

Archaeological Chemistry: An Emerging Discipline

Archaeology, the study of the excavated remains of past human cultures, and especially archaeological chemistry, the analysis of organic and inorganic archaeological materials, represent multidisciplinary efforts to reconstruct the course of human culture independently of or in concert with written records. Both fields have emerged only in the last hundred years, and their full potential in illuminating the human past, including the Scientific Revolution itself, has been only partly realized.

Archaeological chemistry is an essential part of the larger field of archaeology. All the finds from an archaeological excavation are materials (pottery, soils, glass, stone, bones, textiles, paints, etc.) that require chemical analysis to be understood fully. This was already appreciated when the first systematic excavations were carried out in the late nineteenth century at Nineveh and Babylon by Austen Henry Layard and at Troy by Heinrich Schliemann. The reports of each of these excavations contained an appendix on chemical analyses of bronzes and glasses by the famous metallurgist John Percy. The study of ancient metal artifacts from private and public collections, principally coins, weapons, and tools, had already been carried out, beginning with Martin Klaproth and George Pearson in the 1790s and continuing with John Davy, J. J. Berzelius, K. R. Fresenius, F. Göbel, and others in the nineteenth century. The value of such studies was evident in

their elucidation of both cultural and scientific phenomena (such as trade connections or corrosion).

When applied to carefully excavated, well-dated materials, chemical analyses have even greater significance in revealing the course of human technological development. Each human artifact has buried within it a "memory" of its past manipulation and use. At the macroscopic level, observations can be made about whether specific tools or molds, which left characteristic marks, were employed in its manufacture. Microscopic and submicroscopic examination of physical and chemical structures and properties, however, can reveal much more information about the sequence of processes that went into manufacturing the object from raw materials, including the original conditions (temperature, pressure, period of time, etc.) at which each step was carried out. Based on the study of well-dated metal artifacts, as well as that of ancient mining, smelting, and refining installations, metallurgists, chemists, and archaeologists together have built up a framework of worldwide human experimentation with metals. We now know that most advances in metal production, involving high-temperature smelting of ores and alloying, occurred in conjunction with the development of urban communities, which had the food surpluses to support full-time specialists and whose elite displayed their status with metal jewelry, sculpture, and weapons. On the other hand, although

the timing and details of some technological innovations (such as the steeling of iron around 1200 B.C. in the eastern Mediterranean) are known (Figures 1 and 2), as yet the evidence is insufficient to determine under what circumstances ancient metal workers would have been motivated toward or capable of shifting from copper to iron metallurgy, the latter requiring much higher smelting temperatures (ca. 1450°C, contrasted to 950°C for copper) and laborious forging.

Chemical analysis of other archaeological materials has provided technological perspectives similar to those derived from the study of changing uses of metals. The pioneering investigations of ceramics, the most ubiquitous fabricated materials found in excavations, were again made by highly respected chemists of the nineteenth century: Humphry Davy, Michael Faraday, and H. de Fontenay were among those who studied pigments and pottery glazes. A ceramics program I initiated at the Museum Applied Science Center for Archaeology (MASCA) in the University Museum at Penn is concerned with reconstructing the ancient technology of pottery and silicates (glass and faience) by detailed study of the finished artifacts. By using a variety of complementary analytical techniques (e.g., xeroradiography, petrography, scanning electron and proton-induced X-ray spectroscopy, neutron activation analysis), the starting materials and additives, the original firing temperatures, and the fabrication methods of the ancient craftsmen can be reconstructed. In general, innovations in ceramics do not follow one after another in temporal succession, with progres-

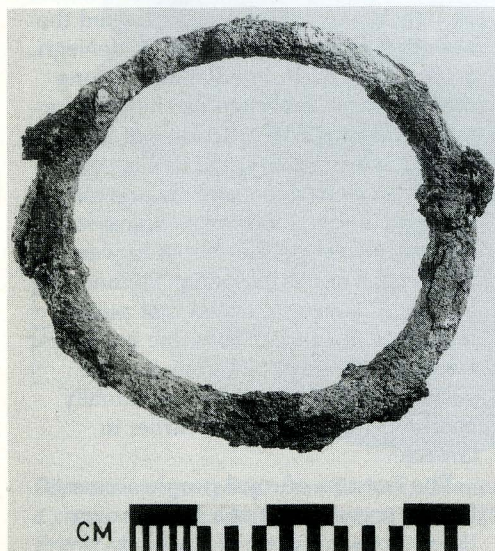


Figure 1. One of the earliest steel artifacts yet discovered—an anklet from an Iron IA (12th century B.C.) burial in central Transjordan. See P. E. McGovern, *The Late Bronze and Early Iron Ages of Central Transjordan: The Bag'ah Valley Project, 1977–1981* (University Museum Monograph No. 65) (Philadelphia: University Museum, 1986). Photograph by N. Hartmann.

Figure 2. A highly magnified ($\times 3000$) scanning electron image of the steel structure of the anklet in Figure 1. Unusually coarse spheroidized carbides are present within a pearlitic matrix. Photograph by H. Moyer.



sively more sophisticated materials and methods, as they do in ancient metallurgy as it went from copper to bronze to iron manufacture. Rather, the most important techniques in pottery manufacture (tempering, the use of slips and paints, firings above 1000°C) were already known and practiced at a high level of expertise, often exceeding that of later times, when pottery first appeared in the archaeological record in the Middle East during the Neolithic period. It is true that the slow and fast wheels, introduced later, represented major advances in pottery production, but hand-building techniques were never totally displaced.

A particularly interesting example of the potting industry gradually reverting from wheel-throwing to coil-building has been documented in the Late Bronze and early Iron Ages (ca. 1550–1050 B.C.) of central Transjordan. The shift from one technique to another was accompanied by lower-fired wares with more inclusions. From a ceramic viewpoint, the change appears to be correlated with the mass production of pottery at the end of the Late Bronze Age. Clay beds with low percentages of inclusions were probably worked out, and less time was taken in cleaning up the clays. Since clays with more inclusions can actually be formed more efficiently by hand than by throwing, it is not surprising that the more "primitive" technique came to be preferred in the early Iron Age. Before our study had been carried out, archaeologists had assumed that the evident changes in pottery forms and styles were due to the invasion of a new people, such as the Ammonites or Israelites. The shift in potting techniques, however, occurred prior to the disruptions around 1200 B.C. and over an extended period of time. Neutron activation analysis also demonstrated that the same clay source was used over the entire five-hundred-year period.

The emergence of the glass industry at the beginning of the second millennium B.C. in upper Mesopotamia might be considered the forerunner of the modern "high-tech" enterprise concerned with computer chips, fiber optics, and other silicate materials. The industry had spread to Palestine by 1550 B.C. (Figures 3 and 4). In antiquity a wide range of transition metal colorants, including manganese, cobalt, antimony, and lead, were developed as colorants and opacifiers. Manufacturing procedures and chemical recipes, as well as the invoca-

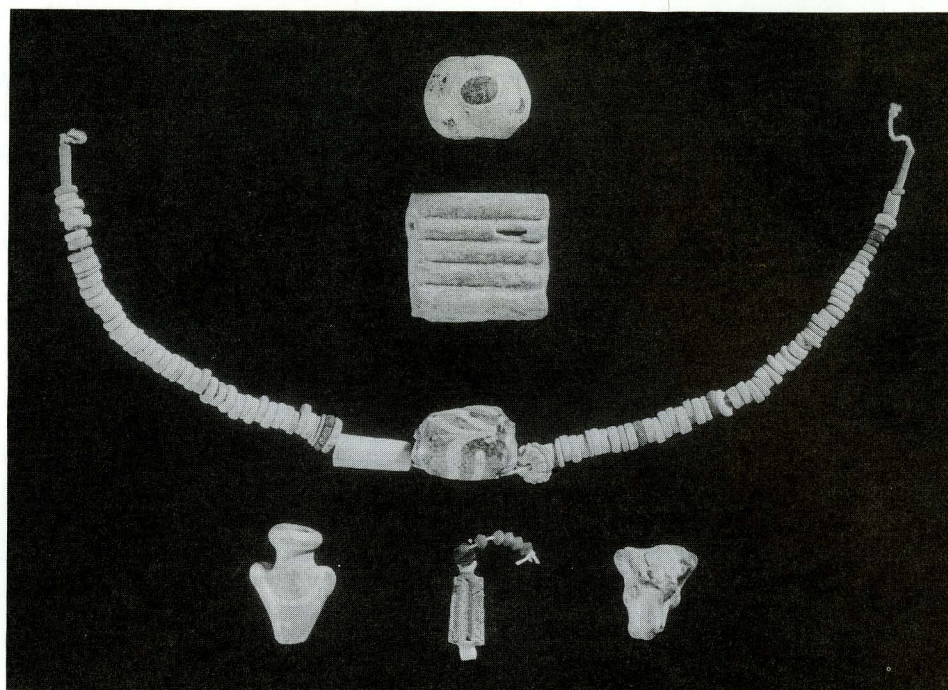


Figure 3. Jewelry found under the altar steps of the Late Bronze II Egyptian temple at Beth Shan in Israel. Various bead shapes and pendant types of glass and faience are shown (note the Egyptian "heart" at the lower left and the Syro-Palestinian ram's head at the lower right). Photograph by P. E. McGovern.

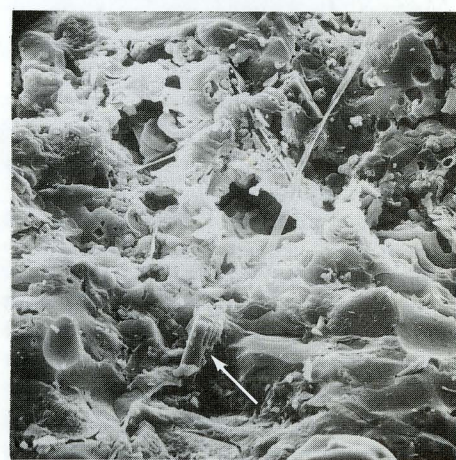


Figure 4. Scanning electron image of a bead, made of Egyptian blue frit, from a burial in central Transjordan. A platey crystal of Egyptian blue ($\text{CaCu Si}_4\text{O}_{10}$) can be seen embedded in the glassy matrix at the lower center (see arrow). Photograph by P. E. McGovern.

tion of gods at various stages in the process, are detailed (using a highly specialized vocabulary) in contemporaneous texts, written in Akkadian using cuneiform writing on clay tablets. The process of weathering in ancient glasses has also been a focus of chemical inquiry. Because they are not crystalline but supercooled liquids, glasses are thought to be more resistive to radioactive decay products, thus possibly providing a means with which to dispose of nuclear waste safely. The aging properties of glasses of known compositions from archaeological contexts represent long-term experiments—admittedly with few controls—for appraising this proposal.

Because they degrade easily, organic compounds are less often the province of archaeological chemistry. Royal purple (dibromoindigotin), probably the most

famous and valued dye of antiquity, is an exception to the rule. With the rise of modern chemistry, the dye attracted the attention of B. Bizio, A. and G. deNegri, R. Dubois, and P. Friedländer, among others, who established its chemical formula and properties. Because of its extended aromaticity, the dye is very stable. Ancient dyers and writers may not have understood the chemical structure of the compound, but they were well aware of this property. Plutarch, in his *Life of Alexander*, noted that purple textiles seized in Persia by the conqueror were as intensely colored as if made yesterday, although they had actually been produced 170 years earlier in Greece.

The fastness of royal purple accounts for the preservation of a sample over three thousand years old, which

Rudolph H. Michel and I studied recently. We employed a variety of analytical techniques (infrared, electron, proton-induced X-ray emission, and mass spectrometry), in conjunction with wet chemical tests for indigoid dyes, to examine a purple sediment on the interior of pottery vessels from a thirteenth-century B.C. industrial context at the site of Sarepta along the Lebanese coast; we identified it positively as dibromoindigotin (see *Analytical Chemistry* 57 (1985), 1514A–1522A). Besides being the earliest chemical attestation of the dye, the finding had important implications for the dyeing process itself. For example, one vessel type (Figure 5), whose interior was covered with the dye, had a wide mouth and a spout at the bottom that would have been ideal for separating the dye solution from organic residues of the mollusks from which the dye is derived. The dyeing was also carried out in the vicinity of pottery kilns, which might have provided the heat necessary to reduce the compound in vat dyeing. Hypothetical reconstructions of the exact stages of the dyeing process are made difficult by the limited archaeological data, and, more important, the lack of documentary evidence for another thousand years. Even the lengthy, authoritative description of the process in the *Historia naturalis* by Pliny the Elder, written in the first century, has been variously interpreted. By attempting to replicate Pliny's process in the laboratory,

modern chemistry can help to resolve some of the translational difficulties. As one example, it has been shown that the dye can be reduced to the leuco base for vat dyeing only by tin in an alkaline solution (Figure 6). In Pliny's account of boiling the extract in a vessel of *plumbum*, therefore, the Latin is best translated as "tin" (*plumbum album*) rather than "lead" (*plumbum nigrum*). With ever-accumulating chemical, archaeological, and linguistic data, our understanding of ancient chemical processes will be progressively refined. Still, a point will eventually be reached at which the empirical observations and procedures of antiquity will defy explanation in modern chemical terms.

Besides shedding light on the course of human technological and cultural development, archaeological chemistry provides the means to date absolutely ancient physical remains (both written and unwritten). The details of the carbon-14 dating method, which Willard Libby discovered in 1947, need not be repeated here, except to say that it has become the most widely applied technique for dating remains of the last 10,000 years, when human culture has undergone the most profound changes (developments in mass spectrometry promise to extend its effective range back to 100,000 years before the present). It is also the most accurate method yet developed, once corrections have been made for changes in the amount of car-

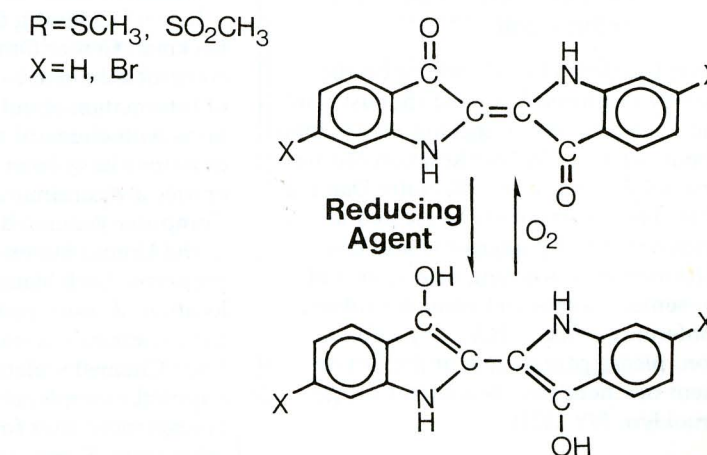
bon-14 in the environment, possible contamination by more recent carbon, and differences in the uptake of carbon-14 by different plant and animal species. In contrast, other dating methods (e.g., thermoluminescence, amino acid racemization, obsidian hydration) either have a much more limited application or are more affected by past environmental conditions (e.g., groundwater contamination, climatic changes) that cannot be readily assessed.

Chemical techniques have also become increasingly important in the actual discovery of archaeological sites. The inorganic and organic materials that constitute human settlement debris, whether foodstuffs, construction elements (stones, plaster, wood), or specialized artifacts (metals, ceramics, etc.), have specific chemical compositions and properties as originally constituted and as they undergo reactions in a soil matrix. A variety of geophysical and geochemical detecting devices (magnetometers, resistometers, ground-penetrating radar, phosphate analyzers) make use of chemical and physical differences (e.g., magnetic susceptibility, electrical conductivity, acidity) between archaeological features and the surrounding medium to locate subsurface remains. Often the most interesting archaeological remains (intact burials, industrial installations, archives) have been intentionally hidden or covered over by relentless geological forces. In addition to the more



Figure 5. A spouted vat from Sarepta, Lebanon, which contained a purple sediment identified as royal purple. Photograph by J. B. Pritchard.

Figure 6. Dibromoindigotin (royal purple) undergoes reduction in a vat dyeing process to form the almost colorless leuco base. Once this compound is chemically bound to the textile, it can be reoxidized to the purple dye. If hydrogen is substituted for the two bromines (marked by X in the figure), the blue dye indigotin results.



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spectacular discoveries made by such methods, they are of value in developing efficient, cost-effective excavation strategies.

The scope of archaeological chemistry is enormous, and only a very small portion of the field has been discussed above. The discovery, dating, and interpretation of excavated remains continues with the conservation of selected artifacts and whole buildings, requiring a host of considerations on how best to stabilize chemical constituents. The detection of forgeries by chemical methods has an auxiliary function to play, since the replication of antiquities, as a profitable enterprise, can easily lead to a falsification of the past (e.g., the Piltdown Man hoax).

Even though it has already accomplished much, archaeological chemistry is best described as an emerging discipline. Since World War II, its subject matter and the tools it employs for answering specific questions have been defined. Nevertheless, the individual scientists at work in archaeological chemistry are widely dispersed in various scientific fields. The Archaeological Chemistry Section of the American Chemical Society's Division of the History of Chemistry brings together some of the interested, active parties on a periodic basis, and an effort has been made to map out the long-range goals and needs of the discipline. Without adequate funding and a defined place in the academic curriculum, however, the discipline will remain a stepchild of better-established fields and never attain its full potential in elucidating the history and prehistory of chemistry.

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Call for Information

Leon Gortler, who is working on the history of physical organic chemistry in the United States, is seeking information about the first Organic Reaction Mechanisms Conference held at Notre Dame in 1946. He is particularly interested in finding a list of participants and any information concerning discussions of presented papers and plans for future conferences. If you have any information, please contact him at the Department of Chemistry, Brooklyn College, Brooklyn, NY 11210.