

FEBRUARY 21, 1983

CHEMICAL & ENGINEERING

NEWS



Archaeological Chemistry
Page 26

Archaeological Chemistry

Physical science helps to unravel human history

Pamela S. Zurer, C&EN Washington

Archaeologists surveying central and southern Jordan in the 1930s found few artifacts from the middle and late Bronze Ages (about 1900 to 1300 BC). In explanation, they theorized that the area at that time had been the home only of nomads or had had a few major settlements at most. But suddenly, in late 1977, high-quality pottery dating from the late Bronze Age—hardly the work of nomads—turned up for sale in Amman. It was traced to a looted burial cave in the hills surrounding the Baq'ah Valley, northwest of Amman. These clues, which suggested that people had lived in the region in settled communities, appeared to contradict the nomad theory.

Patrick E. McGovern, research specialist at the University of Pennsylvania's University Museum's Applied Science Center for Archaeology (MASCA) in Philadelphia, systematically surveyed and excavated the Baq'ah Valley in the following years, uncovering a wealth of undisturbed evidence that had been missed by earlier archaeological explorations. His work in the Baq'ah illustrates the important role the physical sciences are playing in archaeology. And McGovern's multifaceted training (he studied chemistry as an undergraduate before obtaining a Ph.D in archaeology and working in radiocarbon dating) reflects the broad scope needed to wed the disciplines successfully. From the initial survey of a potential site to the laboratory analyses that can last for years after the digging is over, archaeologists and physical scientists are collaborating to learn more about the past than ever could have been surmised using classical methods alone.

For example, McGovern's team surveyed the Baq'ah with geophysical prospecting instruments—a cesium magnetometer, resistometer, and electromagnetic detector. Soil in filled-in caves gives rise to areas of higher mag-

netic intensity than the surrounding bedrock, and the magnetic variations led the researchers to a series of burial caves dating from about 1550 to 1050 BC.

Back in the U.S., McGovern studied the pottery, metal, and glass artifacts from the Baq'ah both at MASCA and in collaboration with other laboratories. Drawing on the masses of field and lab data he accumulated, McGovern concludes the earlier theory of Bronze Age nomads is misleading and overstated: People had lived settled lives in the Baq'ah. The fine pottery that had first alerted archaeologists to the importance of the region was shown to be of local origin by its chemical similarity to a nearby claybed. Moreover, Mycenaean and Cypriot pottery imports, Egyptian scarabs, and Mesopotamian cylinder seals show the people living in the Baq'ah were part of the late Bronze Age trade network.

Many glass beads, which were studied chemically and microscopically, are comparable to examples from northern Syria, where glassmaking is believed to have been invented about the same time (approximately 1600 BC). And pieces of iron jewelry from an early Iron Age cave are the earliest verified examples of steelmaking from Jordan and among the earliest examples ever found.

Relying on their backgrounds in art, anthropology, and ancient languages and history, archaeological scientists such as McGovern seek to answer myriad questions about ancient artifacts: How old is it? Who made it? How did the people who made it live? What's it made out of? Where did the raw materials come from? What was it used for?

Just a few decades ago, scientists could use only their eyes to place each newly uncovered potsherd, metal fragment, or shaped stone into its proper place in the jigsaw puzzle of what is known about earlier times.

But visual methods are severely limited. And today political and religious unrest block access to many ancient sites; a growing sense of nationalism and pride in the past prevents the removal—and even the excavation—of artifacts from many countries; and construction and environmental pollution threaten to destroy many ancient remains. Archaeologists, working with physical scientists, must extract as much information as possible from every small clue they can dig up.

Archaeometry (the physical sciences as applied to

archaeology) generally is applicable to four areas of archaeological research: conservation of artifacts; prospecting—that is, location of archaeologically interesting sites; dating; and composition of materials. Most archaeological scientists in the U.S. also would include environmental reconstruction in archaeometry, although there's an ongoing discussion of just what the term should encompass. Most scientists using chemical methods are involved in dating and materials analysis.

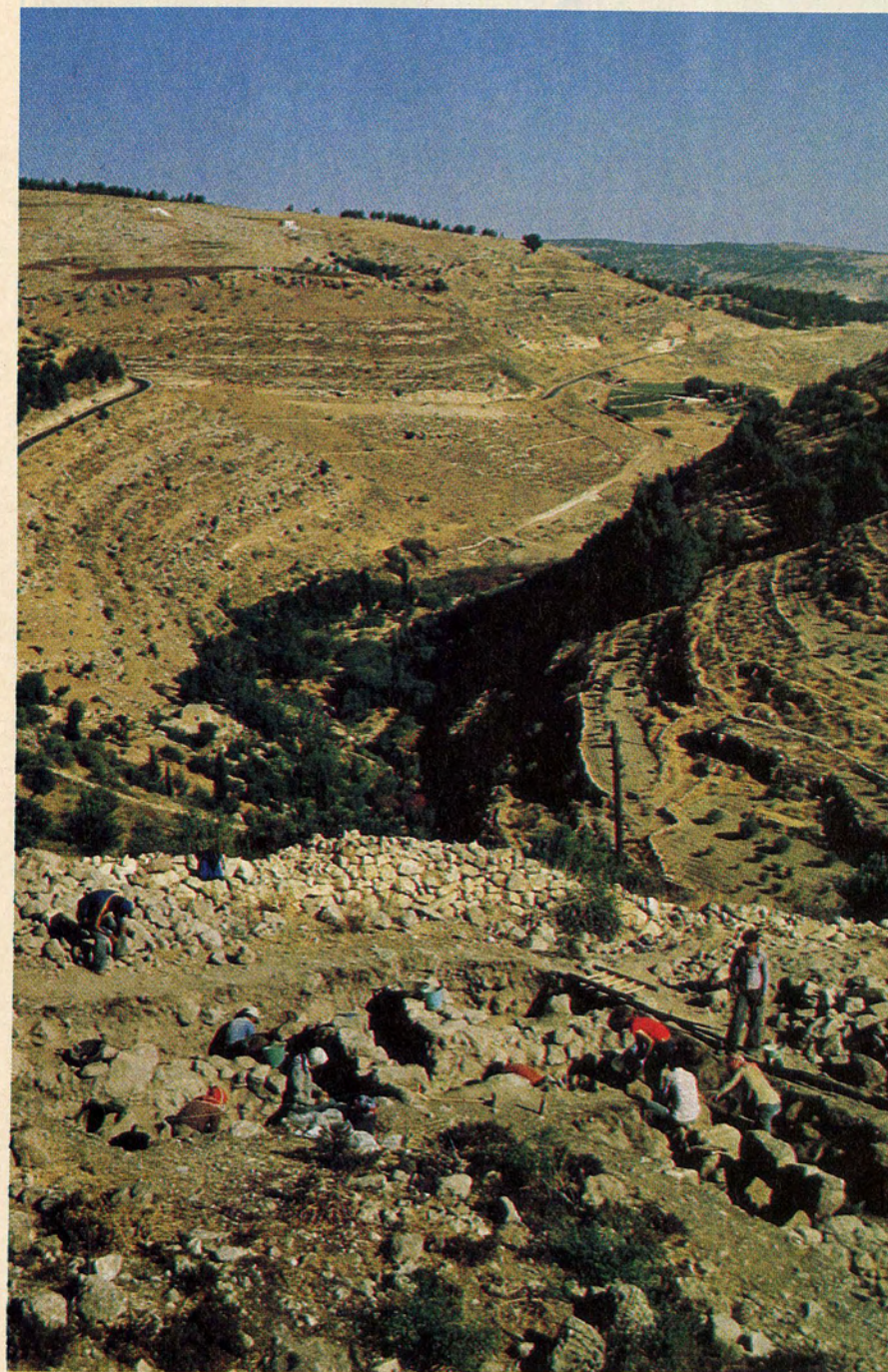
Dating—absolute or at least relative placement in time—is essential for developing chronologies and authenticating materials. And knowing the composition of bone or of artifacts such as metal, pottery, and glass helps archaeologists sort out ancient raw material sources, technologies, trade patterns, and diets.

Dating methods such as carbon-14 isotope dating and thermoluminescence rely on the principles of physical chemistry. Amino acid dating and obsidian hydration dating, in contrast, are based on classical chemical changes. Techniques used to analyze materials include standard analytical methods such as x-ray fluorescence, atomic absorption, optical emission, nuclear magnetic resonance, and infrared spectroscopy, as well as the less accessible proton-induced x-ray emission and neutron activation analysis.

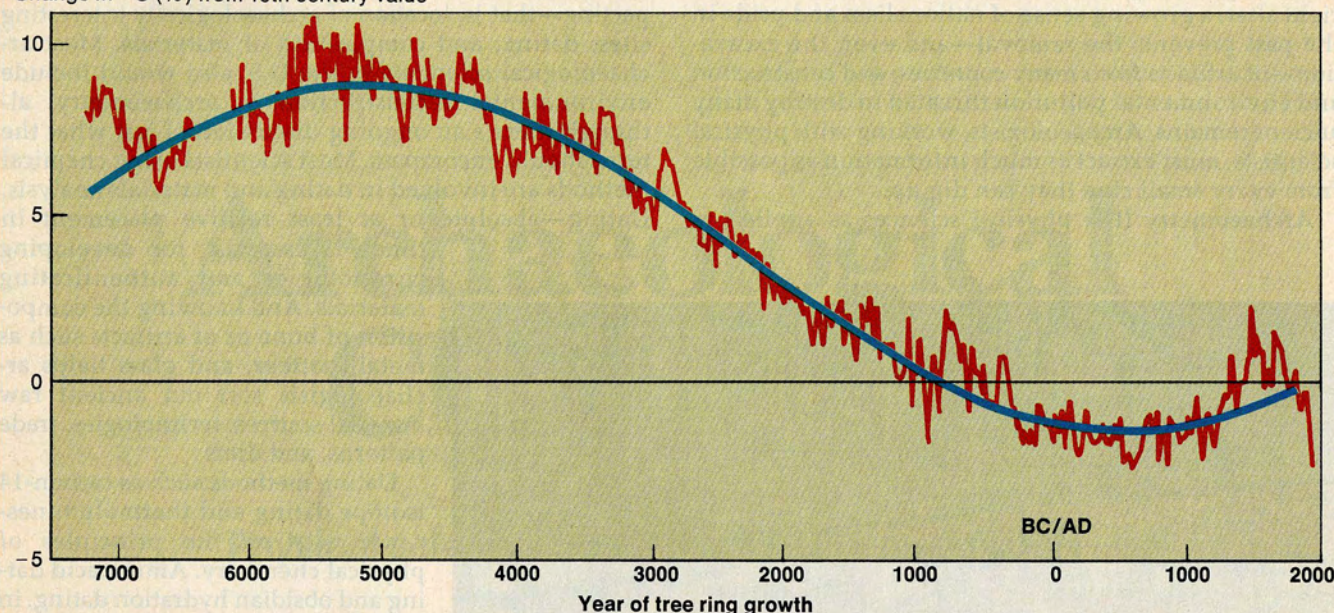
Radiocarbon dating

The question of age is one of the first that scientists studying evidence of early humans seek to answer. An iron spear point found at a Palestinian site may be unremarkable if it dates from 800 BC, in the middle of the Iron Age. But it is worth a lot more study if it stems from 500 years earlier, when Middle Eastern peoples were working mostly with bronze. Chemistry's most well-known contribution to archaeometry is a dating technique: radiocarbon (carbon-14) dating.

Using the radioactive isotope of carbon— ^{14}C —to date carbon-containing matter was proposed in 1947 by Willard F. Libby, who later won the Nobel Prize in chemistry for his work in the field. The method compares the ratio of carbon-14 to stable carbon isotopes in an ancient sample to the same ratio in modern samples. The technique relies on the fact that carbon-14 continually is being created in the upper atmosphere, where

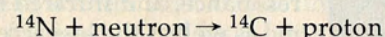


Archaeologists excavate large building, probably Roman, in Jordan's Baq'ah Valley. Site also was occupied in late Bronze and early Iron Ages

Long-term variation in atmospheric ^{14}C activity approximates a sine curveChange in ^{14}C (%) from 19th century value

Source: Hans E. Suess, La Jolla Radiocarbon Laboratory

neutrons produced by cosmic rays collide with nitrogen:



The radiocarbon then is oxidized to carbon-14 dioxide, which mixes with carbon-12 and carbon-13 dioxides and is dispersed throughout the atmosphere and oceans.

Radioactive carbon enters the food chain as plants take up carbon dioxide through photosynthesis. Animals and humans feed on the plants, incorporating carbon-14 into their tissues. Once the organism dies and thus no longer ingests any radiocarbon, the ratio of carbon-14 to the stable isotopes of carbon decreases as the radiocarbon decays with a half-life of about 5730 years. Thus, a carbon-containing artifact 5730 years old will retain only half the carbon-14 of a living sample, one 11,460 years old retains only a quarter, and so on.

Radiocarbon dating is based on the assumption that the pool of radioactive carbon dioxide has remained constant throughout time. But that assumption turns out not to be true. Archaeologists began to notice that radiocarbon dates for some samples didn't match ages that they had determined in other ways. For example, carbon-14 dates for some Egyptian artifacts don't jibe with the chronology of the dynasties derived from ancient written sources. Dendrochronology—the science of dating using variations of growth recorded in the wood of tree rings—confirms that the carbon-14 pool constantly has been changing, according to Minze Stuiver, professor in the department of geological sciences and the quaternary research center at the University of Washington, Seattle.

The biggest changes have been in the twentieth century. Burning of fossil fuels has injected carbon dioxide

depleted of carbon-14 into the atmosphere. And in an opposing trend, man-made carbon-14 has entered the atmosphere from nuclear weapons' tests.

But archaeology is not much concerned with dating samples from the twentieth century. More worrisome is the variation in the production of carbon-14 that is the result of natural, not man-made, causes. A long-range cycle with a period of about 10,000 years is thought to be tied to changes in Earth's geomagnetic dipole field, which influences incoming interstellar cosmic radiation. A short-term variation over a few hundred years, superimposed on the first trend, may be due to solar fluctuations.

"The long-term difference may be as much as 800 years if you go back 8000 years," Stuiver says. His research group, as well as others at MASCA, the University of Arizona, and the University of California, San Diego, have been working to create radiocarbon calibration curves that can correct for atmospheric fluctuations in carbon-14. Their studies are the reverse of ordinary radiocarbon dating: They take tree fragments whose calendar ages are known through dendrochronology, and precisely measure the remaining carbon-14.

Dendrochronologists use several long-lived species of trees in their studies. Chronologies longer than the life of any one tree are built up by matching wiggle patterns—the variations in width of rings caused by fluctuating climate—from living, dead, or fossilized trees whose ages overlap. In this way, Douglas firs from the Pacific Northwest have been dated to about 1800 years ago, California sequoias to about 3200 years, and Bristlecone pines back about 7000 years. A German chronology on oaks from the Rhine Valley extends back 6000 to 7000 years.

Stuiver creates his precise calibration curves by using 50 g of wood for one sample—a huge amount by radiocarbon standards—and counting the decay rate over a period of about four days. The correction factors that Stuiver so determines uncover a complication in finding the true age of an artifact. "If you find one radiocarbon age, you may have more than one [corresponding] calendar age," Stuiver says. Because of the carbon-14 pool fluctuations, tree-ring samples from different years can contain the same amount of carbon-14.

But even with that complication, the correction factors can clear up conflicts between historical and radiocarbon ages. For instance, Icelandic sagas tell of Leif Eriksson landing in 1000 ± 2 AD at a place he called Vinland, located west of Greenland. Archaeologists studying L'Anse aux Meadows, Newfoundland, found Viking-style artifacts and a terrain that matched closely Eriksson's description of Vinland. But radiocarbon dates on numerous samples from the purported Viking settlement placed them at 895 ± 30 AD, a hundred years before Leif Eriksson's time. Applying the dendrochronological correction factors, however, gives an age of about 997 AD, Stuiver says, right on the money.

Despite precise calibration curves, radiocarbon dating faces certain inherent limitations. Even with the newest instrumentation, it can't date materials older than about 60,000 years, as the amount of radiocarbon in a sample after 10 half-lives is simply too small.

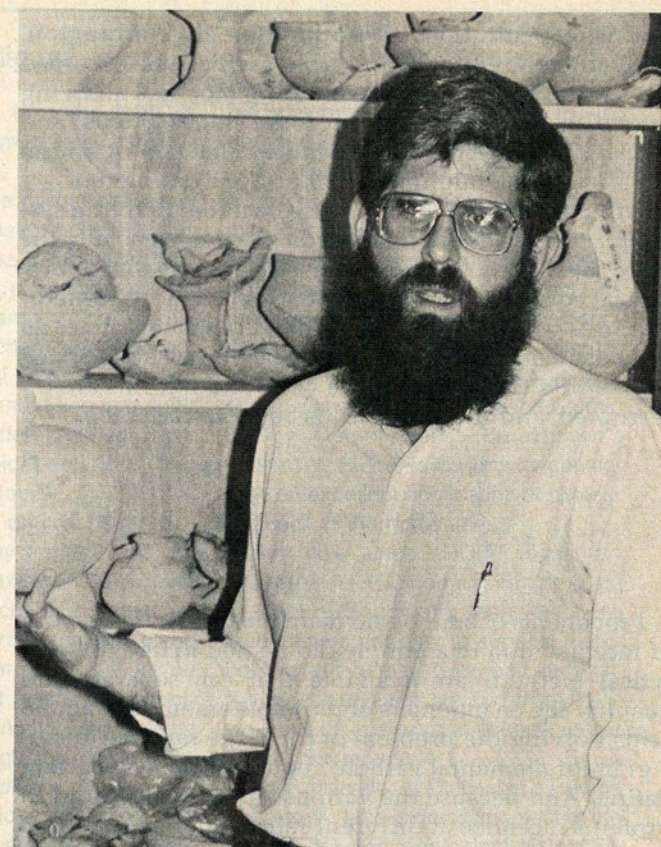
Another problem is that often the organic material available to be dated is not related directly to the finds whose age archeologists want to know. Charcoal, for instance, is often analyzed to determine the age of bones or artifacts found at the same site. But the radiocarbon age found for a charcoal sample tells only when the wood it was made from died—and that could have been centuries earlier. It would be better to date bones or man-made objects directly. The mineral portion of bone, however, is notoriously subject to ion exchange with the environment and therefore analysis of bone carbonate can be misleading. And often there is not enough of the nonmineral part of bone, mostly collagen, to get a radiocarbon date with standard techniques.

Thermoluminescence

Unfortunately, radiocarbon dating more often than not is useless for the most common archaeological find, pottery. Fired ceramics, which have been used by humans in the Near East since about 7000 BC, contain little or no carbon. But about 20 years ago a new technique, thermoluminescence (TL), was developed to date pottery on the basis of radioactivity inherent in clay.

All clays contain a small amount of naturally occurring radioactive materials such as uranium, thorium, and potassium-40. As these atoms decay they excite electrons to metastable electronic levels. When clay is heated above 400°C , the stored energy is released as visible light, called thermoluminescent glow, as the electrons fall back to stable levels. The light intensity can be measured and depends on how long ago the clay was last heated and the rate of radioactive bombardment.

When a piece of pottery is fired, the natural thermoluminescence from the clay is released: The TL clock is



MASCA's McGovern traces origins of pottery and other artifacts through their elemental compositions

set back to zero. Over time, radiation damage builds again within the clay. Heating a sample of pottery and measuring its thermoluminescent glow gives an indication of how long it has been since the piece was fired.

But although archaeologists once had great hopes for TL dating, it now is used primarily to expose modern ceramic fakes, where a high degree of accuracy is not required.

"Once we got into the physics of thermoluminescence dating we found it was too complex for routine use in archaeological contexts, and was thus very expensive," says Stuart J. Fleming, a physicist who is scientific director of MASCA. The error level is around $\pm 7\%$, he says, too high for most archaeological studies, particularly for work in historical times.

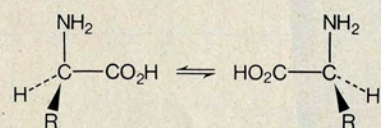
Fleming is excited, however, about TL's use in studying human's early use of fire 30,000 to 40,000 years ago. "There are early hearths of baked clay in Australia," he says, "and no other method of dating is applicable to them."

Amino acid dating

Whereas archaeologists agree that TL's use as a dating technique is limited, the jury's still out on another new dating method. Advocates of the controversial technique of amino acid dating assert it can overcome radiocarbon's problems with sample size and age range. The idea was conceived in the 1950s by Philip H. Abelson, then of the

Carnegie Institution of Washington in Washington, D.C., and now editor of *Science* magazine, who observed that amino acids—essential building blocks of all living organisms—were present in fossil bones, shells, and teeth. He suggested that chemical changes in amino acids over time might be the basis for a dating tool.

Amino acid dating rests on the fact that in living systems, amino acids occur in optically active (generally the *l*) form. If they were in chemical, as opposed to biological equilibrium, one would expect a racemic modification—an equal amount of *l*- and *d*-isomers. Once an organism dies, the biochemical reactions that had been preventing the equilibration of *d*- and *l*-forms are interrupted, and the amino acids begin to racemize.



Proponents of amino acid dating maintain the amount of racemization in a sample can be tied to its age. Analytical methods are available that can separate and quantify the enantiomers of picomole amounts of amino acids, solving the problem of the large samples (about a gram of elemental carbon) required for radiocarbon dating. And because the various amino acids found in proteins racemize at different rates, the time span that can be studied depends on which amino acids are considered. For instance, at 25 °C and neutral pH, the half-life for racemization of aspartic acid is about 3000 years. Under the same conditions, alanine's half-life is about 12,000 years, according to the work of Jeffrey L. Bada, professor of marine chemistry at the University of California, San Diego.

Because racemization is a chemical process, the extent of reaction can be affected by factors other than time. Bada has studied both free amino acids and those bound in proteins and concludes that temperature is the most important variable. For example, at 0 °C the half-life for racemization of aspartic acid is 430,000 years, more than a hundred times longer than at 25 °C.

"You've got two unknowns in the date question," Bada says, "age and the rate constant, which is primarily a function of temperature." To date a bone by the amino acid method, Bada studies a sample from the same geographical area whose age is known through radiocarbon dating or some other independent means. He determines the *D/L* ratio of the dated sample and then works backward to determine the average integrated temperature in the region of interest. He then uses that calibration temperature to date bone samples of unknown age from a presumably similar temperature environment.

Bada has used amino acid dating to address the question of when humans first inhabited the New World, a controversial topic among North American archaeologists. The majority think humans migrated across the Bering Sea from Asia about 10,000 to 20,000 years ago. But some anthropologists, including the late Louis S. B. Leakey, believe certain artifacts and traces of human presence point to humans arriving about 100,000 years

ago. Reliable dates on human skeletons from the Americas could go a long way toward resolving the question.

Using a carbon-14 age of 17,150 years for a skeleton from Laguna, Calif., for calibration, Bada determined the amino acid racemization age for another California skeleton known as the Del Mar individual. Later, with a modified temperature calibration, he dated a skeleton from Sunnyvale. He concluded that the skeletons were 48,000 and 70,000 years old, respectively, from the extent of racemization of aspartic acid in the bones. These ages have generated a lot of controversy, because, if they are correct, they imply that anatomically modern humans (*Homo sapiens sapiens*) appeared earlier in North America than in the Near East or Europe.

Another investigator interested in the problem of when humans came to the New World has studied the same Sunnyvale skeleton by carbon-14 dating. R. Ervin Taylor, professor of anthropology and director of the radiocarbon laboratory at the University of California, Riverside, exploited the new radiocarbon technique of tandem accelerator mass spectrometry, which requires only milligram samples. Working with the new National Science Foundation Regional Accelerator Facility at the University of Arizona, Taylor finds the Sunnyvale individual is only about 3500 to 5000 years old, confirming a measurement made in his own lab.

The two ages determined for the same individual by two different techniques differ by an order of magnitude and lead to profoundly different conclusions about early humans in North America. Each scientist stands by his findings.

"The problem that you have with carbon-14 dating is that there is a very low protein content remaining [in old bones]," Bada says. "They don't make any efforts in the ¹⁴C business to isolate pure fractions, so samples may be contaminated with secondary inputs which result in lower ages." As an example, Bada points to some material he studied from Olduvai Gorge, Tanzania. The bones were collected from a level called the middle Stone Age, which is dated by classical stratigraphic means to about 30,000 years ago. Bada's amino acid analyses gave ages of about 35,000 years, whereas radiocarbon ages of the bones were about 3000 years.

Taylor agrees that the problem of samples contaminated with modern carbon is severe. In fact, much of his research centers on that problem. A few tenths of a percent of modern carbon can make a 50,000-year-old sample appear thousands of years younger, he says. But Taylor points out that he prepared three separate samples of Sunnyvale skeleton material in three different ways, and the ages determined from each fraction agreed within a thousand years.

"A lot of people say amino acid racemization dates are generally in error—I don't," Taylor says. "In some cases it apparently works and in some cases it doesn't. It suggests some other factors have to be considered."

A scientist who has been looking into those other factors is P. Edgar Hare, staff member of the geophysical laboratory at the Carnegie Institution of Washington. He believes the amount of water that bone is exposed to affects profoundly its amino acid content.

Funds for archaeological projects difficult to dig up

Although competition for money is fierce in all areas of research, archaeological chemists are finding the struggle for funds particularly tough. "To develop any sort of major funding in this area is simply impossible," says Joseph B. Lambert of Northwestern University.

As chairman of the American Chemical Society's Division of the History of Chemistry's Subdivision of Archaeological Chemistry's task force on funding, Lambert polled archaeological scientists on their source of funds. The group found that about 35% of the researchers received most of their support from their own institutions. In fact, 30% of the respondents had never gotten any outside funds.

For example, Eastern Michigan University's Giles F. Carter for years has been studying Roman coins on a shoestring budget from the university. Sometimes he's even had to use his own money.

Those workers who receive outside grants get them from an odd conglomeration of sources, including the National Science Foundation, the National Endowment for the Humanities, private foundations, and even private individuals, the ACS study finds. Although NSF has funded the largest number of grants, it also rejects a greater proportion of proposals than any other agency. And

NSF support tends to come from its anthropology program, not its chemistry division.

"We support research in chemistry itself, not projects that use chemistry as a tool," says Thomas L. Isenhour, NSF program director for chemical analysis, to explain the program's lack of activity for archaeological chemistry. Isenhour says he tries to find a home for every proposal and will send those that don't fit his purview to a different NSF division. For the archaeological sciences, that division is anthropology.

Indeed, the NSF anthropology program supports many projects with an archaeological chemistry component. Radiocarbon researchers, in particular, praise NSF's support for upgrading and replacing equipment. But pressure on the shrinking social science research budget is great and many proposals by chemists fall through the cracks between the two disciplines.

"NSF [anthropology program] will fund proposals that are clearly of relevance to solving an archaeology problem," Lambert says. "But if one is trying to develop a method of applying chemical technique, it's not interested."

Lambert thinks this reflects a breakdown of the peer review system. "The reviewers may be scientists working in the same area," he says, "but the peo-

ple who make the decision as to who gets funds are not peers."

The likelihood of getting funds from other federal agencies is not great either. Because of lack of support by the Department of Energy, the long tradition of collaborative work between archaeologists and chemists at Brookhaven National Laboratory is in danger of dying. "Our work was very well supported when we were under the Atomic Energy Commission," Brookhaven's Edward V. Sayre says. "It was considered an excellent application of nuclear methods to the humanities."

But now under DOE, young archaeologists who come to Brookhaven to learn archaeometry techniques are being asked not only to support themselves, but to pay overhead as well. "With less and less support from DOE, we won't be in a position to continue our work," Sayre says.

The University of Minnesota's George R. Rapp Jr., who is president-elect of the Society for Archaeological Sciences, summarizes the concern of researchers who are trying to use the methods of the physical sciences to understand the human past. "A lot of people have never had outside funds," he says, "and the field is moving very slowly. The field is suffering from poor development because of lack of funding."

Water is essential for the racemization reaction to take place, Hare says. Even apparently dry bones have a small percentage of water in their matrix, which lets the reaction proceed. But if bones have survived in a damp location or one that's been flooded periodically, complications set in.

The major organic part of bone is the protein collagen, which has three long peptide chains coiled around each other like a rope. In addition to racemizing the individual amino acid components of the chains, water can react with the peptide bonds, hydrolyzing collagen to gelatin. Once the protein is hydrolyzed, it can more easily leach out of bone.

"I can get virtually any *D/L* ratio with the same reaction temperature and time by varying the amount of water," Hare says, describing artificial aging experiments he performs on cow bone. If he preheats the bone to remove water, he finds no racemization. If he exposes the bone to water vapor, he finds essentially complete racemization. But if he immerses the bone in excess water, he finds an intermediate amount of racemization in the amino acids remaining in the bone.

The excess water allows free amino acids to leach out of the bone, Hare says. The free amino acids are significantly more racemized than those in the intact collagen, he explains, so the material remaining in the bone appears to be less racemized—younger—than would be expected.

This sensitivity to water can wreak havoc with the calibration technique developed by Bada, Hare says. If the bone used for calibrating the temperature history has been wetter—more extensively leached—than the bones of unknown age, the calibration bone will appear too young and the unknown bones too old. And if the bones of unknown age have been in greater contact with water, they will seem too young. "There are too many variables," Hare concludes. "There is still a lot of research to be done on amino acid dating."

But Hare is enthusiastic about amino acid dating of shells, which are often found among human remains. "Shells are potentially easier to work with than bone—mainly because they approach a closed system," he says. Using a portable liquid chromatograph, Hare and his coworkers have developed an assay system which lets

Archaeology provides insight into nuclear waste and environmental problems

While the physical sciences are becoming more and more integrated into archaeological research, archaeology is contributing its part toward finding solutions to some difficult technological problems. For example, the study of ancient glass is helping to formulate methods of nuclear waste disposal. And old refuse heaps may contain information important to environmental studies.

Safe long-term storage of high-level radioactive waste has been a major stumbling block to public acceptance of nuclear power. Some methods under scrutiny involve fusing the waste with glass and then storing it deep underground. Solids gradually are damaged by radiation. But because glasses are not crystalline but are supercooled liquids, they are intrinsically more stable toward radioactivity. Questions remain, however, as to how well glass can stand up to time and weathering.

At least some of the answers are contained in ancient glass artifacts. "We've got glass that's been around for 3500 years," says Maureen F. Kaplan, an archaeologist who works at Analytic Sciences Corp., a consulting firm in Reading, Mass. Kaplan prepared a handbook for the Department of Energy summarizing what is known about the aging properties of ancient glass.

Kaplan found that the deterioration of glass depends more on its chemical composition than on its age. Criz-

zling—the leaching of chemicals and water from glass that causes it eventually to crack into masses of flakes—may be tied to too little lime, for example.

Equally important to how well glass survives is the kind of weathering it endures. For instance, Roman glass from Europe that has been subjected to freezing and thawing has fared less well than glass of similar composition that was buried in the milder climates of the Middle East or Egypt.

Kaplan also is looking into designs for markers to warn future generations to keep away from land-based repositories of nuclear waste. Whatever label is used must last 10,000 years and unambiguously tell people to keep out. "There are marking systems that have lasted for 5000 years," she says, referring to the pyramids, Stonehenge, the Great Wall of China, and Serpent Mount in Ohio. "Some of them we understand today, and some we don't."

Establishing environmental baselines from archaeological materials is the goal of research by Elizabeth A. Coughlin, a chemist who is administrator of the Center for Archaeological Research & Development of Harvard University's Peabody Museum. She notes that regulating environmental pollutants is often complicated by uncertainty over the natural levels of toxic elements. Changes in elemental content of archaeological samples from preindustrial

times indicate how the environment has been altered, she says.

Coughlin and graduate student Cheryl P. Claassen, now assistant professor of anthropology at the University of Cincinnati, dug into trash piles of quahog shells on the North Carolina coast. The clam shells were discarded by Indians who collected them 2700 years ago as food and wampum. The researchers compared the elemental composition—determined by neutron activation analysis—of prehistoric shells with that of modern shells.

"Clearly, there are elements present in modern shell that weren't in the old shell," Coughlin says. A 15% increase in the levels of arsenic may be due to runoff from agricultural uses, specifically pesticides containing arsenic compounds.

Coughlin links five elements that show increases of 45 to 50% to military activity at a nearby Marine Corps base, Camp LeJeune. Tellurium, hafnium, gold, holmium, and niobium are used in electromagnetics, and aerospace, demolition, and nuclear technology, she says, and the military base has active bombing and artillery ranges.

As a followup, Coughlin wants to collect shells from the entire East Coast to check whether the concentrations of these elements have increased everywhere. But from her work so far she is confident that shells are an excellent environmental indicator.

in obsidian at various temperatures to find a hydration rate and activation energy for each type of obsidian. They calculate the effective hydration temperature from mean annual air temperatures and the range of temperature in the region where the artifacts were found. Knowing the obsidian's chemical composition, its hydration rate, and the effective temperature, they can find the artifact's age from the thickness of the hydration layer.

"Most researchers are convinced that it is now an operational technique" that can give reliable dates, Michels says. For example, the obsidian dates on 72 different samples from East Africa agreed with independent radiocarbon ages and stratigraphic successions, he says. He also is working on artifacts from Easter Island, Guatemala, and Sardinia. Michels thinks the method potentially could date objects from 500,000 years ago. He now is studying some hand axes from Ethiopia that are at least 120,000 years old.

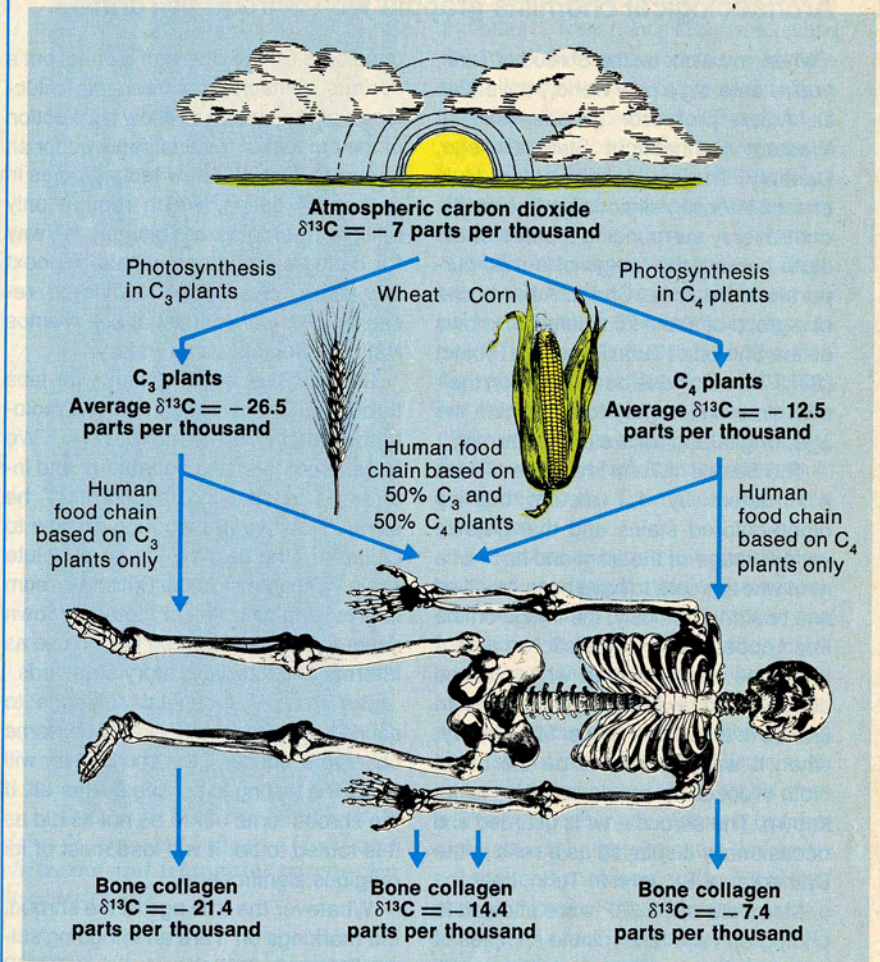
Bone offers clues to diet

In addition to trying to determine the age of bones, scientists are looking at human skeletal remains for clues as to what ancient people ate. Knowing whether they ate mostly meat or grains, for example, or cultivated vs. wild plants, archaeologists can surmise something about the lives of early humans.

The mineral portion of bone is mostly $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ —hydroxyapatite—but trace elements collect in bone, reflecting what people eat. For example, the strontium levels in plants are higher than in animals, because animals have biochemical mechanisms that discriminate against strontium's substituting for calcium, even though the two elements are in the same chemical group in the periodic table. Therefore a relatively high strontium content in human bone indicates a plant-based diet. Similar arguments relate higher levels of vanadium and manganese to a primarily vegetarian diet, whereas elevated zinc and copper levels point to meat consumption.

But a lot of pitfalls attend trace element analyses of bone. In fact, until recently bone studies were not often undertaken. Bone is much more likely to have decayed than other archaeological finds like pottery or stone, and surviving bone can be badly contaminated by the soil around it. Although the concentrations of elements of interest can be determined without too much difficulty using standard analytical techniques, archaeologists have to be very careful in interpreting the results.

Ratio of ^{13}C to ^{12}C in human bone reflects diet



Note: $\delta^{13}\text{C}$ = difference, in parts per thousand, of the ratio of ^{13}C to ^{12}C in a sample and the ratio in a reference standard of marine carbonate. For example, the ratio of ^{13}C to ^{12}C in atmospheric carbon dioxide is 7 parts per thousand smaller than in the reference material, so the $\delta^{13}\text{C}$ for atmospheric carbon dioxide is -7 parts per thousand.

Source: *American Scientist*, 70, 602 (1982)

them find a rough amino acid-based date in the field as they collect shells.

And Bada stands by the use of amino acid racemization as a dating tool for bone. "There's been no real controversy with the method outside of the Del Mar and Sunnyside work," he says. Bada points to numerous others working with the technique and to his own work in Tanzania, in Europe, and in China studying Peking man. Certainly amino acid dating will continue to be a chemical tool exploited by archaeologists, but the results must be placed carefully in the context of other evidence.

Obsidian hydration dating

Obsidian dating is another method whereby some of the limitations of radiocarbon dating can be overcome, according to its proponents. Obsidian is a glassy volcanic material which flakes easily. It was used widely by early humans who shaped it into cutting tools or weapons with sharp edges. Exposed surfaces of obsidian, like

those of other kinds of glass, slowly absorb water. As the water diffuses into the obsidian, a hydration layer forms that grows with time and can be measured under a microscope.

In 1959, Irving Friedman, a geochemist with the U.S. Geological Survey in Denver, suggested that the thickness of the hydration layer on an obsidian artifact could be related to how long ago the piece was crafted. However, as is the case with amino acid dating, other variables besides age affect the process. The rate of water diffusion depends on both temperature and the chemical composition of the obsidian but is independent of relative humidity, Friedman found. Exposure to sunlight also is a factor.

Recently, Joseph W. Michels, professor of anthropology at Pennsylvania State University, University Park, reported new experimental methods for determining specific hydration rates for obsidian samples of various compositions. Michels and his coworkers at Penn State's obsidian dating laboratory induce hydration

Archaeological chemists grapple with Shroud of Turin

"When you work on the Shroud of Turin, you're entering a new world," says Alan D. Adler, professor of chemistry at Western Connecticut State College, Danbury. The world Adler refers to is one of intense religious and scientific controversy surrounding a piece of old cloth bearing the image of a man purported to be Jesus Christ. Adler is one of a group of about 25 scientists, known as the Shroud of Turin Research Project (STURP), who have been trying on their own time and money to determine the age, origin, and nature of the shroud.

The Shroud of Turin is a piece of linen 4.3 meters by 1.1 meters bearing blood-colored stains and the life-size yellow image of the front and back of a man who appears to have been crucified and beaten. Curiously, the image on the linen appears more realistic on a photographic negative than when viewed directly. It first was displayed in southern France in the middle of the 14th century, when it was claimed to be the burial cloth of Jesus. Its previous history is not known. The shroud now is guarded and occasionally displayed as a relic in the Cathedral of St. John in Turin, Italy.

Members of STURP were allowed to photograph and take minute samples of the cloth for chemical analysis when it was displayed in 1978. They also undertook various spectroscopy, infrared thermography, and x-ray experiments. A 15th-century accident in which the shroud was scorched and damaged by water left evidence of how the cloth and image react to heat and water.

The researchers are trying to find out how old the cloth is, what makes up the image and bloodlike stains on the linen, and how the markings were formed. But Eric J. Jumper, associate professor at the Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio, says STURP can never prove that the man pictured in the shroud was Jesus, although that question is the root of the intense interest in the shroud. "Science at most can supply a negative answer," Jumper says.

The question of the cloth's age may be most important, for if the linen is younger than the first century AD, it definitely could not have the religious significance that is claimed for it. The linen fiber of the shroud makes it a prime

candidate for radiocarbon testing, but a serious obstacle has been the reluctance of the church to allow destruction of the amount of material required for an accurate date. But new technologies in carbon-14 dating, which require only milligram samples, are clearing the way for dating experiments within the next few years, says Robert H. Dinegar, research physical chemist at Los Alamos National Scientific Laboratory.

Dinegar has been talking with labs throughout the world that can do radiocarbon dating on a microscale. "We have about five labs capable of and interested in studying the shroud," he says. "Now we are working on how to calibrate [the results] on an absolute scale." Dinegar says the British Museum is providing samples of cloth of known dates for the radiocarbon labs to use as internal and interlaboratory standards.

But even if technical solutions to dating the shroud are near at hand, some observers wonder if the church ever will allow the testing to proceed. After all, if the shroud turns out to be not as old as it is touted to be, it will lose most of its religious significance.

Whatever the true age of the shroud, the markings on it are an intriguing scientific puzzle in their own right. STURP researchers have studied the shroud by computer enhancement and image analysis, the techniques used to extract information from photographs sent from space satellites. They find the body image appears to encode three-dimensional information, as if it were formed while the cloth was draped over a human figure. Studying the shroud under a microscope shows that only the tops of the threads are yellow-colored, and that the colored fibrils are all about the same shade. Certain areas appear darker to the eye—the top of the nose, for instance—because more threads in that area are colored. It is as if the image were a half-tone photograph such as those published by newspapers.

The reddish stains on the shroud that appear to be blood from wounds are indeed blood, according to STURP researchers. Chemical tests are positive for the presence of proteins and heme and bile pigments, they say. The most convincing evidence, according to STURP, is that immunological tests

show samples of the bloodstains react as does human blood.

Adler and other team members believe the coloring agent that forms the body image is simply a degradation product of the cellulose of the linen itself, rather than an added pigment. Infrared and ultraviolet spectra are consistent with an α,β -unsaturated carbonyl giving rise to the yellow color. Such a chromophore can be formed by a number of pathways during oxidative degradation of cellulose.

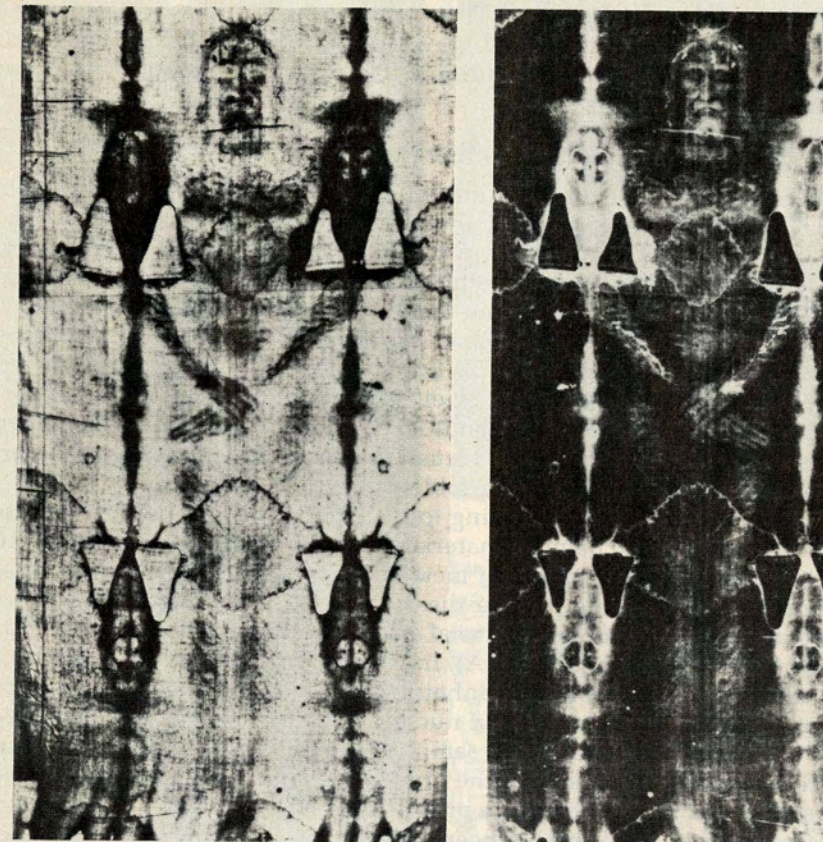
When the STURP researchers studied samples that were lifted from various areas of the shroud using sticky tape, they found inorganic materials which could be pigments, but not enough to give color evident to the eye, in their judgment. Adler concludes that the yellow color of the fibrils of the body image was formed by an acceleration of the normal aging process of linen.

But not everyone agrees. Walter C. McCrone, of McCrone Research Institute, Chicago, who performed his own microscopic and chemical studies of the shroud, believes the image was painted on. McCrone, a microscopist who some years ago proved Yale University's Vinland map to be a modern fraud rather than the pre-Columbian map of America it was purported to be, says the presence of iron oxide, protein, and mercuric sulfide (vermillion) on the sample tapes indicate a gelatin-based paint was used to create the image.

McCrone, who was once a member of STURP himself, generally agrees with the group's explanation of the yellow color on the cloth. But he finds that a pigment of iron oxide and vermillion on top of the yellow fibers makes up the image. "None of the STURP people are microscopists," says McCrone to explain the difference of opinion. "They are not art or painting or pigment experts. I'm doing analyses in parts per billion, while they are looking at parts per million at best."

McCrone also does not believe that the alleged bloodstain areas actually are colored by blood. "The only difference I find between the bloodstains and the body images is the amount of pigment," he says. "The same samples with which they got positive results for blood gave me six negative results."

One of STURP's tests for blood also has been criticized by Irving M. Klotz,



Portion of shroud showing front of body as it appears to the eye (left) and as a photographic negative. Dark scorch marks and triangular patches on either side of the body are result of 15th-century fire

professor of chemistry at Northwestern University, Evanston, Ill. As evidence for serum albumin, Adler cites a color change that occurs when he reacts supposed blood samples with bromocresol-green. But Klotz, who has studied the reaction of dyes and albumin, says the test is not specific: Many other proteins and polymers can give the same color change. Still other observers question STURP's immunological tests on such old samples.

Adler says that McCrone's data may well be correct, but that McCrone has misinterpreted them. For instance, the STURP researchers claim that the protein which McCrone interprets as pigment binder comes from the bloodstained areas of the cloth. And iron present in the linen, Adler adds, could have been absorbed from hard water by the cellulose in the process of manufacturing linen from flax. And STURP researchers say that contamination from the materials of artists who copied the shroud could account for traces of vermillion on the cloth.

Whatever mechanism formed the images on the Shroud of Turin, most members of STURP are convinced it was not painted. "To assume it's a painting would be a greater miracle than the resurrection," Adler says. Adler points out that an artist would find it difficult to paint a reversed negative image that encodes three-dimensional information. And he says that there is not enough iron oxide on the body image areas to show up in the x-radiographs, and so contends there is not enough to be visible to the eye.

McCrone acknowledges that the shroud is not a typical painting, but says there are examples of very transparent paintings from the 14th century. He claims painting reversed images is not so difficult: "I've got a good picture of George Washington that I painted as a negative," he says. And he says there is enough iron oxide to create a visible image, regardless of whether it shows up on the x-radiograph.

These differences of opinion are difficult to reconcile. Neither side hesitates

to question the scientific objectivity of the other. "Their minds are made up and they don't want to be confused with the facts," says Adler of those who believe the shroud is a painting. "The problem with members of STURP is they want to believe it is real so badly that they are blinded to the science," counters McCrone.

McCrone suggests that the sample tapes should be re-examined by art experts to clear up the discrepancies. He and STURP agree that radiocarbon dating must be done. But McCrone points out that a 1st century AD date for the cloth wouldn't necessarily authenticate the shroud. The radiocarbon date would apply only to the linen itself, not to the image on it.

A number of hypotheses aside from painting, dyeing, or staining have been formulated for how the image was formed on the cloth. Among these are: a vapor-phase reaction of ammonia from a decomposing body; physical contact of the cloth with decomposing skin, sweat, and other chemicals such as burial spices; scorching of the cloth with a hot, man-sized statue; a burst of high-intensity light from an unknown source; and a corona or electrical discharge. None of these theories is able to explain all of the properties of the image of the shroud.

A recent proposal suggests that the image was formed by low-energy secondary x-rays emitted by the body in the shroud. The author of the hypothesis, Giles F. Carter, chemistry professor at Eastern Michigan University, Ypsilanti, finds that linen exposed to x-rays in his lab forms a yellow color that looks about right. But as Adler says, the theory is "great physically, great chemically, but absolutely bizarre biologically. Anyone who was that radioactive would be dead long before he was crucified."

Although a lot more is known about the shroud now than was known even five years ago, much more work is needed. The scientists of STURP would like to confirm their assertion that the bloodstains were made by human blood. Everyone is anxious to know the radiocarbon age of the shroud. But the most perplexing question remains: How was the image formed? It will stay a puzzle as long as the researchers involved can't even agree on the data they're trying to interpret.

Photos by Vernon Miller, Brooks Institute

Special Report

electron microprobe to study how elements are distributed in the cross sections of bones. Elements like strontium that are stable to the environment are uniformly distributed across the bone, whereas iron—which tends to infiltrate the bone from the soil—concentrates at the surface, they find.

Lambert and Buikstra compared the trace element contents of male and female skeletons found at a burial site dating from about the second century AD. The element levels are identical for the bones of men and women, indicating they ate the same diet. Varied animal and plant remains found at the site suggest that the people were hunter-gatherers.

In contrast, at another Illinois location where people lived about 800 years later, there is extensive evidence of maize farming and the trace elements in bones are quite different for men and women. Lower strontium levels in the male skeletons from the more modern site imply the men there ate more meat. The difference in diet recorded in the skeletons may reflect how differing sexual roles evolved as the society changed from hunting and gathering to farming, the researchers think.

The carbon content of ancient bones also can reveal something about diet. Researchers are showing that the kinds of plants people eat leave their marks in the ratio of carbon-13 to carbon-12 found in the organic fractions of bone.

As plants convert carbon dioxide into more complex molecules during photosynthesis, the isotopes of carbon react at slightly different rates because of differences in atomic radius and weight. Different metabolic pathways affect the ratio of the stable isotopes of carbon found in plant tissue in different ways. For instance, so-called C_3 plants, including most North American and European plants, first convert carbon dioxide to a three-carbon molecule called 3-phosphoglycerate. These plants use carbon dioxide less efficiently than those that first convert it into four-carbon dicarboxylic acids—the C_4 plants. Maize, sugarcane, and many plants adapted to growing in strong sunlight are C_4 plants. Because of the different chemical reactions involved, plants that follow the C_4 pathway are less depleted in carbon-13 than plants that follow the C_3 pathway. In fact, the characteristically different carbon-13 to carbon-12 ratios in the two kinds of plant can be used to distinguish them.

Michael J. DeNiro, assistant professor in the department of earth and space sciences, University of California, Los Angeles, has been tracing the carbon isotope ratios up the food chain. Feeding experimental animals controlled diets, he finds the carbon isotope ratio in their tissues reflects the isotopic content of their diet. Of course, the more metabolic pathways traversed, the more complicated the trail becomes, but the basic pattern holds.

The characteristic carbon isotope ratios can shed light on human diets. For example, archaeologist Nikolaas J. van der Merwe from the University of Capetown, South Africa, examined skeletons from North American burial mounds. He and coworker J. C. Vogel conclude from mass spectrometry studies that the proportion of maize in the North Americans' diet started at zero, then over a period of about 200 years from 1000 to 1200 AD in-

creased rapidly to account for more than half the carbon in the bones. Their findings suggest that farming as the basis for food very rapidly overtook the hunting and gathering tradition that had lasted for thousands of years.

Metals and metallurgy

Another glimpse into the lives of prehistoric people is afforded by their metal tools, weapons, and jewelry. George R. Rapp Jr., professor of geology, archaeology, and ancient studies at the University of Minnesota, Duluth, studies the trace element profiles of copper artifacts and copper ore deposits. Rapp, a geochemist by training who is president-elect of the Society of Archaeological Sciences, started working with an archaeologist about 17 years ago and as a result changed his research focus from chemical mineralogy to archaeological problems.

"We're trying to trace trade routes—how far people exchanged materials—and the early technology and production of metals," Rapp says. He uses a computer to compare the distinct trace element fingerprints of ore samples and metal objects revealed by neutron activation analysis (NAA). In this technique, first proposed by J. Robert Oppenheimer, artifacts are bombarded with neutrons in a nuclear reactor. The neutron-activated nuclei in the sample then emit gamma radiation characteristic of the kind and amount of elements present, resulting in a profile for each sample.

Rapp has been most successful in tracing the geological and geographical origins of copper in North America, where, unlike most of the world, there are large deposits of native metallic copper. North American pre-Columbian Indians didn't smelt copper or make alloys, according to Rapp, but simply hammered the native metal into shape. As a result, he can tie the trace element content of an artifact to a particular ore deposit.

"Copper ores from near Lake Superior traveled at least 1000 miles in all directions," he says. And although it was once thought that Indians in Minnesota mostly traded for copper from ore-rich Michigan, Rapp finds that ore from the Snake River deposit in central Minnesota shows up in local artifacts. "When Indians came across native copper, they used any bits they could find," he concludes.

Rapp is trying to make similar connections between ore sources and metal artifacts from other parts of the world, but the smelting and alloying technologies that developed outside North America make trade patterns much harder to trace. Robert Maddin, professor of metallurgy at the University of Pennsylvania, Philadelphia, agrees that more sophisticated metalworking techniques make provenance studies very difficult. After a long career in the physics end of modern materials science and engineering, about a decade ago Maddin turned to studying ancient metal artifacts with James D. Muhly, professor of oriental studies at Penn, and Tamara Stech-Wheeler, an archaeologist from Bryn Mawr College. Associated with this research group is the archaeometallurgy section of MASCA, headed by Vincent C. Pigott.



University Museum photos

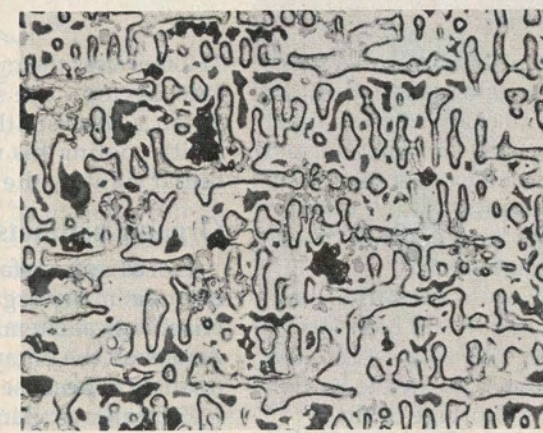
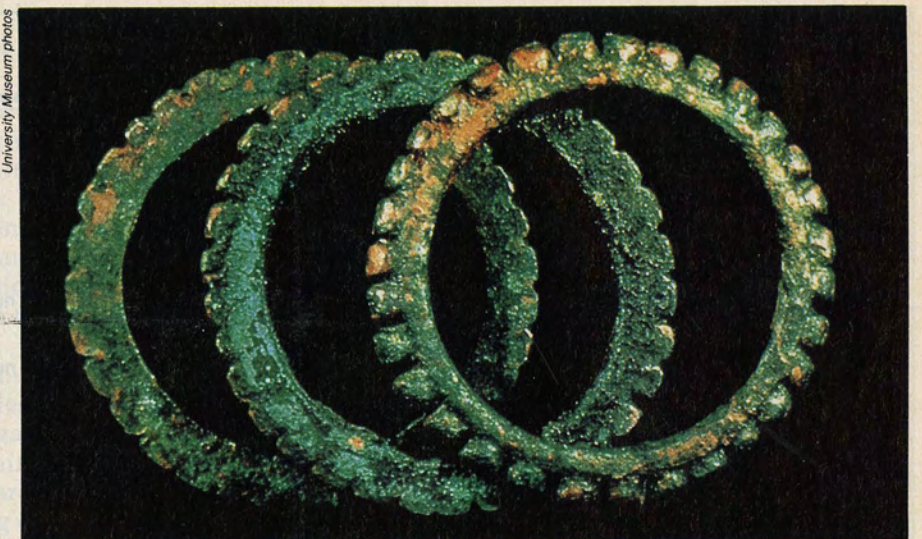


Photo courtesy of Robert Maddin

Many bronze artifacts were found at Ban Chiang, Thailand. Spear point dates from about 2000 BC. Bracelets are about 1000 years younger. Photomicrograph of bronze anklet shows dendritic pattern of cast material

"Archaeologists always ask, 'Where did the ore come from?', and it's almost impossible to answer," Maddin says. In addition to the chemical changes that occur in smelting, he notes that ore deposits are heterogeneous—there can be different mineral compositions a few meters apart in the same deposit. And complicating things further is the problem of remelting. "Ancient peoples always reused their metals," he says.

Yet Maddin finds he can learn a great deal about the technology used in manufacturing metals by studying the artifacts. "The basic theory is that what you did to a metal 10,000 years ago is imprinted in the structure unless you reheat it," he says.

Among other projects, Maddin and Stech-Wheeler have been directing the study of the bronze and iron objects found at Ban Chiang, an archaeological site in northeast Thailand. Until the past decade, archaeologists had considered Southeast Asia a cultural backwater, whose people had borrowed the skills of metallurgy from India or China at a relatively late date. But the rich finds unearthed at Ban Chiang and other Thai sites show sophisticated metalworking developed there independently as early as the third millennium BC.

Elemental analysis of early Ban Chiang metal objects show most were made of bronze—an alloy of copper with about 10% tin, which is abundant in Thailand. A

treelike pattern seen in optical micrographs of the bronze tools, weapons, and ornaments indicates most were cast, according to Maddin. This characteristic dendritic pattern forms as cast alloys cool and different components solidify preferentially. In bronze, the solid components first formed are richer in copper and the last-formed richer in tin.

Other metalworking techniques, such as hammering and annealing, also leave their traces in finished pieces. But the question most interesting to Maddin is what made people turn from working with bronze to working with iron. In the Eastern Mediterranean, the Iron Age began around 1200 BC, though scattered iron artifacts show some much earlier knowledge of ferrous metals.

"Why would iron replace bronze if both were available?" Maddin wonders. "Iron alone is not as hard as bronze, and it corrodes quickly." In addition, iron is much more difficult to work. Whereas bronze can be cast at about 950 °C, temperatures of more than 1500 °C are needed to melt iron. The hottest early furnaces could get was about 1200 °C, Maddin says, so iron had to be laboriously forged. Indeed, the only obvious advantage iron has over bronze is that the ore is much more abundant than copper or tin.

Archaeologists have theorized that some cataclysmic event—an earthquake, a volcanic eruption, perhaps

Archaeological chemists employ broad spectrum of analytical techniques

Analytical method	Best applications	Elements or compounds analyzed	Comments
Atomic absorption spectroscopy	Glass, metals, bone, obsidian	About 50 metals	Simple and accurate, but slow
Neutron activation analysis	Pottery, obsidian, metals, stone, bone, glass	40 to 60 elements	Requires nuclear reactor
Proton-induced x-ray emission	Obsidian, glass, metals	About 25 metals	Nondestructive; analyzes surface of intact artifact
X-ray fluorescence	Metals, glass, pigments	Elements with atomic numbers higher than 22	Nondestructive; best used for surface analysis
Electron microprobe	Metals, pottery, glass, bone	Elements with atomic numbers higher than 22	Ideal for studying variations in composition
Nuclear magnetic resonance; infrared spectroscopy	Organic materials: pigments, amber, resins, oils	Organic molecules	IR best for qualitative analyses; magic angle spinning NMR for solids
Optical emission spectroscopy	Pottery, metals, glass	30 to 40 elements	Versatile and cheap; good for trace elements

drought—around 1200 BC cut off the Middle East's supply of tin, forcing metalworkers to turn to the more difficult iron. A significant cultural change occurs about that time. Many sites show evidence of destruction, and foreign trade appears to be curtailed extensively. "You can't do very much with copper without tin," Maddin says. But he and his collaborators have another theory of why iron became the dominant metal.

"Suppose people learned you could get carbon into iron," Maddin proposes. "Then you would have steel," a much harder, more useful alloy. "We suggest the Iron Age occurred perhaps because people learned to harden iron, rather than [because of] any shortage of tin."

Maddin theorizes that as early smiths struggled to work iron at forges fueled by charcoal, carbon slowly diffused into the metal, changing it to carbon steel to a certain depth below the surface. People didn't realize carbon was the hardener in iron until the 18th century AD, Maddin says, but they knew if you left the material in the furnace longer—all the time adding carbon—you got a harder product.

Maddin is looking for evidence of ancient steelmaking by studying the carbon content of early iron artifacts, very few of which have been analyzed metallurgically. Unfortunately, 90% of the time the iron is badly corroded. Although a ghost structure reflecting the original composition of the metal remains, studying corroded iron is tedious work.

Another metallurgical technique that makes carburized iron harder—and thus in a position to compete with bronze—is quenching. If steeled iron is cooled rapidly from the heated state in which it is worked, it forms a different, harder structure than if it were allowed to cool slowly. Metallurgical analysis of iron artifacts can reveal the characteristic martensite formed by quenching. Maddin delights in pointing to some literary evidence that the process was in use by the eighth or seventh century BC.

"In the ninth book of the 'Odyssey,' Homer describes how Odysseus and his men get the giant Cyclops drunk and then blind him so they can escape," Maddin says.

"Homer uses the metaphor that the hot olive stick going into Cyclops' eye sizzles the way a piece of iron does when a blacksmith plunges it into cold water." So a smith cooling his work in water must have been a familiar sight by the time the "Odyssey" was written.

Organic artifacts

Just as iron artifacts are difficult to study because they corrode, many organic materials pose problems for archaeological chemists because they tend to decompose. And even the organic artifacts that survive may be hard to analyze because they are intractable and insoluble.

"Organic artifacts are pretty tough to do anything with," says Lambert of Northwestern. "There's been very little work on paper or textiles, for example." But Lambert has tackled one difficult, insoluble organic remnant—amber—by using solid-state nuclear magnetic resonance.

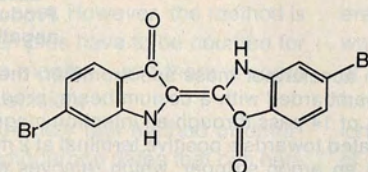
Amber, the fossilized resin of trees, has been used for decorative objects for thousands of years. If archaeologists knew the chemical composition of amber samples, they might be able to trace their geographical origin and perhaps even the kind of tree from which the resin came. Researchers then could map ancient amber trade patterns. But because of the poor solubility in spectroscopic solvents of the noncrystalline material, until recently only infrared spectra of powdered amber have revealed much useful data.

Lambert notes that the problems in analyzing amber are similar to those in characterizing coal. He and his collaborator, James S. Frye, of the Colorado State University Regional NMR Center, Fort Collins, are applying the same approach to amber as has been used successfully for coal and shale oils. Looking at powdered amber samples by high-resolution NMR using magic angle spinning and cross polarization, they find samples can be distinguished by their ^{13}C spectra. Several samples of Baltic amber have identical spectra. The Baltic ambers differed slightly from samples of amber from Sicily and are quite different from spectra of amber from Burma, Romania, and Bohemia.

"It's my hope that solid-state NMR can do for organic artifacts what elemental analysis did for inorganic materials," says Lambert.

An organic dye that was once valued as worth its weight in gold is proving a difficult analytical problem to two separate groups interested in tracing the development of its technology and trade. Tyrian, or royal, purple was prized highly in the ancient Mediterranean. Purple dyes were used by the Egyptians, Greeks, Phoenicians, and Romans and are mentioned in the Old Testament. Pliny the Elder describes the dye and how it was made from certain mollusks.

Modern attempts to reconstruct the dyeing process show the dye was extracted in a colorless, or leuco form, from any of a number of species of gastropods. Acidic oxidation of the extract gives the main purple component, 6,6'-dibromoindigo. One researcher estimates it takes 10,000 sea creatures to make 1 g of dye.



6,6'-Dibromoindigo

McGovern of MASCA is intrigued by a sherd from a pottery storage jar coated with purple sediment that may be Tyrian purple. The sherd was unearthed by another University Museum archaeologist at Sarepta, along the coast of Lebanon, during the first excavation of a Phoenician homeland site. The archaeological site, unfortunately now inaccessible in the chaos of the war in Lebanon, is near the city of Tyre, from which Tyrian purple takes its name.

The purple-tinged sherd dates to around 1300 BC, based on archaeological dates of other pottery found at Sarepta, McGovern says. If the pigment is Tyrian purple, it would be the first verification that the dye was produced by ancient Phoenicians that early.

A study of the sherd by the nondestructive technique of proton-induced x-ray emission (PIXE) showed the colored material contains unusually high levels of bromine. In PIXE analyses, a high-energy focused beam of protons is accelerated onto the surface of a sample, generating characteristic x-ray emissions from each element.

High-resolution mass spectrometry of samples from the sherd confirmed that the purple colorant contains bromine, but McGovern has not yet been able to pin it down as dibromoindigo. Infrared spectra of a reference dye, extracted from modern Lebanese shells following Pliny's description, have thus far given ambiguous results, probably because of the presence of other organic compounds.

A small island in a bay on the coast of Qatar also holds evidence for Tyrian purple manufacture. Christopher Edens of Harvard University's anthropology department has found large ceramic vats and millions of snail remains at a site tentatively dated to 1000 BC. His chemist collaborator, Elizabeth A. Coughlin, research administrator for the Center for Archaeological Research & De-



Polychrome (right) and blue-on-white majolica sherds were found in Mexico City subway excavations

velopment at Harvard's Peabody Museum, is analyzing black residues from the interiors of ceramic sherds. Using chromatographic and wet chemical separations as well as elemental analysis by x-ray fluorescence, she is looking for traces of the purple dye. She notes that degradation of the substance on the sherds—the bane of organic remnant analysis—may make direct identification of dibromoindigo difficult.

Pottery

In stark contrast to the fragility of many artifacts made from organic materials, pottery is among the longest lasting of human creations. Fired-clay pots and sherds are perhaps the most ubiquitous archaeological finds—so much so that before more accurate techniques were developed archaeologists most often relied on the characteristic shapes and styles of pottery to date their sites.

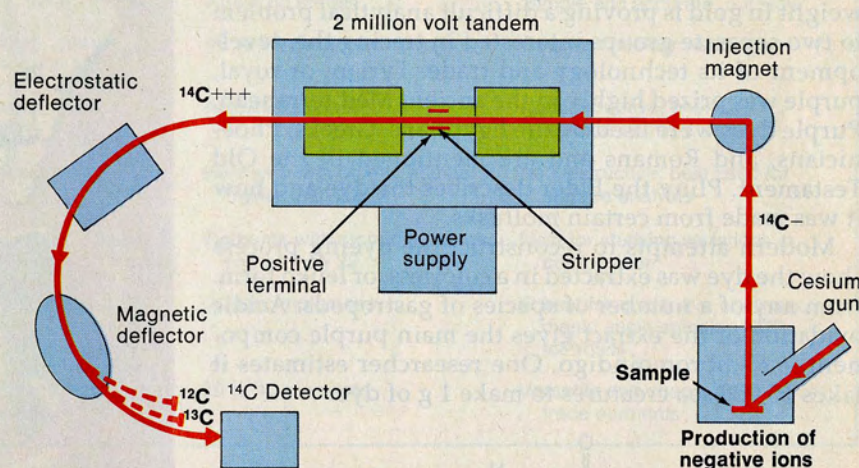
Archaeological scientists today are tracing the patterns of pottery trade and manufacture by comparing the clay composition of sherds found at different sites. An important element in this work is the data bank of more than 10,000 neutron activation analyses at Brookhaven National Laboratory.

Improved instruments allow carbon-14 dating of smaller samples

An archaeologist who has spent a season sweating under the sun to retrieve an artifact is faced with conflicting needs to extract as much information as possible from his or her find while protecting it for future study and appreciation. One question, that of age, sometimes can be answered through the popular, but destructive, technique of radiocarbon dating.

In typical radiocarbon experiments, the carbon fraction of a sample is converted to a gas—usually by burning to carbon dioxide—which is placed in a type of Geiger counter where the rate of disintegration of carbon-14 is measured and compared to that of a reference standard of known age. A routine run requires from a half to several grams of elemental carbon and at least a day of counting time to obtain a date with a precision of about 1%. The older the artifact, the less carbon-14 remains, so larger samples and longer counting times are needed. The oldest radiocarbon ages that can be determined with confidence under such standard conditions are about 40,000 to 50,000 years.

But two recent developments now allow radiocarbon dates to be obtained from much smaller samples—no small thing to archaeologists dealing with artifacts too precious to allow gram-sized



In the University of Arizona tandem accelerator mass spectrometer, the sample in the form of aluminum carbide is bombarded with a cesium beam, producing ions. Negative ions with an atomic mass of 14 pass through an injection magnet into the accelerator. There they are accelerated towards a positive terminal at 2 million volts. At the terminal, ions pass through an argon stripper, which removes electrons to produce ions with a charge of +3. The positive ions are repelled from the terminal and are further accelerated until they have a kinetic energy of 6 million volts as they exit. After passing through electrostatic and magnetic field analyzers, the ions enter a detector, which measures both energy and rate of energy loss

samples to be destroyed or where only a minute amount of material has survived. Microscale detectors for conventional proportional decay counting can work on samples as small as 10 mg.

And mass spectrographic methods, which count carbon-14 atoms—instead of the beta rays those atoms produce as

they decay—require only a milligram or less of material.

A small counter now being used at a number of labs both in the U.S. and the U.K. was developed in the late 1970s at Brookhaven National Laboratory. Garman Harbottle, Edward V. Sayre, and Raymond W. Stoenner undertook the

Edward V. Sayre and Garman Harbottle of Brookhaven's chemistry department have helped numerous archaeologists analyze their pot sherds using NAA. Each analysis is stored in Brookhaven's computer. "As you get more and more data together, your conclusions are much more valid," Sayre says. "Pieces that didn't make sense at one stage may make sense later."

For example, one collaborator of Sayre's looked at pottery samples from Athens that had been made at the Athenian agora. Comparing their composition to that of pots from Marseille, France, which appeared to be Greek imports, the workers found a close match. And other analyses that Brookhaven had on file from pots found in Israel and Cyprus also had profiles very similar to the Athenian material. The earlier data on the computer let the researchers conclude that the pots from France, Israel, and Cyprus had all been made in Athens.

As useful as NAA is for studying pottery—as well as other artifacts and bone—the need for a nuclear reactor limits it severely. Jacqueline S. Olin, supervisor of archaeometry at the Smithsonian Institution's Conserva-

tion-Analytical Laboratory, has been exploring direct current plasma-optical emission spectrography (DCP-OEP) as a complementary method to NAA. For a number of years, Olin has worked closely with Sayre and Harbottle at Brookhaven using NAA on a variety of artifacts.

Olin is using both NAA and the more accessible emission spectrography to trace how Europeans introduced their ceramic technology into the New World. She is studying majolica—a colorful style of pottery which the Spanish brought to their colonies during the 16th century. Olin and archaeologists Florence C. and Robert H. Lister are looking at majolica samples unearthed during construction of the subway in Mexico City. Other majolica sherds come from excavations under the cathedral there, which was built on the site of an Aztec temple dismantled by the Spanish. Still other samples are modern majolica pieces currently being made at Puebla, Mexico.

By comparing the composition of the pottery, the researchers can tell if it was made in Spain or Mexico. The clays from Spain contain calcium, which is essential for

research there with funding from the Conservation-Analytical Laboratory of the Smithsonian Institution, which needed a method to determine the age of an iron artifact of disputed origin from traces of carbon in the iron. The danger of contaminating the sample with modern carbon is an even greater threat when the sample is small, so the Brookhaven workers made the counter mostly of fused silica. Because it has no plastic parts, the entire apparatus can be heated while being evacuated to drive off contaminants.

The Brookhaven microscale detector can be adapted to fit existing conventional radiocarbon equipment at relatively low cost. However, the method is slow—samples have to be counted for about two months—and there is some loss of precision.

An extremely fast method of determining radiocarbon dates that can handle even smaller samples involves counting carbon atoms directly by high-energy mass spectrometry (HEMS). Direct counting capitalizes on the fact that for every carbon-14 atom that decays in a minute and is detected by a Geiger counter, there are 10^9 to 10^{12} more radiocarbon atoms still in the sample. Mass spectrometry offers the capability of directly reading out the relative amounts of various isotopes.

The major obstacle to direct counting of carbon-14 atoms is the necessity of

resolving other entities with the same atomic mass—the much more abundant nitrogen-14 atoms from air and the molecular fragments $^{12}\text{CH}_2$ and ^{13}CH . But use of either a Van de Graaf electrostatic accelerator or a cyclotron to accelerate particles to very high energies (that is, millions of electron volts rather than thousands in conventional mass spectrometers) can overcome that problem.

For example, most labs working on HEMS, such as the new National Science Foundation's Regional Facility for Radioisotope Dating at the University of Arizona, Tucson, use tandem electrostatic accelerators. Tandem accelerator mass spectrometers have three ways of eliminating interfering particles of atomic mass 14. As the sample is ionized, a magnet selects only those ions with a negative charge and a mass of 14 to travel through the instrument. Negative nitrogen ions are not stable, so one interfering factor is removed at the outset.

Interfering molecular fragments are removed at a later stage. After an initial acceleration, the negative ions are stripped of electrons to form multiple-charged positive ions. Fragments such as $^{12}\text{CH}_2$ are broken up, while $^{14}\text{C}^{+++}$ ions are accelerated a second time (thus the name "tandem" accelerator). Finally, after passing through magnetic and electrostatic analyzers, the ions

enter a detector that measures both their energy and their rate of energy loss. This distinguishes them from any remaining chemically different species of the same atomic mass.

The biggest remaining problem with tandem accelerator mass spectrometry, according to Douglas J. Donahue, professor of physics at Arizona and director of the dating lab, is fabricating the targets from which the samples are ionized into the accelerator. Currently the Arizona lab converts samples into aluminum carbide targets, but "we haven't really found anything completely satisfactory," Donahue says. Converting the raw sample into the target material is complicated and not all of the target material ionizes.

Although the NSF facility is still getting the bugs out of its accelerator, it can obtain a radiocarbon date with an accuracy of ± 200 years from a 1 mg sample in about an hour, Donahue says. "We hope that within six months an accuracy of ± 100 years will be routine," he adds. Donahue sets a limit of 50,000 to 60,000 years on the dates the facility can obtain, noting that a 50,000-year-old sample contains only a thousandth of the carbon-14 of a living sample. Many archaeologists, however, hope that HEMS techniques, perhaps in combination with enrichment methods, eventually will allow radiocarbon dating of samples as old as 100,000 years.

making majolica. The pottery is fired, then glazed, painted, and refired.

"You must have a high calcium content or the glaze is unsuccessful," Olin says. "Probably the Mexican majolica potters started using local clay and it didn't work." Eventually they hit upon a solution using a mixture of local calcium- and noncalcium-containing clays, which is still used today in Puebla. "At the cathedral site, we find imported ware and both successful and unsuccessful local ware," Olin says.

Olin finds she can use analytical results from NAA and DCP-OES interchangeably in her pottery studies. Besides the advantage of not requiring a nuclear reactor, DCP-OES detects certain elements such as silicon, titanium, and magnesium that aren't easily determined by NAA.

Ralph O. Allen, professor of chemistry at the University of Virginia, Charlottesville, has used NAA to look at pottery 5000 years older than the material Olin is studying. Geochemist Allen collaborated with archaeologist Michael A. Hoffman, now of the University of South Carolina, to study Egyptian pottery of the

predynastic period (4000 to 3100 BC). Visiting Hierakonpolis, the legendary home of the first pharaohs, they found the ground literally covered with huge amounts of broken pottery. The researchers collected samples from both cemeteries and settlements there, as well as local clays.

"The most significant thing we have found is that the pottery made at each particular site was made of very local material," Allen says. They found different types of pottery: a crude sort tempered with straw, near where people lived; and hard plum-red ware decorated with black tops, at the cemeteries. Originally they thought the finer cemetery material was made of a different kind of clay, "but it's the same, only the technology differs," says Allen.

From looking at the mineral content and the elemental composition of the plum-red ware, the researchers hypothesize that a salt—possibly calcium carbonate—was intentionally mixed with the clay to help fire it at lower temperatures. The increased amount of calcium helps weld it all together. "The belief had been that the technology wasn't good enough to make



MASCA photos

the lanthanide rare earths—can be used to match the manmade objects and the geological bodies where the stone came from.

Allen has had a chance to study some soapstone artifacts from the purported Viking settlement in L'anse aux Meadows, Newfoundland. Most important is a spindle whorl, a little round doughnut-shaped stone like those used as a counterweight in spinning yarn by the Norse in Iceland and Northern Europe. It appears to have been made out of local material from within a few miles of the Newfoundland site, Allen says.

But also found at L'anse aux Meadows was a stone lamp like those made by Dorset Eskimos from the northern regions of Labrador. Allen finds the lamp was made from soapstone from a quarry far away from Newfoundland. "It appears to have been brought there," he says. Unfortunately, chemistry can't reveal whether it was the Vikings who moved the lamp from Labrador to Newfoundland.

Obsidian is another type of stone that was used widely by early humans. Many cutting tools and deposits of obsidian have been analyzed to map the widespread trade in that natural volcanic glass. But more difficult to trace is the spread of technology as humans learned to make glass themselves.

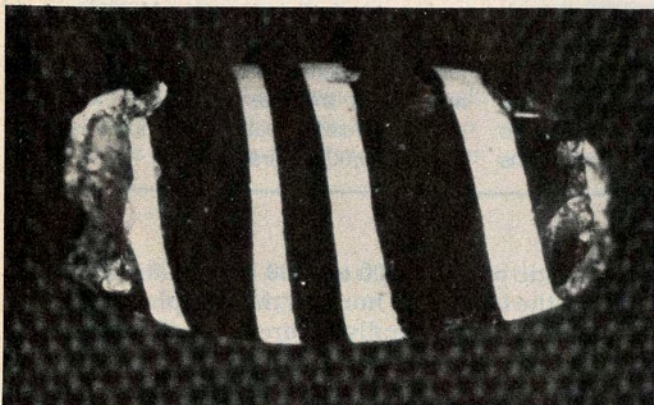
Sand (silica), alkali (a sodium salt or plant ashes), and lime—the basic raw materials for producing glass—are widely available, and early glassmakers could have used pottery kilns as their furnaces. McGovern of MASCA has been approaching the problem of mapping the technology flow by studying the transition metal ions responsible for color in glass.

McGovern has studied a large collection of glass and other beads from a Palestinian site called Beth Shan, dating from 1300 to 1200 BC. Although the material was excavated in the 1920s and 1930s, it languished in the University Museum's basement for many years awaiting further study.

Beth Shan is located between Syria, where there was a strong glass industry, and Egypt, where faience—a silica ceramic with a glass glaze—was made, and McGovern is trying to unravel the complexities of whose techniques influenced whom.

Using PIXE analysis and scanning electron microscopy, McGovern can identify the elements responsible for the colors in the beads. These can be randomly distributed ions in the glassy matrix. Copper, for instance, gives a blue-green in the +2 oxidation state and a red for the reduced +1 valence. Antimony in the +5 state combines with calcium or lead to form crystalline inclusions of calcium (white) or lead (yellow) antimonate. The silvery color of some beads is in fact caused by colloidal silver particulates, he finds.

McGovern is trying computer clustering of the chemical data in hope of tracing the sources of the colorants. But it's difficult, he says, in view of the chemical complexity of the materials and the spotty geological exploration in the Middle East. If the beads were made locally—which is likely because molds and glassmaking refuse were found at Beth Shan—antimony, lead, and silver would have had to be imported. From where is still a question.



Glass beads from Beth Shan date from 13th century BC. Silvery feather decoration (top) results from colloidal silver particles. Spirally banded bead has white antimony (+5) bands over a black (possibly reduced copper) matrix

this kind of pottery," Allen says. But the use of geochemical techniques helped uncover the unexpected skill of the predynastic Egyptian potters.

Stone and glass

Geochemist Allen also has been tracing the origin of North American artifacts made of soapstone. In a project like the Brookhaven computer file of pottery studies, Allen has collected a data bank of NAA analyses of about 700 soapstone objects and quarry samples. Allen finds the patterns of trace elements in soapstone—particularly

Looking for silica/alumina know-how?

Finding the right company to help you develop new products doesn't have to be a gamble. Huber has the experience and ability to tailor our synthetic silicas and silicates to your application.

Whether you are looking for a conditioner, thickener, extender, or reinforcer, our controlled structure technology can meet your specific formulating needs. Whether you are developing new products or modifying current products, Huber offers unbeatable service and economy.

From cosmetics to food, adhesives to coatings, plastics to paper, Huber has the products and skill to suit you.

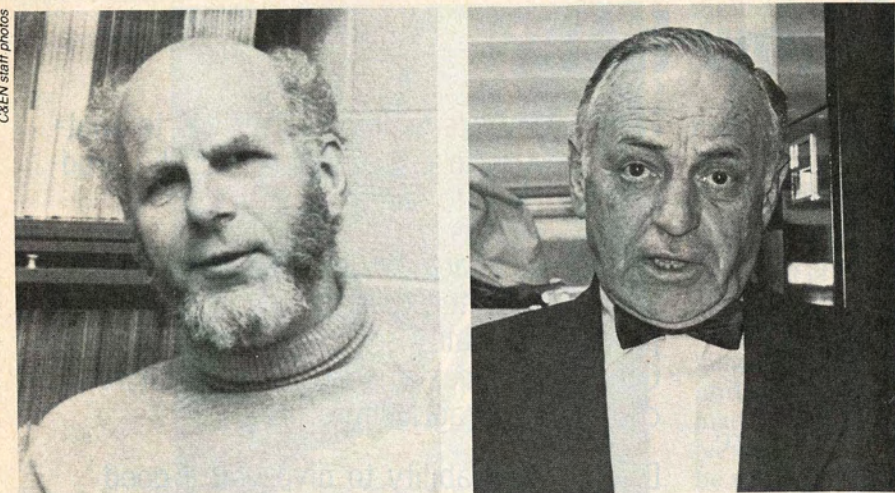
Our products are odorless, tasteless, non-toxic fine white powders that meet all purity and quality specifications of the Food Chemicals Codex and are cleared for food, cosmetic and agricultural uses.

Discover our ability to give you a good hand; call or write us today.

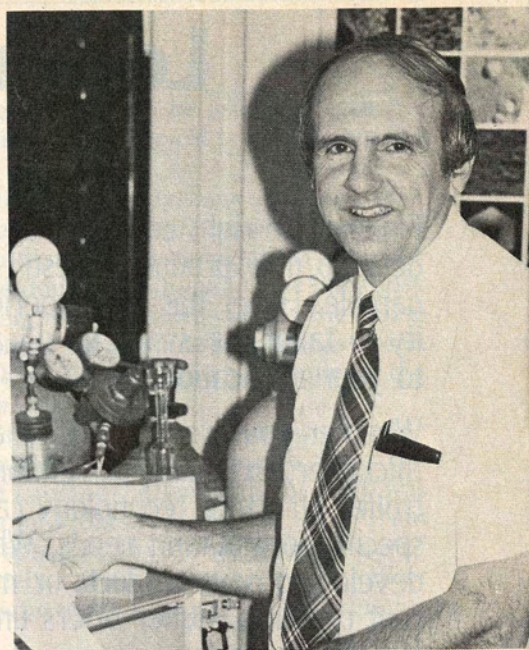
Let Huber response ability give you a hand.



J. M. HUBER CORPORATION
Chemicals Division
Customer Services Department
P.O. Box 310
Havre de Grace, MD 21078
301/939-3500.



Archaeological scientists Stuiver (left), Maddin (center), and Hare study ¹⁴C variability, metallurgy, and amino acid dating, respectively



Future directions in archaeometry

As the methods of the physical sciences are applied more and more routinely to archaeology, making good use of, even simply finding, the masses of data that are accumulating is becoming a problem. "Very often, the archaeologists will put analytical data in an appendix," the Smithsonian's Olin says. "Data can get lost. It costs a lot of money to generate and then it is treated in a cursory fashion."

Wider use of computers may be one way for archaeological scientists to tackle the problem of access to information. Data banks such as Brookhaven's files on pottery give researchers a chance to place their contributions in a broader context. Although Brookhaven's computer currently contains only results from studies done there, eventually it will include data from all over the world, Sayre says.

Some scientists would like to see field instruments that can supply immediate feedback to researchers working at an archaeological site. More and more digs are salvage operations—last ditch efforts before a site is destroyed by highway construction, for example—so there's no going back to re-examine a clue whose significance was overlooked. One step in the direction of immediate feedback in the field is the portable amino acid analyzer developed by Hare of the Carnegie Institution of Washington. Hare's instrument and assay can be used in the field to correlate strata and give the relative ages of fossil shells.

But many archaeological scientists feel that what is most needed to advance their field is not another new instrument or analytical method, but closer cooperation between the disciplines of archaeology and the physical sciences. An archaeologist who simply sends off samples for analysis after the fact is not likely to get all that's possible out of the data a chemist sends back. And most chemists have no way of evaluating what the important archaeological questions are. The most successful projects involve joint planning and research from the start.

"One of the things we've all found is that you can't just

have service work done and get any satisfactory answers," says Suzanne P. DeAtley, assistant professor of archaeology at MIT. DeAtley has worked at the radiocarbon lab at the University of California, Los Angeles, and held a fellowship in materials analysis at the Smithsonian Institution. She, like MASCA's McGovern, is one of a growing number of archaeologists whose training has included work in the physical sciences.

"Chemists are becoming more aware of what really are the anthropological problems," DeAtley says. "And archaeologists are becoming more aware that there are no black-box techniques."

Most chemists working in the field agree that to make a good contribution it's necessary to become an expert in the technology and archaeology of an artifact. But it's not easy, especially for young men and women in universities who aren't yet established in the more traditional specialities.

"As a practical matter, a young person can't work on archaeological problems," says Maddin, the metallurgist from Penn. He notes that pressures to publish and get tenure can force researchers to stick to more state-of-the-art research.

"Generally speaking, the most satisfactory solution is to have a research center where archaeologists and scientists can work together," says DeAtley. Olin agrees. She would like to see a series of labs with the necessary equipment and, perhaps even more important, personnel with backgrounds in archaeology as well as the physical sciences.

"To do this work you must have laboratories," Olin says; "good, well-supported labs where people can work and interact with other scientists and anthropologists." □

Reprints of this C&EN special report will be available at \$3.00 per copy. For 10 or more copies, \$1.75 per copy. Send requests to: Special Issues Sales, American Chemical Society, 1155—16th St., N.W., Washington, D.C. 20036. On orders of \$20 or less, please send check or money order with request.



The winners' choice.

When it comes to Pentaerythritol, manufacturers of alkyd resins, synthetic lubricants, and rosin esters choose Celanese. We're the world's largest and only fully integrated producer with a proven track record of quality, fast delivery, and value. So if

you're in the running for a reliable source of supply for Pentaerythritol, call Celanese at 214-689-4841. Or write, Celanese Chemical Company, Inc., Dept. 5062, 1250 West Mockingbird Lane, Dallas, Texas 75247.

In the long run, you'll be a winner, too.



**CELANESE
CHEMICAL
COMPANY, INC.**

Celanese...There's no substitute for commitment.