analytical chemistry

Review

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Analytical Chemistry in Archaeological Research

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CONTENTS

Archaeology is the study of past human societies through the analysis of material remains. The application of analytical chemistry to archaeological research has increased substantially over the last half-century and today represents a major methodological subfield within archaeological science. This review outlines the analytical methods that archaeologists have successfully incorporated into their research designs, stressing both major advances and necessary limitations that govern the suitability of particular techniques for specific research questions. The broad reviews and treatises of Seaborg,[1] Rainey and Ralph,[2] McGovern,[3] Brothwell and Pollard,[4] Pollard and Bray,[5] Barnard and Eerkens,[6] and Malainey[7] provide the basic principles of analytical techniques and their practical application to archaeological research. The present review focuses on the specific challenges stemming from the analysis of rare and precious archaeological materials, the necessity of knowing the recovery context, including spatial location, time period, cultural associations, and the nature of other associated artifacts, for posing realistic research goals, and major breakthroughs in our understanding of human history that stem from interdisciplinary collaborations between archaeologists and analytical chemists.

The lay conception of archaeology is often one of treasure hunting, the discovery of rare and fantastic exotica, and the collection of fine works of ancient art, the "Indiana Jones" paradigm, partly because of the famous discoveries of Heinrich Schliemann (who excavated the Hellenic city of Troy in the 1870s), Hiram Bingham (who rediscovered the Inka sanctuary of Machu Picchu in 1911), and Howard Carter (who explored the tomb of the Egyptian Pharaoh Tutankhamun in the 1920s). Instead, the best of modern archaeology couches itself as carefully designed, empirical, and data-driven research focused on uncovering the human behaviors and social processes behind the artifact. Today's archaeology is not about finding things; it is about finding things out. The application of analytical chemistry to archaeological materials has become an essential part of modern archaeological investigation.

One of the pioneers in using analytical chemistry to study archaeological objects was Alfred Lucas (1867−1945). An analytical chemist with a background in forensic science, Lucas moved to Cairo in 1898 where he worked for various departments of the British Colonial Service. At the age of 55 he retired from the civil service to pursue his interest in Egyptian archaeology.[8] Shortly thereafter, Lucas became a consulting chemist for the Egyptian Department of Antiquities (a position he held until his death) and was asked by Howard Carter to assist in the examination and preservation of the artifacts from the tomb of Tutankhamun (Figure 1). He remains best known for his book *Ancient Egyptian Materials and Industries* of which many editions have appeared since it was first published in 1926.

Human beings, like all organisms, modify the chemical constitution of themselves and their surrounding environments as they go about daily activities. These range from the quotidian (procuring, preparing, and enjoying food and beverage; discarding waste; production and use of basic tools) to the culturally specific (use of pigments and dyes for decorative purposes; consumption of stimulants and hallucinogens in ritual contexts; embalming and other treatment of the dead) to the seemingly extraordinary (cannibalism; complex metallurgy; genetic modification of plant and animal populations; applying remedies, treatments, and medicines). All of these behaviors provide fundamental information on how human groups organize themselves politically and economically, how cultural norms regulate responses to social and environmental stimuli, how individuals balance their interests against that of a larger group, and beyond the functional necessities of everyday life, how people choose to render their lives meaningful in a complex and often uncertain world.

Analytical chemistry contributes techniques vital for obtaining absolute calendar dates for archaeological sites (radiocarbon and other forms of isotopic dating), linking the raw materials used in prehistory to their geochemical sources (analyses of oxygen, nitrogen, strontium, and other stable

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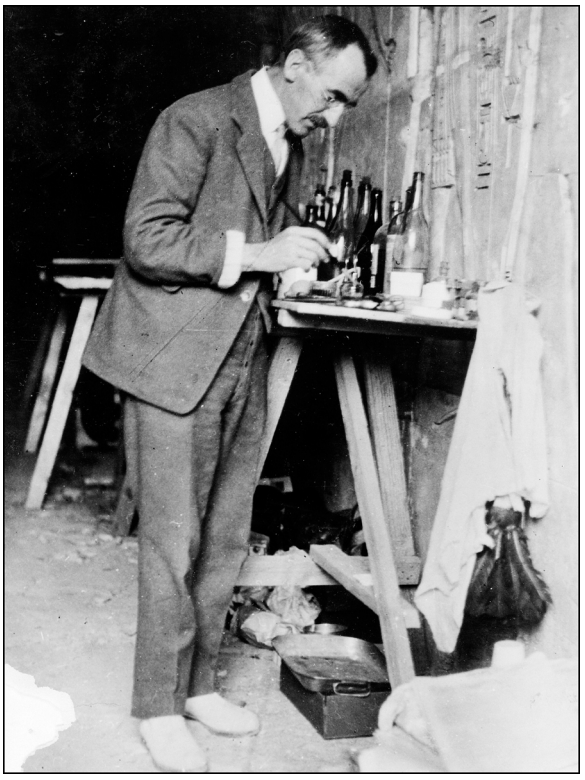

Figure 1. Analytical chemist and Egyptologist Alfred Lucas (1867–1945) at his improvised laboratory in the tomb of Pharaoh Seti II, in the Valley of the Kings near modern Luxor. This is where he, in the early 1920s, directed the analysis and conservation of objects from the tomb of Tutankhamun, directly across the valley, before they were transported to Cairo. Photograph by Bill Warhurst (NICA ID 677877). Copyright News Syndication (London).

isotopes), deducing the elemental composition of artifacts via spectroscopic and elemental fingerprinting (X-ray florescence (XRF), X-ray diffraction (XRD), and neutron activation (NA) analyses), identifying relatively small organic molecules including fatty acids, lipids, sterols, terpenoids, alkaloids, and carbohydrates (combined gas chromatography/mass spectrometry (GC/MS), combined liquid chromatography/mass spectrometry (LC/MS), and combined liquid chromatography/tandem mass spectrometry (LC/MS/MS)) and for identifying larger organic molecules including peptides, proteins, and nucleic acids (radioimmunoassay (RIA), enzyme-linked immunosorbent assay (ELISA), LC/MS, and LC/MS/MS). In their application to varying types of archaeological materials, each methodological technique holds inherent advantages and disadvantages depending on the nature of the sample and the specific type of human activities in question.

Given that budgets are often limited and that the legal and political hurdles to exporting archaeological samples across international borders are often substantial, analytical techniques must be carefully selected to overcome these pragmatic concerns while at the same time optimizing the collection of meaningful data. Analysis now often takes advantage of the wide range of available methods to fully interrogate a sample. Here we loosely organize the extant literature by technique but emphasize that much work involves the application of multiple techniques for assembling complementary and intersecting data sets.

LIMITATIONS AND CONSIDERATIONS

The practice of applying techniques of analytical chemistry to archaeological samples comes with several *a priori* limitations involving the formation of the archaeological record, sampling constraints during fieldwork, the primacy of contextual information, and the nature of experimentation in the field. Analytical chemistry in archaeological applications generally takes one of two forms. First, investigators may conduct a general survey of what has been preserved on a specific artifact if they have no indication of what this might be or, alternatively, to establish baseline data for future testing. Second, the investigators may test specifically for the presence or absence of a predetermined compound. These two approaches address different questions. The first is less specific and will result in more general and broad conclusions, while the second allows specific methods to be developed and precise but narrow conclusions to be drawn. Upon the recovery of a ceramic vessel, for example, one may ask if the pot was used for utilitarian purposes or purely for decoration, an exploratory analysis to identify the compounds present in the vessel would, in part, address this question. Alternatively, if a similar pot was found in association with the remains of a historically recorded ancient brewery, it may be hypothesized that the sample played a key role in the brewing process. Then, the presence of fermentation byproducts in the ceramic fabric would justify acceptance of the hypothesis. This second example highlights the all-important role of context in archaeological sampling. Artifacts that lack information on their depositional context are, for scientific purposes, practically useless. Information on the spatial and temporal provenience of the artifact in question, the assemblage of data and other artifacts that were recovered alongside it, and the history and treatment of the object since recovery in the field should be accounted for before destructive and possibly misleading chemical analyses are applied. Lack of contextual information renders the results of any additional analyses useless for answering meaningful research questions.

Archaeological samples are often rare and nonduplicable, presenting a further set of limitations on the nature of the intended experimentation. In the strict sense of the term, there are no true controls for the chemical analysis of artifacts, because all samples are contextually unique. While it seems possible to reproduce a ceramic vessel, we do not know and thus cannot reproduce the totality of the environments to which it was exposed, and it is impossible to recreate the centuries (or millennia!) of deposition, inducing oxidation, leaching, etc., to which it had been subjected. What is more, trials cannot be run indefinitely, for time constraints but also due to limitations in the amount of material available to test. Analyses are often destructive and require the permission of national governments and sovereign peoples (who usually hold a legal claim to archaeological materials). Most of these analyses cannot be performed in a fieldwork environment, and samples therefore must be exported at no insignificant cost. Furthermore, field collection and handling of samples may alter the chemical signatures of a given artifact; thus, archaeologists must consider the potential analyses that they wish to run, advisibly *before* actually recovering the sample. To avoid these and related pitfalls, we suggest that the use of chemical-analytical methods for archaeological materials must be governed by carefully crafted research questions with clearly outlined hypotheses that are embedded in a larger anthropological research project (Figure 2). While this may seem

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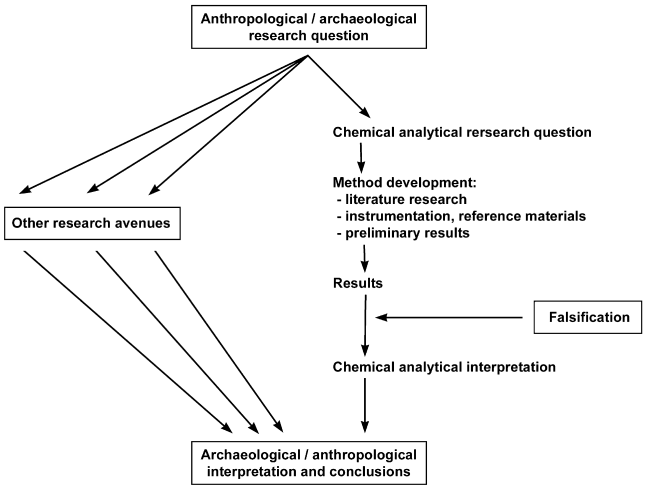

Figure 2. Chemical analytical research alone can never be expected to provide complete answers to anthropological research questions but has to be embedded in a larger archaeological research project for which information from many sources is combined. On the other hand it should not be presumed that existing analytical methods can be used unaltered; instead a significant effort to develop an applicable method is to be anticipated. Falsification is used here in the epistemological sense, meaning that alternative explanations (including those not based in archaeology) for the observed phenomena must be considered in their interpretation.

obvious among practitioners of the natural sciences, the role of archaeology as an exploratory science and interdisciplinary bridge between the social sciences, humanities, and natural sciences calls for more explicit attention to methodology and its application.

RELATIVE ABUNDANCE OF STABLE AND UNSTABLE ELEMENTAL ISOTOPES

Isotopic analysis is being increasingly used to investigate the age or geographical origin of ancient artifacts, including human remains. Measurement of the amount of remaining unstable isotopes with half-lives suitable for measuring time on an archaeological scale, such as ^{14}C and ^{238}U, have become mainstays of modern archaeological practice for dating organic materials. In addition, various geological, climatological, and biological processes result in global variations in the distribution of different isotopes of most elements. As a result, the relative abundances of such isotopes can be used to determine the origin of local raw materials as well as organisms, including humans. Comparison of the relative abundance ratios of the isotopes of elements such as H, O, S, Cu, Sr, Sn, and Pb, thus provide an effective means of accurately locating the geographical origin of archaeological finds and have become an important means of addressing human migration and trade. Subsistence products may also leave isotopic signatures. Differences in the photosynthesis pathways between C-3 and C-4 plants lead to variation in the relative uptake of ^{12}C and ^{13}C, a difference that is reflected in the $^{13}C/^{12}C$ ratio of plant consumers. Furthermore, the relative amount of ^{15}N compared to ^{14}N increases approximately 3‰ with each step of the food chain, an effect especially notable in marine environments with long food chains. Measurement of the relative abundances of these isotopes in bones and organic residues can thus provide important information on dietary practices.

The advent of radiocarbon dating is arguably the most significant methodological innovation in the history of archaeology.[9,10] Prior to radiocarbon assays, archaeologists measured time as a series of relative, stratigraphic relationships wherein deeper layers in an excavation are interpreted as older. In parts of the world with a tradition of written history, material remains could sometimes be dated by linking them to textual accounts. This is of course mute in areas with no or yet undeciphered scripts (in the ancient civilizations of North and South America, for example). Willard Libby et al. developed the radiocarbon method using organic artifacts of known origin and date, including samples from wooden ships and coffins recovered in historically documented Egyptian tombs, portions of a wooden floor from a Syrio-Hittite palace (northwestern Syria) recovered in association with imported Greek pottery of a stylistically datable decoration, and samples of long-lived trees whose age was known from growth-rings (dendrochronology).[9,11] These early advances in unstable isotope dating, obtained through β-radiation counting, were costly and destructive by today's standards, requiring, for example, an ounce of wood (8 g of carbon) per sample.[11] The development of accelerator mass spectrometry (AMS), in which the abundance of ^{14}C is measured relative to the more abundant ^{12}C and ^{13}C isotopes, replaced the β-radiation counting method because of greater precision and increased the effective range of radiocarbon dating techniques to at least 40 000 years before present (defined as 1950) and reduced sample sizes from grams to milligrams.[12] While still a destructive form of analysis, this significantly broadens the number of contexts that can be dated.

Accurate radiocarbon dating requires a calibration curve from which the age of a sample is deduced by interpolation, rather than directly from the measured $\delta^{14}C$.[13−15] The reason for this is that, contrary to Libby's initial assumptions, the production of ^{14}C in the upper stratosphere is not constant (Figure 3, top) but rather fluctuates with the amount of cosmic radiation. Furthermore, carbon can be trapped for prolonged periods of time in oceans and geological formations. Periods of increased mixing of the oceans, volcanic eruptions and erosion, as well as the burning of large volumes of fossil fuels can thus result in the release of radiocarbon-depleted materials.[16−18] Atmospheric nuclear tests on the other hand have resulted in very large amounts of circulating ^{14}C. Several continuously updated calibration curves have been compiled from dendrochronology[19,20] and uranium/thorium dates ($^{214}U/^{230}Th$) from the layers in coral formations (Figure 3, bottom).[21−23] The usefulness of unstable isotopic dating is also affected by interpretations of archaeological context and fieldwork decisions. The reuse of organic artifacts in antiquity (the so-called heirloom effect), for instance, must be considered and may explain apparent discrepancies in the dating data for objects from the same site.[24] Ideally multiple radiocarbon dates should be obtained from each archaeological context, as singular samples prove insufficient for drawing reliable conclusions.[25]

Comparison of the relative abundance of isotope ratios of oxygen ($^{18}O/^{16}O$), nitrogen ($^{15}N/^{14}N$), carbon ($^{13}C/^{12}C$), strontium ($^{87}Sr/^{86}Sr$), hydrogen ($^{2}H/^{1}H$), and other elements that are incorporated into organic tissues provides an opportunity to address questions about human mobility, migration, and dietary practices. For example, the relative abundance of strontium isotopes in rocks and soils varies naturally.[26] Strontium is taken up by plants and animals, eventually being incorporated in low abundance into the

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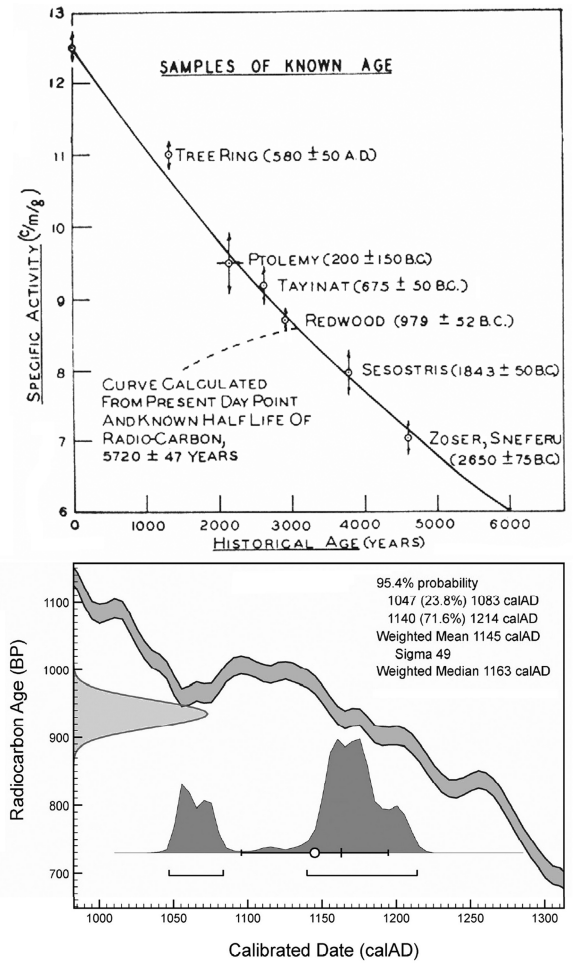

Figure 3. (Top) The first of several graphs published by Willard Libby in the early 1950s providing proof for the concept of radiocarbon dating by showing a near-linear relationship between known age of the tested objects (on the abscissa) and the measured ^{14}C decay (on the ordinate). Reprinted with permission from J. R. Arnold and W.F. Libby. Age determinations by radiocarbon content: Checks with samples of known age. *Science* **1949**, *110*, 678−680 (Figure 1). Copyright 1949 American Association for the Advancement of Science. (Bottom) Modern radiocarbon calibration curve (OxCal v4 1.3 for the southern hemisphere) for charcoal found in an archaeological context in southern Peru. The bell-curve on the left represents the $^{14}C/^{12}C$ measurement, the diagonal curve the $^{14}C/^{12}C$ ratio to be expected at different periods in time, and the curve at the bottom the inferred (calibrated) calendar date of the object (in this case either 1047−1083 or 1140−1214 AD).

mineral matrix of bones and teeth. In bone, calcium and strontium are continually exchanged with dietary sources and, assuming a negligible isotope effect on uptake, the ratio of the isotopes reflects the ratio in the local environment. Tooth enamel is not renewed and, with the same assumption, the ratio of isotopes reflects the ratio in the surrounding environment at the time of formation of the teeth. Provided that the body was not relocated after death, the relative abundance ratios of the strontium isotopes in bones and teeth can indicate whether an individual migrated a significant distance from their birthplace.[27−30] In some cases, culturally specific practices of population disbursal and relocation make it possible to infer additional social information about individuals. For example, Sr, O, and Pb analyses of human remains at the Inca sanctuary of Machu Picchu show significant heterogeneity in relative abundance ratios, suggesting that the resident population was cosmopolitan, drawn from multiple Central Andean populations.[31] In another case, water molecules containing ^{18}O will be slightly more reluctant to evaporate and slightly more prone to fall as rain. Chenery et al. used this phenomenon in combination with Sr isotope analyses to demonstrate that the Roman army stationed in the British Isles was composed both of recruits from the local population and nonlocal soldiers that were apparently born in warmer climates.[32,33] In both cases, strontium ratios were examined alongside secondary lines of isotopic evidence, including carbon, nitrogen, oxygen, and lead, providing for robust conclusions.[34,35] Stable isotope ratios also provide a method for sourcing rare and desirable ancient materials, when such materials are unamenable to trace elemental analysis. For instance, examination of hydrogen ($^{2}H/^{1}H$) and copper ($^{65}Cu/^{63}Cu$) relative abundances among turquoise assemblages from the American southwest has linked turquoise sources with artifacts.[36] These data allow the recreation of exchange networks that constitute important vectors for the flow of materials, people, and ideas in the ancient world.

Oxygen ($^{18}O/^{16}O$) isotope ratio combinations, which differ depending on the distance from the coast, are also used for determining residential patterns and the composition of households.[37] For example in the Moche Valley in northern Peru, investigators compared phosphate oxygen isotope combinations ($\delta^{18}O_p$) in local freshwater sources with that from human remains in local tombs, including the bodies of sacrificial victims.[37] Their results suggest that it was common for women to move from their home communities to that of their husband. Elite males appeared to be locally born, spending most of their life near their place of birth. In contrast, male victims of ceremonial sacrifices show different isotopic signatures, indicating a different geographical origin for sacrificial victims.[37]

The measurement of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) isotope ratios in human remains allows for a determination of the use of C-3 versus C-4 plants, especially wheat and barley (C-3 plants) versus corn (maize) and millet (C-4 plants).[38−41] Studies focused on nitrogen isotope ratios allow for the identification of high levels of fish in the diet, although high levels of ^{15}N levels may also result from particular manuring or grazing practices.[42,43] Beyond ^{15}N, trophic level effects have been demonstrated for ^{2}H and ^{13}C.[44] This again demonstrates the importance of modern experimentation as a source of reference for interpreting the dietary practices of ancient human populations.

■ ELEMENTAL FINGERPRINTING

Elemental fingerprinting techniques by XRF, instrumental neutron activation analysis (INAA), or inductively coupled plasma mass spectrometry (ICPMS) provide a means of sourcing raw materials, allowing for the reconstruction of procurement and trading practices. The effectiveness of XRF for archaeological sourcing relies upon the assumption that chemical composition is homogeneous throughout the sample. This makes the technique effective for sourcing well-mixed materials incorporated into artifacts, such as volcanic glasses.[45−50] Sourcing of clays used in the production of ceramics is also undertaken, for instance in Mesoamerica and Egypt (Figure 4),[51] although these provide greater methodological and interpretational challenges because of sample heterogeneity.[52,53] Portable XRF (pXRF) instruments allow

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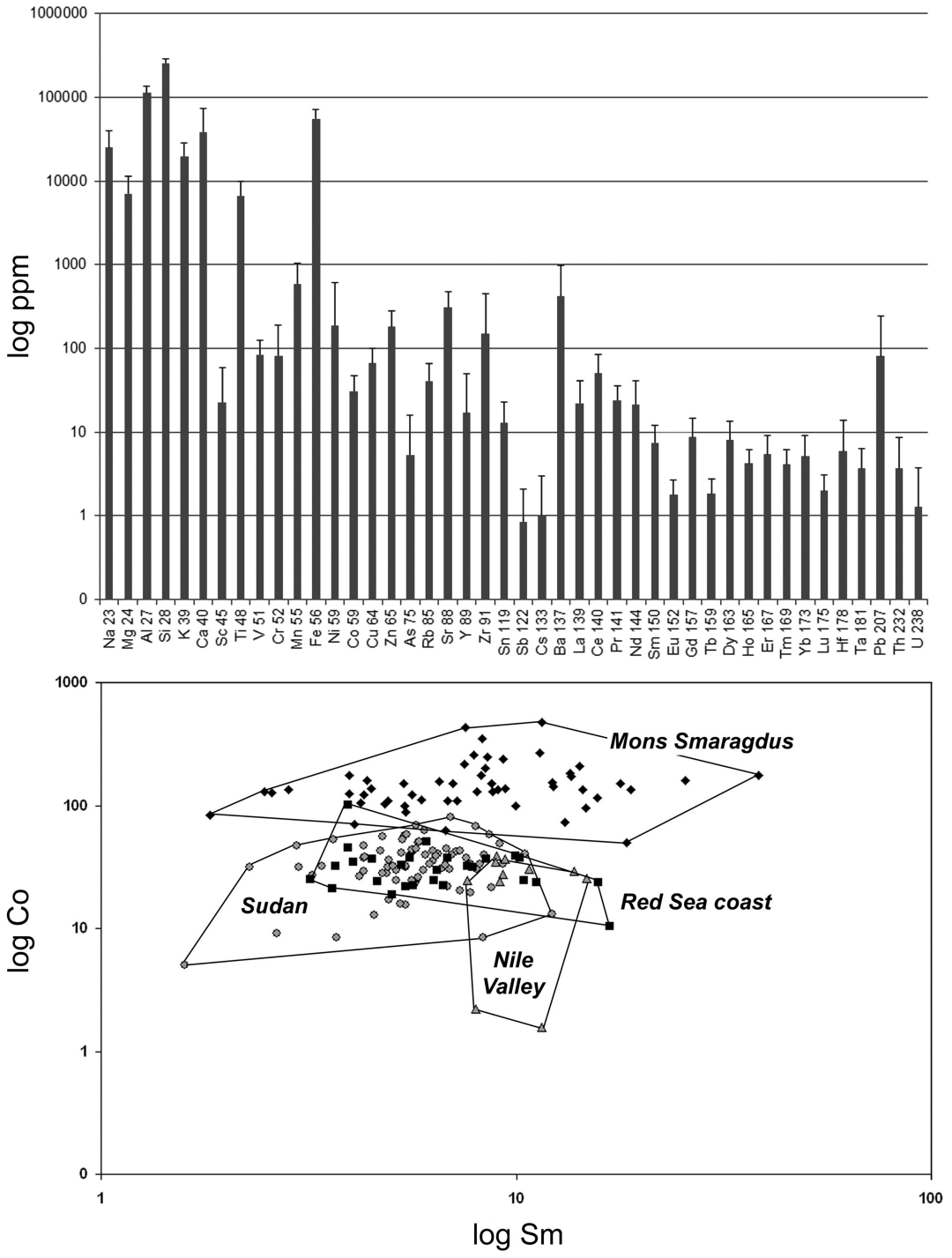

Figure 4. (Top) Abundances in parts-per-million, established by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), of 44 selected elements in the ceramic matrix of a type of pottery produced in Egypt and Sudan during the 4th−6th centuries common era (CE, also known as AD). The data represents average abundances resulting from 189 measurements made on 137 different potsherds, and the error bars indicate the standard deviation of the average abundances. (Bottom) Biplot comparing the abundances of cobalt and samarium in the same data set indicates compositional differences between sherds found in different regions (eastern Sudan, the Red Sea coast, the Egyptian Nile Valley, and the Mons Smaragdus region in eastern Egypt). The two elements were selected after principle component analysis (PCA) of the whole data set.

for timely and low-cost analysis in the field, but the accuracy, comparability, and statistical validity of pXRF measurements continue to be debated.[54−59] Direct comparison with laboratory-based elemental fingerprinting shows that pXRF accurately depicts compositional groups, though less so than INAA, making the two effective complements.[60,61]

From a practical perspective, INAA and ICPMS approaches differ from pXRF in that they must be deployed in a laboratory, requiring the exportation of samples, and are destructive. While INAA and ICPMS are more sensitive and can deal with an expanded set of elements (and in some cases their isotopes), equipment and laboratory costs are significantly higher. INAA was first tested against archaeological samples of known origin

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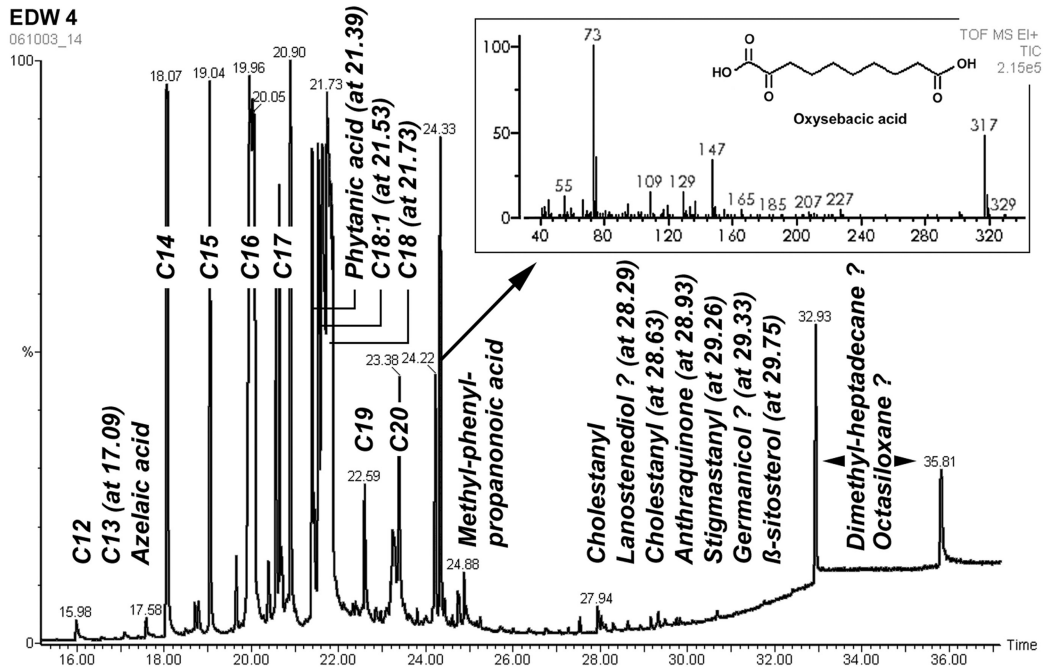

Figure 5. Annotated gas chromatogram (total ion current display, relative abundance in percent on the ordinate, retention time in minutes on the abscissa) of the organic residue extracted from an unglazed, 4th−6th century CE ceramic vessel from southern Egypt, after conversion to the trimethylsilyl derivative. The molecules in the sample were identified by electronic comparison of their EI mass spectra with the spectra in the 2002 version of the NIST/EPA/NIH Mass Spectral Library. The combination of plant hormones and saturated as well as unsaturated fatty acids and their decay products was interpreted as originating from berries or seeds (including cereals).

by Sayre et al. as part of a consortium of archaeologists and chemists convened by J. Robert Oppenheimer in March of 1956.[62] Using terracotta ceramics recovered from archaeological contexts in the Mediterranean and the Near East, the investigators established that decay patterns of irradiated sherds were distinct in accordance with their geographical origin. The method has been much revised since these early experiments, and improvements in accuracy now provide the opportunity to address ever-more specific spatial relationships, making INAA a staple of archaeochemistry.[63,64] In some cases INAA laboratories have developed their own archaeological specialties.[65] These data have been used to reconstruct village trading patterns[66] and migratory routes,[67] as aids in chronology building,[68] and to infer how ancient societies organized the production of specific goods.[69]

Volcanic materials, such as obsidians and pumices, have elemental compositions specific to their geological sources. Large eruptions also leave a physical, stratigraphically visible signature of tephra (volcanic ash) in the archaeological record. INAA can link these visible geological layers to particular, historically documented eruptions, thus aiding in the creation of specific chronological markers for fieldworkers.[70] Establishing the transport of pumices, obsidians, and basalts away from their source is a principle means for reconstruction of long distance trading networks and distribution economies.[71−73] The elemental signature from INAA analysis of clays and ceramic paints allows for the identification of pottery production centers and distribution patterns.[74] Finely made pottery often served as a status good in many parts of the ancient world, and as such reconstructing the movement of finewares provides a proxy for the movement of the people that transported them. As such, recent applications of INAA have been instrumental in identifying phenomena such as pilgrimages.[75,76] Drawbacks of INAA include issues associated with irradiating samples as well relatively high costs.

Like XRF and INAA, application of ICPMS generally focuses on elemental characterization that links artifacts to geochemical sources. ICPMS provides a relatively sensitive means for elemental and isotopic fingerprinting.[77] The technique has been used to identify groups of mineral-based paints and particular paint and glaze recipes on ceramics, to source ceramic pastes,[78] and to provenience metals.[79,80] In a number of these cases, the resolution of ICPMS allows the sourcing of materials based on the relative abundance of isotopes rather than elements, further increasing the efficacy of the method.[81−84] In some cases, attempts have been made to connect agricultural products to the soils in which they were grown.[85]

The destructive nature of sample preparation and the general heterogeneity of archaeological materials provide two major hurdles for ICPMS analysis. As a consequence, a variety of sample introduction techniques are used in an attempt to balance sample preservation against the material characteristics of the samples selected for analysis. Laser ablation (LA) is minimally destructive but highly targeted. Because of this, analysts must be aware of heterogeneity across the surfaces of the sample.[86] On the other hand, LA can be targeted at specific pigments or ceramic inclusions of interest.[87] Acid dissolution overcomes problems of sample microheterogeneity and, while destructive, produces more accurate results when compared to competing techniques such as INAA.[88,89] Other alternatives, including microwave digestion (MD) and alkaline fusion vary in suitability depending on the chemical characteristics of the artifact in question.[90] A final important issue with these techniques is that the ancient sources of raw materials often remain unknown and thus unavailable for comparison. In these cases, geochemical fingerprints can still be used to group

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artifacts by tentative source, even though this cannot be related to a geographical place.

MONOMERIC ORGANIC MOLECULES

Specific organic molecules associated with archaeological contexts or artifacts have been identified primarily through the use of mass spectrometric methods.[91] Thus, questions can be addressed about the production, distribution, and use of organic substances in the ancient world. Most organic materials are subject to leaching as well as microbial and chemical degradation, and thus useful biomarkers are only those that are sufficiently robust to survive long-term deposition, such as fatty acids, terpenoids, and sterols, sometimes the decay products of less stable parent compounds. Samples have been analyzed from a variety of media, including but not limited to soils from hearths,[92] packed earthen floors,[93] and human hair and tissue.[94,95] Ceramic matrixes are excellent loci for the preservation of organic molecules as their porosity allows for retention and, to some degree, protection from destructive forces. Ceramics are also among the most commonly preserved artifacts in the archaeological record.

GC/MS has been available since the two techniques were first married in the 1960s but did not find its way into archaeology until the late 1970s, with major methodological advances made in the 1990s.[96] At present, GC/MS has proven useful to identify the production and use of specific subsistence practices involving meat, dairy, and vegetable consumption,[97−99] cacao beverage flavorings,[100] medically significant plants,[101] organic pigment binders,[102] wines,[103] perfumes like frankincense,[104] molluscan dyes,[105] oils,[106] cosmetic creams,[107] waxes,[108] triterpenic resins,[109,110] tars,[111] bulk fats used on sounding leads,[112] psychoactive substances including mescaline[113] and tobacco,[114−117] among other compounds. These substances relate to specific behaviors in the ancient world, and thus analyses must be designed within a contextually appropriate frame of research. GC/MS is also applied in museum and conservation settings to better understand degradation and preservation processes, for example, in atmospheric studies of museum display cases,[118,119] to find the origin of proteinaceous paint media,[120−124] and as a means to better understand the decomposition of waterlogged wood.[125,126]

The utility of GC/MS in part lies in the ease with which the data can be used to identify unknown molecules by comparing electron ionization (EI) fragmentation patterns to reference mass spectral libraries. This allows analysis of organic residues left in archaeological ceramics, thus providing information on the food that these vessels once contained (Figure 5), although the interpretation of the data remains challenging. Other advantages include the quantitative nature of the process and the superb chromatographic resolution of contemporary GC. The advantages of analysis by GC/MS are offset somewhat by the need for adequate thermal stability of the analyte, which often has to be obtained by chemical derivitazation. GC/MS remains the technique of choice for most archaeological investigations of organic residues.

There are no true experimental controls when subjecting unknown archaeological materials to analytical tests. The complex, mixed, and degraded nature of archaeological samples often necessitates the development of specific, tailor-made analytical protocols. Additional considerations include highly region-specific organic materials, such as teff (*Eragrostis tef*) or quinoa (*Chenopodium quinoa*) as a major food source, and the use of materials that are unexpected as they are no longer commonly used in modern society, such as spermaceti from sperm whales (*Physeter macrocephalus*) which was once widely used to make candles. Usually, analysts first develop experimental protocols with known samples, which are then tested against archaeological materials. Suitable protocols thus occupy a significant portion of the literature, for example, in establishing detection methods for fatty acid methyl esters to interrogate seed-processing residues on Great Basin ceramics and lithics;[127] terpenoids from varying species of frankincense (*Boswellia* spp.) that allow for fine-grained sourcing studies;[128] yellow flavonoid textile dyes;[129] the effects of differing depositional environments on beeswaxes and the establishment of useful biomarkers for different foodstuffs;[130,131] and the decay products of opium alkaloids.[132] In addressing the need for cross-pollination of methodological techniques to solve such problems, Barnard et al. initiated a "round robin" experiment wherein samples of a known organic residue (created by cooking milk of *Camelus dromedarius* in a newly purchased unglazed ceramic vessel) were sent to several laboratories for analysis.[133] While a variety of proteomic, lipid, and stable isotope analyses were performed, none of the seven participating research groups could identify the origin of the residue to species level. This conclusion points to the need for multiple and intersecting lines of evidence to address unknown residues in archaeological samples and careful attention to contextual and historical information accompanying the recovery of samples.

LC combined with a variety of detectors has been applied to archaeological research since the 1980s for the analysis of residues in ceramics and organic dyes on textiles. Advantages of LC combined with laser desorption (LD) and electrospray ionization (ESI) MS over GC/MS include the fact that molecules need not be thermally stable, thus avoiding the need for chemical derivatization that is often unavoidable for GC/MS. Because of this advantage, LC/MS addresses a greater range of organic molecules. However, the lack of fragmentation obtained during LD and ESI often complicates the identification of unknowns. Although fragmentation patterns can be obtained through the use of MS/MS, the interpretation of such patterns is not as well developed as the interpretation of EI fragmentation patterns and libraries. Sensitivity comparisons often favor LC/MS, in part because of the practical limitation imposed by the proportion of a sample that can be reliably injected. Like GC/MS, LC/MS can be used for quantitative analysis, particularly when internal standards are employed. LC/MS has been used, for example, in differentiating Baltic and Romanian archaeological ambers based on varying concentrations of succinic acid.[134,135] High sensitivity can minimize the amount of sample required, thus reducing destructive sampling. Washburn et al. used LC/MS to detect low picomole amounts of theobromine in Hohokam pottery by simply washing out the pots with water and then sampling the washings, thus demonstrating the importation of cacao-based drinks from Mesoamerica into the American Southwest.[136] LC linked with ultraviolet and visible light detectors, including multiple simultaneous wavelength diode array detection, has proven useful for detecting and distinguishing between multiple textile dyes and their decay products.[137−144]

Some research projects require a level of sensitivity and specificity that can only be achieved with tandem mass spectrometry configured to perform multiple reaction monitoring (MRM) experiments. For example, while tartaric acid found

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naturally in red wines may be identified in ceramic matrixes based on LC/MS data, the identification of malvidin, the pigment in red wine and a more specific marker of grape products, required a more sophisticated strategy.[145−148] In the case of Barnard et al., it was necessary to remove as much free syringic acid as possible from the ancient ceramic samples by solid phase extraction.[149] The samples were subsequently treated with base that converted a proportion of any residual malvidin into newly formed syringic acid which was detected by LC/MS/MS-MRM. The signal intensity from the final sample was about 50-fold above the limit of detection of the assay and equivalent to what would have been recovered from 30 nL of commercial red wine.[149]

MS/MS, combined with a variety of sample introduction methods, also provides the specificity necessary to discriminate between dairy and adipose fats of multiple animal species via triacylglycerols, allowing for a more nuanced understanding of the evolution of ancient economies.[150] Garnier et al. used infrared multiphoton dissociation (IRMPD) MS/MS to build a species-specific database of vegetable oils and animal fats, which they then applied to determine the fuel source for lamps recovered from the ancient settlement of Olbia (modern Ukraine) dating to the 5th century before the common era (BCE, also known as BC).[151] LC/MS/MS approaches prove useful for solving museum conservation challenges related to the storage of archaeological materials in modern facilities, for instance, to identify problematic pigments in rubber stabilizers that cause flint artifacts to suddenly change color during storage.[152]

Used in parallel, GC/MS and LC/MS are effective for characterizing samples that purposefully contained multiple organic products, for instance, in pitch-lined wine amphorae from the ancient Mediterranean,[153−155] lamp fuels based on seed oils and animal fats,[156,157] for vessels which were reused for multiple purposes over their lifetimes,[158,159] for ship coatings,[160] for large assemblages of vessels expected to vary widely in content,[161] and simply as a means of cross-validation of results.[162] Because ancient residues are often complex compositional mixtures of plant, animal, and mineral origin, both techniques are often used alongside other research strategies, for instance, in the case of paint consisting of inorganic pigments and organic binders.[163,164]

POLYMERIC ORGANIC MOLECULES

Detection and identification of DNA and proteins is of great utility for studying ancient societies. The relative chemical instability imparted by the ribose moiety (in contrast to the greatly increased stability resulting from the absence of the hydroxyl moiety in the 2′ position of deoxyribose in DNA), and the ubiquity of RNase enzymes, account for the absence of this polymer in ancient samples, while polysaccharides are presumably easily lost by leaching and microbiological attack. It is perhaps surprising that both residual DNA and proteins can be recovered from ancient artifacts, but the evidence is incontrovertible. Under favorable circumstances, including low temperatures, low humidity, and anaerobic environments, these compounds appear to survive much longer than expected based on every-day experience. In contrast to monomeric organic molecules, an important advantage of DNA and proteins is that their identification may be genus or even species specific.

The rapidity with which archaeologists recognized the value of bottom-up proteomics for identifying species-specific proteins in residues from ancient samples reflects the growing interaction between archaeologists and analytical chemists. Both ESI and LD ionization strategies have been successfully employed. These developments have expanded our ability to discuss ancient herding and dairying practices, and the broader impact of proteomics research by zooarchaeologists extends beyond archaeology into the world of conservation biology.[165]

The species-specificity associated with bottom-up proteomics is particularly useful for studying domestication timelines and paleodietary practices. Various mammalian species are identifiable via peptides from bone collagen samples. This allows zooarchaeologists to identify particular food species, even when samples are too fragmented to rely on visible anatomical markers.[166] Traditional zooarchaeological limitations, such as differentiating between sheep and goats based on bone morphology, may be aided through proteomic approaches.[167] Indeed, small and degraded samples have yielded to peptide-based bottom-up techniques. For instance, bovine milk proteins have been identified in >4000 year old ceramics from artifacts excavated as long ago as the early 19th century.[168] Extending proteomic data to subsistence production practices, Yang et al. identified dairying practices associated with the earliest known cheese, a kefir from Bronze Age Xinjiang, produced through fermentation by *Lactobacillus kefiranofaciens* and yeasts.[169]

Similar analyses have been applied to plant foods. Shevchenko et al. deployed a LC/MS/MS analysis of samples in a gel medium to identify grain species left as burial offerings in tombs from the Turpan Basin, Shanshan County, in the Xinjiang Uighur Autonomous Region.[170] The investigators found that sourdough breads made from a mixture of broomcorn millet and barley (the latter domesticated in the Near East) was a well-established food item in western China by 500 BCE, providing residents with a significant source of fiber, B-vitamins, essential minerals, and antioxidants.[170] Beyond food products, similar approaches have been used to determine the faunal source of secondary products such as furs and skins. Hollemeyer et al. demonstrated that Otzi the Iceman, the famous 5000 year-old mummy found in an Alpine glacier, wore ovid and bovine skins, suggesting that he practiced animal husbandry at an early date or at least that he was in touch with pastoral peoples.[171] Chambery et al. used an LC system to distinguish between egg yolk, egg white, and alpha casein proteins in binding agents in early 20th century mural paintings.[172]

Keratins are particularly stable proteins that can be found in ancient hair, skin, and nails and along with collagen, another stable protein (mentioned above), are being used through bottom-up proteomic analyses to assign species identity to ancient samples and in some cases trace lineages.[173,174] Badly degraded samples require unusually stringent conditions for dissolution and reduction of disulfide bonds that are particularly abundant in keratins. As with all organics, a crucial issue is the extraction of the material from the ancient artifact. Methods for improving the efficiency of the extraction process have received attention in recent years. Microwave-assisted extraction and digestion has been used with success for identifying proteins from ceramic media.[175]

In addition to bottom-up analysis of protein residues to identify subsequences within the macromolecule, other aspects of protein chemistry provide yet other potential avenues to date ancient samples. These include fragmentation, oxidation, disulfide reduction, and racemization. Of these, racemization seems to be the only property that has been used thus far. Moini et al. have exploited the time-, temperature- and context-

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dependent racemization of L-aspartic acid released from proteins after acid hydrolysis to date ancient silks.[176] The difficult separation of the D- and L-isomers requires either capillary zone electrophoresis or derivatization with a chiral reagent prior to chromatographic separation.

The application of immunological techniques for the identification of proteins in ancient samples has paralleled those of mass spectrometry. An essential requirement here is that the antigenic determinants for antibody recognition remain preserved in proteins from ancient samples. Heating of proteins may render them immunologically undetectable; experimental studies suggest that ceramic cooking media provide poor preservation environments for immunologically detectable proteins.[177] An advantage over mass spectrometry is the extreme sensitivity that can be achieved with antibody-based techniques. Crossover immuno-electrophoresis (CIEP), RIA, and ELISA have all been used to link protein residues from ceramics and stone tools to particular animal species. Each technique utilizes different physical properties (movement in electrophoresis, color-production under UV light, radioactive detection) to identify positive association between antibodies and antigens.[7] Variable affinity of different proteins for lithic and ceramic surfaces requires attention to the extraction methods employed.[178] Importantly, issues of antibody cross-reactivity, particularly in the case of highly homologous proteins originating in different species, have resulted in disputes over the interpretation of the findings.[179−182]

CIEP was first introduced to archaeological research in the late 1980s, when Newman and Julig sampled proteins on lithic tools from a Boreal Forest site in Canada.[183] Blood proteins from stone tools continue to occupy the largest subset of analyses,[184,185] although the technique has also been applied to proteins from ancient human feces and soils.[186] CIEP analyses generally deal with archaeological contexts of great antiquity. Recently, Yohe II and Bamforth used CIEP to identify the remains of horse, bear, and camel proteins on stone tools found in Colorado. Given the premodern context of the cache and the fact that native horses and camels disappeared from North America during the late Pleistocene, their study both identifies prey species and supports the great antiquity of the recovered assemblage.[187]

ELISA analyses use antibody recognition linked to a colorimetric reporter assay to identify the target compound. These assays are 100 to 1000 times more sensitive than CIEP.[188] This approach has been successfully used to identify the species of small fragments of osteological material, for example, from battlefield remains spanning the Bronze Age to the English Civil War[189] and from cremation and burial remains.[190,191] Blood proteins on lithic materials are also detectable with ELISA,[192] making it a compliment or alternative to CIEP. Research has demonstrated that certain burial environments and diagenetic processes, rather than simply age, may govern the survivability of particular protein biomarkers,[193,194] and thus the context of samples must be carefully considered before ELISA analyses are undertaken. Recently, Palmieri et al. developed a method using ELISA to detect the daughter products of denatured bovine dairy and chicken proteins from painting microsamples.[195]

Protein RIA provides a sensitive method for distinguishing between human and animal blood proteins on lithic tools. Used in archaeological research since the mid-1980s,[196,197] techniques have improved significantly in recent decades.[198,199] Much as is the case with ELISA, diagenetic processes may produce cross-reactions that affect the interpretation of results.[200]

■ ANCIENT DNA

The recovery and analysis of ancient DNA from plants, animals, pathogens, and humans is of great interest for reconstructing premodern society, both as a means of investigating population dynamics and for illuminating the relationship between humans and nonhuman species. Key to the study of ancient DNA (aDNA) is overcoming the degraded and fragmentary nature of samples that come from the archaeological record. The development of the polymerase chain reaction allowed investigators to amplify small samples but carries with it a greater sensitivity to contamination by modern organisms and thus demands careful attention to sample recovery and treatment.[201−203] While originally conducted for archaeological purposes through varying modifications of the Sanger diodeoxy sequencing method, more recent sequencing takes advantage of automated "next-gen" sequencing instruments.

In 1984, Higuchi et al. succeeded in extracting DNA from 150 year-old quagga muscle (*Equus quagga*, an extinct relative of the zebra) stored in the Museum of Natural History at Mainz, Germany.[204] Investigators derived aDNA directly from archaeological samples the following year, when Paabo succeeded in rehydrating and cloning DNA from the 2400 year-old mummy of an Egyptian child.[205] These early successes provided definitive proof that DNA can survive long-term deposition in certain environments, opening the door for broader archaeological applications. Taphonomy issues relating to aDNA continue to be approached through replicative experimentation.[206,207]

Ancient DNA extracted from plant and animal foodstuffs provides a specific determination of dietary health, especially when samples are not amenable to macroscopic analysis. DNA from the intestinal contents of Otzi the Iceman (see above) identified his last two meals: one of ibex meat (*Capra ibex*), dicot plants, and possibly cereals, followed by red deer (*Cervus elaphus*) and possibly cereals.[208] In addition, the determination of these prey species suggests that Otzi's final journey was from subalpine coniferous forests to the high altitude environs where his body was recovered, providing archaeologists with specific spatial information on his final movements. aDNA also plays a central role in tracing animal management strategies when morphological differences between species are difficult or impossible to track macroscopically. Barnes and Young used aDNA analysis to differentiate between remains of wild and domestic geese from postmedieval settlements in Flixborough, U.K., demonstrating that both hunting wild geese and domestication of them played a part in village subsistence economies.[209] In some cases, tracing genetic changes in a single food species over millennia can aid in reconstructing long-term human dispersal events, for instance changes in pig (*Sus*) genetics that accompanied the peopling of Polynesia.[210]

Long-term changes in human disease ecology may be traced through aDNA analysis in conjunction with paleopathological analysis of skeletal remains when analyses are carefully controlled.[211] Certain diseases that affect osseous tissue have been under aDNA investigation for some time, for instance, tuberculosis.[212] In the case of tuberculosis in Iron Age populations from Siberia, aDNA allowed Murphy et al. to differentiate between typical human (*Mycobacterium tuberculosis*) and livestock forms (*M. bovis* and *M. tuberculosis*).[213] The authors suggest that lesions on lumbar vertebrae in their

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sample population were related to gastrointestinal infection by the bovine form, given that the ingestion of infected dairy products is the most likely vector for *M. bovis*. Genetic approaches to paleopathology have been applied to leprosy,[214,215] septicemic plagues,[216] and parasitism[217,218] among other maladies. Some pathologies may be difficult to detect on a molecular level despite leaving skeletal markers, such as venereal syphilis,[219] and a healthy amount of methodological debate remains concerning the broader application of aDNA to paleopathological research.[220−222]

Studies of human population demographics have of course benefited greatly from the introduction of aDNA analysis,[223] including the initial peopling of the Americas (Figure 6),[224] the genetic impact of European colonialism on New World populations,[225] tracking the descent of modern populations from Neolithic groups,[226] identifying kinship patterns among individuals buried in collective tombs,[227] reconstructing the Neanderthal genome (*Homo neanderthalensis*), and whether humans and Neanderthals interbred.[228−230] Several of these issues remain controversial and are continuously debated, especially as additional new data is retrieved.[231,232] Recently this was the case when it was shown that the remains of a young female who died about 12 000−13 000 years ago on the Yucatan Peninsula (Mexico) preserved mitochondrial DNA of the same type as Native Americans despite displaying characteristics of the Paleoeamerican facial phenotype (Figure 6).

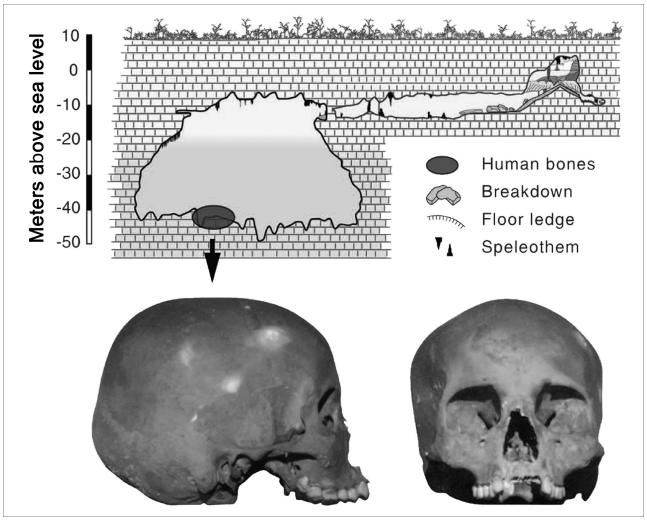

Figure 6. Photograph and location of the skull of a female estimated to have been 15−16 years old when she died. Her skeleton was found in the Hoyo Negro sinkhole in the Yucatan Peninsula (Mexico) and was dated to 12 000−13 000 years ago. Despite displaying characteristics of the Paleoeamerican facial phenotype, which is different from the Native American phenotype and sometimes suggested to indicate a different ancestry, mitochondrial DNA recovered from the skeleton is of the same type as from other groups native to the New World. This finding corroborates the hypotheses that both Paleoamericans and Native Americans derive from a single group that crossed the Bering Strait around 26 000−18 000 years ago. Reprinted with permission from J. C. Chatters et al. Late Pleistocene Human Skeleton and mtDNA Link Paleoamericans and Modern Native Americans. *Science* **2014**, *344*, 750−754 (Figure 1C,D). Copyright 2014 American Association for the Advancement of Science.

COOPERATION BETWEEN ARCHAEOLOGISTS AND CHEMISTS

Archaeological research projects with a biochemical/analytical component almost invariably entail the cooperation of scholars and scientists with widely varying expertise and research interests. Given the different backgrounds and research interests of anthropological archaeologists and analytical biochemists, there exists an inevitable disconnect between them. This gap is especially large in the United States, where basic education in science, technology, engineering, and mathematics (STEM) is widely available but mostly benefits students who have an interest in it,[233,234] while education in the history and philosophy of the discipline is almost entirely missing from scientific curricula.[235,236]

Within the field of archaeology, publications on organic residues are mostly in *Archaeometry* and the *Journal of Archaeological Science*.[6] When published elsewhere, they often appear in specialized biochemical journals and biochemists sometimes use archaeological samples to address biochemical rather than archaeological research questions.[237] Archaeologists do not regularly read *Analytical Chemistry* nor biochemists *Archaeometry*, which hinders the two groups from connecting, although online search engines increasingly remove this issue. More difficult to alleviate is the fact that journals are reluctant to publish complete analytical (in the case of archaeology journals) or anthropological (in the case of biochemistry journals) research backgrounds because they are considered outside their scope or expected to be common knowledge among their readership. Valuable information thus fails to make its full impact in the larger scholarly and scientific communities leading to misunderstandings and sometimes heated debates, such as those over blood residues on ancient stone tools[197,238−240] and cannibalism in prehistoric North America.[241−244] The latter flared up upon the finding of human myoglobin in pottery and feces preserved in a settlement in Cowboy Wash (in southwestern Colorado) dating to around 1150−1175 CE (Figure 7).

There is an ongoing debate between those active in the field on the relation between archaeology, anthropology, and the natural sciences.[3,245−249] Archaeological theory is mostly anthropological theory but also includes elements of (evolutionary) biology, (art) history, and physics.[250,251] As such, archaeological investigation is ideally positioned to serve as a place of collaboration for these highly specialized fields. This needs to be encouraged rather than rejected in an effort to establish the priority of one set of useful theories and tools over another.[5] The issue is not whether archaeologists should become biochemists or biochemists archaeologists but rather how scholars and scientists from different fields can cooperate effectively to tease as much information as possible out of the material remains of the human past.[1−3,5] Without a specific research question, careful sampling, feedback between methods, results and data collection, and the ultimate integration of all information, biochemical analytical research is just that and not of immediate interest to the archaeological and anthropological communities.

The most important requirement for achieving productive cooperation within an archaeological research project is an open dialogue between all participants. Communication should be aimed at a critical understanding of the methods, prospects, and limitations of all deployed research techniques. Archaeologists should not enter such a project with unrealistic

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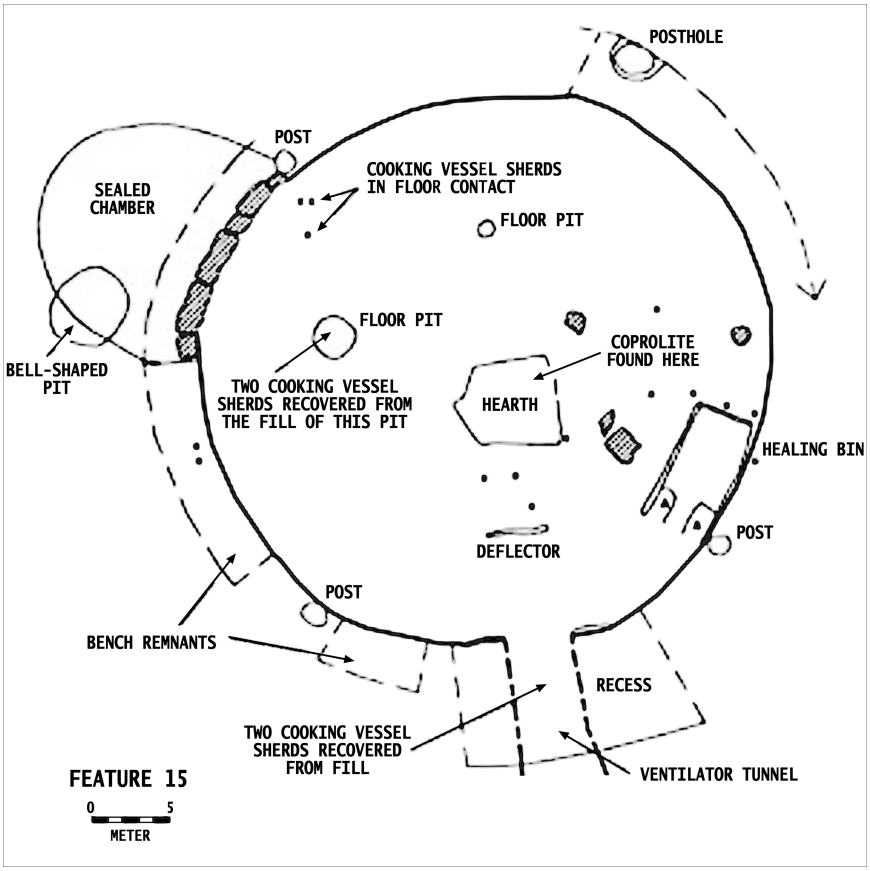

Figure 7. Plan of the ancient structure in Cowboy Wash (in southwestern Colorado) in which pottery and feces (labeled "coprolite" in the image) dating to around 1150−1175 CE were found. These were shown to contain human myoglobin by sandwich-ELISA. Additional research convincingly indicated that this finding should be interpreted as evidence for cannibalism. Reprinted with permission from R. A. Marlar et al. Biochemical evidence of cannibalism at a prehistoric Puebloan site in southwestern Colorado. *Nature* **2000**, *407*, 74−78 (Figure 1, insert). Copyright 2000 Macmillan Publishers Ltd.

expectations, partly resulting from a literature in which failures are underreported. Usually there is a significant amount of method development to be realized before ancient specimens can be analyzed. Such groundwork is time-consuming and potentially costly, while archaeologists are often anxious to produce archaeological data rather than develop a new methodology. Analytical biochemists, on the other hand, should understand that the identification of molecules from an archaeological sample is only part of the research project. Translating the presence of one or two biomolecules into broader statements about human behavior, without paying attention to issues of sample selection and archaeological preservation, is unrealistic. Another challenge is establishing consistency in the generation and interpretation of data.[252−254] There seems to be too little effort to standardize methodologies or cross-check results, opening the field to more severe challenges than otherwise warranted.[133,181,182,197,238,240−244,255−258] Archaeologists need to spend more effort on establishing the accuracy and robustness of individual approaches and continually evaluate the efficacy of the field as a whole.

Less focused research, resulting in insignificant and unreliable conclusions, is among the reasons that the initial enthusiasm about the field of organic residue analysis has occasionally changed into skepticism. In these cases, flawed sampling strategies and interpretations, rather than analytical protocols and instrumentation, are largely to blame. If, on the other hand, the research question is well articulated and the samples and methods are chosen accordingly, more definite conclusions may be expected. In these cases, the results of organic residue analysis are not severed from their archaeological origins but rather become another property of the artifact, next to weight, age, color, shape, context, etc. Only when firmly embedded in archaeological practice and anthropological theory, enabled by an intimate cooperation between archaeologists and analytical biochemists, can the field reach its full potential and realize elements of its original promise.

■ CONCLUSION

The application of carefully selected analytical-chemical techniques to archaeological research provides a host of qualitative and quantitative data otherwise not available to investigators. Some analytical approaches (e.g., radiocarbon dating) are used nearly ubiquitously in archaeological projects and have become crucial tools for successful field research. Other techniques best address context-specific and carefully formulated research questions. Stable isotope analyses provide a host of information on material sourcing patterns and the movements of goods and people by taking advantage of geochemically heterogeneous distributions of elemental isotopes; they also extend archaeologists' ability to determine culturally specific residency patterns and diet preferences. Elemental fingerprinting approaches (INAA, ICPMS, XRF) are useful for similar questions of migration and sourcing and are

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generally minimally destructive, making them excellent candidates for rare archaeological materials. The recent dramatic increase in the use of portable XRF instruments allows chemical analysis to be undertaken directly in the field. Monomeric and polymeric organic biomarkers may be identified through a variety of MS and related techniques, and their role as specific target molecules requires analytical techniques carefully tailored to the research question at hand. Proteomic and DNA analyses can identify the use of specific organisms and their interaction with human communities, whether prey species, diseases, or domesticates, not to mention the genetic history of human groups themselves.

Next to research design and monetary costs, destructive versus nondestructive approaches may govern the choice of technique, in combination with the possibility for it to be carried out in a fieldwork environment. Once selected, proper analysis must account for burial environment, local biomes and geochemistry, and the culturally specific circumstances surrounding the deposition of the artifact in question. Analysis of any sort is scientifically unsound in the absence of careful control over archaeological context. Laboratory experimentation is often required in order to configure analyses in accordance with artifact specific conditions.

No two archaeological sites, or artifacts, are exactly the same. The challenge faced by archaeo-chemists is to develop broadly applicable analytical techniques and procedures that yet provide the flexibility that archaeological science demands. At present, analytical chemistry and archaeology are bound in a fruitful and rewarding relationship. Chemists have faithfully taken up the mantle of investigating the hidden fragments of the ancient world and together with archaeologists have expanded our knowledge of what it means to be human.

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Kym F. Faull Ph.D. is a Professor in the Department of Psychiatry and Biobehavioral Sciences at the UCLA David Geffen School of Medicine, a member of the Jane and Terry Semel Institute of Neuroscience and Human Behavior at UCLA, and Director of the Pasarow Mass Spectrometry Laboratory. After receiving a Ph.D. in Plant Physiology in 1976 at the University of Adelaide, Australia (on gibberellin biosynthesis in plants), he changed fields to mammalian biochemistry and mass spectrometry during postdoctoral studies at the University of Wollongong, Australia, and following that at Stanford University Medical Center. At UCLA since 1990, his publication record reflects a background in biochemistry and experience in the characterization and quantitation of biomolecules by mass spectrometry. This includes experience with metabolic screening using gas chromatography/mass spectrometry for organic acidurias and other inherited diseases of metabolism and work on biogenic amines and related compounds in the major neuropsychiatric illnesses (major depressive disorder, schizophrenia, etc.). His experience with contemporary mass spectrometry and chromatography for the identification and quantitation of compounds in complex samples extends to electrospray and matrix-assisted laser desorption/ionization studies of peptides, proteins, carbohydrates, lipids, and other biomolecules and the application of these techniques to the study of human biochemistry. He also continues to direct an active research program that includes multiple collaborations including some with archaeologists, most notably Hans Barnard, and is involved in teaching and administration at the UCLA campus.

Hans Barnard M.D., Ph.D. is Adjunct Assistant Professor Archaeological Sciences at the Department of Near Eastern Languages and Cultures at the University of California, Los Angeles, as well as Assistant Researcher at the Cotsen Institute of Archaeology, also at UCLA. As an archaeological surveyor, photographer, and ceramic analyst he has worked on sites in Armenia, Chile, Egypt, Iceland, Panama, Peru, Sudan, Syria, Tunisia, and Yemen. He is currently involved in research projects investigating the interaction between the Tiwanaku and Wari polities in the Vitor Valley (near Arequipa, Peru) and between the Phoenician and Roman Empires in Zita (near Zarzis, Tunisia). With W. Z. Wendrich and R. M. Bridgman he has published "*Report on the Baynun Mapping Project*" (Leiden 1999), with J. W. Eerkens "*Theory and Practice of Archaeological Residue Analysis*" (Oxford, 2007), with W. Z. Wendrich "*The Archaeology of Mobility: Old World and New World Nomadism*" (Los Angeles, 2008), and with K. Duistermaat "*The History of the Peoples of the Eastern Desert*" (Los Angeles, 2012).

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