Studying Archaeological Remains
A Great Challenge for Modern Chemistry

by Giuseppe Spoto

Chemistry plays an important role in the study of archaeological materials. It has in fact allowed us to infer trade routes by studying ancient artefacts and also 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 also intervenes in the understanding of the mechanisms which cause archaeological material to degrade. The modern analytical methods today available have been used to study a wide range of archaeological inorganic, organic and biological materials. A short overview of some of the most relevant achievements reached by applying chemical methods to archaeology is here reported.

Archaeology studies past human life, culture and activities as shown by material evidence in the form of surviving artefacts, 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 important events and can be affected by the human tendency to represent the writer's 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. It has also allowed us to infer trade routes by studying ancient artefacts and also 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 also intervenes in the understanding of the mechanisms which 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 artefacts. Archaeological materials are studied from a chemical point of view mostly using the variety of instrumental methods today available to chemists [2]. Such methods have led to the development of new approaches that satisfy specific requirements to a greater degree such as micro-destructiveness or non-destructiveness of the sample to be analysed. In this context, the use of spatially resolved analytical techniques have provided new opportunities for micro-destructive and, at times, completely non-destructive analyses thus opening up new diagnostic approaches for the study of archaeological ad artistic samples [3, 4].

G. Spoto, Dipartimento di Scienze Chimiche - Università di Catania.
gspoto@dipchi.unict.it

Chemical methods in archaeology over the last three centuries

The chemical methods used in the study of antiquities go back to the 18th century. Eminent scientists such as Humphry Davy, Jöns Jakob Berzelius, Michael Faraday, Marcelin Berthelot, Friedrich August von Kekulé and Wilhelm Conrad Röntgen 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 19th century thanks to a number of other investigators, most of them operating in isolation. 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. The concept of *provenance* is still active in the field [5] and the development of instrumental methods and of new ways to mathematically treat data sets [6] have allowed to better define the potential and the limitation of scientific provenance of archaeological material. The use of scientific examination in order to shed light on the past was greatly fostered when major museums began to establish laboratories for that purpose on their premises. 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 Of-

Figure 1 - Obsidian studies have allowed to infer ancient trade routes in the Mediterranean area

fice tunnel as protection against possible war damage 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 [7].
The pioneering approach developed in museum science laboratories was followed by the involvement of university laboratories which 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.

Materials study

Chemistry plays an important role in the study of archaeological materials. Such study has a variety of aims. When artefacts are studied some of the most important aims are to shed light on 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 [8]. By interpreting such information it is possible to better understand the behaviour 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.

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 artefacts to their use, re-use and ultimate discard" [8]. 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. In particular, flint was used from the Paleolithic Period onwards for a variety of purposes such as cutting and pounding. The advent of farming during the Neolithic Period expanded the need for flint that was extracted from mines or quarries and transported to different regions. Chemical studies aimed at establishing what distance the flint travelled from its source are based on the premise that it is possible to source the flint chemically to a particular location [9].
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. Obsidian is a glass formed when highly viscous volcanic lava of high silicon and aluminium contents 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 [9, 10]. Now we know that the acquisition of obsidian developed in different ways, ranging from local collection over land or sea. The Mediterranean area represented an important source for obsidian [11]. Elemental chemical analyses 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 [12]. Central Mediterranean regions were mainly supplied by the Italian islands of Lipari, Sardinia, Palmarola and Pantelleria [11].

Ceramics - The discovery of fire allowed humans to process natural materials to improve or simply change their characteristics (ca. 1,600,000 years ago) [13]. One of the earliest uses of fire concerned cooking. Food became safer and tasted better after cooking. Later, stones were heated to improve their hardness (ca. 80,000 b.C.).
The complex technology required for the making of pottery was not to develop 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 b.C. [14]. The development of pottery is still, however, a subject for debate and its origins have been placed between 12,000 and 10,000 b.C. [10]. 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 which have led to the various modes of pottery production, distribution and consumption has been recently discussed [15]. Pottery has been certainly 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 [16].

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 ca. 2000 b.C. [10].
Glazing technology may, however, have anticipated the origin of glass [10, 17]. 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 b.C. 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. 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 [18]. Five elements were determined by using INAA and expressed in term of oxides: magnesium, potassium, manganese, antimony and lead. Ancient soda-lime glasses dated between 1500 b.C. and 800 b.C. and 800 b.C. and 1000 a.D. 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 b.C. and 200 b.C. were identified as a separate group. Islamic glasses were grouped as high magnesium containing glass produced between 840 a.D. and 1400 a.D. and high lead glasses produced between 1000 a.D. and 1400 a.D. 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 b.C. and 700 b.C. were obtained by innovating the raw materials used [19]. Later in Medieval north-Europe high potash glasses were used to produce church windows and vessel easily subject to degradation [16]. High potassium and barium oxide glasses were produced under the Chinese Han Dynasty (206 b.C. - 221 a.D.) [20]. New materials were also used in India from the first millennium a.D. to produce high alumina glasses [21].

Metals - The advantages offered by metals compared other materials used by ancient people such as stone or wood were discovered not before 10,000-12,000 years ago in Southwest Asia. The advent of metallurgy with the development of farming and of the 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 shaping of native copper was a well-established custom in Southwest Asia from ca.10,000 b.C. onwards. 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 b.C. (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 from 4000 b.C. onwards, the resulting alloy being *bronze*. Lead and zinc were two other important elements in forming or modifying the characteristics of copper alloys. The beginning of the Early Iron Age [22] - fixed as being 1200 b.C. - coincides with the ability of people from West Asia to smelt iron and alloy carbon so as to obtain steel.
Up to 1500 b.C. the Hittites had the most developed technology for the working of 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 b.C. Iron smelting technology presumably dates back to the Bronze Age as the temperature required for smelting iron (1,100-1,150 °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 [23]. Glass-like materials, or *slag*, were formed during smelting due to a reaction between the silica impurities present in the ore and fluxes.

Organic and biomolecular archaeological materials

Most of the research studies carried out in archaeological science over the last fifty 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. The approach consists in identifying molecular markers capable of identifying unknown organic samples on the basis of their presence in contemporary natural substances [24]. Lipids, in particular, have been shown to be of particular important as biomolecular markers.

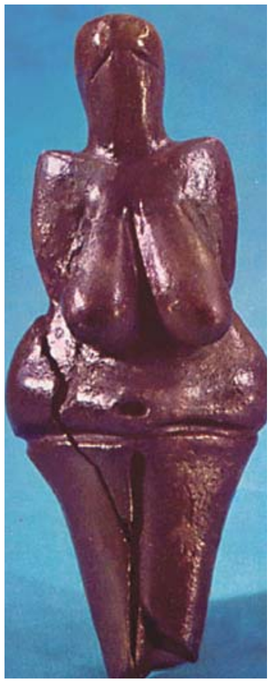

Figure 2 - A Paleolithic woman's statuette made of terracotta. The statuette, found in Dolni Vestonice, Czech Republic, is known as the Black Venus of Dolni Vestonice and is dated to about 24,000 b.C.

Archaeological lipids - Lipids occur ubiquitously in plants and animals and preserve under favourable 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 cou-

pled with mass spectrometric analysers has contributed to studies of artefact use patterns and food consumption through the identification of lipid residues. Lipids are extracted from the powdered original matrices by using organic solvents, they are properly derivatized and then analysed by GC or GC/MS techniques or by GC-C-Irms for isotope ratio studies [25]. Degradation processes cause lipids to be hydrolysed or oxidated. Secondary ketones are commonly found in 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, for instance, 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 [26]. 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 [27]. 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.

Figure 3 - The Ramses II mummy

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 the chemical evidence of the transformation of fats into adipocere indicates submersion of the body in water for several months before its freeze-drying [28]. Cholesterol is another lipid that persists in long-buried bones of humans and animals and its evidence can be used as a source of paelodietary information [29]. Recently, lipid biomarkers have contributed to shed light on chemical treatments used in ancient Egyptian mummification [30].

Proteins - Proteins have rarely survived to the archaeological record [31]. Only under unusual burial environments have they survived microbial degradation and proteins in hard tissues such as tooth, bone, and shell, are prevalently protected. 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. As a consequence of the above it should be expected 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 [32]. Immunological methods have also been used as extraction methods of protein from mineral surfaces, however, a yield of about 0.0025% was evaluated for the proposed methods. Recently, a new immunological method that allows protein extraction yield up to 0.1% has been proposed [33].

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 [34]. Ancient DNA studies were boosted by the invention of the Polymerase Chain Reaction (PCR) [35] that 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 [36]. Moreover, a deep understanding of the degradation processes which concern post-mortem DNA and of the conditions under which DNA preserves is required [36-37].
DNA is a record of ancestry. For this reason ancient DNA can be used to determine kinship relationship within a group of specimens. Moreover, ancient DNA can express some of the biological characteristics of an archaeological specimen. Biological sex or genetic diseases can be inferred by studying archaeological DNA. Studies carried out on DNA sequences older than one million years ago (antediluvian DNA) have concluded that such ancient sequences cannot be reproduced or derive from contaminations [38]. A variety of studies on DNA sequences dated up to 100,000 years ago from extinct animals have revealed phylogenetic the relationships of extinct animals [36]. For instance, the extinct *moas* of New Zealand have been shown to be related to flightless birds in Australia rather than extant kiwis in New Zealand [39]. The study of ancient human DNA sequences have opened a new exciting view of our ancestry [36]. It is today known that Neanderthal hominids, that lived in Europe and Western Asia until about 30,000 years ago, were not directly related to modern Europeans. The common ancestor of modern Europeans lived about 170,000 years ago possibly in Africa. However, a mixture of modern humans and Neanderthals coming to Europe from Africa about 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 which involved its transportation from northern to southern Europe around 5000 b.C. 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 [40]. Differences in the absorption patterns generated by the vibrational stretching of C-O bonds (1,110-1,250 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 [41].

Degradation of archaeological materials

Most of the materials studied by the archaeology have survived for long time in the ground and survived to a plethora 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 to 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. 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 and comes from the Greek word ταφοζ (taphos, grave). 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 [42].
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”* [42]. Diagenetic studies thus involve also post-depositional changes that affect the structure of metal, glass or ceramic during burial. In this perspective geochemical modelling have been used to provide a deeper understanding of the complex variety of post-depositional processes affecting inorganic materials such as ceramics [42]. Great progress has been also made in understanding taphonomic processes affecting bone [43]. 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 below in this text, can be obtained from lipids, proteins and DNA often preserved in bone. For these reasons attention is increasingly placed on understanding all taphonomic processes involving bone.

References

[1] C. Renfrew, P. Bahn, Archaeology: Theories, Methods, Practice, 3rd Ed., Thames and Hudson, London, 2000.
[2] Modern Analytical Methods in Art and Archaeology, E. Ciliberto, G. Spoto (Eds.), John Wiley & Sons, New York, 2000.
[3] G. Spoto *et al., Chem. Soc. Rev.,* 2000, **29,** 429.
[4] G. Spoto, *Acc. Chem. Res.,* 2002, **35,** 652.
[5] L. Wilson, A.M. Pollard, in Handbook of Archaeological Sciences, D.R. Brothwell, A.M. Pollard (Eds.), John Wiley & Sons, New York, 2001, 507.
[6] M.J. Baxter *et al.* in Modern Analytical Methods in Art and Archaeology, E. Ciliberto, G. Spoto (Eds.), Wiley, New York, 2000, 681.
[7] A unique overview of the history of scientific conservation was provided by Harold J. Plenderleith with a lecture held at the British Museum in 1978. The text of the Plenderleith’s lecture has been recently published in H.J. Plenderleith, *Stud. Conserv.,* 1998, **43,** 129.
[8] M.S. Tite, in [13], 443.
[9] J. Henderson, The Science and Archaeology of Materials, Routledge, London, 2000.
[10] J.B. Lambert, Traces of the Past: Unraveling the Secrets of Archaeology Through Chemistry, Addison-Wesley, Reading, Massachusetts, 1997.
[11] R.H. Tykot, *Acc. Chem. Res.,* 2002, **35,** 618.
[12] O. Williams-Thorpe *et al., J. Archaeol. Sci.,* 1984, **11,** 183.
[13] R.M. Rowlett, *Science,* 1999, **284,** 741.
[14] P.V. Vandiver *et al., Science,* 1989, **246,** 1002.
[15] M.S. Tite, *J. Archeol. Meth. Theory,* 1999, **6,** 181.
[16] A.M. Pollard, C. Heron, Archaeological Chemistry, The Royal Society of Chemistry, Cambridge, 1996.
[17] M. Tite *et al., Acc. Chem Res.,* 2002, **35,** 585.
[18] E.V. Sayre, R.W. Smith, *Science,* 1961, **133,** 1824.
[19] J. Henderson, *Archaeometry,* 1988, **30,** 77.
[20] L. Jiazhi, C. Xianqiu, Archaeometry of Glass, in H.C. Bhardwaj (Ed.), Indian ceramic Society, Calcutta, 1987, 21.
[21] R.H. Brill, Archaeometry of Glass, in H.C. Bhardwaj (Ed.), Indian Ceramic Society, Calcutta, 1987, 1.
[22] R. Maddin *et al., Sci. Am.,* 1977, **237**(4), 122.
[23] H. Hodges, Artifacts: an Introduction to Early Materials and Technology, Gerald Duckworth & Co. Ltd., London, 1989.
[24] R.P. Evershed, *World Archaeology,* 1993, **25,** 74.
[25] R.P. Evershed *et al., Acc. Chem. Res.,* 2002, **35,** 660.
[26] S.N. Dudd, R.P. Evershed, *Science,* 1998, **282,** 1478.
[27] I.D. Bull *et al., Antiquity,* 1999, **73,** 86.
[28] B.X. Mayer *et al., J. Chromatog. B,* 1997, **692,** 1.
[29] R.P. Evershed, A.W. Stott, *Anal. Chem.,* 1996, **68,** 4402.
[30] S.A. Buckley, R. P. Evershed *Nature,* 2001, **413,** 837.
[31] A.M. Gernaey *et al.,* in [13], 323.
[32] R.P. Evershed, N. Tuross, *J. Archaeol. Sci.,* 1996, **23,** 429.
[33] O. Craig *et al., Nature,* 2000, **408,** 312.
[34] S. Paabo, *Nature,* 1985, **314,** 644.
[35] R.K. Saiki *et al., Science,* 1988, **239,** 487.
[36] M. Hofreiter *et al., Nature Rev. Gen.,* 2001, **2,** 353.
[37] H.N. Poinar, *Acc. Chem. Res.,* 2002, **35,** 676.
[38] T. Lindahl, *Nature,* 1993, **365,** 700.
[39] A. Cooper *et al., Proc. Natl. Acad. Sci. USA,* 1992, **89,** 8741.
[40] C.W. Beck, *Appl. Spectr. Rev.,* 1986, **22,** 55.
[41] J.B. Lambert, G.O. Poinar, *Acc. Chem. Res.,* 2002, **35,** 628.
[42] L. Wilson, A.M. Pollard, *Acc. Chem. Res.,* 2002, **35,** 644.
[43] R.E.M. Hedges, *Archaeometry,* 2002, **44,** 319.