

The First Wine & Beer

Chemical Detection of Ancient Fermented Beverages

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Organic analysis applied to archaeological remains, especially the contents of pottery vessels, has developed rapidly over the past two decades. Lipids, resins, dyes, perfume ingredients, drugs, and other compounds—some less than a milligram in weight and some thousands of years old—have been identified by using a wide range of chemical and physical techniques. As these methods are further refined, archaeological chemistry promises to open up new chapters in human and environmental history, including ethnicity and genetic development, diet, dis-

ease, and materials processing.

Under certain conditions, in either very dry or waterlogged environments where microbial activity and autoxidation are reduced, some organic compounds or their degradation products are preserved in ancient archaeological contexts. We previously demonstrated the presence of royal purple, one of the most famous dyes of antiquity, on pottery sherds (*Anal. Chem.* **1985**, *57*, 1514 A). In this article, we report our investigations of another luxury item of many cultures: wine. This investigation, in turn, has led to discoveries about another, perhaps less prestigious but no less important, fermented beverage: beer.

Wine and archaeology

The chemical detection of a fermented beverage such as wine or beer is a greater analytical and archaeological challenge than that of royal purple (6, 6'-dibromoindigotin), which occurs only in certain marine mollusks and is stable because of its resonance structures. Wine is a processed beverage made from grape juice or must. It is an unusually



complex mixture of water and organic compounds (Figure 1), including alcohols, aldehydes, acids, carbohydrates, proteins, esters, and polyhydroxyaromatics such as tannins, anthocyanins, flavonols, and catechins, all of which contribute significantly to its color and taste.

Phenolic carboxylic acids, which are the degradation products of polyhydroxyaromatics, are relatively stable and are a distinguishing group of compounds found in grapes that might be sought in an analysis. Even more specific is tartaric acid and its salts, which occur in large amounts only in grapes. The survival of the latter compounds, however, is not assured, especially in view of their finite water solubilities.

Once a compound such as tartaric acid or potassium bitartrate is identified, there is still the problem of how to distinguish between grape juice, grape syrup, another fruit juice (e.g., from dates or pomegranates) that has been adulterated with grape juice, and wine. If written or pictorial evidence exists, such as inscriptions on the sides of vessels detailing their contents, interpretation is eas-



*Vintage scene from the tomb of Nakht, Western Thebes, New Kingdom. (Davies, N., *The Tomb of Nakht at Thebes*; reprinted with permission from the Metropolitan Museum of Art, New York.)*

ier. For prehistoric periods, however, there is only the “mute” archaeological record. From this—at best, only a partial record—the researcher attempts to infer whether a pottery vessel might have served a special purpose or whether the presence of grape pips (seeds) in a certain context points to wine-making, consumption of the whole fruit, or some other activity.

Wine-making in the highlands of Iran?

Archaeologists under the direction of T. Cuyler Young, Jr., of the Royal Ontario Museum in Toronto were faced with a puzzling set of evidence during their excavations of Period V remains at Godin Tepe, located in the Zagros Mountains of western Iran. Period V, dating between approximately 3500 B.C. and 2900 B.C. (the Late Uruk period), is contemporaneous with the beginnings of complex urban life as we know it.

Lowland Greater Mesopotamia, comprising the wide alluvial plains of the lower Tigris and Euphrates rivers in modern Iraq and of Khuzistan in southwestern Iran, was

home to one of the oldest literate civilizations in the world: the Sumerian and Elamite city-states. Here, clay tablets incised with pictographic characters were unearthed. The growing population was supported by irrigation agriculture and horticulture of domesticated plants (e.g., cereals, figs, and dates). Traders and adventurers exploited surrounding areas for precious commodities such as gold, copper, lapis lazuli, carnelian, and timber, which were un-

graphic tablet, and other artifacts were discovered within an oval complex of well-constructed symmetrical rooms enclosing a central courtyard, the Citadel Mound complex. These findings, which were contemporary with the earliest lowland city-states of the Late Uruk period, can be understood within the broader cultural developments of the time. It is plausible that Godin Tepe was an early Sumerian and/or Elamite trading post, administrative center, and/or

ANALYTICAL APPROACH

available in lowland Greater Mesopotamia.

The Zagros Mountains, bordering lowland Greater Mesopotamia, provided some of these raw materials and were tied into the wider trading network. Godin Tepe is located along the High Road or the Great Khorasan Road (the famous Silk Road of later times) in the central Zagros Mountains. Pottery, an early picto-

military base for protecting the trade route.

Other finds are more difficult to understand. An unusually large funnel, about half a meter in diameter, and a circular “lid” of smaller diameter were recovered from one room of the Citadel Mound complex. McGuire Gibson of the University of Chicago’s Oriental Institute proposed that the funnel, covered with a coarsely wo-

ven cloth (long since deteriorated), might have served as a strainer for grape must. Such large funnels are known to have been used much later in wine-making installations in the Middle East. It is possible that grapes were heaped into the funnel, the lid was used to apply weight and pressure, and the juice was directed into a jar.

This was a plausible scenario, but it lacked hard evidence. No grape pips, which are often well preserved, were found in the room, and the funnel might have been used for another liquid. The lid might have been just that—a lid for a wide-mouthed vessel. The wine-making hypothesis, however, became more compelling when one of us (VRB) noted a red deposit on the insides of several jars (Figure 2) from two rooms that were directly across the courtyard from the room where the funnel and lid were found. Could the red deposits have been wine deposits? One room

appeared to have been a residence where wine might have been consumed; the other room might have been used to distribute wine and other goods to merchants, soldiers, and others through two windows facing the central courtyard.

The jars with the red deposits are a unique pottery type that has a rope design applied as two inverted U shapes along opposite exterior sides of each vessel. During the Late Uruk period, rope designs often indicated the placement of real rope. The shape and placement of the inverted U suggested a means by which these vessels could have been supported on their sides. In fact, the red deposits on the interiors of one whole vessel were confined to the base and the sidewall (Figure 3). The red residue was on the same side of the vessel as the applied rope decoration on the outside. The deposit was precisely where materials would have settled out from a liquid if the vessel had been stored on its side.

The inference that this jar once contained a liquid was supported by another stylistic peculiarity. These jars have relatively narrow mouths and tall necks, compared with other jars of the same period. A narrow-mouthed, tall-necked vessel would be better suited for storing and pouring liquids.

It also seemed likely that the jars had once been sealed, because two unfired clay stoppers—slightly smaller than the mouth and neck diameters of the jars—were found discarded in other rooms of the complex. The clay could have functioned like a modern-day wine cork, absorbing liquid and expanding to keep out the oxygen, if the vessels had been laid on their sides. Such precautions make sense if wine were the intended final product.

Grape juice quickly ferments to wine. The trick is to stop it from becoming vinegar, and this could have been accomplished by a technique still used today: stoppering the vessel and storing it on its side.

Identification of tartaric acid

Clearly, hypotheses about wine production and consumption at Godin Tepe stand or fall on whether the jars did indeed contain organic compounds derived from grapes.

Transmission and diffuse-reflectance FT-IR spectrometry (DRIFTS) are versatile techniques that are particularly useful in an archaeological chemical investigation when one must determine whether the sample

is an organic or inorganic residue. DRIFTS has the advantage that the archaeological sample need not be damaged, and it eliminates the need for preparing an optically transparent potassium bromide wafer. The spectra from either technique will show the same absorption bands at the same wavelengths.

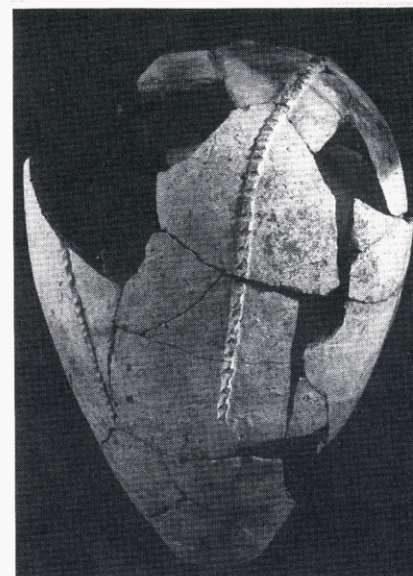


Figure 2. Godin Tepe wine jar, late Period V.

(Courtesy William Pratt, Royal Ontario Museum.)

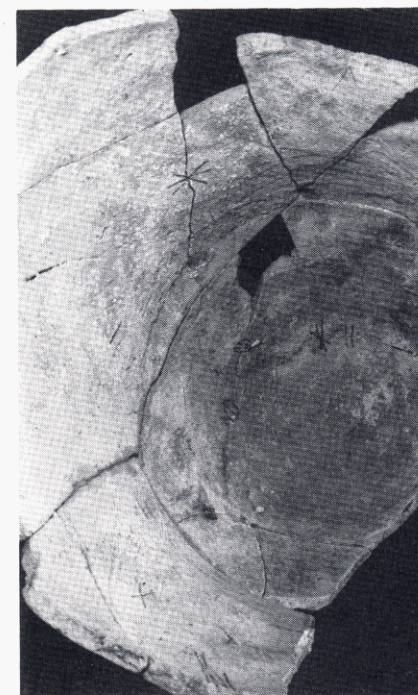


Figure 3. Red deposit (dark patches) visible on the interior base and one side of the Godin Tepe jar in Figure 2.

(Courtesy William Pratt, Royal Ontario Museum.)

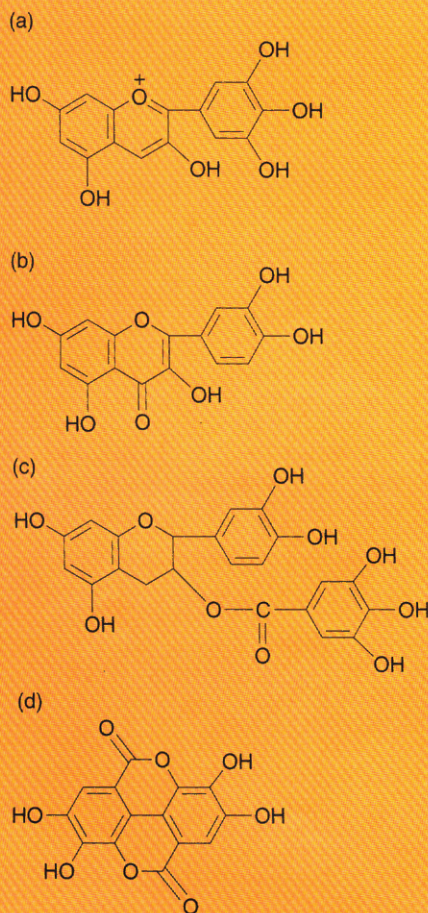


Figure 1. Compounds found in wine.

(a) Delphinidin, an anthocyanidin. (b) Quercetin. (c) Catechin-3-gallate. (d) Elagic acid, which is esterified with sugars to yield elagotannins.

The DRIFT spectrum of the surface scrapings of the interior red deposit of one Godin Tepe jar revealed the presence of organics but was dominated by silicates. More definitive results were obtained by extracting several sherds with boiling acetone. The sample was evaporated to dryness, yielding 6–7 mg of resinous solid for both a 17-g sample (with a visibly thicker deposit) and a 73-g sample (with a thinner deposit). Because whole sherds were extracted, it is not known whether this relatively small amount of solid derives from the reddish deposit, from the interior of the vessel, or from both areas. A control sample from a deposit-free area of one jar, however, showed no organics.

For a reference sample of an ancient wine residue, a dark-colored deposit from a storage jar or amphora (Figure 4) was chosen from the ancient Nubian site of Gebel Adda, now submerged by the waters of Lake Nasser behind the Aswan Dam. There was little doubt that this vessel once contained wine, because it belongs to a special pottery type. Such jars were imported in quantity from Upper Egypt into Nubia during the late Byzantine period (fourth to sixth centuries A.D.). Whole villages in Nubia were composed largely of taverns, and empty amphorae, like the one tested, were piled in heaps around the taverns.

The DRIFT spectra of the Godin Tepe jar extracts (Figure 5a and 5b) and the ancient Nubian reference sample of wine (Figure 5c) have many similarities, including an intense C–H peak around 2900 cm^{-1} ; a sharp, intense carbonyl peak, with a shoulder, at $1720\text{--}1740\text{ cm}^{-1}$; and carboxylic acid-related bands between $1385\text{ and }1470\text{ cm}^{-1}$ and $1240\text{ and }1250\text{ cm}^{-1}$. Of particular interest is the $1720\text{--}1740\text{ cm}^{-1}$ carbonyl band, which is at the upper end of the range for carboxylic acids ($1680\text{--}1740\text{ cm}^{-1}$) and is characteristic of carboxylic acid groups located near strong electron-withdrawing groups, such as halogens and carbonyls. In addition, the bands at $1600\text{--}1650\text{ cm}^{-1}$ suggest the presence of carboxylic acid salt(s). The hydroxyl bands at $3400\text{--}3500\text{ cm}^{-1}$ are broad and result from the presence of several types of hydroxyls. The strong band at 2900 cm^{-1} and the numerous absorption bands from $1550\text{ to }800\text{ cm}^{-1}$ indicate a variety of organics, possibly some of those listed above as wine or grape components.

The DRIFT results strongly sug-

gest that the carboxylic acid in the extracts is tartaric acid. For comparison, we examined the spectrum of the naturally occurring L-(+) isomer of tartaric acid (Figure 5d). Because the three stereoisomers (Figure 6) have very similar DRIFT spectra, racemization of the unknown would not affect the results. Most significant for comparison are the bands at 1445 cm^{-1} and 1250 cm^{-1} as well as the doublet peaks at $1740\text{ and }1720\text{ cm}^{-1}$, all of which exist because of carboxylic acid groups in the molecule. These values are very close to those of the unknown deposit and extracts.

Although the DRIFT analysis provides strong evidence for tartaric acid, it does not unambiguously identify the compound. Separation and characterization of tartaric acid by chromatography, followed by spectroscopic analysis, is one way to gain greater certainty. Although future investigations may provide such confirmation, a simpler approach is to test the unknown mixture with a highly specific Feigl spot test for tartaric acid.

In this test, β,β' -dinaphthol and concentrated sulfuric acid are used

to convert tartaric acid to a compound that exhibits green fluorescence under UV light. Samples from the Godin Tepe jars and the Nubian amphora, as well as synthetic L-(+)-tartaric acid, all gave the same characteristic green fluorescence.

Another unanswered question is why tartaric acid is present primarily as the free acid and not, to any considerable extent, as its salt. The free acid is more soluble in water than the monopotassium salt (the form in which it crystallizes from wine) and would be expected to dissolve and disappear through groundwater percolation. One might conjecture that this dihydroxy dicarboxylic acid was strongly adsorbed on silicates by hydrogen bonding. Thus it could be removed from the hydrolysate of the bitartrate and preserved in the pottery matrix. The equilibrium between the acid and the salt would shift to the acid side as more acid was bound up in the ceramic.

Implications for wine-making

The chemical authentication of tartaric acid in the Godin Tepe jars agrees with the archaeological scenario that the jars originally contained a grape product. But although the presence of tartaric acid is the crucial link in the chain of arguments, it is insufficient for establishing whether the grape product was a liquid and, if so, whether it was fermented to wine. For these inferences, we must rely on the archaeological evidence. The available data (e.g., the narrow mouths and elongated necks of the jars and the red deposits that had formed from materials settling out) point to the jars having been filled with liquids. Under normal conditions and at room temperature, grape juice easily and quickly ferments to wine.

Grape must fermentation proceeds rapidly because a variety of wild yeasts, primarily the genera *Saccharomyces* and *Candida*, are present in the "bloom" of the grape skins. The ability of yeasts to ferment grape sugars depends on the presence of specific enzymes. Oxygen respiration is required for the growth and multiplication of the yeast cells and consequently for the course and degree of fermentation. The continued availability of oxygen after fermentation has ceased leads to the multiplication of the bacteria (*Acetobacter*) that are responsible for the conversion of ethanol to acetic acid. The precautions that were taken in storing the liquid contained in the Godin Tepe

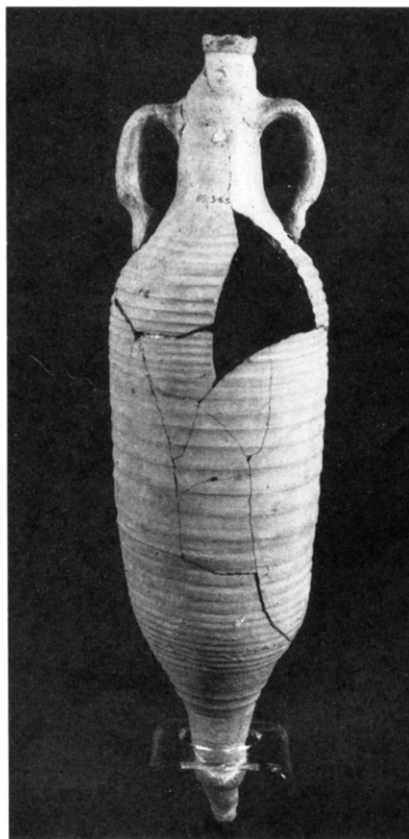


Figure 4. Nubian wine amphora.

(Courtesy William Pratt, Royal Ontario Museum.)

jars—stopping the vessels and laying them on their sides—makes the most sense if this liquid were wine. Air was prevented from entering and nourishing the bacteria that convert wine to vinegar.

The actual processing of grapes into wine need not be very complex, as the textual and pictorial evidence for wine-making from the ancient world clearly shows. In Egyptian wine-making, the grapes were tread on in crushing vats to extract the juice or must. A bag press was also used to squeeze out any juice remaining in the solid residue. Pottery jars were then filled with the juice, which quickly fermented to wine by natural processes. The jars were completely stoppered only after most of the fermentation had occurred.

A similar series of steps was probably used to produce the wine contained in the Godin Tepe jars and, indeed, this process of wine-making might well have been discovered at many times and in many different

places. Even the development of specialized pottery vessels and storage techniques for wine-making were not beyond the expertise of village or small-scale household vintners.

Although the Godin Tepe jars very probably contained wine, it is still uncertain whether the beverage was produced on site from grapes grown locally. The evidence for a local wine-making installation is only a large funnel and a putative lid for pressing the grapes. Nevertheless, if one were searching for an early center of wine production, Godin Tepe—centrally located on a major trade route in the central Zagros Mountains—would be an excellent place to begin. The people from the Transcaucasian region, approximately 600 km to the north where the wild grapes still grow today, likely were in contact with Godin Tepe in Period V. The emerging cities of lowland Greater Mesopotamia, especially their elite classes, represented a large potential market for wine. The entrepreneurial and experimental spirit of the period, quite evident in the extensive trade connections, urban development, agriculture, and horticulture of the lowlands, might well have been applied to viticulture and viniculture in the highlands.

Another fermented beverage

Recently, one of us (VRB) observed a curious crisscross pattern of long incisions on the interior of a Late Uruk double-handled jug from one of the same rooms containing the wine jars at Godin Tepe. The incisions were filled with a pale yellowish residue. The early Sumerian sign for beer shows a pottery vessel with internal linear markings. Together, the archaeological and pictographic evidence strongly suggests that this

vessel served as a beer container.

Calcium oxalate is a principal component of “beerstone,” which settles out at the bottom and along the sides of beer fermentation and storage tanks, and it characterizes barley beer. This salt is soluble in water to only 6 mg/L at 18 °C, and the compound would be expected to accumulate on the inside of a storage vessel, especially one with a greater surface area caused by incising.

A Feigl spot test (which is sensitive to 10^{-6} g) provided definitive evidence that the pale yellowish deposits in the incisions of the ancient Iranian sherds contained an oxalate, most probably calcium oxalate. Reduction of the oxalate in an acidic medium to glyoxalic acid, followed by reaction with phenylhydrazine and hydrogen peroxide, gives a distinctive pinkish red color. Another ancient beer sample, as well as pure calcium oxalate, were run as controls. Scrapings from an Egyptian New Kingdom blue-painted “beer-bottle,” belonging to a type used in a “bread and beer” ritual and clearly intended for beer (according to tomb paintings and reliefs), tested positive. We also tested modern beerstone from a brewer’s vat, which gave a pinkish red color.

In addition to beerstone, oxalates occur naturally in relatively large amounts (~5–10% by fresh weight) in spinach and rhubarb, species of which grow in the Iranian highlands today. Compared with cereals, however, these plants make up a minor part of the human diet, and it is unlikely that they or their derived products were stored or processed in the ancient incised vessel. Minor sources of oxalic acid or oxalate salts, which are widely distributed in nature, were ruled out. Feigl

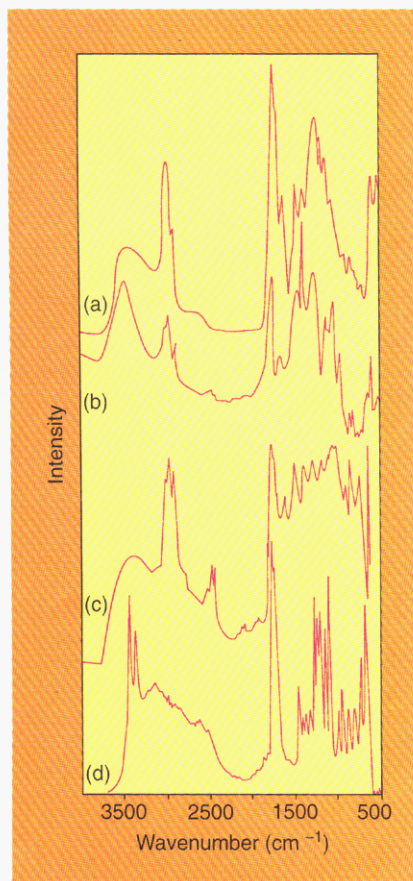


Figure 5. Spectra of extracts and tartaric acid.

(a, b) DRIFT spectra of Godin Tepe jar extracts mixed with KBr. (c) DRIFT spectrum of Nubian amphora wine deposit mixed with KBr. (d) IR transmission spectrum of L-(+)-tartaric acid.

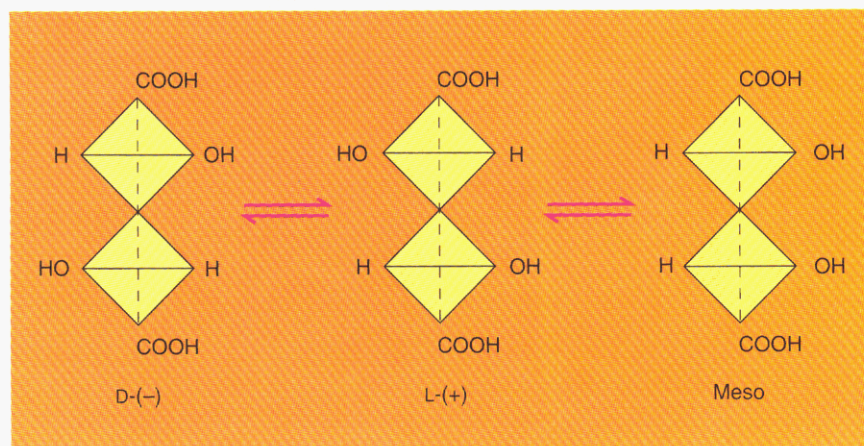


Figure 6. Stereoisomers of tartaric acid.

spot tests of exterior scrapings of the vessel and from the interior of one of the wine jars gave negative results.

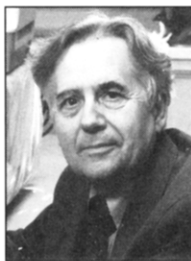
The discovery of oxalate inside the Godin Tepe jug confirmed the archaeological and pictographic evidence that the vessel was a beer container. This result should not be surprising, given that the site was in close contact with lowland Greater Mesopotamia, where beer was the preferred drink. The beer at Godin Tepe was likely made from locally grown barley because carbonized six-row barley predominated in the archaeological material recovered from Period V.

Wine and beer connoisseurs may disagree about many matters, but neither group can as yet claim that wine or beer was the earliest fermented beverage. The inhabitants of Godin Tepe in the Late Uruk period obviously appreciated the nutritional and psychotropic benefits of both drinks.

We thank T. Cuyler Young, Jr., and Edward J. Keall of the Royal Ontario Museum in Toronto for providing samples from the Godin Tepe vessels, and Nicholas B. Millet, also of the Royal Ontario Museum, for providing samples from the Egyptian vessels. A modern sample of beerstone was scraped out of a fermentation vat at the Dock Street Brewing Company of Philadelphia, PA. Bruce Chase and his staff, in particular N. Rapposelli and E. Matthews, at the Experimental Station of The Du Pont Co. in Wilmington, DE, ran the DRIFT and transmission spectra. Vernon Singleton, professor of enology at the University of California-Davis, kindly advised us on the characteristic components of wine and beer as well as the appropriate analytical techniques for their identification. Andrew Waterhouse of the University of California-Davis recently consulted with us on chromatographic analyses. The barley from Period V at Godin Tepe was identified by Naomi F. Miller of MASCA.

Suggested reading

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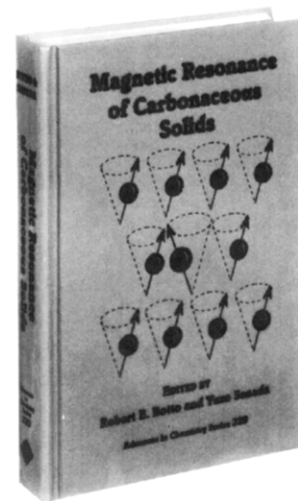
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Patrick E. McGovern received his A.B. degree in chemistry from Cornell University and his Ph.D. in Near Eastern archaeology and literature from the University of Pennsylvania. He joined MASCA as a research scientist in 1979. He engages in a wide range of research in archaeological chemistry, including radiocarbon dating, cesium magnetometer surveying, colorant analysis of ancient glasses, pottery technology, and organic analysis of vessel contents and dyes.



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