CHEMICAL METHODS IN ARCHAEOLOGY

1. Introduction

Archaeology is the study of past human life, culture, and activities, which is shown by material evidence in the form of surviving artifacts, biological and organic remains, and a variety of other evidence recovered by archaeological excavation (1). It differs from the other historical disciplines since these reconstruct the past on the basis of documentary sources. Documentary sources mostly testify to important events and can be affected by the human tendency of a writer to represent his/her own subjective reality. Archaeology, by contrast, tells about the past by studying materials that entered into the life of common people.

In its endeavour to study material evidence, archaeology has strongly interacted with almost all scientific disciplines. Among these, chemistry has certainly played an important role. Chemistry has developed methods to date archaeological material and has also allowed us to infer trade routes by studying ancient

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artifacts and to shed light on the technology used to make them. The diet and customs of ancient peoples have also been discovered by applying chemical methods. Chemistry intervenes in the understanding of the mechanisms that cause archaeological material to degrade in order to set up procedures aimed at stabilizing decay and preventing further deterioration. It also tries to find the best way to restore ancient artifacts.

Today, a number of resources are available to researchers involved in studies dealing with chemistry and archaeology. *Archaeometry* and the *Journal of Archaeological Science* are two specific journals devoted to the interactions between the sciences and archaeology. A variety of different conference proceedings contain results from chemical studies in archaeology. Between them those published by the American Chemical Society (2–6) and the Materials Research Society (7–12) are of particular relevance. Several books cover topics of relevance to archaeological chemistry. The comprehensive book edited by Brothwell and Pollard (13) represents a landmark in the field of archaeological sciences and replaces the outdated book edited by Brothwell and Higgs (14,15). A broad introduction to archaeological chemistry was provided by Goffer (16) in 1980 while the most recent book from Pollard and Heron (17) concentrates on a series of case studies. The books from Lambert (18) and Henderson (19) are based on the study of a series of archaeological materials. Techniques of analytical chemistry applicable to archaeology have been discussed in the book edited by Ciliberto and Spoto (20). Methods used to date archaeological materials are discussed in the books by Aitken (21) and Taylor and Aitken (22).

2. Chemical Methods in Archaeology Over the Last Three Centuries

The chemical methods used in the study of antiquities go back to the eighteenth and nineteenth century. Eminent scientists such as Humphry Davy (17 Dec. 1778–29 May 1829), Jöns Jakob Berzelius (20 Aug. 1779–7 Aug. 1848), Michael Faraday (22 Sept. 1791–25 Aug. 1827), Marcelin Berthelot (25 Oct. 1827–18 Mar. 1907), Friedrich August Kekulé von Stradonitz (7 Sept. 1829–13 Jul. 1896), and Wilhelm Conrad Röntgen (27 Mar. 1845–10 Feb. 1923) turned their attention to ancient coins, glasses, pigments, pottery, and other remnants of the past during the course of their studies. Similar investigations continued throughout the nineteenth century thanks to a number of other investigators, with most of them operating in isolation (23–25). Important basic concepts in the field started to be introduced at that time when European chemists suggested that chemical composition could be used to identify the source of archaeological materials (25). The concept of *provenance* is still active in the field (26) and the development of instrumental methods and of new ways to mathematically treat data sets (27–29) have allowed us to better define the potential and the limitation of scientific provenance of archaeological material.

The use of scientific examination to investigate the past was greatly fostered when major museums began to establish laboratories for that purpose on their premises. After a scientific laboratory was established in 1888 at the Königlichen Museen in Berlin, the director Friedrich Rathgen (30) provided the first manual dealing with practical procedures for the conservation and restoration of antiquities (31). This handbook remained for many years the only collected scientific documentation in the field. It was in 1920, as a direct result of the First World War, that one of the leading laboratories in the field was established at the British Museum. The discovery of the alterations suffered by many of the objects stored in 1918 in the Holborn Post Office tunnel as protection against possible war damage (32) moved the Trustees to invite Alexander Scott to carry out an investigation. On the basis of his report, an emergency laboratory was set up in 1920 within the precincts of the British Museum. At this time, Alexander Scott was aged 70 and was a senior fellow of the Royal Society, Superintendent of the Davy-Faraday Laboratory of the Royal Institution and President of the Chemical Society. His interests, ranging from sciences to arts, led to the systematic application of chemical methods to the study of ancient objects held in museums (33). Just a few years later the first research facility devoted to the study and the conservation of archaeological and artistic objects was established in the United States. In fact, in 1928 the Center for Conservation and Technical Studies was opened at the Fogg Art Museum of Harvard University by its Director Edward W. Forbes.

The pioneering approach developed in museum science laboratories was followed by the involvement of university laboratories that ensured the continuous development of new chemical methodologies for the investigation of remnants of the past. In spite of this continuous evolution, only in the past four decades has the use of advanced analytical instrumentation, together with the increased knowledge of statistical methods for the elaboration of coherent data-sets, established a fundamental link between instrumental analytical chemistry, art, and archaeology. The opening in 1955 of the Research Laboratory for Archaeology and the History of Art at Oxford University was certainly a starting point for this process. Today, science departments are normally active within the major museums while departments and institutes devoted to studies of relevance for chemistry applied to archaeology are present in most of the world's university institution.

3. Materials Study

Analytical chemistry plays an important role in the study of archaeological materials and has a variety of goals. When artifacts are investigated, some of the most important aims concern the study of the technology used to produce them, to reconstruct their distribution from the production areas, and to understand the use to which they were put in the past (34). By interpreting such information, it is possible to better understand the behavior of ancient people. Long-term storage often tends to obscure chemical information that contribute to the above mentioned aims. It is thus important to understand, at the deepest possible level, all the altering processes that intervene in the life cycle of the archaeological material.

3.1. Instrumental Methods for Chemical Analysis.

Archaeological materials are studied from a chemical point of view by using the variety of instrumental methods available today to chemists (20). However, all chemists involved in studies concerning samples of archaeological interest will recognize how important it is to make an appropriate selection of the analytical method to use in their studies. The main questions raised usually concern how the proposed analytical procedure will affect the integrity of the object under examination. From this point of view, only those techniques that do not alter the integrity and appearance of archaeological objects can be considered as "ideal" techniques. Techniques that operate *in situ*, making sample-taking unnecessary, come close to this ideal.

In the attempt to find a balance between the requirements of scientific methods and the need to maintain the integrity of the object under study, the only alternatives to *in situ* analysis require the object itself to be placed in the analyzing chambers of the equipment or tiny fragments of samples to be scraped from its surface. The former approach cannot be applied in all cases, since only small objects such as coins, certain jewelry, and statuettes are of a size and shape that will fit into common analytical tools. The destructive approach thus remains as a last resort for the extraction of chemical information from archaeological samples.

Tremendous improvements have been made with regard to the scope and efficiency of today's chemical instrumental methods, which has led to the development of new methodologies that satisfy specific requirements to a greater degree such as micro-destructiveness or nondestructiveness of the sample to be analyzed. A wider range of information is now available and the greater sensitivity and reproducibility of analyses is thus ensured. In this context, the use of spatially resolved analytical techniques have provided new opportunities for micro-destructive and, at times, completely nondestructive analyses, opening up new diagnostic approaches for the study of archaeological samples (35).

Instrumental chemical methods used to study archaeological materials include elemental analytical techniques (36) and molecular analytical techniques (37).

X-ray fluorescence (XRF) has been popular for elemental analysis since the 1960s. Major and minor element composition of a great variety of solid archaeological materials including stones, metals, glasses, ceramics, bones, paintings and other materials is daily obtained in most archaeometry laboratories making use of energy dispersive XRF (EDXRF) or wavelength dispersive XRF (WDXRF) equipment (38–40). Synchrotron radiation XRF (SRXRF) has been recently proposed as a technique that significantly improves the performance of the standard XRF (41). However, its use is limited by the small number of synchrotron radiation facilities available. Particle-induced X-ray emission (PIXE) also has been widely used to study archaeological materials by using multiproject facilities (42,43). A facility dedicated to the study of museum artifacts has been developed at the Research Laboratory of the Museums of France in Paris (44).

Trace element analyses contribute to chemically fingerprint archaeological material. Provenance is often inferred by evaluating results from trace element analysis. Optical emission spectroscopy (OES) has been used for analysis of elements present at concentration up to $\sim$0.001% since the 1930s. It was largely replaced by atomic absorption spectroscopy (AAS) during the 1970s and by the inductively coupled plasma (ICP) techniques during the 1980s (45). Instrumental neutron activation analysis (INAA) (46) has been the technique of choice in provenance investigation for a long time, largely due to the high sensitivity to many trace elements along multiple dimensions of element concentration (47). It also ensures good precision and accuracy of data compared to other techniques (46). However, ICP–mass spectrometry (ICP–MS), less costly equipment, today rivals INAA in provenance investigations (45,48).

The above mentioned methods for trace element analysis require samples, often in the range of tenths of milligrams, to be properly treated. Inappropriate procedures have been shown to affect the precision of the results (49). Efforts are placed today in trying to minimize the destructive impact of trace element analysis. In this perspective, the use of the laser ablation–ICP–MS has been investigated (50–53). Laser-induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy (LIPS) or laser ablation spectroscopy (LAS), has been recently proposed as a new micro-destructive method for major, minor, and trace element analysis in the study of archaeological material (54).

Isotope analysis plays an important role in the study of archaeological material. The quantitative determination of the relative amount of isotopes of interest allows us to hypothesize on the provenance of metal objects and also to support paleodietary research. Thermal ionization mass spectrometry (TIMS) has been used largely for the analysis of heavy metal isotopes for provenance purposes (55). More recently, the multi-collector–ICP–MS (MC–ICP–MS) has been shown to attain the required reproducibility for lead isotope analysis (56,57). Archaeological investigations based on the study of stable isotopes such as ^{13}C, ^{15}N, or ^{18}O are carried out by making use of isotope ratio mass spectrometry (IRMS) based techniques (58,59).

Molecular analytical techniques are used in archaeological science with a variety of purposes. The identification of organic materials is one of them. These organic materials are for the most part natural products and, hence, composed of complex mixtures of biochemical components. Detailed compositional information from such materials are derived making use of a wealth of instrumental methodology, most of which are based on organic mass spectrometry (MS) methods (60,61).

Gas chromatography mass spectrometry (GC–MS) has become the workhorse of organic analysis in archaeology thanks to its ability to separate and analyze mixtures of thermally stable volatile compounds or compounds that can be volatilized by the application of heat. Liquid chromatography mass spectrometry (LC–MS), more often in the form of high performance liquid chromatography mass spectrometry (HPLC–MS), is used when thermally unstable or not volatile organic mixtures are going to be analyzed. The use of different mass analyzers allows for improved performance of the above mentioned techniques. Tandem mass spectrometry (MS^n) has also been shown to contribute to the study of organic remains. In fact, GC–MS–MS has been used to confirm the presence of DNA residue in ancient seeds (62).

However, the possibility of studying solid samples offered by cross-polarization magic angle spinning NMR (CP–MAS–NMR), coupled with the ability to analyze less sensitive elements such as silicon and aluminium, has recently allowed the demonstration of the potential of this technique in studying ancient organic residues, archaeological bone and wood, fossilized resins, and a range of other archaeological materials (63).

Both Raman spectroscopy (64) and Fourier transform infrared spectroscopy (FT–IR) (65) have been used increasingly in archaeology to study a wide range of both inorganic and organic archaeological materials. Modern applications tend to favor the microdestructive approach guaranteed by the use of micro-Raman spectroscopy and FT–IR microspectroscopy (35).

A variety of other analytical techniques have been used to solve specific archaeometric questions. Among them surface sensitive analytical techniques (see SURFACE AND INTERFACE ANALYSIS) such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) have been sparingly used, mostly to investigate degradation processes and to microdestructively characterize both inorganic and organic material (66–69).

The fundamental contribution of statistical methods in the understanding of data generated by the variety of analytical methods used to investigate archaeological material should not be overlooked. The exploratory multivariate methodologies have been extensively used in interpreting analytical data from archaeological materials (27,29). Recently, the Bayesian approach has been used as a statistical modeling of data (28,29).

3.2. Inorganic Archaeological Materials. It has been clarified that "*The primary aim of materials studies in archaeology is to contribute to the investigation of the overall life cycle or chaîne opératoire of surviving artifacts.... This life cycle starts with production that includes the procurement and processing of the raw materials through to the fabrication and decoration of the artifacts. It then continues through distribution of the artifacts to their use, re-use and ultimate discard*" (34). Inorganic materials better survive the degradation processes that increase with time and thus have more easily been subjected to such investigations.

Stone. Stone is certainly one of the earliest inorganic materials used by humans (70). In particular, flint was used from the Paleolithic period onward for a variety of purposes such as cutting and pounding thanks to its properties to produce sharp blades with characteristic conchoidal fractures when worked. The advent of farming during the Neolithic period expanded the need for flint, which was extracted from mines or quarries and transported to different regions. Chemical studies aimed at establishing what distance the flint traveled from its source are based on the premise that it is possible to source the flint chemically to a particular location (19). Earliest works were able to distinguish between broad geological areas in western Europe in which flint occurs by using the amount of a single element (thorium) as a discriminator (71–73). Successive studies demonstrated that a more precise sourcing was possible by detecting aluminium, iron, magnesium, potassium, sodium, calcium, and lithium at levels >50 μg/g (74). In such a way, the chemical composition of flint was linked to specific areas in England.

Obsidian is certainly the lithic material providing archaeologists with the clearest evidence of contact between different cultures. In fact, obsidian is almost the ideal material for source characterization by elemental analysis and was the material of choice for the manufacture of a variety of cutting tools. Moreover, it is shiny and attractive, and for this reason was used in the past for ornamental purposes. Obsidian is a glass formed when highly viscous volcanic lava of high silicon and aluminium content cools rapidly, usually at the margins of a lava flow, such that the process of mineral crystallization is precluded. The presence of obsidian far from any source of volcanic activity represented an intriguing puzzle to the archaeologists (18,19). Now we know that the acquisition of obsidian developed in different ways, including local collection over land or sea. For this reason, sourcing archaeological obsidian is of great assistance in the investigation of the cultural, social, and economic development of ancient societies.

Early works based on chemical elemental analysis carried out with optical emission spectroscopy showed that it was not until 7500 BC that obsidian artifacts were moved beyond their immediate environs of source areas in the Near East (75–77). The advent of LA–ICP–MS has allowed us to improve our ability to precisely source obsidian. Nine separate Cappadocian sources have been clearly separated with a minimal impact of the destructiveness of the analysis (78). The Mediterranean area also represented an important source for obsidian (17,79). Elemental chemical analyses carried out by OES in early works and successively by INAA, XRF, and ICP–MS have identified the island of Melos as the source for obsidian for Greece, Crete, and the Aegean islands. Northern Italy and Macedonia were supplied by Carpathian sources (80,81). Central Mediterranean regions were mainly supplied by the Italian islands of Lipari, Sardinia, Palmarola, and Pantelleria (79). The obsidian source located in the area between east-central Mexico and Guatemala, called Mesoamerica, have been studied in an attempt to shed light on ancient trade routes set up when important cultures such as Aztecs and Maya were present in the area (82,83).

Ceramics. [See FINE ART EXAMINATION AND CONSERVATION (19).] The discovery of fire allowed humans to process natural materials to improve or simply change their characteristics (~1,600,000 years ago) (84). One of the earliest uses of fire was for cooking. Food became safer and tasted better after cooking. Later, stones were heated to improve their hardness (~80,000 BC). The complex technology required for making pottery was not developed until thousands of years after fire had been discovered. Paleolithic objects from Dolni Vestonice in the Czech Republic are probably pottery's earliest ancestors and can be dated to 24,000 BC (85). The development of pottery is still, however, a subject for debate and its origins have been placed between 12,000 and 10,000 BC (18,86). Pottery technology evolved with time and more and more complex procedures allowed the production of finely finished ceramic artifacts that combined aesthetics with usefulness. The introduction of glaze certainly improved both the appearance and utility of pottery, especially when the use of proper fluxes provided suitable glazes for curved surfaces such as those of pots (87,88). Flat surfaces were in fact already being glazed in Egypt in ~5000 BC but the glazed pots found in Syria have been dated to a later period, ~1700 BC.

Different methods for finishing pottery required control of the oxidizing/reducing atmosphere during firing. The most famous and striking examples of this procedure were provided by the Greeks after the invention of the so-called "red-figures" technique (89). On the basis of documented evidence, most attribute this technique to the painter Andokides, dating it to ~530 BC. It involved producing red and black paints on pottery as a result of switching from an oxidizing firing atmosphere to one that was reducing to form Fe_2O_3 (red) or Fe_3O_4 (black) on the surface of the pottery previously covered with suitable clay materials. The complex decorations developed during the Middle Ages and the Renaissance bear witness to the tremendous evolution of pottery decoration techniques through successive ages.

Ceramics are synthetic materials whose production is affected by choices and actions taken by humans during each stage of production that reflects their cultural symbolism, tradition, and individual preferences. Their study can thus improve our knowledge of past societies. The complex range of parameters that led to the various modes of pottery production, distribution, and consumption recently has been discussed (90). Pottery has been the biggest class of material to be studied for provenance purposes. In the simplest approach, the chemical composition of the fired ceramic is considered indicative of the composition of the raw clay material. However, a number of factors could influence the final composition of the final products and thus it is a normal procedure to compare the finished pottery composition with that of fired pottery of certain provenance (17). Since the 1970s INAA has been the preferred analytical technique for pottery trace analysis (46,91). More recently INAA has been rivaled by ICP–MS in this field. The limited length of this article does not allow us to account for the enormous literature developed in an attempt to provenance archaeological ceramics. The reader is addressed to further readings for a detailed list of case studies (17–19,46,90–92).

Glass. (See GLASS.) The development of the technology necessary to obtain glass could be linked to the smelting of metal ores or to the manufacturing of glazed pottery. The earliest known glass material are supposed to be linked to smelting technology and have been dated to ~2000 BC (93,94). Glazing technology may, however, have anticipated the origin of glass (18,88). In fact, the first vitreous materials were glazed stones and ground quartz bodies coated with a glaze called faience. Mesopotamia was probably the region in which glass production was first established but it was in Egypt after 1500 BC under the XVIII dynasty that glass production found its first prominence.

The early chemical analyses carried out with the aim to create ancient glass composition data sets began in the 1950s (95). However, it was only in 1961 that the first report as to where ancient glasses were grouped in term of chemical composition and correlated to both geographical and chronological criteria were published (96). Five elements were determined by using INAA and expressed in term of oxides: magnesium, potassium, manganese, antimony, and lead. Magnesium was an impurity in the alkali used as flux, potassium was both an impurity in the alkali and an alkali itself. Both manganese and antimony were used to eliminate the pale green color of glass with iron impurity and obtained under oxidizing conditions (17,19). Ancient soda-lime glasses dated between 1500 and 800 BC and 800 and 1000 AD were categorized as being high magnesium (HMG) and low magnesium (LMG) containing glasses. The amount of magnesium put in relation to the potassium contents reflected the use of mineral (natron) or plant-ash sources of alkali. High antimony soda-lime glasses produced between 600 and 200 BC were identified as a separate group. Islamic glasses were grouped as high magnesium containing glass produced between 840 and 1400 AD and high lead glasses produced between 1000 and 1400 AD.

Today, a number of other ancient glass composition groups have been identified. Each of them reflecting changes in the raw material or in the technology used to produce the glass. Low magnesia, high potassium oxide glasses produced in Europe between 1150 and 700 BC were obtained by innovating the raw materials used (97). Later in Medieval northern Europe high potash glasses were used to produce church windows and vessels easily subject to degradation (17). High potassium and barium oxide glasses were produced under the Chinese Han Dynasty (206 BC–221 AD) (98). New materials were also used in India from the first millennium AD to produce high alumina glasses (99).

Metals. [See FINE ART EXAMINATION AND CONSERVATION (18,19).] The advantages offered by metals compared to other materials used by ancient people, such as stone or wood, were discovered 10,000–12,000 years ago in Southwest Asia. The advent of metallurgy with the development of farming and domestication of animals allowed the rise of urban civilizations. The exploitation of metals enhanced previously existing trade routes and the specialization required by metal working encouraged social stratification.

Copper in its native state is believed to be the earliest metal used by humans even though native gold could have preceded its use due to its beauty and resistance to corrosion. The production of copper and copper alloy objects developed alongside the evolution of the technology linked to the extraction of the metal from ores—smelting, the improved ability to work the metal and, finally, the ability to form alloys (100). Much of this evolution was a consequence of the ability of metalworkers to discover and control processes that allowed them to heat the metal, in its native state or in ores containing copper compounds, at increasingly high temperatures so as to reach the temperature necessary to melt copper (1083°C).

The shaping of native copper was a well-established custom in Southwest Asia from ~10,000 BC onward. This area was by far the most advanced in copper-work technology. In fact, evidence for the smelting of copper-based ores, which leads us to suppose that casting skills were already established, has been dated to 7000–6000 BC (Çatal Hüyük, Anatolia).

The addition of elements other than copper to form alloys with better properties in terms of castability, hardness, and appearance may originally have been accidental. Arsenic, the first element used to form copper alloys, was alloyed with copper during Chalcolithic times, possibly using arsenic-containing copper ores. Tin was the most important alloying element in the Old World after 4000 BC until the resulting alloy being *bronze*. Lead and zinc were two other important elements in forming or modifying the characteristics of copper alloys. The former was used especially by the Greeks who intentionally added lead to the tin-bronzes used to make statues both to improve the fluidity of the molten alloy and to enhance appearance. The intentional alloying of zinc—thus forming *brass*—was certainly lead to the use of the mentioned elements in copper alloy preparation. The earliest brass objects were probably manufactured in eastern Turkey during the first millennium BC. With the *calamine process* been established and perfected, brass production increased rapidly thanks to its use in minting coins during the Roman Empire (17).

The smelting of lead was assumed to precede that of copper. The lower temperature required for lead smelting (800°C) is the most obvious reason for this assumption. Lead use was at its height when the Greeks used it with copper-tin alloys to make statues. However, during the Roman Empire lead production increased tremendously and reached levels of production that were to be reproduced only after the Industrial Revolution (101). Under the Romans, lead was used to produce a great variety of objects ranging from coins to pipes for the distribution of water.

The beginning of the Early Iron Age (102)—fixed as being 1200 BC—coincides with the ability of people from western Asia to smelt iron and alloy carbon so as to obtain steel. Up to 1500 BC, the Hittites had the best developed technology for working iron. The advantages of iron over copper and its alloys had, however, been known since the Bronze Age. Evidence of uneven uses of iron, sometimes in its native state, have been dated to 2500 BC. Iron smelting technology presumably dates back to the Bronze Age as the temperature required for smelting iron (1100–1150°C) is similar to that required for copper. However, iron smelting necessitated a more accurate control of the carbon and oxygen present in the furnace so as to maximize the percentage of iron present in the spongy mass, or *bloom*, obtained after the furnace was cooled (103). Glass-like materials, or *slag*, were formed during smelting due to a reaction between the silica impurities present in the ore and fluxes. The formation of slag, inevitably containing certain amounts of iron, was sometimes due to the intentional addition of fluxes to the furnace to help rid the ore of silica impurities.

Lead isotope analysis has been used for provenancing metal objects (104). The applicability and the use of the method has caused discussions mainly centred on the evaluation of the correct interpretation of the use and limitation of lead isotope analysis in the investigation of ancient metal production (105–107). Nevertheless, lead isotope analysis has allowed better identification of sources of copper used in the Mediterranean Bronze Age. Mines at Laurion were the largest sources of lead in the late Bronze Age. Lead found at Knossos on Crete from Middle Minoan to Mycenaean times was excavated at Laurion. Also, Egyptian artifacts from Amarna and Abydos have proven to be derive from metals excavated at Laurion.

3.3. Organic and Biomolecular Archaeological Materials. Most of the research studies carried out in archaeological science over the last 50 years have been devoted to the investigation of inorganic material. This situation was due to the idea that biological and organic material can only survive in the archaeological record under exceptional circumstances. After a few pioneering investigations in the 1980s, the use of increasingly sophisticated organic techniques have since demonstrated how a variety of organic and biomolecular archaeological residues can be studied. This approach consists in identifying molecular markers capable of identifying unknown organic samples on the basis of their presence in contemporary natural substances (108). Lipids, in particular, have been shown to be particularly important as biomolecular markers (109).

Archaeological Lipids. Lipids occur ubiquitously in plants and animals and preserve under favorable conditions in association with a range of different classes of archaeological materials ranging from unglazed pottery, soil, human and animal remains, resins, and a range of other amorphous materials. The use of modern chromatographic techniques coupled with mass spectrometric analyzers (60) has contributed to studies of artifact use patterns (110) and food consumption (111) through the identification of lipid residues. Lipids are extracted from the powdered original matrices by using organic solvents. They are properly derivatized and then analyzed by GC or GC/MS techniques or by GC–C–IRMS for isotope ratio studies (112).

Degradation processes cause lipids to be hydrolyzed or oxidated. Secondary ketones are commonly found in the lipid extracts of ancient cooking vessels. The contribution of isotope ratio studies carried out by GC–C–IRMS in differentiating ancient lipid residues has been clearly demonstrated, eg, by distinguishing between cow milk and adipose fats using the $\delta^{13}C$ values of their $C_{16:0}$ and $C_{18:0}$ fatty acids (113). The identification of lipid biomarkers also provides insights into ancient anthropogenic activities. In fact, soil lipid profile is affected by different agricultural practices, while detection of ancient faecal inputs to the soil may allow the location of ancient cesspits (114,115). In such studies 5β-stanols, bile acids, and *n*-alkyl lipids act as useful biomarkers. Lipids help also in studying decay processes associated with human remains. Lipid analysis of skin tissue from the Tyrolean Ice Man showed that some acyl lipids were preserved. However, it was noted that all triacylglycerols with more than one double bond were completely degraded. The combined histological evidence of loss of epidermis with chemical evidence of the transformation of fats into adipocere indicates submersion of the body in water for several months before its freeze–drying (116). Cholesterol is another lipid that persists in long-buried bones of humans and animals (117) and its evidence can be used as a source of paelodietary information (118). Recently, lipid biomarkers have helped to shed light on chemical treatments used in ancient Egyptian mummification (119). Organic material from Egyptian mummies dating from 1900 BC to 395 AD have been studied by GC–MS, thermal desorption (TD) and pyrolysis (Py)–GC–MS. In Egyptian mummification, natron was used as the desiccant while a variety of organic materials were used to prevent the decomposition of the body. Plant oils and, to a lesser extent, animal fats were used to protect tissues from degradation thanks to the cross-linked network they generate after polymerization. Both coniferous resin, identified by the presence of diterpenoid components, and beeswax, identified by the presence of alkanes, wax esters, and hydroxy wax esters, were increasingly used with time for their antimicrobial and antibacterial properties. A number of other plant derived components of the embalming mixture also have been identified while no component coming from petroleum bitumens were detected. The latter evidence contradicted the previously supposed use of natural bitumens in mummification (120).

Proteins. Proteins have rarely survived to the archaeological record (121). Only under unusual burial environments have they survived microbial degradation and proteins in hard tissues such as tooth, bone, and shell, are prevalently protected (122). Temperature plays the main role in protein preservation, however, deposition within small pores whose dimensions physically excludes enzymes and close interaction with minerals have been proposed as situations that enhance protein preservation (121,123). As a consequence, we should expect that it is possible to obtain protein residues from ancient ceramics that may have been in contact with protein-rich foodstuff for prolonged periods of time. However, protein extraction from mineral and ceramic surfaces is difficult. Most of the proposed methods disrupt the macromolecular structure of the protein residue (124–126). Immunological methods have also been used as extraction methods of protein from mineral surfaces, however, a yield of $\sim$0.0025% was evaluated for the proposed methods (127). Recently, a new immunological method that allows protein extraction yield up to 0.1% was proposed (128,129).

Other Organic Residues. Organic residues have been identified by making use of FT–IR. In particular, this technique, in combination with other spectroscopic and chromatographic analytical techniques, has provided chemical evidence of ancient food and beverages (130,131).

Food is fundamental for all human society, not only for nutrition and health but also in economic, social, and ritual life. Information about prepared food is therefore critical for an understanding of ancient cultures but unfortunately examining the food of the past is extremely difficult. Food is normally consumed and leftovers usually decay. These problems are of particular relevance when residues of ancient beverages are to be studied. Fermented beverages are made from a variety of sugar-containing materials. Barley (*Hordeum vulgare* L.) was probably the first to be domesticated and used to make beer. This beverage first appeared in Mesopotamia ~6000 BC (18). Wine followed this early beer production.

A small fragment of the yellowish residue present in a Neolithic jar found in the Hajji Firuz Tepe village (North of Iran) and dated 5400–5000 BC was analyzed by means of diffuse-reflectance FT–IR spectroscopy (130). The spectra showed features attributed to calcium tartrate. After comparison with ancient and modern reference samples, this result, confirmed by means of chromatographic and ultraviolet (UV) spectroscopic methods, was the earliest chemical evidence for wine since tartaric acid occurs naturally in significant amounts (~1%) only in grapes (*Vitis vinifera* L.). The calcareous environment of the site had converted the acid into calcium tartrate. Moreover, the shape of the jar confirmed its use as a liquid holder. A detailed study of the spectra (with peaks centred at 2926 and 2858 cm^{-1}) and their comparison with reference samples, together with the analytical evidence obtained from chromatographic and UV spectroscopic investigations, also confirmed the presence of an oleoresin extracted from the *Pistacia atlantica* Desf. terebinth tree. Alcohol soluble resin was used to inhibit bacterial growth and improve the wine in taste and odor.

A similar analytical approach also led to the identification of the ancient organic material present in vessels found at Gordion (Turkey) in a tomb dated ~700 BC (131). The tomb is assumed to be that of the Phrygian King, Midas. The study of the region at 1420, 1390, 1170, and 1120 cm^{-1} in the diffuse-reflectance FT–IR spectra of the methanol extracts of 14 food samples indicated that a mutton or goatmeat-based dish had been left in the vessels. The contemporary presence of bands due to long-chain esters of beeswax, calcium oxalate, and calcium tartrate in the diffuse-reflectance FT–IR spectra of the methanol extracts of 16 beverage samples instead provided evidence of a mixed fermented beverage of grape wine (calcium tartrate), barley beer (calcium oxalate, also called "beerstone"), and honey mead (beeswax).

This study, which revealed one of the most comprehensive Iron Age drinking sets ever found, suggested that such food and drink was eaten at a feast before the interment of the king, thus providing fundamental chemical evidence for ancient cuisine in the Mediterranean area.

Ancient DNA. DNA entered the archaeological record from the second half of the 1980s. In fact, before then it was not imagined that long-term preservation of DNA was possible. A breakthrough in the field was a study published in 1985 where the successful detection of intact genetic information in a 4000-year old Egyptian mummy was presented (132). Ancient DNA studies were boosted by the invention of the polymerase chain reaction (PCR) (133), which allows a targeted stretch of DNA to be amplified millions of times so as to be properly sequenced. Unfortunately, the high sensitivity of the method renders contamination from modern DNA highly probable if appropriate procedures are not set up (134). Moreover, a deep understanding of the degradation processes that concern postmortem DNA and of the conditions under which DNA preserves is required (134,135).

DNA is a record of ancestry. For this reason, ancient DNA can be used to determine kin relationship within a group of specimens (136). Moreover, ancient DNA can express some of the biological characteristics of an archaeological specimen. Biological sex (137) or genetic diseases (138) can be inferred by studying archaeological DNA. Studies carried out on DNA sequences older than 1 million years ago (antediluvian DNA) have concluded that such ancient sequences cannot be reproduced or derive from contaminations (139). A variety of studies on DNA sequences dated up to 100,000 years ago from extinct animals have revealed the phylogenetic relationships of extinct animals (134). For example, the extinct *moas* of New Zealand have been shown to be related to flightless birds in Australia rather than extant kiwis in New Zealand (140). The study of ancient human DNA sequences opened up a new and exciting view of our ancestry (134,141). It is today known that Neanderthal hominids that lived in Europe and western Asia until ~30,000 years ago, were not directly related to modern Europeans (142). The common ancestor of modern Europeans lived ~170,000 years ago, possibly in Africa (143). However, a mixture of modern humans and Neanderthals coming to Europe from Africa ~40,000 years ago cannot be excluded.

Amber Provenance. *"It will, of course, for ever remain a secret to us whether this amber is derived from the coast of the Baltic or from Italy, where it is found in several places, but particularly on the east coast of Sicily."* With this sentence of his book "Mycenae: a narrative of researches and discoveries at Mycenae and Tiryns" the German archaeologist Heinrich Schliemann (1822–1890), discoverer of the ruins of Troy and Mycenae, seemed to be challenging scientists to solve the puzzling question of the provenance of amber. Amber is a fossil resin, derived from coniferous trees. It comprises a complex mixture of molecules based primarily on monoterpenoid and diterpenoid structures. It has been used for ornamental purposes since prehistoric times when it was believed that amber was sunlight solidified by sea waves. Understanding the provenance of amber made it possible to establish the earliest known trade routes that involved its transportation from northern to southern Europe ~5000 BC. In the 1960s, IR spectroscopy contributed greatly to this discovery by providing evidence of differences in composition between Baltic amber and Sicilian amber. Transmittance IR spectra acquired from hundreds of amber samples made it clear that the vast majority of amber from prehistoric Europe derives from material originating in the Baltic coastal region (144). Differences in the absorption patterns generated by the vibrational stretching of C–O bonds (1110–1250 cm^{-1}) provided the analytical evidence of Baltic or non-Baltic provenance.

CP–MAS–NMR has also been shown to be able to characterize both modern and fossil amber on a worldwide basis by distinguishing them in both their botanic as well as geographical differences (145,146).

Amino Acid Racemization Dating. Amino acids are the "building blocks" of proteins and up to several hundred of such building blocks can be contained in a protein. All of the amino acids that occur in proteins, except glycine, have at least an asymmetric carbon atom and thus can occur in two optical isomers called D and L. In life, the amino acids making up the proteins of higher eukaryotes consist solely of the L form. Metabolically active tissues contain specialized enzymes known as racemases that maintain a disequilibrium in our cells of only the L isomers. After death, the enzymes in living organism cease their activity and amino acids undergo racemization thus interconverting the L isomers in to the D isomers at a time dependent rate. In the late 1960s, the dating method based on the racemization of the amino acids in fossil organisms was first announced (147,148). The method was expected to extend beyond the radiocarbon range (40,000–150,000 years BP) (for an overview on dating see FINE ART EXAMINATION AND CONSERVATION) but acquired a controversial reputation after errors made in some of the dating carried out in the mid-1970s. The dating of Californian paleoindian skeletons carried out by quantifying the aspartic acid racemization led to an estimated age for the fossil bones of ∼50,000 and 60,000 years (149). Such result suggested an early colonization of North America. Later, after more precise calibration by AMS radiocarbon dating, the bones were redated to 5000–6000 years (150). [A review on amino acid racemization of Californian paleoindian remains may be found in (17).] Today, it is clear that fluctuation in the burial environments and the degree of degradation of the protein can affect the dating and that studies carried out on protein extracted from well-preserved bones can led to more reliable dating (151,152) even though a variety of factors may render the method prone to contamination by exogenous or degradated proteins (153).

4. Degradation of Archaeological Materials

Most of the materials studied by the archaeology have survived for long time in the ground and to a variety of degradation processes. Degradation processes affect different materials to a different extent and follow different paths. For this reason, certain materials entered the archaeological records more often than others. Stone survives almost unaltered while materials such as metal, glass, and certain organic material such as amber, undergo some degradation but often survive in a recognizable form. Biological materials such as skin and hair survive only under exceptional condition such those that preserved the Tyrolean Ice Man in the Alps on the Austrian–Italian border (154). Biological hard tissues such as bone, tooth, and shell undergo complex degradation processes.

The overall degradation processes that act on organic remains after death are studied by *taphonomy*. The term was first introduced in 1940s (155) and comes from the Greek word ταφοζ (taphos, burial). Taphonomy studies all the natural and anthropogenic processes that affect the organism in its transferral from the living word (biosphere) to the sedimentary record (lithosphere). Taphonomy includes two different stages. The first one, *biostratinomy*, includes all the interactions involved in the transferral of the living organism from the living world to the inorganic world, including burial. *Diagenesis* includes all the transformation occurring after burial (156,157).

More recently, these concepts, referring only to living organisms, have been broadened and diagenesis is now "… *the cumulative physical, chemical and biological processes that alter all archaeological materials in the burial environment, and is consequently a fundamental characteristic of the archaeological record*" (156). Diagenetic studies thus also involves postdepositional changes that affect the structure of metal, glass or ceramic during burial (158,159). In this perspective, geochemical modeling was used to provide a deeper understanding of the complex variety of postdepositional processes affecting inorganic materials such as ceramics (156). Also, great progress has been made in understanding taphonomic processes affecting bone (160–162). Bone is an important component of the archaeological record due to the wide range of information its organic and inorganic components carry. Paleodietary information is obtained by the elemental and isotopic analysis of bone components while a variety of other information, partially described above, can be obtained from lipids, proteins, and DNA, which are often preserved in bone. For these reasons, attention is increasingly being placed on understanding all taphonomic processes involving bone.

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