host rock and the subsequent transport and redistribution of the constituent particles. This illustrates the difficulties involved in locating potentially useful ore deposits. Another problem is that some ore minerals are hydrothermal, ie they were generated when the residual liquid magma penetrated into unrelated, pre-existing rock formations. Additionally, where there is a primary association between the ore and the surrounding geology, this can be disrupted by subsequent weathering, erosion, and metamorphism.

Detailed geological surveys exist for many countries but their interpretation hinges on the subjective definition of what constitutes a viable ore body: witness the unresolved problem of the sources of tin in the Near East (Dayton

Table III Gross correlation between tin and arsenic content of European Bronze Age material

Number of artefacts with		
a	tin and arsenic contents both zero	1455
b	tin less than 3% and arsenic < 1%	1988
	arsenic 1-3%	1860
	arsenic > 3%	209
c	tin more than 3% and arsenic < 1%	2393
	arsenic 1-3%	372
	arsenic > 3%	8
<i>Source of the analyses: Junghans et al (1968)</i>		

1973/74; Muhly 1973). There are no fixed ground rules because an ore is merely a metalliferous mineral in a high enough concentration to be exploited economically. Ores with only a 5% copper content overall can be worked profitably today, but they are unlikely to have been very attractive in the Bronze Age. Because of these problems, most initial attempts to determine the raw materials in the early metallurgy of Britain focused not on the ores but on the composition of the metal products. Much of this work has now been superseded, but it is worth considering because of its residual influence.

Early analyses by Coghlan and Case (1957) and Brown and Blin-Stoyle (1959) indicated that Bronze Age metalwork from Britain and Ireland underwent changes in composition, related to some extent to chronological factors, and a similar pattern emerged from more wide ranging programmes on European material (Table III). Local perturbations can be easily swamped in a mass of data, and the chronological picture that emerged was the use of fairly pure copper, followed by copper with an appreciable content of arsenic, antimony, nickel and/or silver, with the copper-tin and copper-tin-lead alloys being introduced in the later stages of the Bronze Age. It was then argued, most cogently by Tylecote (1962), that this sequence could be related to changes in the type of raw material used. In this model, it was assumed that the earliest copper objects were made directly from native copper. Once smelting had been introduced, the oxidized ores were used first and these in turn were replaced by complex ores (eg tennantite/tetrahedrite) that gave the arsenic- or antimony-rich material. The final development was taken to be alloying, leading to the copper-tin bronzes and the copper-tin-lead alloys. An explanation was then needed for these changes, and it was suggested that they could be related to the stratigraphy within some types of ore body. With the native copper on the surface and the primary sulphide ores at the lowest depths, the sequence of raw material use could have been achieved simply by working down through a deposit and extracting each layer in turn. The introduction of alloying with tin still required an explanation, and arsenic was given the pivotal role. Arsenic contents of 1-6% improve the mechanical properties and castability of copper (Vaders 1954) to an extent that can be recognized and, as enriched ores can produce metal of this composition directly, it seemed logical that their use would have been favoured. Following the mechanistic theory, once the enriched ore zone had been exhausted the primary sul-

Table IV Selected analyses of Bronze Age metalwork

Period	Provenance	Object	%Sn	%As	%Sb	%Ag	%Pb
EBA	Castletown Roche, Cork Ireland Ireland Conlohan, Clare Portara Ford. Lough Erne Falkland, Fife	flat axe		2.0	0.93	0.28	0.20
		flat axe		1.38	0.34	0.20	
		flat axe		1.59	0.14	0.30	
		halberd		1.23	0.24	0.13	
		halberd		1.71	0.36	0.20	
		halberd		2.10	0.70	0.41	
	<i>Source: Coghlan & Case (1957)</i>						
LBA	Old Kilpatrick Edmonton Marsh Essex Reach Fen Ireland Essex	spearhead	8.9	n.d.	<0.05		0.02
		spearhead	12.5	0.26	0.085		0.13
		sickle	10.2	n.d.	<0.05		7.0
		chisel	6.2	<0.1	0.08		4.8
		knife	6.4	<0.1	0.12		4.1
		sword	8.2	<0.1	0.21		5.6
	<i>Source: Brown & Blin-Stoyle (1959)</i>						
LBA	Andover Wilburton Guilsfield Guilsfield Isleham River Thames	sword	9.42	1.09	0.90	0.27	1.5
		spearhead	9.26	2.15	5.24	0.43	8.9
		spearhead	5.54	0.98	0.63	0.17	8.7
		cake	9.92	0.93	1.57	0.20	6.5
		axe	6.91	0.58	0.69	0.22	10.5
		socketed tool	0.35	2.25	1.69	0.35	5.9
	<i>Source: Northover (1982)</i>						

phides would have been encountered and the quality of the copper reduced through a lowering of its natural impurity levels. A process of experimentation would then have been needed before it was found that the addition of some form of tin would improve the product.

This model usefully emphasizes the relationship between the composition of the raw material and the metal produced from it but, even there, some of the assumptions require modification. For instance, the purity of the metal was thought to be an indication of the use of native copper, and some native copper is indeed extremely pure. However, this is not always the case, and Maddin *et al* (1980) demonstrate that composition alone is a far from adequate criterion. Also, more recent analyses have shown that even Late Bronze Age tin bronzes can have high arsenic levels (Table IV), thus disrupting the supposed relationship between these two elements and, as was mentioned above, any arsenic or antimony found in a copper can derive from sources other than tetrahedrite/tennantite ores (eg Craddock 1979). However, the materialistic model was never meant to be a description of the actual situation at any given time or place. It was an attempt to explain change and its most abiding legacy has been the concept of Bronze Age metallurgy as a single self-propagating industry, isolated from external factors and motivated by its own logic, whereas much of the current archaeological debate views technology as only a minor component and the major influences as social and economic. It is of little value to suggest that improvements in the mechanical properties of the material were a motivating factor if the final products are viewed as non-utilitarian. As with any material, technical comments tend to promote the idea of progress and the optimization of resources, without allowing for stagnation or decline. They can therefore only achieve full relevance within the

total archaeological framework, although they can contribute to its modification.

Britain and Ireland are rich in metallic ores (Bowie *et al* 1978) but the deposits themselves provide little direct evidence of prehistoric usage. Most of the major sources, from the Shetlands to Cornwall, have been worked at some time, but extraction pits and mines are notoriously difficult to date. With an early date for workings at Alderley Edge resting on inconclusive evidence (Warrington 1981), and even the dating of the Irish mines at Mount Gabriel (Jackson 1980) being questioned (Briggs 1983), no metal ore mine in the British Isles can be securely dated to the Bronze Age. Thus the sources themselves provide no clear guidance on the areas, or even countries, from which resources were drawn. The absence of smelting sites or slag debris is equally inconclusive, as it is always possible that they await discovery, and ideas on the scale of the industries based on the distribution of the products are prone to subjective interpretation. One of the original views of metalworking was that it was a very important, specialized development, concentrated initially in only a few areas. The Neolithic stone axe trade (Davis, this volume, 33-5) offers some parallels, involving as it does long-distance transport of raw materials or semi-finished objects into areas that were not totally deficient in their own resources. However, several of the axe factories are in remote areas, and this suggests a degree of geological knowledge or, at the very least, that considerable areas must have been surveyed before suitable materials were located. If this interest in lithic materials is translated into the Bronze Age, it is highly unlikely that colourful ore deposits would have gone unnoticed. The idea that local ores would have been known, and therefore possibly exploited, was the basis of an influential paper by Scott

(1951) on the 2nd millennium BC in Scotland, and persists in some literature today. Thus, there are two extreme approaches—the idea of a highly organized, concentrated industry, comparable to those focused on the Bronze Age mining areas at Rudna Glava in Yugoslavia (Jovanovic 1979), Aibunar in Bulgaria (Chemik 1978), Anatolia (Giles & Kuijpers 1974), and Austria (Pittioni 1951), or the concept of small-scale localized activity. There is not necessarily any conflict because several different types of industry are likely to have been in operation during the long period occupied by the Bronze Age.

During the last decade, the study of British Bronze Age metallurgy has developed along three main lines—experimental work, a continuation of the analysis programmes, and a renewed archaeological interest in what the products of metalworking—actually represent. Experiments in smelting, conducted by the author in the field and others in the laboratory, have confirmed the theoretical predictions of the conditions needed for smelting and the changes in composition between ore and metal (eg Tylecote *et al* 1977). Loss of volatile elements like zinc, arsenic, and antimony can be appreciable, but it depends very much on the type of smelting process. The changes produced by the smelt, plus the addition of constituents—from the fuel within the furnace, all contribute to the final composition of the metal. -However, the analysis of a sample from an object has never been more than an estimate of the current composition of that particular part of the object, and the effects of smelting merely join experimental error, segregation, corrosion, alloying, etc as factors to be considered when analyses are interpreted. Despite these problems, gross changes in impurity patterns or the presence of specific elements can be used to classify analyses, and this is 'discussed further in Northover's paper in this volume (56-9).

In this paper, the discussion has concentrated on copper. This does not mean that the origin of the tin has been definitively resolved, but the possible sources in Cornwall, France, Spain, and Ireland are very limited. Lead isotope analysis has proved very potent in tracing the geological sources of lead and the silver derived from it, and one of the most interesting developments could be the application of this method to traces of lead in copper ores (Gale & Stos-Gale 1982). Whatever technique is adopted, the continuing problem of raw material exploitation will only find a solution through collaboration between the archaeologists and the laboratories.

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Introduction

The refractory ceramics found either on major metal-production sites or on metalworking sites which usually occur in a more general archaeological context include (1) fragments from smelting furnaces together with the associated tuyeres, (2) crucibles used for the purification of the metal and for melting the metal for casting, (3) moulds for casting ingots, artefacts, and coin blanks, and (4) fragments of crucible furnaces and forging hearths, again together with the associated tuyeres. In addition to their obvious typological characteristics, these metal-production and metalworking ceramics are distinguished by their vitrified or slagged surfaces, as well as by the slags and metal prills found in association with them.

In the scientific examination of these ceramics, the first aim must be to establish that they are indeed associated with metal-production or metalworking rather than with, for example, glassmaking, which makes use of a range of refractory ceramics that are often similar in appearance. Secondly, the scientific examination must be directed towards identifying the processes in which the ceramics were used: for example, what ores were smelted in the furnaces and what metals were melted in the crucibles or cast in the moulds? Thirdly, the technological details of these processes must be investigated: for example, what was the smelting temperature and the duration of smelting, and how were the crucibles and moulds heated, and to what temperatures?

In order to illustrate the range of information that can be obtained from the scientific examination of the refractory ceramics associated with metal-production and metalworking, results are presented for ceramics from a pre-Roman silver production site at Rio Tinto (Spain) and an AngloSaxon metalworking site at Netherton (Hampshire), together with those for a small group of Iron Age coin moulds.

Experimental procedures

Examination of the ceramics with a binocular microscope and the analysis of their surfaces using an X-ray fluorescence (XRF) spectrometer provides the first indication of the nature of any surface contamination and hence of the processes in which the ceramics were used. However, in order to carry out a full scientific examination of the ceramic, it is necessary to prepare a polished thin section from a slice cut from the ceramic as far as possible perpendicular to its surfaces. The polished thin section is then examined using a scanning electron microscope (SEM), an electron microprobe, and, to a lesser extent, a petrological microscope.

The extent of vitrification (ie glassy phase) and the pore structure developed as a result of firing are studied using

the SEM (Maniatis & Tite 1981). Typically, it is found that, with increasing firing temperature, the degree of interconnection between the particles making up a ceramic body increases until an essentially continuous glass matrix containing bloating pores develops (see Figs 23 and 24). Subsequently the bloating pores increase in size and become less angular (see Figs 19 and 20) until finally the ceramic suffers terminal distortion involving either massive bloating or slumping. Thus the vitrification 'gradient' developed across the ceramic as a result of its use in metal-production or metalworking processes can be defined. Typically continuous vitrification with coarse spherical pores (>50 μm diameter) is observed at the front surface of the ceramic which had been subjected to the highest temperature and either continuous vitrification with fine bloating pores (1-10 μm diameter), fragmented vitrification, or no vitrification is observed at the back surface.

The firing temperatures associated with the different degrees of vitrification observed in the as-received state are estimated by comparison with the vitrification developed in samples either taken from the lowest fired parts of the ceramics or taken from mineralogically similar ceramics and refired to known temperatures in a laboratory furnace. Hence the maximum temperature reached at the surface of the ceramic and the temperature gradient existing through the ceramic when it was in use are estimated. The temperature gradient reflects the extent to which heat penetrated the ceramic from the surface during use, and hence the length of time for which the maximum temperature at the surface was maintained. This time of operation for the process for which the ceramic was used can therefore be estimated from the temperature gradient data using the appropriate solution of equation for heat conduction (Tite *et al* 1982). Operating times for typical temperature differences ($T_s - T_i$) between the surface and various depths below the surface are given in Table V.

The contamination at the surface of the ceramic resulting from the metal-production or metalworking processes is analysed qualitatively using the X-ray spectrometer attached to the SEM, or quantitatively using the electron microprobe. In addition, trace concentrations of metal contamination are detected by the analysis, using optical emission spectroscopy, of scrapings taken from the inner surface of the ceramic.

Results

The information obtained on the metal production and metalworking processes from the examination of a range of refractory ceramics from Rio Tinto and Netherton and from the examination of Iron Age coin moulds are presented separately in the following sections.

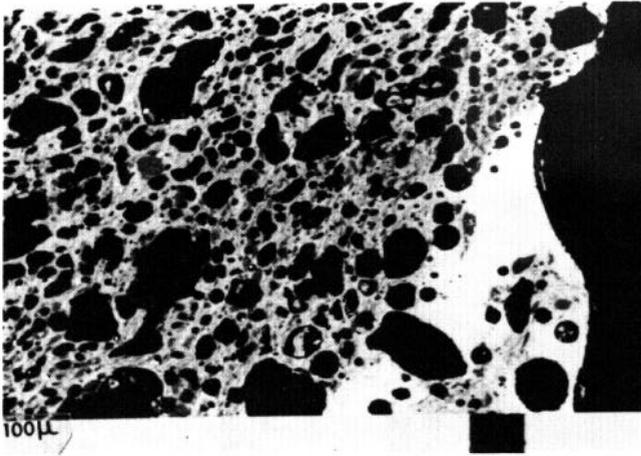


Fig 16 SEM photomicrograph showing patch of slag (white) and continuous vitrification with coarse bloating pores at the inner surface of Rio Tinto wall fragment (RT 68)

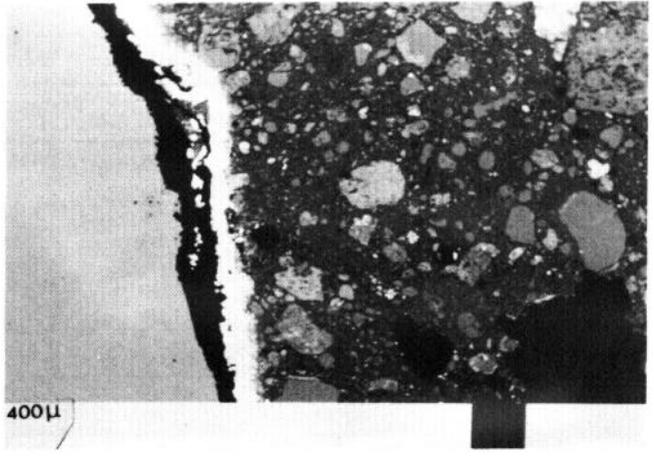


Fig 17 SEM photomicrograph showing layer of lead-rich glass (white) and no vitrification at concave outer surface of Rio Tinto wedge-shaped ceramic (RT 169)

Rio Tinto

Furnace wall fragments and wedge-shaped ceramics found with slags, ore, and metal in a deposit within the very massive ancient slag heaps at Rio Tinto (Spain) were examined. Rio Tinto was a major mining and smelting site at which silver production started about 800 BC, and at which both silver and copper were produced during the Roman period until the 2nd century AD. The group of material investigated was associated with pre-Roman silver production (Iberian : and-1st centuries BC) in which silver was extracted from jarosite ore (mixed metal sulphates) by smelting in the presence of lead. The silver was subsequently recovered from the lead by cupellation.

The vitrification 'gradients' observed through the furnace wall fragments (RT 68, RT 95) indicated that the maximum temperatures reached at the inner surfaces were about 1150-1200°C and that these temperatures were maintained for about 3-10h, a time which is consistent with the smelting of jarosite ores. Only small

patches of slag were adhering to the inner surfaces (Fig 16). This fact, together with curvature of the fragments, suggests that they originated from the upper part of the furnace.

The wedge-shaped ceramics (RT 154, RT 169) were characterized by a concave outer surface which was oxidized and an irregular slagged inner surface which was reduced. The concave surface was covered with a 50-100 um thick layer of lead-rich glass (Fig 17, Table VI), which contained immiscible globules of lead and trace concentrations (0.05-0.1%) of silver. The clay at this surface was not vitrified, suggesting firing temperatures of less than 900°C. At the slagged surface, the clay matrix was penetrated to a depth of 10-15mm by sinuous fingers of a fayalite slag (Fig 18) similar in composition to the plate slags found in association with the

Table V operating times determined from temperature gradients

Depth below surface (mm)	Operating times*		
	T _s = 1100°C T _i = 1000°C	T _s = 1200°C T _i = 1100°C	T _s = 1150°C T _i = 1100°C
5	30 min	35 min	2 h
10	2 h	2½h	9 h
15	4½h	5½h	20 h
20	8 h	10 h	34 h
25	13 h	16 h	

* Operating times are calculated assuming linear heat flow perpendicular to the surface of the ceramic and a thermal diffusivity of 0.005cm²/s. T_s is the temperature at the surface throughout the operation and T_i is the maximum temperature reached at specified depths below the surface.

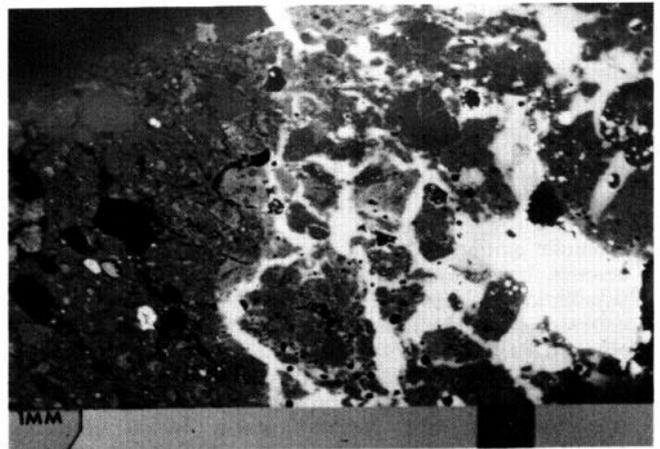


Fig 18 SEM photomicrograph showing sinuous fingers of fayalite slag (white) and continuous vitrification with coarse bloating pores at inner surface of Rio Tinto wedge-shaped ceramic (RT 169)

Table VI Electron microprobe analysis (%)

Oxide (% wt)	Rio Tinto			Nether-ton		
	1	2	3	4	5	6
Si O ₂	19.24	36.29	30.66	35.49	36.09	43.54
Ti O ₂	—	—	0.36	—	0.38	0.27
Al ₂ O ₃	5.83	4.94	4.46	3.94	6.04	4.86
Fe O	1.662	38.89	36.57	0.81	0.62	0.69
Mn O	0.14	—	0.08	—	—	—
MgO	0.34	0.50	0.70	0.37	—	—
Ca O	0.62	3.09	3.75	2.63	1.66	1.17
Ba O	—	9.70	8.56	—	—	—
Na ₂ O	—	0.70	0.20	—	—	—
K ₂ O	1.37	3.27	1.75	1.37	0.24	0.38
PbO	67.57	1.02	1.12	40.86	47.26	23.82
Cu O	—	—	0.09	6.54	5.78	16.35
As ₂ O ₃	2.00	—	—	—	0.52	9.92
Zn O	—	—	—	8.01	—	1.82
Sn O ₂	—	—	—	0.72	1.88	—
Total	99.67	100.04	88.30	101.09	100.85	102.89

1 Lead-rich glass on concave surface of Rio Tinto wedge-shaped ceramic (RT 154)

2 Slag penetrating Rio Tinto wedge-shaped ceramic (RT 154)

3 Plate slag from Rio Tinto (RT 181)

4 Lead-rich glass on surface of Nether-ton crucible (N 1664a)

5 Lead-rich glass on surface of Nether-ton crucible (N 1684a); metal droplets containing 70% Cu and 30% Ag also present

6 Lead-rich glass on surface of Nether-ton crucible (N 1705a); precipitated copper oxide also present in glass

refractory ceramics (Table VI). The degree of vitrification of the clay matrix indicated a maximum temperature at this surface of about 1150-1200°C, and the depth of penetration of the slag suggested a prolonged contact period.

The purpose for which the wedge-shaped ceramics were used is not at all clear. The similarity of the temperatures and heating times for the wedge-shaped ceramics and furnace wall fragments, and the similarity between the compositions of the slag on the wedge-shaped ceramics and the plate slags, suggests that the wedge-shaped ceramics formed part of a smelting furnace. If this suggestion is correct, the layers of lead-rich glass on the concave outer surfaces of the wedge-shaped ceramics could have resulted either from roasting lead-bearing ores against the furnace wall or from pouring impure lead, obtained from smelting, over the surface in order to promote oxidation of other metals (copper, antimony, arsenic, bismuth, etc) extracted from the ore, prior to cupellation. Either use would have been cost-effective in terms of using the heat generated in the furnace. In any reconstruction of the furnace, however, the fact that the clay used for the wedge-shaped ceramics contained abundant tuff fragments and was therefore different from that used for the furnace walls, which contained abundant shale fragments, must be taken into account.

Nether-ton

Crucible fragments from a metalworking area at the Late Saxon site at Nether-ton (Hampshire) were examined. In

addition to the crucibles, the evidence for metalworking at Nether-ton included hearths, pits containing charcoal, metal fragments (ie droplets, scrap, and artefacts), possible mould fragments, and some slag. Analysis of the metal finds indicated that copper alloys (ie bronze and brass, both leaded and unleaded), silver, and gold were being cast and worked on the site. There was, however, no evidence at this site for the extraction of these metals from their ores.

The crucibles examined were either shallow dish-shaped or more steep-sided thimble-shaped: both types were relatively thin-walled (5-7mm thickness). The vitrification observed in the SEM indicated that the operating temperatures for both types of crucible were typically in the range 1100-1200°C. For the dish-shaped crucibles, the vitrification tended to be slightly greater at the inner surface, suggesting that they were heated from above. In contrast, for the thimble-shaped crucibles, the vitrification tended to be slightly greater at the outer surface (Figs 19 and 20), suggesting that they were heated from below.

The inner surfaces of three of the dish-shaped crucibles (N1684a, N1664a, N1705a) were covered with a 200-400 µm thick layer of lead-rich glass (Fig 21) which contained significant concentrations of copper (both in solution and precipitated), zinc, arsenic, and tin (Table VI). This glass was most probably formed as a result of the reaction between molten lead and the body of the crucible. Metal droplets containing c 70% copper and c 30% silver were also detected at the surface of one of

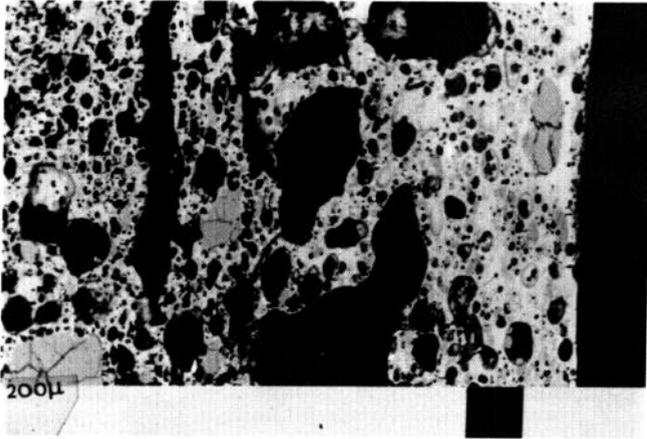


Fig 19 SEM photomicrograph showing continuous vitrification with coarse bloating pores at outer surface of Netherton thimble-shaped crucible (N 1608)

these crucibles (N1684a). On the basis of the surface contamination, these three crucibles could have been used either for the cupellation of scrap metal in order to retrieve the silver, or for melting leaded copper alloys prior to casting. In principle, it should be possible to distinguish between these two processes on the basis of the redox conditions (ie oxidizing for the former, and reducing for the latter), but unfortunately, the colours of the body fabrics do not unambiguously establish the redox conditions. However, in view of the (at least partially) oxidizing atmosphere implied by the colours and also the presence of Cu-Ag droplets in one crucible, it seems more likely that they were used for cupellation. Similar Late Saxon dish-shaped crucibles with lead-rich surface layers have also been found at Lincoln, York, Thetford, and Northampton (Bayley 1983).



Fig 20 SEM photomicrograph showing zinc-enriched layer (lighter grey) and continuous vitrification with medium/coarse bloating pores at inner surface of Netherton thimble-shaped crucible (N 1608)

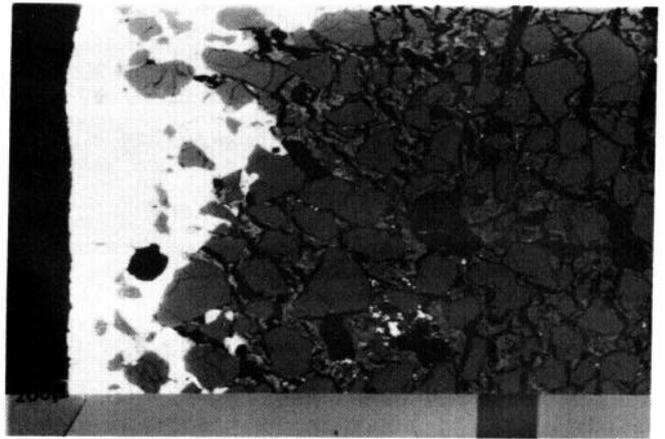


Fig 21 SEM photomicrograph showing layer of lead-rich glass (white) and fragmented vitrification at inner surface of Netherton dish-shaped crucible (N 1664a)

A fourth dish-shaped crucible (N1644) had occasional gold particles adhering to the surface and a comparatively high density of silver particles dispersed through the vitrified body at the surface (Fig 22). It seems probable therefore that this crucible was used for melting silver and gold alloys prior to casting.

A fifth dish-shaped crucible (N1553a) and two thimble-shaped crucibles (N1608, N1553b) exhibited no very obvious surface contamination when examined in cross-section in the SEM. Some dispersed zinc was observed in two cases (N1553a, N1608: Fig 20), but, in view of the high volatility of zinc, its presence at the surface is of very little assistance in determining the uses to which these crucibles were put. However, trace concentrations of copper and silver, which were higher at the inner sur-

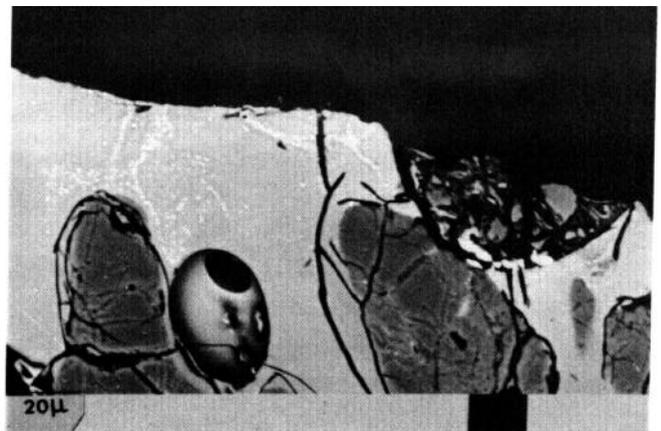


Fig 22 SEM photomicrograph showing gold particles (white) adhering to the surface on the right and small silver particles (white) dispersed through the continuously vitrified body at the inner surface of Netherton dish-shaped crucible (N 1644)

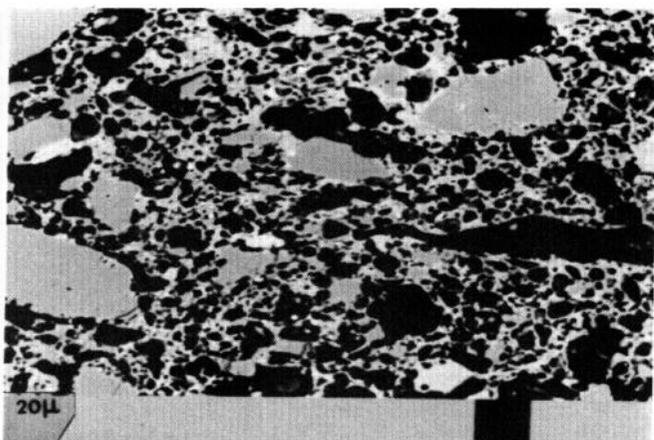


Fig 23 SEM photomicrograph showing continuous vitrification with fine/medium bloating pores at top surface of Cressingham A coin mould

faces than in the body of the crucibles, were detected by optical emission spectroscopy. This result suggests that these crucibles were also used for melting silver, and possibly copper, alloys prior to casting.

Coin moulds

A small group of Iron Age coin moulds from Braughing (Hertfordshire), from Cressingham (Norfolk), and Old Sleaford (Lincolnshire) were examined in an attempt to establish how they were used and to identify the metals cast in them. The coin moulds consist of fired clay blocks some 10-20mm thick in which there are a series of hollows some 5-10mm deep. The coinage metal was melted in the hollows to form blanks from which the coins were struck.

The SEM examination of the moulds indicated that the vitrification was greatest at the top and bottom surfaces

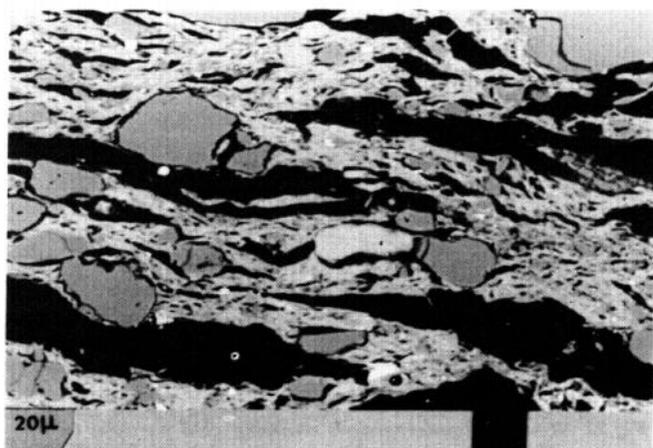


Fig 24 SEM photomicrograph showing fragmented vitrification at bottom of hollow in Cressingham A coin mould



Fig 25 SEM photomicrograph showing silver particles (white) adhering to the surface of a hollow in Cressingham C coin mould

of the mould blocks (Fig 23) and decreased towards the centre of the block. Similarly, the extent of vitrification at the bottoms of the hollows in the mould (Fig 24) was less than that at the surfaces of the mould block. The temperatures reached at the surfaces of the mould blocks were in the range 950-11150°C, with the higher temperature being reached at the bottom surface for some moulds and at the top surface for others. The temperatures reached at the bottoms of the hollows were in the range 950-1050°C. These results suggest that coin moulds were not only heated from above as proposed by Tylecote (1962) and Tournaire *et al* (1982), but that heat was supplied from both above and below.

Examination of the polished sections in the SEM for traces of the coinage metal melted in the moulds met with only limited success. A few small particles of silver were found adhering to the surfaces of the hollows in two of the moulds (Cressingham C and Braughing) studied (Fig 25), but no metal particles were found on the other three moulds. However, the analysis by optical emission spectroscopy of scrapings taken from the hollows revealed trace concentrations of both silver and copper on these latter three moulds (Cressingham A; Old Sleaford 1703 and 1750) whereas only trace concentrations of copper were found in the scrapings taken from top surfaces of the mould blocks. Hence all the moulds were almost certainly used for the production of silver coinage. For this purpose, the temperatures reached at bottom on the mould hollows (950-1050°C) would have been more than sufficient to melt the silver which, when alloyed with some 5-10% of copper, has a melting point in the range 900-950°C. Furthermore, it should be noted that the temperature estimated from the observed vitrification assumed a heating time of about 1h, and shorter times at higher temperatures would have produced the same vitrification.

Conclusions

The examples presented above provide some indication of

the range of information that can be obtained from the examination of refractory ceramics associated with metal production and metalworking. Firstly, analysis of the surface contamination of the ceramic fragments clearly assists in the identification of the processes involved, although it must be appreciated that the necessary diagnostic contamination is not always present on the ceramics and therefore success in identifying the processes cannot be guaranteed. Secondly, the study of the vitrification 'gradient' within the ceramics can provide valuable information on the technological details of the processes involved. However, it must be emphasized that, in order to obtain the full story of the metal-production and metalworking processes at a site, it is essential to supplement the results from the refractory ceramics with those obtained from the examination of any slags, ores, and metal fragments found at the site.

With regard to the availability of material for further work, metalworking sites tend to be associated with settlements, and in Britain those dating from the Roman period onwards are frequently found in urban contexts. They are therefore likely to be located in the course of general rescue excavations. In contrast, metal-production sites tend to be located close to the source of the ores in more rural contexts. Their excavation is therefore more likely to occur in the context of research projects whose specific aim is the investigation of early metallurgy. Possible topics for such research in Britain include Bronze Age copper mining and production sites such as Alderley Edge (Cheshire) as well as Bronze Age and later tin mining and production sites in Devon and Cornwall. When undertaking the excavation of metal-production sites, it must be remembered that metallurgical debris (ie ores, slags, refractory ceramics, etc) is essentially anonymous and cannot by itself be readily dated. For example, furnaces at Rio Tinto which were recorded in the 19th century as being Roman because of their proximity to Roman remains were almost certainly 18th century. In collecting metallurgical debris for detailed technological investigation, it is therefore essential that it is excavated from stratified deposits and that it is as fully representative of the overall range of available material as possible. Since many key ancient metal-production sites, including Rio Tinto, are currently being destroyed, a fully representative collection of such material is crucial, both for immediate examination and in order to provide a repository of samples for future study as the scientific techniques available progressively improve.

Finally, it must be emphasized that having attempted to reconstruct, for example, a smelting process from the study of the refractory ceramics and slags, the next step should be to carry out an experimental smelting based on this reconstruction. Comparison of the ceramics, slags, and metal from the experimental smelting with the ancient material then provides the basis for confirming the proposed operating parameters. At the same time, of course, the experimental smelting will provide invaluable information on many other aspects of the entire operation.

Acknowledgements

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The word 'complete' is in the title of this contribution to emphasize the interdependence of archaeological and technological approaches to the study and interpretation of metalwork from archaeological contexts of all periods. Too often the applications of metallurgy have been regarded as a separate, specialized entity and the benefits of a complete synthesis with more 'conventional' archaeological approaches have been lost. The ultimate aim should be to provide as effective a contribution to our knowledge of the social and economic environment of a site, or even a class of artefacts selected for research, as environmental studies now provide about the natural, human, and agricultural environment. The word 'non-ferrous' has been dropped from the original title to indicate that the thoughts set out here apply to all classes of metalwork. The sections below are designed to consider the overall approach to archaeometallurgical work in the context of an excavation or research project, ways of developing the external and internal examination of metalwork, the back-up that must be provided via experimental physical metallurgy, and ultimately some ways in which the conclusions might be presented. Space being extremely limited, the suggested procedures are set out as tables of questions, annotated where appropriate, which are designed to permit a common approach to all classes of metalwork.

Approaches

Historically, there have been two approaches to the direct examination of archaeological metalwork. The first approach, until recently applied virtually exclusively to non-ferrous and precious metalwork, comprised extensive programmes of compositional analysis and was overwhelmingly concerned with the provenance of the metal used. This work was inhibited for a long period by untested and erroneous assumptions about the organization of metal-working in the periods concerned, particularly with regard to the effects of recycling. In fact, provenance should be the final aim of analysis, as will become clear. The first steps should be to group material on the basis of common compositional and microstructural traits without any initial regard to provenance but always with due attention paid to the archaeological relationships of the material. From this, the standard alloys and techniques of an industry or site, or the lack of them, can be understood. As this type of data is accumulated, it becomes apparent that these change constantly with time and an important relative metallurgical chronology can be built up. Similarly, it becomes apparent that the sources of metal used in a particular area vary in the same way, and this conclusion does then demand an approach to the question of provenance. This can occasionally be solved, with luck, very quickly, but it generally requires a knowledge of metal compositions over a wide area, which takes time to

acquire. Nevertheless, the value of analysis in answering these questions has been demonstrated up to late Saxon times and there is no reason why it should not continue beyond. There are no *a priori* grounds for rejecting an analytical approach, as an adroit use of analysis and metallography, with a proper understanding of the archaeological record, can unravel the workings of an industry based entirely on scrap metal. It does not matter if the necessary data are not generated from a single site or find. Growing experience and a growing data base will eventually provide a full answer, although there is always an immense amount to be gained from just a single site.

The second approach is metallography, where an acid-etched surface is examined with a special microscope to investigate the microstructure of the metal. By this method, a corpus of data has been built up relating to metalworking, and this has been associated with the recording of alloy content and, increasingly, impurity patterns and inclusion analysis. This is very much becoming the standard in this country for both ferrous and non-ferrous metals and provides a much clearer view of the metallurgical history of each object, and a much greater range of data for reconstructing industrial traditions and groupings and habits of metal use. Indeed, it should become the rule that analysis and metallography are always combined, for a full interpretation of one is impossible without the other. All ancient metal objects are inhomogeneous and the adoption of such a system as this can exploit to the full the information contained in such inhomogeneities. This work should always be backed up by experimental studies of the alloys concerned because we are either dealing with unfamiliar alloys or with familiar compositions in unfamiliar situations, and increased knowledge of their physical metallurgy is urgently required.

Having established the general outlines of the metallurgical approach we must define the questions to be asked in just such an investigation. The metallurgical objectives can be summarized by asking:

Metallurgy:

- What is it?
- What is it made of?
- Where did the materials come from?
- How was it made?
- Why was it made like that?
- How was it used and how did use affect it?

These questions have their archaeological counterparts, some of which can probably only be answered with the metallurgical data so obtained:

Archaeology:

- What is it for and what is it doing on the site?

Where did it come from?
 How did it get there?
 How did its use affect the site or its users?
 Why was it found where it was in that particular state?

These two groups are clearly closely interrelated; although the archaeological and metallurgical data relating to an artefact, group of artefacts, context, or site may be acquired by separate processes, ideally their inter-relationship should be expressed by handling the two data sets as a single whole and presenting an integrated set of conclusions. Practical experience has shown that there cannot be strict demarcation between the archaeological and metallurgical approaches, and the organization of a particular piece of work should be dictated by the material and resources available and not by any *a priori* assumptions about its nature. Some of these questions can be answered for and from a single artefact, especially the what and the why. The where, and often the how, are likely to demand reference to a wide range of similar or contemporary material, but in many cases, from both the metallurgical and archaeological points of view, the necessary information is not easily available or does not yet exist. The necessary data bases can be constructed, but doing so requires the recognition that all metalwork recovered from excavations or archived in museums is potentially the source of such information and cannot be discounted. Only by the systematic study of all types of material, especially excavated metalwork with a well defined context, can the data bases be built up that will allow the fullest understanding of future recoveries. The routes to that understanding are outlined below.

External examination

The detailed external examination of any metalwork should be designed to be as productive as possible of both archaeological and technological data, if, indeed, they can be separated, and should be combined in a single description. The archaeological description is aimed at providing typological and chronological data, considering the external connections of a site as represented by the affinities of the objects, assessing the significance of decorative features, the effects of use, and so on. All too often in the past the examination has stopped there. Extending it to a range of technological questions not only generates specifically technological data, but also reflects on the archaeological interpretation; too frequently typological niceties have been debated at length and the fact that an object is in scrap condition completely ignored, with a biased interpretation as a result. The questions to be asked in an external examination are presented here in tabular form, classified into discussion of condition and techniques of manufacture, with a third section relating to industrial debris (excluding slag, the subject of the paper by Bayley, this volume, 41-4):

Conditions:

As-cast (untrimmed, occasionally still with runners and risers, signs of inverse segregation, etc)
 Semi-finished (trimmed but unworked)

Finished (wrought, fabricated, ground, polished, decorated)
 Used (signs of hafts, wear, sharpening, repair, etc)
 Worn/damaged (objects at the end of their life through wear or damage)
 Failed castings (cold shuts, poor filling, gassing, etc)
 Failed objects (in-service fractures, etc)
 Scrap (deliberate signs of breaking up, etc)
 Reworked objects for new uses

Techniques:

Mould type (permanent, ephemeral, investment)
 Mould/pattern/die links and sequences
 Worked areas (extent and character of working)
 Working techniques (hammered, rolled, drawn; tool types, etc)
 Finish (abrasive types and grades; decorative working)
 Coatings (plating, cladding, inlays; bronze, brass, (gold, silver, tin, iron, niello, etc)
 Decorative techniques (schemes and tools)
 Fabrication techniques (riveting, welding, brazing, soldering, burning-on, etc)
 Repair techniques

Industrial:

Casting jets, runners, risers
 Casting debris
 Chills, cores, etc
 Moulds
 Ingots
 Scrap
 Refractories
 Fixings (rivets, etc)
 Stock (bar, sheet, wire)

Analysis

For any real understanding of an object an analysis must be partly destructive, in that a sample is required. The primary aim of sampling is to present the metal in the most suitable form for the analytical technique required and to mitigate the effects of corrosion. Even if an object is to be examined whole, a part of the surface still needs to be cleaned. The routines described here are based on those for electron probe microanalysis as used at Oxford. This demands a solid sample that is mounted as a standard metallographic sample, and is also used as such so that metallography and analysis reinforce each other. The microprobe forms a focused beam of electrons which, when they strike the sample, produce a characteristic X-ray spectrum. The position of the lines in the spectrum is a function of the identity of the elements present and their intensity is a function of concentration. The spectrum is then analysed and the data used to produce a corrected composition, usually in weight-%. The instrument can be set to analyse points either singly, or in arrays or small areas. Detection limits are more than adequate for our present understanding of the metallurgy of the materials analysed, although ultimately the more sensitive analytical techniques available might be useful for the study of specific elements at very low levels when their behaviour is better understood. The microprobe can also function as a scanning electron microscope and can

provide a variety of images useful in an analytical context. The analytical routines regularly used are designed to provide information about alloying, impurities, and inhomogeneities which will relate to technique, industrial tradition, and provenance. The results should be examined with the following questions in mind:

Alloying:

Elements--Cu, As, Sb, Sn, Pb, Zn, Ni, O for copper alloys

Ag, Au, Cu, Pb, Sn, Zn for silver and gold alloys

Fe, C, P, N for iron alloys

(Assessing whether a particular composition represents a deliberate alloy or not can require considerable data and experience)

Concentrations of alloying elements

Distribution of alloying elements, which is an indicator of manufacturing techniques and metallurgical history

Estimation of control of alloying elements:

- 1 Direct control/mixing of individual elements
- 2 Modification of scrap supply by realloying
- 3 Modification of scrap supply by recognition and sorting of alloy types
- 4 Unmodified use of scrap supply

These questions can rarely be solved without reference to the associated archaeological data.

Impurities:

Elements--As, Sb, Pb, Co, Ni, Fe, Ag, Au, Zn, Bi, etc for copper alloys

Ag, Au, Cu, Pt, As, Sn, Zn, Pb, Cd, etc for precious alloys

P, S, Mn, Cr, Co, Ni, As, Cu, etc for iron alloys

Concentrations of elements; determination of usefulness as an indicator of provenance or of technology, or both

Distribution of elements

Distribution of elements at trace levels (eg Au, Zn, Bi in copper alloys; Pt in gold)

Correlation between elements

Inhomogeneity: Macroinhomogeneity

Normal, inverse, and gravity segregation as a function of manufacturing processes

Matings and other coatings

Microinhomogeneity

Dendritic segregations

Second phases

Insoluble components and their distribution (eg Pb, Bi in copper alloys)

Intermetallics (eg Pt group in gold alloys, speiss in copper alloys)

Non-metallic inclusions (oxides, sulphides, slags). These can be fossils of their manufacturing processes and (very importantly with slag inclusions in iron)

can be a very helpful indicator for grouping with provenance in mind. The importance of measuring particle size and distribution of these inclusions is also beginning to be realized

Porosity

Metallography

The techniques of optical metallography have been applied to archaeological questions for a very long time. It is possible that too much of an element of the routine has entered into this application. The integration of microanalysis with metallography has suggested that increased care in the identification of microstructural features is both desirable and necessary as there have been frequent misidentifications in the past. The images now available to us from the microprobe and the SEM enhance our metallographic abilities, and the availability of on-line image analysis techniques allows a much more quantitative approach to metallography. The purposes of metallography are to determine the microstructure of an artefact and to work out the processes that produced that microstructure. The questions to be asked are equally applicable to ferrous, non-ferrous, and precious alloy systems; they are divided below into general questions of microstructure and the investigation of special features, all of which can benefit from a combination of micro-analytical investigation. An important element in this work, although not detailed below, is the question of specimen preparation. Although there are standard routines, these usually have to be adapted for specific applications, and the question is too complex to discuss here. In metallography we consider:

Microstructures:

As cast (chilled, slow-cooled, furnace-cooled)

Homogenized (cast structure removed by high-temperature anneal)

Wrought

Wrought/annealed

Wrought/annealed/residual cold work, etc

Special features:

Dendrite spacing (gives indication of cooling rate, mould type, etc)

Grain size

Final cold work from manufacture or use

Residual coring in some cast structures (gives an indication of annealing temperature and number of working/annealing cycles)

Inclusion types

Inclusion morphology and deformation

Particle size distribution for inclusions and second phases (related to manufacturing methods)

Diffusion zones around particles, in bonding layers, etc

Hardness (macro and micro)

Examination of welded, brazed, and soldered joints

Examination of plating and cladding

Micro-examination of surfaces (abrasives/decorative techniques/fractography etc)

There are special features to the metallography of ferrous metallography, relating to the measurement

of carburization, the identification of nitriding and high-phosphorus phases, the deformation of inclusions, and the study of weld areas.

Experiment

With all the alloy systems considered there are many areas relating to extraction, mechanical and heat-treatment properties, and microstructure which are inadequately documented, and for which an extensive programme of experimental metallurgy is required. Fortunately this work is rapidly gathering momentum and vastly increasing our understanding of ancient metallurgy. The areas of interest include:

Replication:

Smelting techniques (furnace conditions, ores, fluxes, fuel, slag, refining)
 Casting techniques (behaviour of mould types, mould life, pouring conditions and their impact on microstructure, cooling rates, heat-flow parting compounds)
 Working techniques (tools, annealing cycles, etc, and resultant microstructures; effect of inclusions, major impurities)
 Finishing techniques (grinding, polishing, plating, etc)
 Special processes (coining, etc)

Economics:

Measurement of inputs (fuel, metal, refractories, labour, skill, etc)

Properties:

Mechanical properties of alloys; effect of minor alloying additions; heat-treatment properties
 Relationship between microstructure and processing
 Relationship between microstructure and composition
 Relationship between microstructure and properties
 Relationship between properties and impurity composition.

The objective of this work is to be able to use the data generated to interpret any microstructure for an archaeological context in terms of its manufacturing history and subsequent use, and to relate its condition to its context. In this way such experimental work is an important source of social and economic data, as well as more strictly metallurgical information.

Presentation

The presentation of archaeometallurgical data of the types described above is still evolving. This section is included simply to list what appear at present to be some of the most desirable objectives:

- 1 In cataloguing finds, the archaeological and metallurgical data for any single object should be combined.
- 2 For data processing, it is of assistance to reduce these data to simple variables, eg numerical description of typology, single variables to encode impurity pattern, hardness, grain size, alloy type.

- 3 Examination of behaviour of individual features such as alloying elements on a site, regional, or chronological basis.
- 4 Examination of behaviour of groups of elements.
- 5 Examination of other variables such as hardness, grain size, etc.
- 6 Comparison of metallurgical variables with:
 - typology
 - distribution
 - chronology
 - context
- 7 Development of multivariate statistics to combine metallurgical and archaeological variables.
- 8 Preparation of an integrated history of metallurgy and metal-use on individual sites, and viewing this in the social and economic context presented by the other aspects of the archaeology of the site. It is essential that the application of the procedures outlined above is not wasted by being presented as an isolated specialist report, although, of course, the data used may well be catalogued or processed separately. The conclusions are as much part of the interpretation of the site as any other.

Concluding remarks

Despite the brevity demanded by the format of this publication, I hope that sufficient indication has been given of the potential range of the metallurgical contribution to archaeology when freed from the rather limited applications made until recently. The procedures described above are appropriate to any site and any period. There are, despite the lengthy list of topics already given, important areas that really require a separate contribution: two such are the study of corrosion of artefacts, which occasionally uneasily straddles the division between metallurgy and conservation, and the use of stable isotope analysis, principally of lead, as a powerful indication of the provenance of some metals. In fact the issue of provenance has to some extent been deliberately avoided here. Experience has shown that in most cases a consideration of the immediate source of the metal, primary or secondary, is generally more important than identifying the hole in the ground from which the metal ore originally came. Only when considering the organization of extractive industries is a detailed consideration of provenance essential. The question of provenance in the past has tended to be related to non-ferrous metals only. Recently the provenancing of iron has become important, once it had been recognized that the widespread distribution of iron ore did not automatically mean equally widespread extraction. This leads to a useful concluding remark: archaeometallurgy is still beset by many fallacies, which only the development of a much closer relationship between metallurgy and archaeology will solve. One of the most tenacious of these is that if an ore resource was available locally it was necessarily exploited. In fact the economic demands of metal extraction generally meant that it was always easier to use a scrap supply if one was available, and this applies as much to iron as to copper. Equally importantly, the source of such a scrap supply might be totally different to the sources of technical inspiration of a site or industry.

Over the past few years the Royal Numismatic Society has taken a special interest in the chemical and physical analysis of coins, and this interest has come to practical fruition in the publication of two important reports. The first, *Methods of chemical and metallurgical investigations of ancient coinage*, produced after a conference on this subject had been held under the auspices of the Royal Numismatic Society, and edited by E T Hall and D M Metcalf, includes discussions of most of the methods available for analysis, together with a selection of type studies on coins of different metals, by a variety of different methods. This volume appeared as a Royal Numismatic Society Special Publication (No 8) in 1972. Analyses, once provoked in this fashion, continued unabated, so that in 1980, D M Metcalf and W A Oddy edited a further special publication (No 13), which included a selection of recent papers to continue the discussion of methods used, and their applications to coinages from the 6th century BC up to the post-medieval period. This volume, *Metallurgy in numismatics*, has the tentative suffix 1 in the hopes that it may become a continuing feature of the scientific numismatic world, perhaps to appear as necessary when there is an amount of good material awaiting publication. These two volumes, together with their bibliographies, give a very firm basis for future work and thought; I have introduced them in detail, rather than consigning them to impersonal footnotes, so that those not in continuous touch with the numismatic world may know something of their aims, their scope, and their genesis. Their contents form an excellent guide to current methods (see Table VII).

Almost all of these studies to date have been devoted to coins from recently found hoards or from specimens preserved for some time in museum collections. These coins are uniformly in good condition with little or no surface corrosion, and one would not expect them to deviate in any remarkable way from their composition as struck by the mint. The problem of surface enrichment or leaching out of metals preferentially from the surface of the coin can be minimized, and steps can be taken during analytical work to check its importance. I want to examine a completely different set of possibilities which arise from the future analysis of the great mass of coins found during excavations, the only coins of direct relevance to practical excavators and conservators, wherever they work.

I shall leave gold coins out of account. Coins from known contexts have a much greater archaeological value than museum specimens of the same coins whose origins are unknown. Only one or two in every hundred thousand coins that are excavated are gold. When these very rare finds are made they are often of types which to museums are 'common', so that they would add little information to the general sum of knowledge if they were examined

analytically. If any general analysis is to be done on such classes of coin, the museum specimens are more expendable than archaeological specimens.

Silver coins occur more commonly as finds both on excavations and in chance discoveries. These, in general, have been studied in detail (Table VII), although there remain certain gaps in our knowledge. Again, those gaps will probably best be filled from the study of good museum specimens or from the analysis of large numbers of coins of one type occurring together in a hoard. This leaves us with coins of bronze, which may contain an admixture of silver, lead, or other unexpected metals.

Whereas methods for the analysis of gold and silver coins have clear, easily definable objectives, and can thus employ standard techniques, the analysis of bronze coins is practised far less, and is open to much greater experiment. The study of gold coins has to date been principally concerned with the gold content of each coin, the

Table VII Methods of analysis

I = Hall & Metcalf 1972
II = Metcalf & Oddy 1980

<i>Chemical analysis</i>	Roman Imperial silver and bronze, I, 3-47
<i>Specific gravity</i>	Axumite gold, II, 73-82 Merovingian gold, I, 75-87
<i>Activation analysis</i>	Various gold and silver, I, 93-5 and 127-48 Merovingian gold, I, 88-92 Ancient gold, silver, and copper, I, 183-93 Crusader gold, II, 119-50
<i>X-ray fluorescence</i>	Roman republican silver, II, 55-72 Roman Imperial silver, II, 168-73 Roman Imperial bronze, II, 157-67 Various silver, I, 153-69 Byzantine base silver, I, 211-8 Byzantine copper, I, 2 19-34
<i>Lead isotopes</i>	Archaic Greek silver, II, 3-49 Ancient gold, silver, and bronze, I, 279-303
<i>Atomic absorption</i>	Medieval silver, II, 180-5 Anglo-Saxon silver, I, 195-210 Oriental silver, I, 195-210
<i>Comparative studies</i>	Greek electrum, II, 194-215 Various fine and debased gold, I, 171-82 Anglo-Saxon debased silver, II, 83-98
<i>Bibliographies</i>	Greek and Roman, I, 327-70 Early India, I, 371-81 Medieval and Islamic, I, 383-434

admixture of copper or silver, and the possible determination of trace elements which might help to determine the source of the gold coined. Silver coins have been analysed to determine their silver content; the associated lead has been examined by isotope analysis, again to try to locate the silver sources used. Trace metals may be considered for groupings of coins, or for sources of metals (see Table VII), although the risks of metal production influencing metal composition must be kept in mind. Since precious metals were continually re-used in the ancient world, time-consuming methods of analysis with the aim of pinpointing metal sources are seldom attempted unless there is particular reason to think that the coins being examined are free from re-used coin bullion. In these examples a particular metal is being followed in order to generate particular, and predetermined, information. These techniques have sometimes been extended to bronze coinage, but less time has been spent on them.

My purpose here is to follow a very different path. Rather than starting out in solution of particular problems, by agreed methods, on perfect specimens of coinage, I want to advocate the opposite: the experimental analysis of examples of the great quantity of very poor specimens of coinage, to see what happens. My justification is quite clear: the material is there and is not being exploited. The results are, by definition, not clear, even to the extent of not knowing in what area the answers might lie.

One or two negative points may be made. The results of such work will be of very little interest to pure numismatists, and even less to pure chemists. The pure numismatist is concerned with criteria of importance for coins related to the place of the coin in a historical framework, its place in a sequence of development, its face value, purchasing power, silver content, or place in a sequence of dies, punches, or moneyers. To the archaeologist most of these are irrelevant. What matters is that certain coins of minimal numismatic interest turn up in certain numbers in certain places, and are deserving of study as archaeological objects. The methods to be used in their study must be developed by pragmatic experiment: the right methods will be those that give interesting and repeatable results. They must, of course, be supplemented by orthodox analyses, but this might be the only point at which they touch the main body of chemical theory as it moves forward. The methods of study will be chemical only in so far as they have been developed by chemists; the subject will be numismatic only in as much as the matter for study consists of coins. The information derived from such studies will seldom help in the construction of the orthodox coin report, dates will be no more precise, nor will descriptions of emperors or reverse types be changed. Such information can be derived with reasonable accuracy simply by the coin specialist making use of what he can see on the coin as mediated through his experience of coin identification. What then are the positive points that might grow out of such a study?

Firstly, we need to know what happens to a coin when it is buried for two thousand years, and subjected to the leaching effects of weak solutions of humic acids, alkaline soils, or, in extreme examples, a graveyard environment. A very simple experiment on these lines would be to

section coins of very complex composition in order to check the complete metal content across the section: simple in concept, that is, though it could have considerable problems in execution. Such experiments would have to be carried out on coins of similar composition which had been buried under differing conditions: on the surface of bare chalk, in rubbish pits dug in limestone, in shell and acid sand, acid subsoils, and complex organic environments such as waterlogged rubbish pits and graves.

Armed with the knowledge which such analyses would provide, we could move on to the investigation of groups of coins. There are two main divisions here: the coins which belong to one site which will include many different types of coin, and the coins which belong to one coin type which will be spread over many different sites. The first group provides few obvious leads unless the site is particularly rich in one group of coins. Even then the information is likely to be gained by attacking the problem of types of coin rather than coins grouped by find-spot.

The types of coin must be detailed by time and space; where they came from, and when. Most of the coins found which belong to the first two centuries AD will be official products of the mint of Rome, produced according to an accepted and moderately well known standard. They will occur on British sites in small numbers and will generally not produce much new information. However, there are classes of early coin which will repay analysis, and these are the copies of official products, such as copies of Claudius I coins in copper or bronze. Since they seem to have been struck in response to an absence of official coin, their metal should be quite different from the coinage metals of the central government, and may well be freshly mined. It seems unlikely that they were all struck in one place or from the same supply of metal; they should therefore show differences of metal content, but whether this will concern whole percentages of difference in lead contents, or parts per million of difference in their trace elements, we do not know. This is the point at which empirical methods must be tried. Claudian copies ought to be analysed site by site to see if the differences in composition, which are bound to show up, vary according to the site. They should also be considered by weight, by stylistic grouping (excellent copies, reasonable, or execrable), and by diameter of the die and the flan. If the within-group variations in metal contents are greater than the between-group variations, we must assume a general homogeneity of production, while waiting for new ideas.

Similar questions regarding regular coins and copies arise in the 3rd and 4th centuries. The coins of the period AD 260 - 90 come from the regular mint of Rome or elsewhere in Italy, from the Gallic Empire mints of Lyon or Cologne, or 'from barbarous mints in France and Britain. While Italian and Gallic mints can be reasonably well identified stylistically, little progress has been made on the general attribution of barbarous radiate coins. Some of these barbarous coins were definitely made out of regular radiate coins which contained a percentage of silver; others were made out of worn sestertii which contained a percentage of zinc; others may be made of almost

pure copper. There is, of course, nothing to stop one barbarous workshop from starting production with one set of dies on metal produced by melting down sestertii, continuing with the same dies on some ingots of Welsh copper, and finishing off one or two batches from melted-down regular radiates. In this case the differing metal contents would say nothing about the place of production. But if Welsh finds had a high number of barbarous radiates made of copper, and sites in the south-east of England had a high number of coins containing zinc, progress would have been made.

Most important, once the initial analyses had established the standard levels of silver or zinc, or some other ingredient, levels of the order of whole percentages might be detected by very quick and simple spot tests. In this way whole collections of coins could be processed in one or two days. The presence or absence of silver could well be established by filing the edge of the coin until clean metal is seen, scratching the metal on an unglazed tile, and then treating some twenty 'smears' with dilute nitric acid to dissolve them, and with suitable reagents to effect the spot-test. Alternatively, X-ray fluorescence (XRF) would provide reliable results. Such mass-produced simple tests obviously depend for their success on previous exploratory analyses such as I have described above.

The question of minting of barbarous radiates is seldom in dispute; coins tend to be firmly classified as products either of the official mints or of barbarous mints. In the 4th century the division between regular coins and copies is far less clear, and here a large programme of analysis might well clear up many of our present problems. Thus there is a large number of coins of AD 330 - 41 on almost every site in Britain. Many of these coins are from the regular Gallic mints. Some of these coins have blundered legends, inappropriate *reverse* types, or very small flans, and these can immediately be classified by any worker, however inexperienced, as irregular copies. But there remain in every group of site-finds a number of coins which are not obviously regular, nor yet obviously irregular. The more experienced the worker the more of the doubtful group of coins he will classify as irregular. Thus our present uncertainty gives coin lists from different sites, by different workers, which are not comparable. It is suspected that all regular coins of this period contain a small but detectable amount of silver; a very small number of irregular coins of this period from the site of Wood Eaton (Oxon) have been shown not to contain any silver (King 1978). A programme of analysis is needed to establish the variations in silver content of undoubted regular coins, and to characterize irregular coins from as many different sites as possible. If some general principles can be established, whenever coins of this period are published an analysis can be included as an objective judgement of their place in the series.

It will easily be seen that I favour the development of this work without the imposition of rules. Our knowledge at present is so limited that we are not in any position to impose rules of research. Progress in the subject depends, as in archaeology in general, not on the plodding application of standard procedures, but on the flash of perverse insight which strikes out along new, and often insecure

lines. Once some guidelines have been established there might be a time when progress will be the swifter for the harnessing of effort in set ways to determined ends: we are not there yet. There is a quantity of material, there are students looking for topics for research, there are methods of analysis which are nondestructive or only slightly disfiguring. We need a period of putting these together in almost random order to select some ideas for future research.

Perhaps a postscript would be in order to consider, tentatively, the priorities which exist for the use of ancient coins. Any coin which has lost its archaeological co-ordinates is totally expendable unless it has a rarity in its own right as one of a small group of scarce coins. This does not mean that it *should* be destroyed, but that it may be destroyed if its owner considers that its destruction will further his interests or his knowledge. Any coin with an archaeological context is the preserve of the archaeologist. The first requirement is to find out what the coin is, and to derive all possible dating and other information from it. If the coin is obscured it must be completely cleaned. If there are a large number of coins to be cleaned (say 3 000), this is a matter not of ethics but logistics. In the absence of ten laboratory technicians with expert knowledge and a time span of ten years before the report is to be written, the answer lies in stripping the 3 000 coins to identifiable copper by the speediest methods available. If such methods limit the information which can later be derived from those coins, that is unfortunate, but cannot be helped. Any site which has produced 3 000 coins in one campaign is likely to yield a further sample if the site is revisited in order to collect more coins for a more ordered programme of analysis. And such limited sampling must (one hopes) shortly be recognized as a valid archaeological procedure.

Coins from unstratified deposits may be preserved without any chemical treatment for future sampling for chemical analysis. Such coins are then still the preserve of the archaeologist, not the museum curator who gives them shelf-room. Their purpose is to further knowledge, and they are therefore fair game for nondestructive analysis, with the inevitable concomitant of filed and scratched edges and polished surfaces. In rare cases, and with much heart-searching, they may be destroyed.

It is worth ending on a reflective note: that our current preoccupation with, and uncritical reverence for, the past, is a disease rare in history.

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Glass is an excruciatingly difficult material to interpret. As an artefact form it is not easily evaluated by analytical means: indeed, scientific research taken in isolation is a futile tool in assessing its archaeological significance. Glass is best understood by integrating the whole plethora of research fields that apply, including manufacturing technology, artefactual typology, social environment, and, not least, the historical framework in which it evolved. During the last two decades of glass studies the traditional emphasis has been on visual typology, from which has emerged the forms and seriations normally used as reference sets in archaeological reports. By contrast, a number of scholars have turned to 'black box' solutions, analysing specific items or groups of glasses by various methods in an attempt to solve pertinent problems that the material was seen to offer. These have included problems of colouring properties, decay mechanisms, compositional phenomena, or any of a string of issues specific to the material in question. What has been lacking, however, perhaps uniquely to glass studies, is the overview of the material technology which is the necessary preparatory stage before these issues can be most accurately investigated. The groundwork is formidable. It includes delving into the mundanity of the nature of the materials from which glass is made, into geochemistry, into the compositional attributes of organic materials, into the problems of changing sources, into furnace dynamics, and into the chemical complexities of colouring agents, each of which will influence, perhaps only in a discrete way, the character of the final product.

In Britain, vessel and window glass first arrived as a consequence of Roman forces and subsequently appeared with such ubiquity that the sources of manufacture, methods of distribution, the social market, and the general sequences of types are either known or can be inferred with reasonable conviction. It is when the Roman period ceases in Britain, the time at which Britain looks (unsuccessfully) to its own defence and becomes a technological eunuch, that the problems of glass studies are highlighted and the deficiencies of approach emphasized. The difficulties are easily illustrated. The questions that one would like to ask from the broad period AD 400-1500, such as 'where was glass made' or 'what exactly was it made from', are surprisingly unanswerable. The main part of the problem is caused by the nature of the material itself.

As a substance glass is enigmatic. It is essentially a supercooled liquid with an immense compositional tolerance, so much so that at one extreme its composition can be akin to ceramics and at the other to metal, although its physical state excludes it from being either. The fundamental composition relied on two readily available raw materials: a silica product, usually sand, and an alkali component which in theory could be provided by

either suitable geological deposits or by any one of an enormous range of plant or wood ashes. As far as the Roman and post-Roman period is concerned, the extant glasses can be divided into two very broad compositional types, the difference between them being not so much the relative proportions of sand and alkali as the nature of the alkali itself. The earlier alkali (Sanderson & Hunter 1980) was a substance called natron, a saline evaporite found in parts of Africa, and the later alkali was derived from organic ashes (typically from bracken, beech, or oak) and thus relevant to no specific location. The date of transition is discussed below. Analytically the two types are distinct in their major element concentrations, notably with regard to potassium, sodium, and calcium (Sanderson & Hunter 1980). This is perhaps an irrelevance to the archaeologist on the grounds that the difference is also visual. The later organic 'forest' glasses were much less durable than the 'natron' glasses in the extent of surface weathering, gradual opacity, and a predisposition towards disintegration. The broad differences between the two types are best illustrated using ternary diagrams (Iliffe & Newton 1976), which plot the glasses in terms of their molecular structure and express *relative* durability. However, the method does not show any discontinuity separating the two broadly distinct types, partly because of the range and overlap of concentrations in each group and partly because of the extent of experimental error. With regard to the latter, mention must be made of the surface properties of glass, which can affect the reproducibility of data derived from surface analytical techniques. This has now been studied in detail (Cox & Pollard 1977) and methods of surface preparation subsequently applied (Sanderson *et al* 1984). The two basic glass groups can be inferred but not fully resolved, nor for that matter can any additional 'concealed' groups be identified with any statistical conviction.

Until recently the knowledge we possessed about early glass was derived more from documentary records than from any pursuit of analytical investigation. These comprised passing, and often oblique, references such as those of Bede and Pliny, the more dogmatic manuals dating from the Assyrian cuneiform tablets through to Theophilus, Agricola, and Neri, and finally the accounts and rolls of the higher ranking medieval court and ecclesiastical records. This total corpus of sources, irrespective of bias, accuracy, or credibility, shows one corroborative phenomenon hard to equal in any other early material, that of the conservative nature of glass technology. In some respects this conservatism is understandable. From the point of view of chemistry glass is a material with such enormous flexibility of chemical composition that *a priori* changes which may have occurred may not even be observable within the tolerance of the final composition. Less understandable, however, is the conservatism of production techniques

which shows, for example, a furnace design in 17th century Jamestown, Virginia (Harrington 1952) virtually unchanged from our first recorded illustration belonging originally to the 8th/9th century and attributed to Hrabanus Maurus (reproduced in Hunter 1981, fig 99).

Changes, when they occurred in glass composition, did so for a variety of reasons. Glass manufacture was a process amenable to great flexibility and vulnerable to varying levels of human skills. It is unlikely that an awareness of chemical change or furnace dynamics was held by early glass practitioners. Craft is a more appropriate term than science. The changes which we have regarded as being significant and measurable are probably only red herrings. Given the generally nomadic character of glass production in north-west Europe, these changes are little more than proof of the glass industry's ability to adapt to different working environments, irrespective as to whether that environment and its resources belonged to the eastern Mediterranean, the Normandy forests, the Surrey Weald, or any other known location where production flourished. Compositional variation is the hallmark of a nomadic industry, and one might expect to observe it in either or both of the raw materials, the silica and the alkali components. This factor of itinerance signifies that compositional differences do not occur by design, but are the effects of change by accident, and are thus of some significance with respect to issues of provenance or dating. This alone makes the problem hard enough, but one must also include compositional variation caused by simple methods of pre-treatment of raw materials (Sanderson & Hunter 1981), changes in fuels, and the effects of that change not only on redox conditions but also when the spent fuel ash is used as the alkali source itself. Temperature and oxidizing atmospheres, combinations of which may oxidize certain elements present, accidentally *or* otherwise, into coloured states, must also be considered factors of change. The presence of cullet (glass scrap) and additives for colouring or decolouring have obvious significant compositional effects, and the two-phase process of manufacture itself—the fritting (the solid-state reaction between the two raw materials) and the melting (the glassy state achieved)—provides its own variables. The parameters for potential innovation either independently or in combination are infinite. Hence, if one wishes to determine latent factors of characterization or provenance, this maze has to be untangled and sorted into its component areas across the whole spectrum of elemental composition, major, minor, and trace.

The most surprising aspect, given the vulnerability to change in so many quarters, is that so little *visual* innovation appears to have taken place within the appearance of the final product. The wide tolerance of glass chemistry is partly a cause, and to some extent this belies the skills of the maker whose craftsmanship lies not simply in his ability to produce glass *per se*, but to produce it at a respectable level of clarity, despite variation in composition, contamination, and the inconstancy of a recalcitrant furnace. Within the total infrastructure of potential change a certain sublevel of compositional change must be attributed to the rectification of the effects that accidental innovation by these means might have created.

The prime feature of glass was clarity, unobtainable in any other artefact material, and therefore preservation of this aesthetic quality was critical to the production process. Perhaps the choice of materials was not always within the glass master's control, but at least he had some powers by which their detrimental effect on the final product might be rectified. It is along these lines that some form of quality control must have been exercised, perhaps even to the extent that compositional phenomena in a group of glasses reveals not so much the idiosyncrasies of slightly different materials but rather the skill of the glass master in counteracting their effects. Suffice it to say that his activities are heavily disguised in the analytical data.

Colour is particularly relevant here. Coloured states could be achieved to a certain level, and within a certain range, without the use of deliberate additives simply by exercising appropriate control of melting conditions. A glass melt containing iron and certain levels of manganese or antimony could be decoloured in this way, and more recent work has shown that a whole range of other colours might be similarly produced, depending on the contaminant elements present. Beechwood, for example, contains sufficient manganese to act in this way, and its usefulness was noted as early as the medieval period by Theophilus. The problem, however, is that, unless detailed knowledge is obtained regarding the exact composition of the raw materials (perhaps through methods of elemental correlations), it is difficult to determine whether a particular colouring/decolouring element represents an impurity or a deliberate addition. An essential research area now lies in providing an objective method of colour assessment for glass by which colour definition plotted on chromatic co-ordinates can be related to analytical data. This may provide the link between aesthetics and expertise in early glassmaking, and preliminary results have already demonstrated its value (Hutchings & Sanderson 1981). One possible example can be gleaned from early post-Roman Europe at a time which one might justifiably consider to be a period of general political instability. Barbaric taste was different to classical taste, the supplies of essential materials were likely to have been disrupted, and the somewhat inferior wares produced (initially at least) appear to reflect lower standard of craftsmanship. Throughout Britain and the Continent large numbers of vessels occur exhibiting unusual, but not displeasing, colours typically of brown, ochre, yellow, mauve, dark blues, and greens. Although it is possible that these were the products of deliberate colouring, it seems more likely that they represent declining standards in which strict control of furnace conditions was either not followed or was deemed unnecessary. Hence the colours that emerge are the results of the minor and trace components of raw materials whose combined effects would under normal circumstances have been counteracted or neutralized by the expertise of the glassmaker. There is no discernible major compositional change that marks a Roman vessel from an Anglo-Saxon vessel, but there is this aesthetic change which might be put down to technological differences in the broadest sense.

The early glass industry was conditioned by a number of

economic and social factors, the effects of which may be of some significance in interpreting analytical data. At one extreme are the lives of the workers who produced the gigantic 9t block of glass at Beth Shearim in the Middle East, and at the other the workers in the English Weald who eked out a semi-nomadic existence. Through patronage, the former could rely on supplies of consistent raw material, thus retaining compositional tradition, as opposed to the latter, who relied on medieval market forces, constantly moving from place to place and inadvertently providing innovation to their glass composition. It would be more helpful to the analyst if more furnace sites could be identified to provide a better perspective for localized compositional characterization, but the archaeological picture is bleak, and provenance theories are largely unproven.

Only a handful of furnace sites can be identified from the Romano-British period, and thereafter it is not until Blunden's Wood (Surrey), dated to the 14th century (Wood 1965), that subsequent examples are known. The intervening period contains a number of possible sites: at Glastonbury (Radford 1958), at Coppergate, York (P V Addyman, pers comm), and at Saxon Hamwih (M Brisbane, pers comm), but in all three the evidence is frustratingly tantalizing. The problem also applies to a late 7th century spate of ecclesiastical glazing now evident on a small number of sites, notably at Winchester (Hunter, forthcoming) and the monasteries of Jarrow and Wearmouth (Cramp 1970). Windows were glazed with highly coloured quarries of durable glass cut into mosaic shapes, and provide a sharp reminder of the skills of the period. Continental craftsmen were probably imported to carry out the work, but as yet it is not possible to determine whether they brought ready-made glass with them or whether they started from scratch with local materials. The difference is between glass-working and glass-making respectively, the former being significantly less technologically demanding, and known to have occurred on a number of Dark Age sites in western Britain and Ireland. The strength of Christian patronage cannot be overestimated. Together with Gothic architecture, it provided the main impetus for glazing skills in the Middle Ages and has numerous implications. Apart from the introduction of decorated windows in the late 7th century, it was also responsible, several centuries later, for the glazing of Wolvesey Palace, Winchester, using a specially created durable glass at a time when non-durable (forest) glass was being used elsewhere in the town. Patronage, it seems, had revived a recipe and re-introduced a former tradition.

Archaeologists are understandably concerned with matters of provenance and dating to which glass studies are particularly unsympathetic, mostly for reasons of compositional difficulties outlined above. The majority of investigations into early glass have centred on the nature of raw materials through major element concentrations. It is, however, *not* to the major elements that the problems of provenance or localized manufacture can be set, partly because the major elements are not the most promising discriminants and partly through the lack of known furnace material on which to base a discriminant programme. Some likely raw materials, vegetable ash in

particular, can exhibit bulk compositional variation within a single locality, and this may mean that major element compositions are only consistent to a high degree of precision within a single pot batch of glass. This was the case in the analysis of window glass from Repton, St Wystan (Sanderson *et al* 1984, table 4), where the elemental standard deviations were considerably smaller than those of other groups of glass. One is essentially obliged to define as closely as possible the character of each raw material, and the analytical approach assumes that these component sources actually possess characterizing attributes. The assumption is a fair one for a geological material (ie natron), which, according to modern research, was geologically deposited in only a small number of locations in Africa, the most accessible being the Wadi Natrun in Egypt. There is little doubt that this produced the durable Roman and early post-Roman glass, although at the same time it is hard to believe that natron was still traded across the length of Europe during the course of Barbarian and Islamic uprisings. There may indeed have been a more local substitute, but its characteristics are not apparent at major element levels and its existence thus remains unverified. The later forest products lack the overall consistency of natron-type glasses and thus provide a broader spread of analytical data, making characterization extremely difficult. These forest products were not thought to have occurred in Britain until the end of the 1st millennium, after which time they characterize the glass composition of the medieval period proper. However, more recent excavations, notably at Winchester, have produced forest glass of similar composition undisputedly dated to the late 9th or early 10th century (Yates 1983), clearly demonstrating that durable and nondurable glasses were contemporary and that no absolute date of changeover can be determined. The Winchester evidence alone shows an overlap period of approximately 300 years. This observation is relatively new and has passed hitherto unnoticed, partly through the decay characteristics of the forest glass. Depending upon buried conditions, forest glass could decay not only to a point at which it became unrecognizable as a vitreous material, but also to a point of total disintegration due to internal decomposition. Its absence may be the simple result of its inability to survive. Glass studies now need the archaeologist to come forward with stratigraphically dated pieces in order that the true lifespan of this type of glass can be more accurately ascertained.

What must be already clear is that, although glass is potentially a valuable material to investigate by analytical means, much of the groundwork still remains to be done and the pertinent issues of provenance and dating are as yet not fully tenable. It may be possible, taking a full range of elements and using methods of statistical correlation, to identify specific raw-material types and perhaps relate them to visual vessel types. However, the absence of furnace material entails that any characterization that might be inferred is in *vacuo* and impossible to relate either to a specific material or to a particular location. Nevertheless, even the presence of groupings at this level can be of exceptional value if only in indicating the probability of different vessel types

being produced in different centres (Sanderson & Hunter 1982). This at least is a start and hopefully serves to emphasize the difficulties of interpreting this complex man-made material and to stress the total inappropriateness of 'black box' solutions for an artefact study still in infancy.

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Introduction

The important role of the microscope in the identification and understanding of early materials is well known. However, there are unfortunately limitations to the conventional light optical microscope. First, the magnification which can be achieved is limited to about $\times 1\,500$, and secondly, the depth of focus is very small, so that features on the sample which are not at the same height are not in focus at the same time. For this reason planar samples such as the polished metallurgical sample or the biological or geological thin section are generally prepared for detailed studies using light microscopy. The scanning electron microscope (SEM) overcomes the difficulties mentioned so that very fine details on an irregular sample (down to below one hundred-thousandth of a millimetre) may be seen with both the 'hills' and the 'valleys' in focus.

Principles of operation

The basis of the SEM is relatively simple. A very narrow beam of electrons is generated by heating a wire filament (as in a light bulb) to a high temperature under a strong electrical potential. This beam passes down a cylindrical 'column' about 1m long, around which are a series of electromagnetic 'lenses' which allow the beam to be focused and moved. At the base of the column, the electrons hit the sample and generate a number of different types of signal. A signal from the sample may be converted electronically to provide an image of the sample on a TV screen.

Types of SEM image

Two types of SEM image are commonly seen in the SEM photomicrographs reproduced in the archaeological literature, and an appreciation of the essential differences between them greatly improves one's understanding of the information which they convey.

Secondary electron images are based on the signal of the electrons knocked out of the surface of the sample by the incident electron beam. These secondary electrons have low energies, and can easily be drawn into a collector from all over the surface of the sample. Stronger signals received from the 'hills' than the 'valleys' result in the familiar SEM image which shows the relief or morphology of the sample in shades of grey, grading in to one another without sharp boundaries.

Back-scattered electrons are the primary electrons of the beam bounced back from the sample. Heavier elements are more efficient electron reflectors than light elements; thus areas rich in a heavy element such as iron or lead appear brighter than those rich in a light element, eg carbon, silicon, or oxygen. Back-scattered electron images show the make-up of an object in terms of the different

phases or chemical compounds of which it is composed. These are usually separated by sharp boundaries which show up in microphotographs as sharp changes in grey level (eg see Figs 16-25 in Tite *et al*, this volume, SO-5).

Typically, secondary electron images are used in the study of the morphology of materials (eg wood, bone, tool and wear-mark studies), while back-scattered images are used in phase analyses related to chemical technology.

Chemical analysis

A third signal which results from the incidence of electrons on a sample is the generation of X-rays. X-rays are a form of electromagnetic radiation like light, and in the same way may be characterized by their energy or wavelength. Each chemical element emits a spectrum of X-rays of a unique series of energies, and a specimen composed of several elements emits the X-rays of each in proportion to the relative amount of the elements present. Many SEMs have the facility to display this X-ray spectrum on a TV screen, and this spectrum gives a qualitative indication of the composition of the sample, ie which elements are present, and whether they are in high or low concentrations. In principle, it is only a short step to compare the X-ray spectrum emitted by the sample with that of a standard of known composition to give a fully quantitative analysis, but the reality is somewhat more complex. In particular, the conditions under which the unknown sample and the standard are analysed must be identical. In addition, it is desirable that the distance the X-rays generated have to travel through the sample is kept to a minimum. These factors impose design constraints, so that an instrument which is a good microscope is not necessarily a good microanalyser. Thus a second instrument has evolved in addition to the SEM, known as the *electron microprobe*. The microprobe is very similar in major components to the SEM, but incorporates features particularly favourable to accurate micro-analysis, rather than image formation which takes second place.

The X-ray analytical systems typically attached to SEMs analyse the X-ray spectra on the basis of the energies of the X-ray peaks. This technique, known as energy-dispersive analysis (EDA), can detect elements present in amounts down to about 0.1wt-%, but accuracy and precision are poor for concentrations below about 1%. On the other hand, the microprobe allows analysis of the emitted X-rays by their wavelength. Wavelength dispersive analysis is more expensive and time-consuming, but considerably more sensitive and accurate for elements present in small amounts, and its limits of detection are normally about 0.02wt-% element. An additional advantage of wavelength dispersive instruments is the ability to produce X-ray maps. In this case, the electron beam is scanned over the specimen and a dot-density

image is formed on the basis of the number of X-rays associated with a particular element emitted from each area, the density of the dots being dependent on the concentration of the element chosen for analysis.

Cost and availability

Until recently the design limitations discussed above meant that in buying an instrument one was obliged to choose between a good microscope and a good microanalyser, the cost of the latter ranging into several hundreds of thousands of pounds. However, improvements in SEM design and analytical software have led to the development of SEMs with good facilities for fully quantitative energy dispersive analysis for prices in the range £50 000-100 000. This is still prohibitively expensive and if an archaeologist has a problem which requires the application of an X-ray microanalytical technique he/she is obliged to approach an institution which houses a good SEM or microprobe. These are generally university departments-metallurgy for metals and geology for materials such as glass and ceramic which are composed of light elements. Expertise in one material does not necessarily imply that a good analysis will be produced from another. Ideally, one should always consult somebody who has expertise in both the technique and the materials of interest rather than accept a microprobe analysis at face value.

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