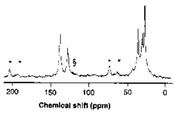
Nuclear magnetic resonance in archaeology



Joseph B. Lambert, Catherine E. Shawl and Jaime A. Stearns

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60025, USA

Received 25th January 2000
Published on the Web 7th April 2000

Nuclear magnetic resonance spectroscopy is a useful analytical tool for the examination of archaeological artifacts. Both organic and inorganic materials have been examined in solution and in the solid. NMR can identify sources of raw materials, verify artifact authenticity, delineate ancient technology, and specify ancient diet.

1 Introduction

Although high resolution nuclear magnetic resonance (NMR) spectroscopy has been an important analytical technique for 40 years,[1] its impact on archaeology until recently has been minimal. The same 40 years saw archaeology grow into a multifaceted discipline that sought input from essentially any source of analytical information, including chemistry, physics, geology, mathematics, computer sciences, and the full range of life sciences.[2]

There are two reasons why NMR, so dominant in structural chemistry, participated minimally in this development. First, for its initial several decades of existence, NMR was primarily a tool for the examination of materials in the liquid phase. If not liquids themselves, the subjects had to be dissolved in an appropriate solvent. At the same time, the primary artifactual materials of archaeology (stone, pottery, glass, metal) were solids with little ability to dissolve and retain their molecular integrity. Secondly, the first decades of NMR focused on hydrogen (^{1}H) and, after the development of pulse Fourier transform methods in the late 1960s, on carbon (^{13}C) as the nuclei of choice. Their favorable properties in terms of sensitivity and resolution served organic chemistry well, but the materials of archaeology at that time rarely contained hydrogen or carbon. Stone, pottery, and glass are composed largely of silicates and aluminosilicates, and metallic materials usually lack hydrogen and carbon. Thus the strong suits of NMR did not match the needs of archaeology.

Three developments have changed this situation: two in NMR and one in archaeology. First, high resolution techniques were developed during the 1970s that applied to solids, particularly for study of the ^{13}C nucleus.[3] The package of new methods included high-powered decoupling, rapid spinning of the sample at an angle designed to remove broadening effects ('magic angle spinning', MAS), and enhanced sensitivity of the carbon signal through a trick called cross polarization (CP) that borrows intensity from hydrogen nuclei. It thus became almost as easy to examine solid as liquid samples. Second, NMR expanded into the rest of the periodic table.[4] Examination of less sensitive elements such as silicon and aluminium became feasible on a routine basis. Third, archaeology began to embrace organic materials that could be examined by traditional proton and carbon NMR methods. Although organic materials had been used for ^{14}C dating, they were treated not so much as a characterizable artifact than as a source of elemental carbon. Archaeologists had new appreciation for foodstuffs, resins, and tars that often exist only as a residue on another material. Thus the scopes of NMR and archaeology began to converge, as NMR developed methodologies for examining solids and nuclei other than hydrogen and carbon, and archaeology became interested in organic materials.

Joseph B. Lambert is Clare Hamilton Hall Professor of Chemistry at Northwestern University, Evanston, Illinois. He received his BS from Yale University in 1962 and his PhD from the California Institute of Technology in 1965. His research is in the areas of organosilicon chemistry, physical organic chemistry, and archaeological chemistry.

Catherine E. Shawl received her BA from Williams College in 1995 with a double major in chemistry and classics. She completed her PhD degree at Northwestern in archaeological chemistry in 2000 and now works as a food chemist at Kraft Foods.

Joseph B. Lambert

Catherine E. Shawl

Jaime A. Stearns

Jaime A. Stearns is a native of Fresno, California. She is currently an undergraduate student in chemistry at Northwestern. Her previous research has included synthesis of phospholipid transfection agents and analysis of palladium nanoparticles.

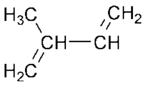
DOI: 10.1039/a908378b

NMR is a means of classifying atoms within a molecule according to their molecular environment.[5] Thus a ^{1}H spectrum provides a series of peaks, or resonances, usually one for each chemically distinct hydrogen. The position of the resonance in relation to a standard is referred to as the chemical shift. This position, as well as the intensity of the resonance and sometimes its splitting by neighboring nuclei into several peaks, is used to characterize the hydrogen in terms of functional groups. The ^{13}C spectrum provides similar information about the carbon skeleton. In this fashion, the overall structure of an organic molecule may be deduced from these spectra. Almost any element may be examined, but success is limited by the natural abundance of a specific isotope and by its sensitivity to the NMR experiment. Hydrogen has both high abundance and high sensitivity. The most common isotopes of carbon (^{12}C) and oxygen (^{16}O) lack appropriate nuclear properties for the NMR experiment, so that recourse is made to the less abundant ^{13}C and ^{17}O.

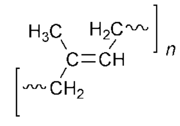
For the purposes of archaeology, NMR can be considered as an analytical technique on the one hand for identifying the structure of a specific organic molecule or on the other hand for providing a census or fingerprint of nuclear types for complex mixtures of compounds, both organic and inorganic. The nucleus most appropriate for the context is chosen for examination: ^{1}H and ^{13}C for organic molecules, ^{31}P for bone, ^{29}Si for silicates, and so on. NMR is relatively insensitive in comparison with mass spectrometry (MS). Thus separation of molecular mixtures into their pure forms by gas or liquid chromatography (GC or LC), followed by mass spectral identification, is a superior technique when only extremely small amounts of material are available. Such a procedure, however, fails for nonvolatile samples that are common in the archaeological context. Moreover, very complex mixtures of organic compounds often are more usefully characterized directly as the bulk rather than by separation into components, and NMR is the method of choice for bulk characterization of mixtures. Thus archaeology is well served by the complementary nature of the MS and NMR experiments. In the subsequent sections, we shall describe NMR applications to archaeology, starting with simple molecules and moving on to molecules and mixtures with increasing complexity.

2 Rubber

The simple molecule isoprene, **1**, combines with itself numerous times in the process called polymerization to form the large rubber molecule containing the repeating unit **2**. In Mesoamerica (Mexico and Central America), the tree *Castilla elastica* supplies a sticky white liquid containing this rubber polymer. It has been processed into rubbery materials by the inhabitants of this region for almost four thousand years. The most frequent rubber artifact encountered is the ball used in the *pelote* game, which was both a religious and a sporting event. A cache of 12 such balls was found at the Olmec site of Manatí in the Mexican state of Veracruz, with dates in the range 1600–1200 B.C. Numerous rubber-containing artifacts also were obtained during the excavation of the sink hole, or *cenote*, at the site of Chichén Itzá in Yucatán with dates in the range 850–1550 A.D., including rubber balls, human figurines of rubber, and a stone tool hafted with a rubber band.



1



2

A recent study[6] of some of the Manatí balls illustrates the types of materials particularly suited for analysis by NMR. As organic materials, the artifacts contain the favorable hydrogen and carbon nuclei. As polymers, they are poorly soluble and nonvolatile. Hence they are not suitable for GC/MS analysis and require examination by NMR directly as the solid. As essentially a single compound, the material should give a very simple spectrum. Indeed, in Fig. 1 the ^{13}C spectrum at the bottom, from a rubber ball artifact, contains only five large peaks, corresponding precisely to the five different kinds of carbons in **2**. This spectrum was taken directly on the solid.

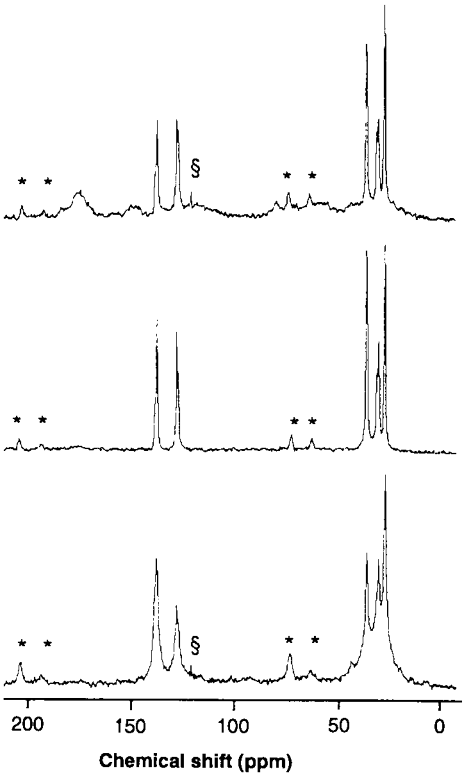


Fig. 1 The CP/MAS ^{13}C spectra of modern latex (top), processed, modern rubber (middle), and an ancient rubber ball from Manatí, Mexico (bottom). Asterisks indicate spinning sidebands. Reprinted with permission from ref. 6. Copyright 1999, American Association for the Advancement of Science.

Unprocessed latex (**2**) does not lead to an object with ideal rubbery properties. Either as a ball or as the thin layers used to construct figurines or bands, the material quickly becomes quite brittle. The ancient Olmecs had to do some chemical processing in order to make a more useful product. Observations by Spaniards during the period of the Conquest but also in Chiapas today have indicated that latex from *Castilla elastica* was mixed with juice from a morning glory vine, *Ipomoea alba*. It was the mixture of these two natural products that exhibited long term rubbery properties. Thus the Olmecs were clearly acting as chemists in order to produce the more useful material.

Hosler *et al.*[6] examined the ^{13}C spectra of pure, modern latex (top spectrum of Fig. 1), of processed, modern material (middle), and of ancient material from Manatí (bottom). They first hypothesized that the morning glory juice induced cross-linking, by which process strands of the polymer **2** are connected through the double bond. This process is analogous to vulcanization, whereby sulfur chains provide the connections between strands. The resulting cross-linked material ought to have greater strength and elasticity and less brittleness. The NMR spectrum of the processed and ancient materials unfortunately did not reveal peaks from cross-linked carbons. It is quite possible that the number of cross-linked pieces is below the detection limit of the NMR experiment.

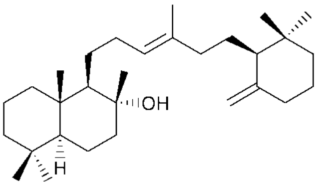
The spectrum of pure latex at the top, however, exhibits some peaks, such as the large, broad peak at δ 173, that are absent from that of either the modern processed material or the ancient artifact. This observation suggests that processing involves purification. Hosler *et al.*[6] suggested that the morning glory juice serves to coagulate the latex, separating organics from water-soluble materials such as proteins (which give resonances at δ 173). The resulting material may be more cross-linked or just more chain-entangled, which would not necessarily show up in the NMR spectrum.

The NMR spectrum of the artifact confirms its identity with modern, processed latex (middle spectrum in Fig. 1). It also suggests that processing enhances elasticity through removal of components, cross-linking, or increased chain entanglement. Without chemical processing, the rubber ball would not have been invented, and the rich culture associated with the *pelote* game would never have developed and become an integral part of Mesoamerican life for thousands of years.

3 Ambergris

Under certain circumstances, NMR also can serve to identify individual, nonpolymeric compounds. A recent study of ambergris, the concretion of organics from the intestinal tract of the sperm whale, illustrates the process and its limitations. Ambergris was a highly valued material for the perfume industry in the 19th century and contributed to the success of the whaling industry and the decline in whale populations. Trade in ambergris was outlawed when the sperm whale became an endangered species, and synthetic organics stepped up to replace it in the perfume industry.

Ambergris today is of historical interest, and a few samples are museum showpieces. Whether such an organic mass actually is authentic ambergris, however, is a question to be asked in each individual case. From characteristics of authentic, modern ambergris, it has been demonstrated that some 24–45% of the total is the single triterpene (+)-ambrein (**3**). Moniz and Hammond[7] examined three alleged ambergris samples from the Whaling Museum of New Bedford, Massachusetts. They attempted to use GC/MS to identify ambrein, but found that it dehydrated (loss of the OH group and an adjacent hydrogen), so that only decomposition products could be found in the MS. Other authors[8] had found that derivatized ambrein could survive the GC conditions, but Moniz and Hammond wanted to work with the pure, underivatized material. They used a process of extraction and chromatography to isolate in one case a pure molecule whose ^{13}C NMR spectrum in solution corresponded to that of authentic ambrein. They calculated that this sample contained 33% of ambrein and concluded that ambrein in ambergris can survive over historical times. This particular piece was said to have been collected in 1910. Moniz and Hammond failed to find anything more than traces of ambrein in two other samples of alleged ambergris from the same museum but without provenance. Either the samples were not ambergris, ambrein had degraded in these cases, or ambergris need not always contain significant ambrein.

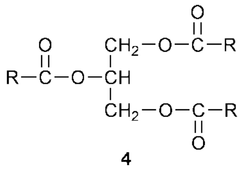


3

Moniz and Hammond started with 2 g samples of ambergris removed from each museum piece. This rather large sample size illustrates the limitations of using NMR to identify single organic molecules. MS typically does the job on a few milligrams. In those cases for which MS fails, however, NMR is a useful alternative when sufficient material is available.

4 Fats, oils, and waxes

Fats and oils consist of triesters of glycerol with long chain carboxylic acids (the so-called fatty acids) (**4**). Fatty acids provide a variety of groups represented by R in the structure.



4

The only difference between fats and oils is that the former are solids and the latter liquids. Waxes are often classified with these substances, but they generally contain several different chemical constituents, including long-chain hydrocarbons, esters, and acids.[9] Thus these classes of materials are a step up in complexity from the pure compounds previously considered. Normally, the constituents are separated by GC, or they can be examined by NMR directly as the mixture.

Beck and co-workers, in one of the earliest applications of NMR to archaeological materials,[10] studied the contents of sealed glass vessels supplied by R. H. Brill of the Corning Museum of Glass. A small flask dated to the 6th–4th century B.C. proved to contain primarily oleic acid or its salts, by direct examination of the ^{1}H NMR spectrum in solution. It was presumed that oleic acid had been the fatty acid attached to glycerol, and the original triester had hydrolyzed. The glycerol had leached out or decomposed, as there was no sign of its resonances. Olive oil contains 85% oleic acid as its side chains in **4**, so that Beck *et al.* concluded that the flask originally contained olive oil.

A similar analysis by Beck *et al.*[10] of the solid residue in a pilgrim flask from the Rhineland dated to the 3rd century A.D. led to the identification of myristic and palmitic acids, constituents of animal fat. The more tentative analysis by another group of an ointment from the 13th or 14th century found in Strasbourg, France, led to assignment of wool fat and Cruciferae (colza) oil.[11] These studies today would probably be carried out more successfully with GC/MS, utilizing less material and obtaining definitive assignments of more components.

Cassar *et al.*[12] examined the ^{13}C NMR spectra of the extractable, waxy material from several royal British seals, used to seal state documents. The materials clearly were mixtures, but the seals used by King Stephen and King John in the 12th century gave spectra identical to that of authentic, modern beeswax. The experiment not only confirmed the nature of the material but also substantiated its long term resistance to chemical or microbial degradation. The later seal of King William IV, however, gave a much more complex spectrum that indicated the presence not only of beeswax but also of resins, whose structure is discussed in a later section. For identification of these substances, NMR is competitive with GC/MS, when there is adequate material.

5 Bone

Organic structures remain largely the same in the solid, liquid, and gas phases (with notable exceptions), so that liquid-phase NMR, MAS analysis of solids, and GC/MS analysis of gases lead to similar conclusions. The same cannot be said of the inorganic materials of interest to archaeology. In general, they are nonvolatile, so that GC/MS no longer is an option. Moreover, dissolution for liquid-phase NMR totally destroys the material and converts it to new structures bearing only a casual relationship to the original artifact. That pushes solid state NMR to the fore as a primary structural tool for the examination of inorganic artifacts. Surprisingly, there have been very few such studies. Instead, inorganic artifacts normally are characterized by their elemental contents, by their X-ray diffraction patterns, or by their infrared (IR) or Raman spectra.

Lee, Klinowski, and Marseglia published a pioneering, though limited, study of a single archaeological bone.[13] Bone is made of calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, containing additional substances such as carbonate, fluoride, sodium, and magnesium ions, with a large, proteinaceous organic portion. The carbonate component is of interest because of possible use in carbon-14 dating and in dietary analysis from carbon isotope ratios. Changes within bone over the time during which the bone is buried, termed diagenesis, can alter conclusions concerning dating and diet.

Lee *et al.*[13] used NMR to try to understand diagenetic processes that occur during burial. They examined a single sample, described as a bovine knuckle, from La Riera Cave in Asturias, Spain. Their analysis required only 10 mg of material. They used both X-ray powder diffraction and MAS NMR to characterize the sample. The X-ray experiments suggested that the bone contained, in addition to hydroxyapatite, some calcium phosphate hydrate ($Ca_3(PO_4)_2$•$(H_2O)_x$) and calcite (a crystalline form of calcium carbonate), and only about 0.5% carbonate ion (the carbonate content of modern bone is 3–5%).

Nuclei are not equally accessible in the NMR experiment. In bone, the main candidates are ^1H, ^{13}C, and ^{31}P. These authors relied mainly on ^{13}C; a ^1H experiment revealed mostly the signal from water. The ^{13}C spectrum of the Spanish bone contained a strong signal at δ 168 characteristic of calcite. A crude estimate based on comparisons with a standard calcite sample indicated that calcite constituted *ca.* 10% of the total. Normal (non-calcite) carbonate in the hydroxyapatite matrix gave no clear signal, in agreement with the lowered proportion found by X-ray diffraction. The only other signals were found in the δ 0–50 region, where saturated organic materials normally resonate.

The NMR and diffraction results were in good agreement. Diffraction, however, had given no indication of the considerable presence of organics. NMR on the other hand could not confirm the presence of calcium phosphate hydrate, as it does not contain carbon. Exploration of ^{31}P spectra might have been useful in this context. The combined methods indicated that diagenesis involves (1) production of calcite and calcium phosphate hydrate, (2) diminished amounts of normal bone carbonate, and (3) retention of a strong organic phase. It is an open question whether the original bone carbonate contributed to the newly formed calcite.

6 Lacquer

Oriental lacquer exemplifies many of the strengths of the solid state NMR method.[14] The sap of a shrubby tree, *Rhus vernicifer*, cures through oxidation-induced polymerization. The resulting product is extremely robust: hard, easily polished, and insoluble in all solvents. It was used in China prior to the Shang dynasty (*ca.* 1800 B.C.) and in Japan by the 9th century A.D. Pyrolysis GC/MS succeeded through pattern analysis to distinguish various lacquers but was destructive and gave little or no structural information.[15]

Raw lacquer contains 20–25% water, 65–70% urushiol, and about 10% gummy substances (carbohydrates). Urushiol is composed of catechols, which are *ortho*-dihydroxybenzenes, further substituted with a 15-carbon side chain, **5**. The chain contains between zero and three double bonds in the R portion, with over 50% of the molecules containing the maximum unsaturation. Interestingly, urushiol differs from the active component of poison ivy only in the arrangement of double bonds. Kumanotani and co-workers[16] suggested a mechanism of curing through oxidation and polymerization to form units of the type **6** (this material represents a dimer, but the actual product would have many more units concatenated).

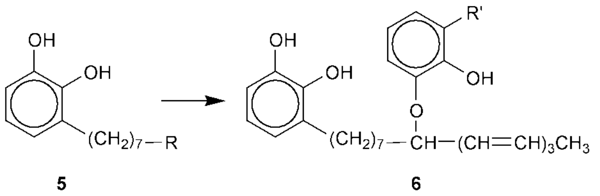


Fig. 2 from the work of Lambert *et al.*[14] shows the CP/MAS spectra of the carbons in four samples of lacquer: from 20th century Japan, from 19th century China, and from 20th century Japan (sampled in two places). The peaks closely mirror the expectations from structure **6**. The side chain CH_2 and CH_3 groups produce the peak in the region δ 20–50. The aromatic and alkene carbons produce the resonances in the region δ 100–160, those with attached oxygens resonating in the higher frequency portion. The small peak at δ 175 is from carboxy groups, either present from oxidation products in the sample or introduced by additives. A key resonance is that centered at about δ 75, a position that is indicative of a carbon with an attached oxygen (C–O). Such a functionality is absent from the starting material **5** but is present in the polymer analogous to **6**. Thus the spectrum confirmed in every way the structure

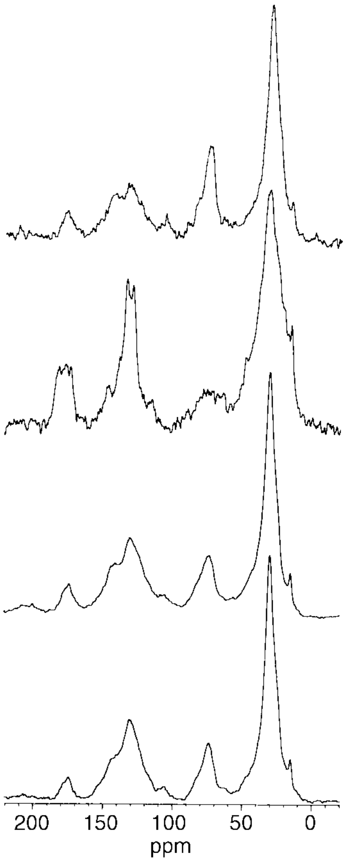


Fig. 2 The CP/MAS ^{13}C spectra of lacquer (top to bottom) from 20th century Japan, 19th century China, and 20th century Japan (sampled in two places). Reproduced with permission from ref. 14.

suggested by Kumanotani.[16] Differences in the size of the δ 75 resonance probably indicate variation in the degree of polymerization. The smaller size of the resonance from the Chinese sample may indicate a smaller degree of polymerization than occurred in the Japanese lacquers.

7 Animal materials

Ancient peoples utilized animal products for numerous purposes other than food, including clothing, coverings in general (shelter, war shields), and writing surfaces (parchment).[17] These materials are not archaeologically robust and tend to decompose quickly. Consequently, discoveries of, for example, silk or parchment, are rare and valuable. Nonetheless, a few NMR studies have been carried out on such archaeological materials.

Chûjô and co-workers examined three silk pieces from 12th century Japan.[18,19] These materials were part of mummy wrappings for three members of the Fujiwara clan in the city of Hiraizumi. The authors comment that, although NMR nominally is nondestructive, simply cutting a sample from a silk object would be considered destructive. In the case of the mummy wrappings, however, such destruction already had occurred during the opening of the mummies, so that silk samples were available. The authors were able to carry out standard CP/MAS ^{13}C studies of these materials.

Their analysis concentrated on the carbonyl resonances in the region δ 170–174, which they attributed to the peptide groups in fibroin molecules. Although there was little fine structure in the illustrated spectra, they were able to attribute specific resonances to glycine and alanine. In this way, they calculated mole fractions of glycine, such as 57% for the silk wrapping of Motohira Fujiwara. Any quantitative work is difficult in NMR studies of solid samples, so these authors correlated their results with electron microscope parameters: filament cross sections and circularity. From dendrochronological data (tree rings), they also had information on temperature variation in the region. In this way they concluded that higher temperatures resulted in lower proportions of glycine in the silk.

Petushkova and Nikolaev used an entirely different NMR method to examine ancient parchment and leather.[20] They measured ^{1}H spin–spin (T_2) relaxation times of water in these materials at very low field (17 MHz). Measurements were made for a sequence of relative humidities, 55–98%, in order to document changes in water content. The relaxation time is considered to be a measure of the mobility of water in the matrix, varying from about 10^{-6} s for frozen water to 2–3 s for liquid water.

They found that the water content increased over this humidity range from 11 to 21% for a 14th century parchment sample, 4–15% for a 19th century leather book binding fragment, and negligibly for a 19th century wool sample. The T_2 values increased from 0.2 to 0.7 ms for the parchment and leather samples, and only from 0.2 to 0.4 ms for the wool sample. These values are characteristic of bound but not rigid water. The results provided a measure of the moistening properties of parchment, leather, and wool. Wool contains less water, and its water is less mobile.

These studies illustrate the type of structural information obtained for relatively simple polymers but also suggest that further examination of water content in organic materials might be profitable.

8 Wood

Wood and seeds are the primary archaeological residue of plants. Seeds are generally examined and identified by botanical methods in studies of diet and climate. Chemically, they are little packets of oils and cellulose. The complex structure of wood is a suitable subject for examination by NMR. Fresh wood is composed of three polymers: 40–45% cellulose, 20–30% hemicellulose, and 20–30% lignin. The first two components are composed of carbohydrate units, whereas lignin is a polymer of phenolic cinnamyl alcohols. Fig. 3 illustrates the CP/MAS ^{13}C spectrum of a modern willow, *Salicaceae salix sp.*, examined as drillings.[14] The carbohydrate resonances are found in the region δ 50–90 and at δ 105. Particularly diagnostic are the prominent peaks at δ 75 from O–C and at δ 105 from O–C–O (the anomeric carbon). The lignin peaks (aromatic and alkenic) are found from δ 110 to 160, and a small carboxy resonance occurs at δ 173.

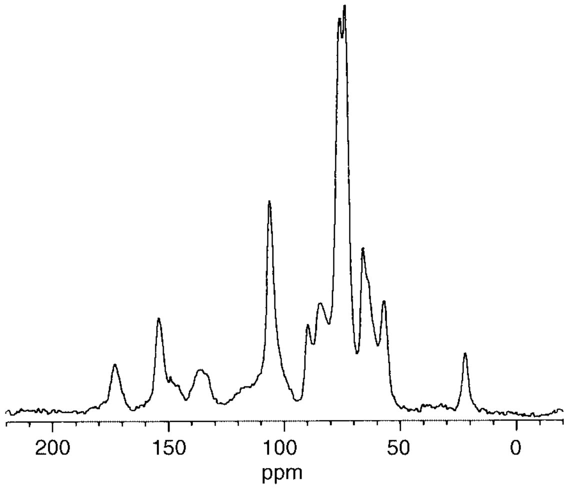


Fig. 3 The CP/MAS spectrum of wood drillings from *Salicaceae salix sp.* (willow). Reproduced with permission from ref. 14.

Hatcher *et al.*[21] first examined the effect of burial on wood. They compared the ^{13}C spectra of a modern spruce sample with those of a spruce log from a 450 year old wood pile in Rotterdam and a 10 000 year old spruce tree from Northern Michigan. The modern spruce spectrum was similar to that in Fig. 3 (species differences are in fact present in the spectra). The Rotterdam sample showed only modest differences, primarily a diminution of the carbohydrate peaks and a growth in the lignin peaks. Carbohydrates are more subject to hydrolysis and leaching. The process continued in the Michigan sample. Although the δ 75 peak was still relatively strong, the δ 105 peak was much weaker. These changes represent the initial steps in coalification, during which unsaturated (aromatic) resonances increase at the expense of saturated aliphatic resonances. Spiker and Hatcher made similar observations on cedar samples[22] and Attalla *et al.* on the New Zealand *Phyllocladus trichomanoides*.[23]

Although NMR can characterize archaeological woods, the results have been more useful in understanding the ongoing process of coalification than in elucidating questions of archaeological interest. Two potential areas of use may be estimating relative ages from the ratio of unsaturated (lignin) to saturated (carbohydrate) resonances, and assessing the level of decomposition of wood prior to conservation.

9 Fossilized plants and animals

Accumulations of plant and animal remains are reworked over geological times into substances such as coal and petroleum that have enormous economic value for modern civilizations. Some of these materials also were used by ancient civilizations and hence provide subjects for analysis. Petroleum products ooze from the earth, for example in the La Brea Tar Pits in Los

Angeles, but more relevantly in numerous locations in Southwest Asia (Iraq, Iran, Turkey). The tarry material, usually called bitumen, was used as an adhesive and a sealant in the ancient world. When processed by the addition of an inorganic filler such as calcite, silica, or gypsum, the material, referred to as asphalt, was used architecturally.

Al-Sammerrai *et al.*[24] examined asphalt excavated from 2000 B.C. Babylon, in modern Iraq, in order to decide where it had originally come from. They compared it with natural materials from the likely sites of Qayarah and Heet (Hit), also in Iraq, by thermogravimetry and solution NMR. They could compare, for example, ratios of various types of saturated and unsaturated proton resonances. They concluded that the archaeological materials had come from Heet, some 200 km northeast of Baghdad. Heet and Babylon, 95 km south of Baghdad, both lie on the Euphrates River, which would have provided a convenient mode of transportation.

As already mentioned, the process of coalification of plant remains involves an increase in aromatic lignin resonances at the expense of aliphatic carbohydrate resonances. Although coal probably was not used in ancient times as a fuel, certain coal-like materials were used as jewelry. Jet is a particular type of carbonaceous material that is clean to the touch, visually attractive in its deep blackness, and easily worked. Artifacts of jet have been found dating back to at least 10 000 B.C. Jet was very popular with Romans. Lambert *et al.* have characterized jet from English and Spanish mining sites[25] and have examined jet artifacts found in the Yucatán peninsula.[26] The jet CP/MAS spectra (Fig. 4) closely resemble that of coal. The ratio of aromatic (δ 100–160) to aliphatic (δ 10–60) resonances places jet among lignites and sub-bituminous coals; the aromatic component is clearly less than that of anthracite and bituminous coal but more than that of peat and brown coal. NMR provides a definitive method to distinguish jet from numerous inorganic, synthetic organic, or natural materials of similar appearance but of less value (horn, glass, onyx, Bakelite, and epoxy resins). There were minor differences between the spectra of the English and Spanish jets.[25] Jet beads from 16th century Tipu, Belize, had spectra that most resembled Spanish sources.[26] They most likely were trade items imported by the Spanish conquerors.

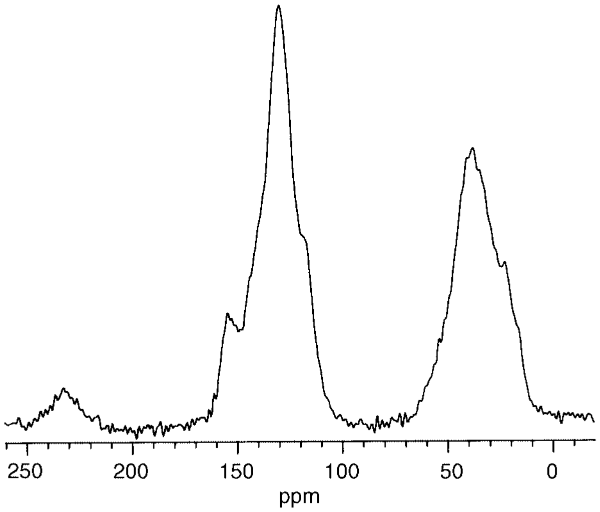


Fig. 4 The CP/MAS ^{13}C spectrum of a sample of jet from Whitby, England. The peak at δ 230 is a spinning sideband.

10 Processed plant materials

Humans became chemists when they started to carry out chemical transformations of raw materials. Processing of inorganic raw materials had long been a part of ceramic, glass, pigment, and metal technologies. Aside from reworking of foodstuffs through cooking, the earliest organic chemistry may have been the processing of plant materials through heating to form tar and pitch (the synthesis of organic dyes was primarily an extraction process, with little chemical transformation). Although the terms tar and pitch have nontechnical connotations, in the archaeological context pitch refers to the residue when organic materials such as wood or peat are heated to drive off volatile components. Tar requires more sophisticated processing, as it is the volatile material condensed when vapors are driven off from heated organics. Tar pitch in turn is the residue when tar is heated to drive off volatiles.

These materials may be examined by IR, NMR, or MS techniques. Each provides a unique approach. The earliest such study combined IR and NMR examination of an organic residue from two urns excavated in Ljubljana, Slovenia.[27] The solution ^{1}H spectrum of the urn residue closely resembled that of birch bark pitch and was quite different from that of beech wood pitch, for example. Infrared spectra of bark pitch from a variety of trees (birch, beech, poplar, oak, elm) were similar but sufficiently distinctive to support the identity of the urn residue as birch bark pitch. Its presence in the urns suggested a trade item, particularly because the birch tree is rare in Slovenia. Birch also was found by NMR to be the source of a wood tar found in Austria.[28]

Evershed and co-workers[29] reported the first general study of these tarry materials. They examined six samples from the Tudor ship the *Mary Rose* (King Henry VIII's flagship, which sank in the Solent channel in 1545) and one from an Etruscan vessel that sank off the island of Giglio *ca.* 600 B.C. some 80 miles northwest of Rome. Pitch or tar was used extensively in naval contexts such as sealants for wood and rope. The authors compared IR, NMR, and MS data with those from natural sources, including coal tar, peat tar, crude oil, Norway spruce wood tar, and pine tar. The solution ^{1}H spectra of the *Mary Rose* samples and the Giglio sample were practically identical to that of pine tar. The infrared and MS data were in agreement. The authors concluded that NMR provided a fast and definitive result, but GC/MS provided more detailed information, such as subtle differences between samples through specific identification of organic molecules present. Evershed has gone on to carry out numerous studies of organic archaeological materials, primarily with GC/MS.

Ghisalberti and Godfrey[30] examined solution ^{1}H and ^{13}C spectra of tars or pitches from several shipwrecks found off of Western Australia and compared them with spectra from the *Mary Rose*. They based their conclusions entirely on the solution NMR spectra. They assigned the materials from the *Vergulde Draeck* (1656), *Rapid* (1811), and *Eglinton* (1852) to pine sources very similar to that of the *Mary Rose*. The sample from the *Belinda* (1824) contained pine tar but also another, more highly aromatic component. The material from the *Fanny Nicholson* (1872), however, more closely resembled coal tar. The authors noted the robustness of these materials, since the conditions of the sites varied from anaerobic waters (*Mary Rose*) to the warm, oxygenated waters of the Indian Ocean, yet spectra of the materials were remarkably similar. Only the material from the *Rapid* exhibited some variations, which the authors attributed to the fact that it was probably of American origin, whereas all the other ships were of European origin.

11 Fossilized resin

Amber is the term usually given to fossilized resins. A variety of trees ooze a sticky material, high in terpenes, probably in response to damage and as a protection. Over geological time (millions of years), the resin becomes fossilized through polymerization, rearrangement, and oxidation reactions. The resulting material, often found with carbonaceous materials such as peat or coal, has also been given the general mineralogical term resinite, as well as numerous terms associated with specific geographic locations (succinite for amber from the Baltic Sea, rumanite from Romania, and so on). Ancient peoples found the golden organic gemstone attractive and easily workable, and it became an object of trade. Amber trade routes crisscrossed Europe, providing the cultures of the Mediterranean with these materials from the north.

Amber is remarkably stable to chemical attack. It is insoluble in water and only partially soluble in organic solvents. As a result, early structural methods relied on IR spectroscopy of the bulk, although Beck examined the soluble fraction by ^{1}H NMR spectroscopy.[10] Thus ^{13}C solid state NMR (CP/MAS) was the first structural method able to examine the entire material and provide information on the carbon skeleton.[31] Fig. 5 from the work of Lambert *et al.*[32] illustrates two NMR methods for examining amber for a sample from the Baltic Sea. At the top is the full spectrum, which contains large resonances from a variety of saturated carbons in the region labeled δ 10–70, a group of very characteristic resonances from double bond carbons in the region δ 100–160, and small resonances from carbonyl carbons in the region δ 170–190. The lower spectrum in Fig. 5 is of the same sample but taken under conditions that select carbons lacking attached hydrogens or carbons moving rapidly in the solid. The technique for obtaining the latter type of spectrum is referred to as interrupted decoupling or dipolar dephasing.

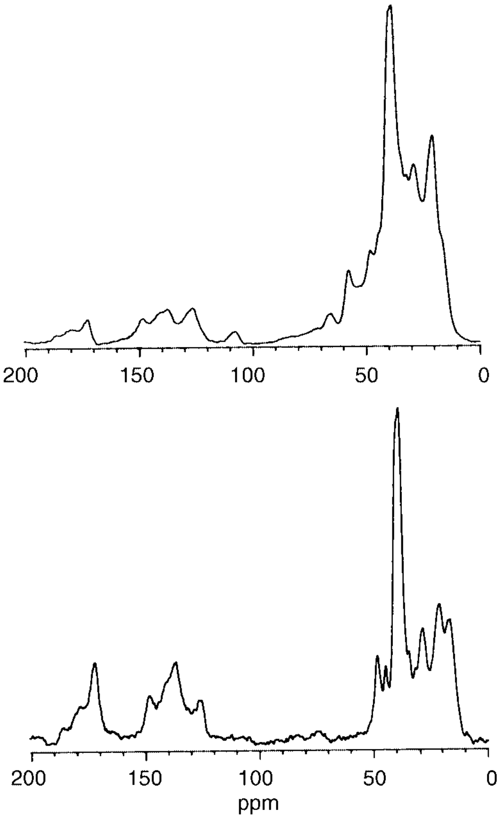


Fig. 5 The CP/MAS ^{13}C spectrum of Baltic amber taken with normal decoupling (upper) and with interrupted decoupling (lower). Reprinted with permission from ref. 32, copyright 1989, American Chemical Society.

The combination of the normal spectrum and the dephased spectrum provides fingerprints for amber and related materials. Lambert and co-workers have characterized fossilized resin from Europe, the Dominican Republic, Mexico, North America, Australia, New Zealand, Africa, South America, Greenland, Southwest Asia, and East Asia.[33] This database of NMR data can be compared with amber found in archaeological contexts. In this way they identified several amber beads excavated at Tipu, Belize, as having a Baltic source.[26] The beads dated to early post-contact Maya burials (*ca.* 1575), and it is likely that they arrived by trade with the conquering Spaniards. Solid state (CP/MAS) ^{13}C NMR spectroscopy also has been used to classify modern resins botanically,[34] to try to understand the structural changes that occur during the process of fossilization,[35] and to assign geological ages to amber.[36] These considerations, however, are peripheral to applications to archaeology.

12 Food residues

The residues left by food in vessels used for cooking, storage, or transport are examined most easily by GC/MS. Such residues usually produce a variety of compounds, which may be separated by GC and identified by MS. Charred material, however, normally is less volatile, in which case NMR becomes useful. Carbon isotope ratios also may be measured for such materials, providing potentially useful information about diet. Oudemans *et al.* first reported solid state ^{13}C NMR studies of food chars.[37] They found that the anomeric carbon of polysaccharides at δ 105 survived charring and burial for Roman pottery from Uitgeest-Groot Dorresgeest in the Netherlands.

Sherriff *et al.*[38] reported the most complete study to date of food residues by solid state NMR. They supported their study of materials excavated from Kame Hills, Manitoba, and southern Ontario with parallel studies of modern food that had been cooked and charred in similar vessels. In this way they were able to recognize distinctions between the remains of plants and animals. Both produced unsaturated resonances in the region δ 100–150 with charring, but charred rice still exhibited the anomeric peak around δ 105. Charred meat or fish also contained a broad, strong peak in the region δ 0–50, characteristic of lipids and proteins.

All of the archaeological samples exhibited resonances in the unsaturated region, confirming that they represented charred food. No spectra, however, contained the anomeric peak. Several of the spectra closely resembled those of artificially charred meat and fish, with two broad resonances at δ 0–50 and 100–150. Polysaccharide-containing foods, such as rice, either were not present or had fully degraded over time. Thus NMR potentially can distinguish food types and serve as a measure of charring.

13 Glass and pottery

Both glass and pottery contain a high proportion of silicon, from sand in glass and clay in pottery. Modern ceramics have been very thoroughly studied by solid state ^{29}Si NMR spectroscopy, but to date there have been no published reports of archaeological glass or pottery.

14 Imaging

When gradient fields are used to obtain spatial information from the experiment, the term magnetic resonance imaging (MRI) has been preferred to NMR. Although information about molecular structure is still possible, MRI normally is used to locate objects in space. In medical applications, MRI has certain advantages over X-ray analysis, as the magnetic fields of NMR are noninvasive in comparison with X-rays, and MRI focuses on soft tissue (X-ray focuses on hard tissue such as bone). There have been news reports of MRI examination of mummies,[39] but the only published studies to date of archaeological material have been of wood. Cole-Hamilton *et al*.[40] obtained images of dry and waterlogged balsa and compared them with the image of an ash sample from the Spanish Armada ship *La Trinidad Valencera*. Annual growth rings were visible on the archaeological sample, and the location of water in specific pores could be defined accurately. The same group[41] obtained nondestructive images of waterlogged timber from the warship *Dartmouth*, which had sunk in 1690 in the Sound of Mull off Scotland. Images were obscured by iron salts. Use of MRI to monitor polymer ingress during conservation was not successful, because of the large background from water signals. Replacement of H_2O by D_2O was demonstrated on modern samples to be a feasible method of improving this technique. Robertson and Packer[42] followed the ingress of D_2O into samples from the *Mary Rose* by MRI. Imaging methods in principle should offer many opportunities for the nondestructive study of the internal structure of archaeological materials, but practical difficulties remain to be eliminated.

15 Conclusions

Nuclear magnetic resonance spectroscopy provides information about the molecular structure of organic and inorganic materials found archaeologically. This information is complementary to that from infrared and mass spectrometry. It is most useful in the overall analysis of insoluble, nonvolatile mixtures of compounds, since other techniques sample selectively. Direct analysis of powdered solids by magic angle spinning and cross polarization techniques provides unique structural information on materials such as rubber, bone, lacquer, silk, wood, asphalt, jet, tar, pitch, amber, and food residues. NMR also can identify specific compounds in solution, as has been done with ambergris, fats, oils, and waxes.

16 References

1 D. M. Grant and R. K. Harris, Eds., *Encyclopedia of Nuclear Magnetic Resonance*, Wiley, Chichester, UK, 1996.
2 M. S. Tite, *Methods of Physical Examination in Archaeology*, Seminar Press, London, 1972; Z. Goffer, *Archaeological Chemistry*, Wiley, New York, 1980; *Modern Analytical Methods in Art and Archaeology*, E. Ciliberto and G. Spoto, Eds., Wiley, New York, in the press.
3 C. A. Fyfe, *Solid State NMR for Chemists*, C.F.C. Press, Guelph, Canada, 1983.
4 R. K. Harris and B. E. Mann, Eds., *NMR and the Periodic Table*, Academic Press, London, 1978; J. B. Lambert and F. G. Riddell, Eds., *The Multinuclear Approach to NMR Spectroscopy*, D. Reidel, Dordrecht, Germany, 1983; P. Laszlo, Ed., *NMR of Newly Accessible Nuclei*, Academic Press, New York, 1983.
5 It is not the intention of the authors to include a detailed description of the principles of NMR in this review. They may be found in many more specialized books, such as J. B. Lambert, H. F. Shurvell, D. A. Lightner and R. G. Cooks, *Organic Structural Spectroscopy*, Prentice Hall, Upper Saddle River, NJ, 1998.
6 D. Hosler, S. L. Burkett and M. J. Tarkanian, *Science*, 1999, **284**, 1988.
7 G. A. Moniz and G. B. Hammond, *J. AOAC Int.*, 1996, **79**, 423.
8 T. F. Governo, R. T. Alessandro and M. J. Prager, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 160.
9 J. S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn., Butterworth Heinemann, Oxford, UK, 1994, Ch. 3 and 4.
10 C. W. Beck, C. A. Fellows and E. MacKennan, in *Archaeological Chemistry*, C. W. Beck, Ed., *Adv. Chem*. 138, American Chemical Society, Washington, DC, 1975.
11 L. Jung, M.-C. Métais and P. Bachoffner, *Ann. Pharm. Fr.*, 1972, **30**, 205.
12 M. Cassar, G. V. Robins, R. A. Fletton and A. Alstin, *Nature*, 1983, **303**, 238.
13 A. P. Lee, J. Klinowski and E. A. Marseglia, *J. Archaeol. Sci.*, 1995, **22**, 257.
14 J. B. Lambert, J. S. Frye and G. W. Carriveau, *Archaeometry*, 1991, **33**, 87.
15 A. Burmeister, *Archaeometry*, 1983, **25**, 45.
16 J. Kumanotani, *Makromol. Chem.*, 1978, **179**, 47.
17 J. B. Lambert, *Traces of the Past*, Addison Wesley, Reading, MA, 1997, pp. 139–152.
18 R. Chûjô, A. Shimaoka, K. Nagaoka, A. Kurata and M. Inoue, *Polymer*, 1996, **37**, 3693.
19 R. Chûjô, *Polym. Prepr.*, 1997, **38**, 896.
20 Y. P. Petushkova and G. M. Nikolaev, *Restaurator*, 1983, **5**, 242.
21 P. G. Hatcher, I. A. Berger and W. L. Earl, *Org. Geochem.*, 1981, **3**, 49.
22 E. C. Spiker and P. G. Hatcher, *Geochim. Cosmochim. Acta*, 1987, **51**, 1385.
23 M. I. Attalla, R. G. Serra, A. M. Vassallo and M. A. Wilson, *Org. Geochem.*, 1988, **12**, 235.
24 F. Al-Sammerrai, D. Al-Sammerrai and J. Al-Rawi, *Thermochim. Acta*, 1987, **115**, 181.
25 J. B. Lambert, J. S. Frye and A. Jurkiewicz, *Archaeometry*, 1992, **34**, 121.
26 J. B. Lambert, E. Graham, M. T. Smith and J. S. Frye, *Ancient Mesoamerica*, 1994, **5**, 55.
27 D. Hadži and F. Cvek, *Arheoloski Vestnik*, 1976, **27**, 128.
28 F. Sauter, E. W. H. Hayek, W. Moche and U. Jordis, *Z. Naturforsch., Teil C*, 1987, **42**, 1151.
29 N. Robinson, R. P. Evershed, W. J. Higgs, K. Jerman and G. Eglinton, *Analyst*, 1987, **112**, 637.
30 E. L. Ghisalberti and I. M. Godfrey, *Bull. Aust. Inst. Maritime Archaeol.*, 1990, **14**, 1; *Stud. Conserv.*, 1998, **43**, 215.
31 J. B. Lambert and J. S. Frye, *Science*, 1982, **217**, 55.
32 J. B. Lambert, J. S. Frye, T. A. Lee, Jr., C. J. Welch and G. O. Poinar, Jr., *Archaeological Chemistry IV*, R. O. Allen, Ed., American Chemical Society, Washington, DC, 1989, pp. 381–388.
33 J. B. Lambert, S. C. Johnson and G. O. Poinar Jr., *Archaeometry*, 1996, **38**, 325 and references therein.
34 A. Cunningham, I. D. Gay, A. C. Oehlschlager and J. H. Langenheim, *Phytochemistry*, 1983, **22**, 965; K. B. Anderson, R. E. Winans and R. E. Botto, *Org. Geochem.*, 1992, **18**, 829; J. B. Lambert, C. E. Shawl, G. O. Poinar Jr. and J. A. Santiago-Blay, *Bioorg. Chem.*, 1999, **27**, 409.
35 D. J. Clifford and P. G. Hatcher, *Org. Geochem.*, 1995, **23**, 407.
36 D. A. Grimaldi, *Amber, Resinite and Fossil Resins*, K. B. Anderson and J. C. Crelling, Eds., American Chemical Society, Washington, DC, 1995, pp. 203–217.
37 T. F. M. Oudemans, J. J. Boon and R. E. Botto, *Archaeometry '92 Conference Abstracts*, 1992, 25.
38 B. L. Sherriff, M. A. Tisdale, B. G. Sayer, H. P. Schwarcz and M. Knyf, *Archaeometry*, 1995, **37**, 95.
39 *Archaeology*, 1984, **32**, 78; *New Scientist*, April 4, 1985, p. 5.
40 D. J. Cole-Hamilton, J. A. Chudek, G. Hunter and C. J. M. Martin, *J. Inst. Wood Sci.*, 1990, **12**, 111.
41 D. J. Cole-Hamilton, B. Kaye, J. A. Chudek and G. Hunter, *Stud. Conserv.*, 1995, **40**, 41.
42 M. B. Robertson and K. J. Packer, *Appl. Magn. Reson.*, 1999, **17**, 49.