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PART I

THE ROLE OF ANALYTICAL CHEMISTRY IN ARCHAEOLOGY

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ARCHAEOLOGY AND ANALYTICAL CHEMISTRY

This chapter aims to place the role of analytical chemistry into its archaeological context. It is a common fallacy that archaeology is about things – objects, monuments, landscapes. It is not: archaeology is about people. In a leading introductory text, Renfrew and Bahn (1996: 17) state that "archaeology is concerned with the full range of past human experience – how people organized themselves into social groups and exploited their surroundings; what they ate, made, and believed; how they communicated and why their societies changed". In the same volume, archaeology is called "the past tense of cultural anthropology" (Renfrew and Bahn 1996: 11), but it differs from anthropology in one crucial and obvious respect – in archaeology it is impossible to interview the subjects of study, or to observe them directly in their everyday life. Archaeology therefore operates at a very different level of detail when compared to anthropology. Inferences about past societies are made from the material evidence recovered by archaeological excavation – sometimes in the form of surviving artifacts or structures (i.e., the deliberate products of human activity), but also from associated evidence such as insect remains, from which environmental and ecological information can be derived. Sometimes it is the soils and sediments of the archaeological deposit itself – their nature and stratigraphy – which provide the evidence, or add information by providing a context. Hence the often acrimonious debate about the effects of looting or the undisciplined use of metal detectors, where objects are removed from their contexts without proper recording. It is always the case that information is lost, sometimes totally, when an object is removed from its archaeological context without proper recording.

Although archaeology is a historical discipline, in that its aim is to reconstruct events in the past, it is not the same as history. If history is reconstructing the past from written sources, then 99.9% of humanity's five million years or more of global evolution is beyond the reach of history. Even in historic times, where written records exist, there is still a distinctive role for archaeology. Documentary evidence often provides evidence for "big events" – famous people, battles and invasions, religious dogma, and the history of states – but such written sources are inevitably biased. History is written by the

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literate, and usually by the victorious. We do not have to look far into our own recent history to realize that it can obscure the past as well as illuminate it. In contrast, archaeology is generally the unwritten story of the unnamed common people – the everyday story of how they lived and died.

At the heart of archaeology is the process of reconstructing past events from material remains. It is this focus on material evidence that creates the need for scientific approaches to the past. Since every archaeological excavation might be thought of as an unrepeatable scientific experiment (in the sense of a data-gathering exercise that can only be done once), there is a practical and moral requirement to extract the maximum possible information from the generally mundane collection of bones, stone tools, shards of broken pots, corroded metalwork, and biological assemblages that constitute the vast bulk of archaeological finds. Trade routes are inferred from fragments of broken glass or pottery manufactured in one place but found in another. The economies of ancient cities are reconstructed from a study of the animal bones found on midden tips. In this respect, archaeology has much in common with modern forensic science – events, chronologies, relationships, and motives are reconstructed from the careful and detailed study of a wide range of material evidence. In order to set the scene, it is instructive to challenge new students in the study of the science of archaeology to name a scientific discipline that has no relevance to modern-day archaeology. One can easily go through the scientific alphabet, from astronomy to zoology, and find many obvious applications. It is possible, of course, to carry out the same exercise in the social sciences, and also in engineering and medical sciences. Since the subject of study in archaeology is the whole of human history, it is not surprising that few (if any) academic disciplines exist that have no relevance or application to archaeology. It is inherently an interdisciplinary subject.

There are a number of more or less comprehensive published histories of scientific analysis applied to the study of past peoples and materials. Caley (1949, 1951, 1967) summarizes the early applications of chemistry to archaeology, and a review paper by Trigger (1988) gives a general overview of the relationship between archaeology and the physical and biological sciences. A collection of recent scientific studies, largely relating to museum objects, including dating, authenticity, and studies of metalwork, ceramics, and glass, can be found in the edited volume of Bowman (1991), and Henderson (2000) provides an overview of the information derived from scientific studies of a similar range of inorganic archaeological materials. Many conference proceedings (especially those entitled *Archaeological Chemistry*, produced by the American Chemical Society [Beck (1974), Carter (1978), Lambert (1984), Allen (1989), Orna (1996), Jakes (2002)], and also the published proceedings of the *International Archaeometry Symposia* [see website]) contain a very wide range of chemical studies in archaeology. Of the several

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books covering the chemical aspects of archaeological science, Goffer (1980) gives a very broad introduction to archaeological chemistry, covering basic analytical chemistry, the materials used in antiquity, and the decay and restoration of archaeological materials. More recent publications include Pollard and Heron (1996), which gives a basic introduction to instrumental chemical analysis followed by seven chapters of case studies, and Lambert (1997), which has eight chapters, each one based on the study of a particular archaeological material. The ‘‘standard works’’ on science in archaeology include Brothwell and Higgs (1963, 1969), Ciliberto and Spoto (2000), and Brothwell and Pollard (2001), but earlier general works such as the eight volume *A History of Technology* (Singer 1954–84), *Thorpe's Dictionary of Applied Chemistry* in twelve volumes (Thorpe and Whiteley 1937–56), and the monumental *Science and Civilisation in China* (Needham 1954–2004) contain, amongst much else, masses of information derived from chemical studies of archaeological material.

1.1 The history of analytical chemistry in archaeology

For the reasons given above, there is a strong moral and practical requirement to extract the maximum information from the material remains recovered during archaeological investigation. Of prime importance in this endeavor is the application of analytical chemistry, now taken to mean instrumental methods of chemical analysis for the detection and quantification of the inorganic elements, but also including a vast array of methods of organic analysis, and (more recently) techniques for the measurement of isotopic abundances for a range of elements. The long history of the relationship between archaeology and chemistry has been described in detail elsewhere (Caley 1951, 1967; Pollard and Heron 1996). Much of this history has focused around the use of analytical chemistry to identify the constituents of archaeological artifacts. Initially this stemmed out of a curiosity to find out what these objects were made from, but, very quickly, more sophisticated questions were asked – most notably relating to *provenance* (or, in the US, *provenience*, but see below). The term here is used to describe the observation of a systematic relationship between the chemical composition of an artifact (most often using trace elements, present at less than 0.1% by weight) and the chemical characteristics of one or more of the raw materials involved in its manufacture. This contrasts sharply with the use of the same term in art history, where it is taken to mean the find spot of an object, or more generally its whole curatorial history. In fact, a recent North American textbook on geoarchaeology has used the term *provenience* for find spot, and *provenance* for the process of discovering the source of raw materials (Rapp and Hill 1998, 134). Although this is an elegant solution to a terminological inexactitude, it has not yet been universally adopted, at least in Europe. Since provenance has been such a dominant theme in

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archaeological chemistry, further consideration is given below to the theory of provenance studies.

The history of analytical chemistry itself has relied extensively on the contributions of great scientists such as Martin Heinrich Klaproth (1743–1817), and it is gratifying to see how many of these pioneers considered archaeological material as a suitable subject for study. Following a successful career as a pharmacist, Klaproth devoted himself to the chemical analysis of minerals from all over the world. He is credited with the discovery of three new elements – uranium, zirconium, and cerium – and the naming of the elements titanium, strontium, and tellurium, isolated by others but sent to him for confirmation. His collected works were published in five volumes from 1795 to 1810, under the title *Beiträge zur chemischen Kenntniss der Mineralkörper*, to which a sixth (*Chemische Abhandlungen gemischten Inhalts*) was added in 1815. In addition to these monumental contributions to mineralogical chemistry, Klaproth determined gravimetrically the approximate composition of six Greek and nine Roman copper alloy coins, a number of other metal objects, and a few pieces of Roman glass. Gravimetry is the determination of an element through the measurement of the weight of an insoluble product of a definite chemical reaction involving that element, and was the principal tool of quantitative analytical chemistry until the development of instrumental techniques in the early twentieth century. His paper entitled *Memoire de numismatique docimastique* was presented to the Royal Academy of Sciences and Belles-Lettres of Berlin on July 9, 1795, and published in 1798. He first had to devise workable quantitative schemes for the analysis of copper alloys and glass; the former scheme has been studied in detail by Caley (1949). He was appointed Professor at the Artillery Officer Academy in Berlin, and in 1809 became the first Professor of Chemistry at the newly created University of Berlin.

Humphry Davy (1778–1829), discoverer of nitrous oxide (N_2O, or “laughing gas”, subsequently used as a dental anaesthetic and today as a general pain-killer), identifier of the chemical nature of chlorine gas, and inventor of the miner’s safety lamp, also played a part in developing archaeological chemistry. In 1815, he read a paper to the Royal Society concerning the chemical analysis of ancient pigments collected by himself in “the ruins of the baths of Livia, and the remains of other palaces and baths of ancient Rome, and in the ruins of Pompeii” (Davy 1815). In a series of letters reported by others in the journal *Archaeologia*, Michael Faraday (1791–1867), the discoverer of electromagnetic induction, showed that he had studied a wide range of archaeological material, including a copper alloy coin, glass, and various fluids (*Archaeologia* XXV 13–17 1835), enameled bronze, glass, fuel residue, food residue, and oil (analyzed by tasting, which is no longer the preferred method!: *Archaeologia* XXVI 306–10 1836), and Roman lead glaze pottery (*Archaeologia* XXXII 452 1847). One of the first wet chemical investigations of ancient ceramics (Athenian pottery from the Boston Museum of Fine Arts) was carried out at Harvard and published in the *American Chemical Journal* by Theodore William Richards (1895). Many other eminent chemists of the nineteenth century (including Kekulé, Berzelius, and Berthelot) all contributed to the growing knowledge of the chemical composition of ancient materials. Undoubtedly, their archaeological interests were minor compared to their overall contribution to chemistry, but it is instructive to see how these great scientists included the analysis of archaeological objects as part of their process of discovery.

The appearance of the first appendices of chemical analyses in a major archaeological report represents the earliest systematic collaboration between archaeology and chemistry. Examples include the analysis of four Assyrian bronzes and a sample of glass in Austen Henry Layard's *Discoveries in the Ruins of Nineveh and Babylon* (1853), and Heinrich Schliemann's *Mycenae* (1878). So distinguished was this latter publication that William Gladstone, the British Prime Minister of the day, wrote the preface. The scientific reports in both of these publications were overseen by John Percy (1817–89), a metallurgist at the Royal School of Mines in London. Percy also wrote four major volumes on metallurgy, which included significant sections on the early production and use of metals (Percy 1861, 1864, 1870, and 1875). Because of his first-hand experience of metallurgical processes now lost, these books remain important sources even today. The analysis of metal objects from Mycenae showed the extensive use of native gold and both copper and bronze, which was used predominantly for weapons. Percy wrote in a letter to Schliemann dated August 10, 1877 that "Some of the results are, I think, both novel and important, in a metallurgical as well as archaeological point of view" (quoted in Pollard and Heron 1996: 6).

Toward the end of the nineteenth century, chemical analyses became more common in excavation reports, and new questions, beyond the simple ones of identification and determination of manufacturing technology, began to be asked. In 1892, Carnot published a series of three papers that suggested that fluorine uptake in buried bone might be used to provide an indication of the age of the bone (Carnot 1892a, 1892b, 1892c), preempting by nearly 100 years the current interest in the chemical interaction between bone and the burial environment. Fluorine uptake was heavily relied upon, together with the determination of increased uranium and decreased nitrogen, during the investigation of the infamous "Piltdown Man" (Weiner *et al*. 1953–6, Oakley 1969). This methodology became known as the "FUN method of dating" (fluorine, uranium, and nitrogen) when applied to fossil bone (Oakley 1963). Subsequently such methods have been shown to be strongly environmentally dependent, and only useful, if at all, for providing relative dating evidence.

The development of instrumental measurement techniques during the 1920s and 1930s such as optical emission spectroscopy (OES; see Section 3.1) gave new analytical methods, which were subsequently applied to archaeological chemistry. The principal research aim at the time was to understand the technology of ancient bronze metalwork, especially in terms of identifying the sequence of alloys used during the European Bronze Age. Huge programs of metal analyses were initiated in Britain and Germany, which led to substantial publications of analytical data (e.g., Otto and Witter 1952, Junghans *et al*. 1960, 1968–74, Caley 1964: see Section 3.5). Unfortunately, there is often an inverse relationship between the size and scope of an analytical project and its archaeological usefulness – perhaps because large size leads to a lack of focus, or simply that size leads inevitably to complexity and, consequently, uncertainty. For whatever reason, these monumental projects (and others like them) have had little lasting influence on modern thinking in archaeometallurgy, and have slipped into semi-obscurity.

As a result of the rapid scientific and technological advances precipitated by the Second World War, the immediate postwar years witnessed a wider range of analytical techniques being deployed in the study of the past, including X-ray analysis and electron microscopy (Chapter 5), neutron activation analysis (Chapter 6), and mass spectrometry (Chapter 8). Materials other than metal, such as faience beads and ceramics, were subjected to large-scale analytical programmes. Faience, an artificial high temperature siliceous material, was first produced in the Near East, and during the second millennium BC it was distributed widely across prehistoric Europe as far as England and Scotland. In 1956, Stone and Thomas used OES to "find some trace element, existent only in minute quantities, which might serve to distinguish between the quartz or sand and the alkalis used in the manufacture of faience and glassy faience in Egypt and in specimens found elsewhere in Europe" (Stone and Thomas 1956: 68). This study represents a clear example of the use of chemical criteria to establish provenance: to determine whether faience beads recovered from sites in Britain were of local manufacture, or imported from Egypt or the eastern Mediterranean. This question was of great archaeological significance, because for many years it had generally been assumed that significant technological innovations originated in the east and had diffused westwards – a theory termed *diffusionism* in archaeological literature, and encapsulated in the phrase *ex Oriente lux* (a term associated with Montelius (1899), but in circulation before then). Although the initial OES results were equivocal, the data were subsequently reevaluated by Newton and Renfrew (1970), who suggested a local origin for the beads on the basis of the levels of tin, aluminium, and magnesium. This conclusion was supported by a subsequent reanalysis of most of the beads using neutron activation analysis (NAA) by Aspinall *et al*. (1972).

During the late 1950s and early 1960s, the diffusionist archaeological philosophies of the 1930s were replaced by radical new theoretical approaches in anthropology and the social sciences. This became known as ''New Archaeology'', and represented an explicit effort to explain past human action rather than simply to describe it. The philosophy of science played a significant role in providing the terminology for this more statistical and quantitative approach to archaeology (see Trigger 1989). This New Archaeology reinvigorated research into prehistoric trade and exchange. The movement of population, via invasion or diffusion of peoples, was no longer seen as the principal instigator of cultural change. Instead, internal processes within society were emphasized, although evidence for ''contact'' arising from exchange of artifacts and natural materials (as proxy indicators for the transmission of ideas) was seen as an important factor and one in which chemical analysis of artifacts and raw materials might be useful. This increased interest in the distribution of materials initiated a ''golden era'' in *archaeometry* (a term coined in the 1950s by Christopher Hawkes in Oxford) as a wide range of scientific techniques were employed in the hope of chemically characterizing certain rock types, such as obsidian and marble, as well as ceramics, metals, glass, and natural materials, such as amber (see Pollard and Heron 1996). These characterization studies were aimed at ''the documentation of culture contact on the basis of hard evidence, rather than on supposed similarities of form'' (Renfrew 1979). Quantitative chemical data formed part of the basis of this ''hard evidence'', which made it necessary for archaeologists to become familiar with the tools and practice of analytical chemistry, as well as the quantitative manipulation of large amounts of analytical data.

Until recently, the applications of analytical chemistry to archaeology focused primarily on inorganic artifacts – the most obviously durable objects in the archaeological record – or occasionally on geological organic materials such as amber and jet. Increasing attention has been directed over the past few decades towards biological materials – starting with natural products such as waxes and resins, but extending to accidental survivals such as food residues, and, above all, human remains, including bone, protein, lipids, and, most recently of all, DNA (Jones 2001). Perhaps surprisingly, the preservation of a wide range of biomolecules has now been demonstrated in a number of archaeological contexts. This is probably due to two main factors: the increasing sensitivity of the analytical instrumentation brought to bear on such samples, and the increasing willingness to look for surviving material in the first place.

It has been shown over the years that, to be of lasting interpretative value, chemical analysis in archaeology needs to be more than a descriptive exercise that simply documents the composition of ancient materials. This is often much more difficult than producing the primary analytical data; as DeAtley and Bishop (1991: 371) have pointed out, no analytical technique has ''built-in interpretative value for archaeological investigations; the links between

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physical properties of objects and human behaviour producing the variations in physical states of artefacts must always be evaluated.'' There has been a constant call from within the parent discipline for meaningful scientific data, which address real current problems in archaeology and articulate with modern archaeological theories. This demand for relevance in the application of scientific analyses in archaeology, although self-evidently reasonable, must be qualified by two caveats – firstly, the concept of what is meaningful in archaeology will change as archaeology itself evolves, and secondly, the fact that analytical data on archaeological artifacts may be of relevance to disciplines other than archaeology. An example of the latter is the use of stable isotope measurements on wood recovered from archaeological sites to reconstruct past climatic conditions. On the former, Trigger (1988: 1) states that ''archaeologists have asked different questions at different periods. Some of these questions have encouraged close relations with the biological and physical sciences, while other equally important ones have discouraged them.'' Only a close relationship between those generating the analytical data and those considering the archaeological problems (ideally, of course, so close that they are encircled by the same cranium) can ensure that costly data does not languish forever in the unopened appendices of archaeological publications.

1.2 Basic archaeological questions

This short introduction has identified the origins of many of the issues addressed by the application of analytical chemistry to archaeology. They can be divided, somewhat arbitrarily, into those projects which use chemical methods to address specific questions of direct interest to archaeology, and those projects which attempt to understand the processes acting upon archaeological material before, during, and after burial. The latter category can and often does address specific issues in archaeology (such as site formation processes), but is perhaps of more general (as opposed to site-specific) interest.

Identification

Perhaps the simplest archaeological question that can be answered by chemical means is ''what is this object made from?''. The chemical identity of many archaeological artifacts may be uncertain for a number of reasons. Simply, it may be too small, corroded, or dirty to be identified by eye. Alternatively, it may be made of a material that cannot be identified visually, or by the use of simple tests. An example might be a metal object made of a silvery-colored metal, such as a coin. It may be ''pure'' silver (in practice, a silver alloy containing more than about 95% silver), or it could be a silver-rich alloy that still has a silver appearance (silver coins with up to 30% copper can still look silvery, in which case the precise composition may well

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carry information about coinage debasement, which in turn relates to economic history). It may also be an alloy designed to look like silver, but contain little or no precious metal, such as "nickel silver" (cupronickel alloys, such as are used in modern "silver" coinage). It could equally be a coin with a silver surface but a base metal core, such as is produced by plating, or chemical methods of surface enrichment (or as a result of electrochemical corrosion in the ground). Conceivably, it could consist of some more exotic silvery metal, such as platinum, but this would excite great interest if identified in a European context prior to the mid eighteenth century AD since this metal was supposedly unknown in Europe before that date.

Thus, even the simple identification of a material may have important ramifications (expanded upon below), but none of these possibilities could be absolutely confirmed by visual examination alone. Chemical analysis (or chemical analysis combined with physical examination, in some cases) is necessary to identify the true nature of the material. In general, to answer this basic question, the required levels of analysis are relatively simple, subject to the usual constraints posed by archaeological materials (primarily the need to be as nearly as possible "non-destructive"). Consequently, one preferred technique for many years has been X-ray fluorescence (XRF), because of its nondestructive nature (providing the sample can fit into a sample chamber), its restricted sample preparation requirements, and its simultaneous multi-element capability (see Chapter 5). During the 1960s an air path machine was developed in Oxford specifically to allow the nondestructive analysis of larger museum objects (Hall 1960), and since then a portable hand-held XRF system has been produced for use on museum displays or at an archaeological excavation, as well as for geological purposes (Williams-Thorpe *et al*. 1999).

Identification of organic materials in archaeological contexts can pose more problems. The identification of amorphous organic residues (either visible or occluded in another matrix) is addressed in Chapter 7. An example of a situation where the identification of the organically-derived raw material used to manufacture artifacts is important is the discrimination between jet, shale, and various forms of coal. Up until 30 years ago, the classification of small pieces of jewellery made from various black materials was carried out by eye using a number of simple criteria, such as color and physical properties (Pollard *et al*. 1981). Although there is little difficulty when applying these simple techniques to geological hand specimens, the small size of most archaeological finds and the nature of the destructive sampling required for thin sectioning or even streak testing often renders such judgments difficult to make, if not impossible. Such identifications are, however, rather important because of the restricted number of geological sources of jet when compared to other related materials. In the British Bronze Age, for example, if a piece of jet is identified in a Wessex burial context in southern England, then it is automatically taken as evidence of trading links with Whitby on the