Amber: the Organic Gemstone

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ABSTRACT
Resins are produced by woody plants on a worldwide basis. We have found several distinct classes of modern diterpenoid resins based phenomenologically on the solid-state ^{13}C NMR spectra of the bulk material. Resin fossilizes over millions of years into a robust material sometimes called amber. We have characterized several hundred samples of fossil resin by solid-state ^{13}C NMR spectroscopy. We can relate one globe-spanning group of fossil resins to the modern genus *Agathis*, based on spectral evolution over time. A second large group has not been related with certainty to specific modern plants. Fossil resins from Europe fall into two categories, the famous Baltic ambers and another that resembles the *Agathis* group. Fossil resins from the Americas and Africa are closely related to the modern genus *Hymenaea*. Based on spectral distinctions, fossil resin found in an archaeological context sometimes can be assigned to a specific geographical origin on the basis of its ^{13}C NMR spectrum.

Introduction

Almost unique in the mineralogical world is the organic substance amber.[1,2] Other gemstones are inorganic, but amber is a fossilized form of terpenoid plant resins. Numerous genera of plants all over the globe spontaneously or as the result of trauma produce sticky substances that have been termed resins. These substances have been harvested and used throughout history as adhesives, coatings, and binding media for pigments. Some such materials give off pleasant or exotic odors on burning and have been used as incense.

Through evaporation of volatile components and polymerization of dienic functions, resins over geological time can fossilize into extremely hard materials. Because of their attractive appearance, their ability to be carved and polished, and their robust, stone-like texture, such fossilized resins have been treated as gemstones for

FIGURE 1. A box constructed of amber pieces and attached to a chain of amber beads, several hundred years old, from the Museum of the Earth, Warsaw, Poland. Photograph by G. O. Poinar, Jr.

millennia throughout the world (Figure 1). In the European context, these materials have been called amber and have been associated with the eponymous yellow-brown color.

Unworked fossil resin has been found in association with Paleolithic dwelling sites in the Old World[1,2] (prior to about 12 000 B.C.[3]). Worked fossil resin has been found in Mesolithic sites (about 8000–12 000 B.C.). By the Neolithic period (the New Stone Age, associated with farming, from about 8000 B.C.), fossil resin had clearly become a widely traded material. In addition to its attractive appearance, amber is warm to the touch and attracts other objects on rubbing. It is one of the most commonly mentioned gemstones in the writings of Homer (Penelope wore a necklace that was "golden, set with amber, like the radiant sun"). The Greek word for amber was *elektron*. Because of the electrical properties of amber, this word became the root for all English words associated with the terms electron and electricity.

The vast majority of European amber originated around the Baltic Sea, and so trade networks developed to move the supply to Mediterranean markets. Nonetheless, there are natural fossil resin deposits all over Europe and adjacent Southwest Asia, so the actual source of a specific artifact cannot be attributed automatically to sources close to its find site. Schliemann[4] contemplated the rich amber finds at Mycenae by commenting that "it will, of course, forever remain a secret to us whether this amber is derived from the coast of the Baltic or from Italy."

Modern scientific analysis of amber and other fossil resins has proved Schliemann wrong, as spectroscopic

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characterization of the material can indicate geographical source. C. W. Beck[5] pioneered the use of infrared spectroscopy for the characterization of amber. In particular, he found diagnostic vibration patterns for materials from Baltic sources. Mills, White, and Gough[6] used mass spectrometry to identify numerous components in the ether-soluble fraction of Baltic amber. Anderson, Botto, and their co-workers[7] expanded the technique by using pyrolysis gas chromatographic mass spectrometry (GC/MS). Based on the identity of the pyrolysis products, they defined several classifications of fossil resins (which they call resinites). Shedrinski, Grimaldi, and co-workers[8] also used pyrolysis GC/MS, with a focus on identifying amber forgeries. We have employed solid-state nuclear magnetic resonance (NMR) spectroscopy with cross polarization and magic angle spinning (CP/MAS) to characterize both modern and fossil resins on a worldwide basis.[9] Whereas the MS approach focuses on identifying botanical differences based on small-molecule components, the NMR approach uses bulk analysis to examine both botanical and geographical differences. This Account describes the application of NMR to the study of solid resins, with relevance to both archaeology and botany. We begin with characterization of modern resins by NMR, then of fossil resins of known geological provenance, and finally of archaeological materials.

Modern Resins

Resins usually are solid when the constituent molecules contain at least four isoprene units, i.e., when they are diterpenes (C_{20}) or higher. The conifers (order Coniferales) and angiosperms (family Leguminosae) are the most important groups that produce diterpenoid resins.[10] Conifer families that produce such resins include the Pinaceae (pines), Cupressaceae (cypresses and junipers), and Araucariaceae (kauri and others). Diterpenoid resins are particularly prone to polymerization and hence are the predominant source of fossil resins used for cultural purposes. Triterpenoid (C_{30}) resins originate primarily from broad-leaved trees and generally are nonpolymerizing. They have found wide uses as varnish resins for paintings and as incense. Triterpenoid resins include dammars (subfamily Dipterocarpoideae of the family Dipterocarpaceae), mastics (genus *Pistacia* of family Anacardiaceae), and elemis (family Burseraceae, which also produces the famous gum resins myrrh and frankincense).

It is not often possible to distinguish one resin source from another by appearance alone. GC/MS characterization has been very successful at identifying small molecules in either a soluble fraction or a pyrolysate. Our modus operandi has been to examine the solid-state ^{13}C NMR spectrum of bulk resins, with two modes of decoupling. Under normal decoupling conditions, signals should be obtained from all carbons present in the sample. In experiments with interrupted decoupling, signals are selected for quaternary carbons and for some carbons that are moving rapidly in the solid; other signals are edited

out. The two spectral modes serve primarily as fingerprints of the bulk material.

In this way we have examined modern resins from several continents, including the conifer Pinaceae genus *Pinus* (pine), the conifer Araucariaceae genera *Agathis*, *Araucaria*, and *Wollemia*, the angiosperm genus *Hymenaea*, and the triterpenoid family Burseraceae.[11] Samples were harvested from living trees, except for the Burseraceae, which was a commercial sample, probably from the genus *Bursera* from Mexico.

Figure 2 contains five representative pairs of spectra.[11] The spectrum with interrupted decoupling is always the uppermost of the pair. The top two are from *Pinus monticola* from California. The most prolific of the Pinaceae genera, pines probably are the most important source of resins in temperate regions of the northern hemisphere. We found nearly identical spectra for all pine samples, as well as for U.S. Rosin and commercial violin rosin. The most distinctive spectral characteristics are the five peaks in the saturated region of the (upper) spectrum with interrupted decoupling.

The next two spectra from the top are of *Hymenaea courbaril* from the Dominican Republic.[11] This angiosperm genus is the most common source of resins in tropical America and East Africa. Its characteristic resonances include the four peaks in the aliphatic region of the spectrum with interrupted decoupling and the strong exomethylene ($C=CH_2$) resonances at δ 108 and 148 (absent for *Pinus*) of the normal spectrum. Very similar spectra were obtained for samples from Colombia (South America) and East Africa.[11] Long periods of separation as the result of continental drift did not alter the biological or chemical nature of these materials.

Resin-producing trees from the genus *Agathis* occur in the southern hemisphere, particularly in Australasia. The middle pair of spectra in Figure 2 are typical for *Agathis* (*Agathis lanceolata* Lindley ex Warburg, from Sidney, Australia).[11] The most diagnostic aspects are the pair of sharp peaks at δ 40−45 in the interrupted decoupling spectrum, the exomethylene peaks in the normal spectrum, and the six- or seven-peak pattern (one often is a shoulder) in the saturated region of the normal spectrum. This pattern was found for numerous samples from New Zealand and Australia, both modern and semifossilized (ages up to 37 000 B.P.). Copal samples from the Philippines and Wollemi pine (genus *Wollemia*) gave very similar or identical spectra.

A single sample of *Araucaria columnis* (Forster) Hooker from Sidney, Australia, is illustrated in the fourth pair of spectra in Figure 2.[11] Both the normal and the interrupted decoupling spectra are somewhat similar to those of *Agathis*, in particular the pair of peaks at δ 40−45 in the spectrum with interrupted decoupling. A major difference is the series of resonances in the region δ 60−85, derived from carbons attached to oxygen, as found in carbohydrates. Thus, *Araucaria* resin may contain carbohydrates as well as terpenes, as is the case for gum resins.

The bottom pair of spectra in Figure 2 are from a commercial sample from the triterpenoid family Burser-
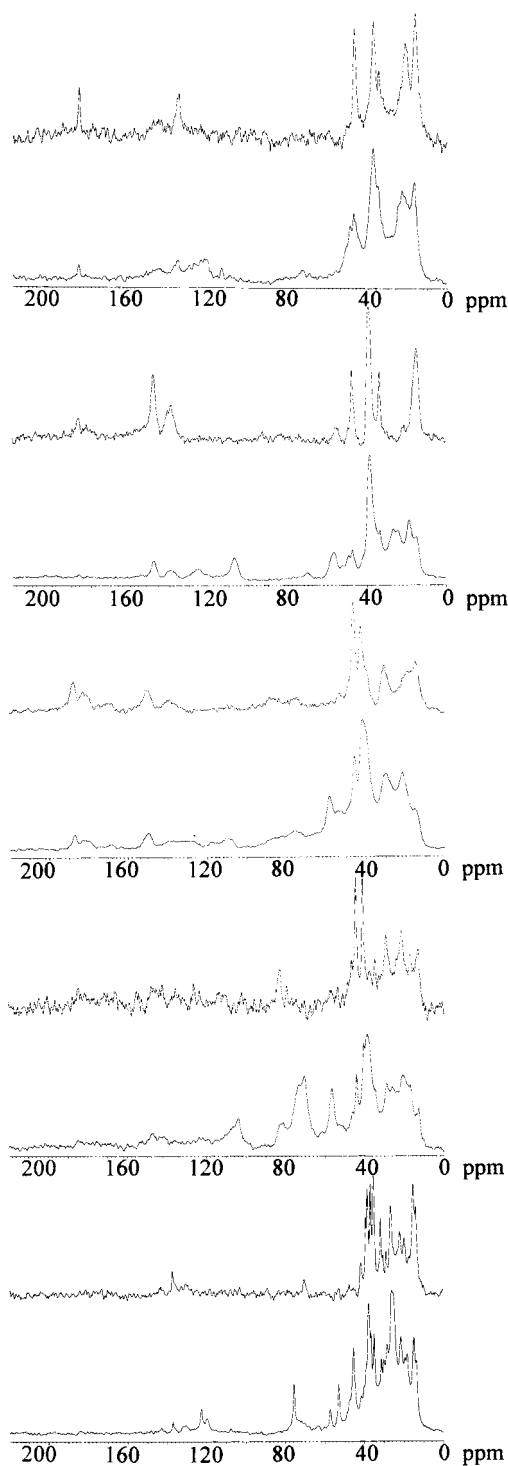
FIGURE 2. ^{13}C NMR spectra of modern resins. There are two spectra for each sample, with interrupted decoupling on top and normal decoupling on the bottom. From the top, the spectra are of *Pinus monticola* from California, *Hymenaea courbaril* from the Dominican Republic, *Agathis lanceolata* lindley ex Warburg from Sydney, Australia, *Araucaria columnaris* (Foster) Hooker from Sydney, Australia, and commercial Burseraceae resin from the O. G. Innis Corp., probably genus *Bursea* from Mexico. Adapted from ref 11.

aceae.[11] There are almost no exomethylene resonances. The peaks in the aliphatic region are more numerous and sharper than those in the diterpene resins, as might be

expected for a material not prone to polymerization. Other samples from Chiapas (Mexico) and Chichicastenango (Guatemala) had similar spectra.

The spectra in Figure 2 represent the most common sources of modern resin, and each may be distinguished from the others. Samples from the temperate zone of the northern hemisphere (*Pinus*), the tropical zone of the northern hemisphere (*Hymenaea*), and the southern hemisphere (*Agathis* and *Araucaria*) give distinct spectra. These diterpenoid resins are easily distinguished from the triterpeneoid resin family Burseraceae. The ability to tell these genera and families apart on the basis of their NMR spectra means that material of an unknown botanical origin can be assigned plausibly to one of these groups, as we have done for several examples.[11] The next question is how these spectra change with aging over geological times.

From Recent to Ancient: *Agathis* and Its Relatives

Modern and fossilized resins are found abundantly in New Zealand and Australia, often in strata that may be dated by association with known geological structures. We examined a series of materials from these regions with known dates moving from the present and recent past (measured in thousands of years) through the Tertiary Period that comprises the Pliocene (1.6−5 million years ago), Miocene (5−24 million years), Oligocene (24−37 million years), Eocene (37−58 million years), and Pale-ocene (58−65 million years) epochs to the Cretaceous Period (starting about 65 million years ago).[13] We divided the samples into five groups according to their spectral appearance. The changes over time correlated smoothly with age. Figure 3 illustrates examples from each group [set (a) with normal decoupling, set (b) with interrupted decoupling]. As the samples move back in time (from bottom to top), the exomethylene resonances at about δ 110 and 150 in the normal spectra diminish and finally disappear. The large peaks in the saturated region (δ 15−65) broaden but change surprisingly little. The peak at δ 60 disappears, and that near δ 20 increases to become the second largest. The dominant peak is always the one near δ 40. Because we can follow the changes that result presumably from polymerization or from degradation over time, we can associate fossilized resin possessing spectra at the top of Figure 3a with *Agathis*-like ancestors. An analogous series of changes occur in the spectra with interrupted decoupling (Figure 3b). The horizontal scales and conditions of Figures 2 and 3 are different, but the lowermost spectra of Figure 3 correspond to the middle pair in Figure 2.

When we compared the spectra of the most ancient samples from New Zealand and Australia (the topmost spectra in Figure 3) with samples from elsewhere in the world, we found essentially identical spectra for materials from widely disparate geographical areas. In East Asia, a Paleocene sample from the Russian island of Sakhalin exhibited this pattern.[14] The same pattern was found in
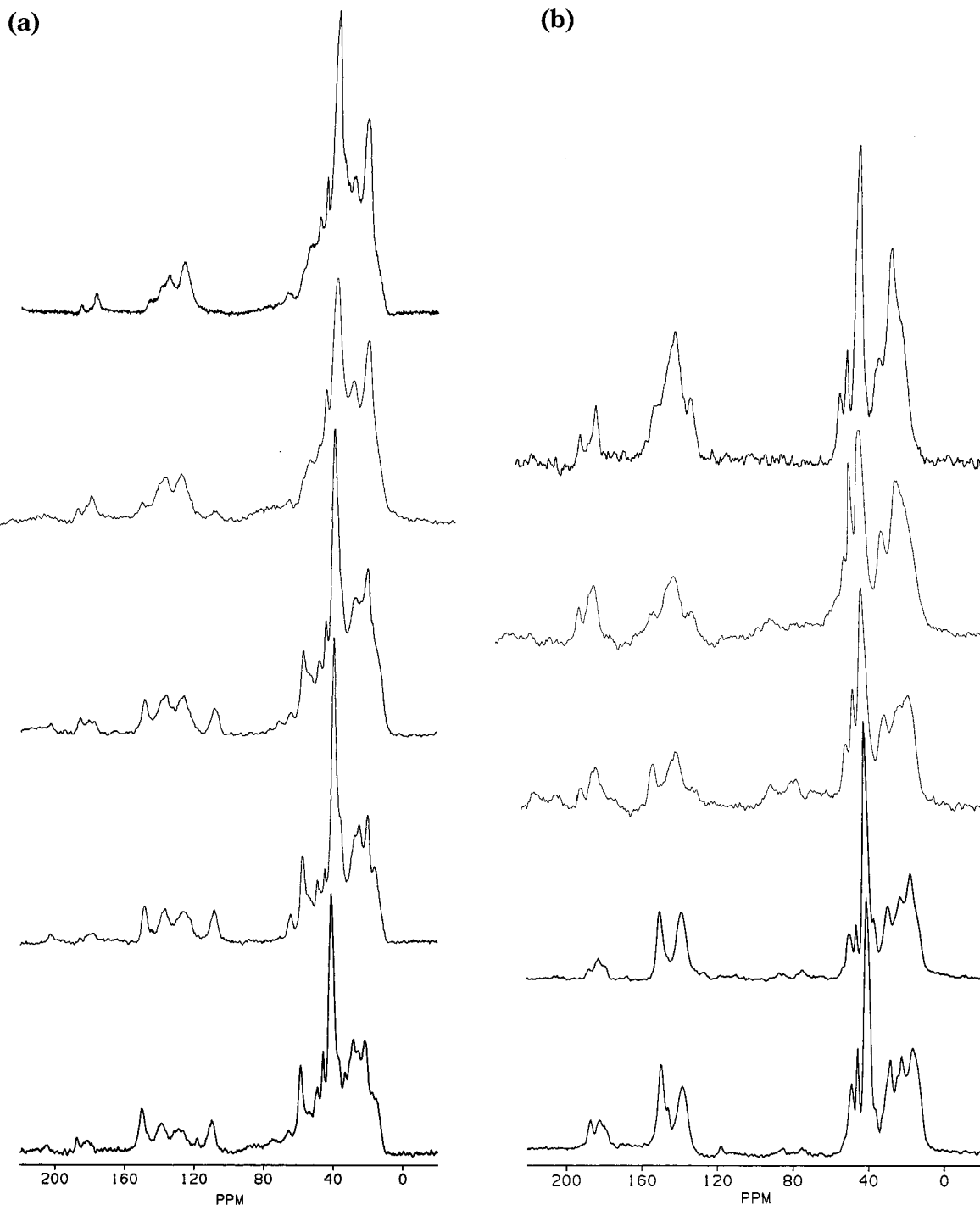
(a)

(b)

FIGURE 3. (a) ^{13}C NMR spectra of resin from New Zealand taken with normal decoupling. From the top, the spectra are from the Hikurangigi Coalfield of the Kamo Coal Measures dating to the Eocene, from the Taupiri Seams of the Waikato Coal Measures of the Rotowaro Coalfield dating to the Eocene, from the Garvey Creek Coalfield of the Brunner Coal Measures dating to the Eocene, from the Roxburgh Coalfield dating to the Miocene, and from a sample off the ground at Awanui associated with a buried kauri log dated at 31 120 years B.P. by ^{14}C. (b) ^{13}C NMR spectra of the same samples taken with interrupted decoupling. Reproduced with permission from Figures 2 and 5 of ref 13. Copyright 1993 John Wiley.

samples not only from Asia and Oceania but also from North America and Europe. Figure 4 (different scale from Figure 3) shows pairs of spectra (normal on the bottom, interrupted decoupling on the top of each pair) for samples from (top) New Zealand (Eocene),[13] New Jersey (Late Cretaceous),[15] and (bottom) France (Late Cretaceous).[16] The normal spectra in Figure 4 and at the top of

Figure 3 have the dominant peak invariably at about δ 40, medium peaks at δ 20 and 28, a shoulder at δ 15, and a sharp peak variably at δ 42. The spectra with interrupted decoupling exhibit these five peaks rather more clearly. The exomethylene peaks are small or absent.

This pattern was observed for numerous samples from Alaska (Cretaceous),[15] Canada (Manitoba and Alberta,
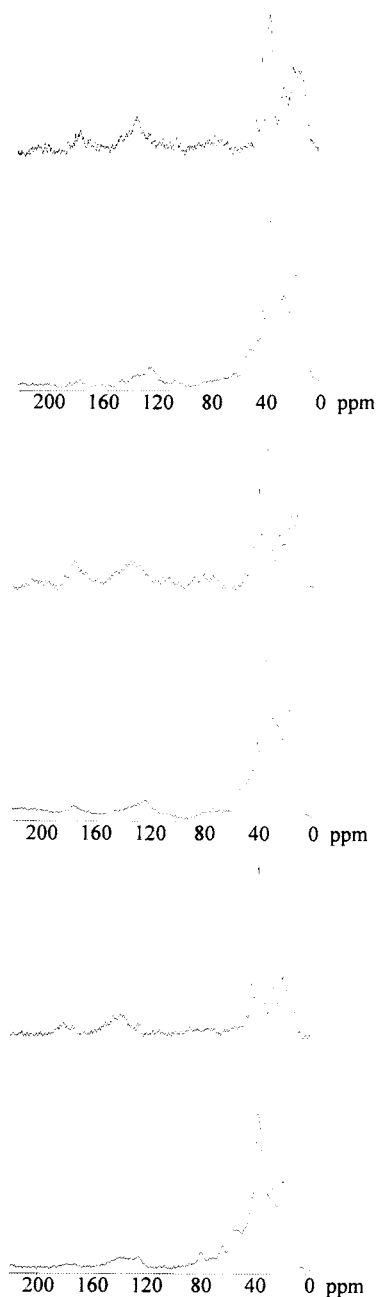
During Cretaceous times, continental drift began to move the deposits to various parts of the world, but living descendants are associated primarily with *Agathis* species in the southern hemisphere.

If this group in fact were the only variety of fossil resin, NMR would provide no insight concerning provenance of archaeological materials. Fortunately, this is not the case, as several other groupings have emerged.

Another Worldwide Group

In our study of Australian fossil resins,[13] we recognized a small group of outliers. We called them Group G at the time and found an affiliation with a sample from Papua New Guinea, which of course is very close by. In our earlier study of North American fossil resins,[15] we also found a set of outliers from the numerous *Agathis*-related samples. This group came from Arkansas. To our considerable surprise, the Australian and Arkansas outliers had essentially identical spectra, as illustrated in Figure 5 (top pair from Australia, middle pair from Arkansas). They have no exomethylene resonances, but the other alkenic resonances are strong in the normal spectrum and become a single, relatively sharp peak with interrupted decoupling. The saturated region has four characteristic large peaks and a shoulder at δ 15, and with interrupted decoupling the region contains generally three sharp peaks. An earlier infrared study[17] of Arkansas resin found the spectra to resemble that of *Shorea* sp., a member of the family Dipterocarpaceae. Species of *Shorea* are found throughout the tropics today. We cannot confirm the relationship of this second group of fossil resin with *Shorea*, because we have not been able to obtain authentic samples for NMR analysis. It would represent a major distinction from the other materials, since this family produces triterpenoid resins.

Originally,[13,15] we were dealing with what appeared to be an anomalous Australia−Arkansas axis. These samples, however, have since been joined by many others. In our recent survey of Asian resins,[14] we found several more representatives of this class, including samples from Burma (uncertain date), Borneo (Early Miocene), Sumatra (Miocene), and India (Gujarat, uncertain date). The sample from Burma represents a famous group of fossilized resins, which have been given the mineralogical name burmite. Its spectra are illustrated at the bottom of Figure 5. It is noteworthy that Sumatra resins also have been attributed to a Dipterocarpaceae source.[19] Thus, we have a second grouping that nearly spans the globe, having members from India, through Southeast Asia (Burma), over the Pacific (Australia, Borneo, Sumatra, Papua New Guinea), and into North America (Arkansas). The absence of contributors from Europe may be suggestive that the source family never became established in that continent or that samples simply have not yet been found there. Samples from Arkansas and Sumatra have been linked with the family Dipterocarpaceae, but we have not established such a relationship based on NMR spectral evolution.
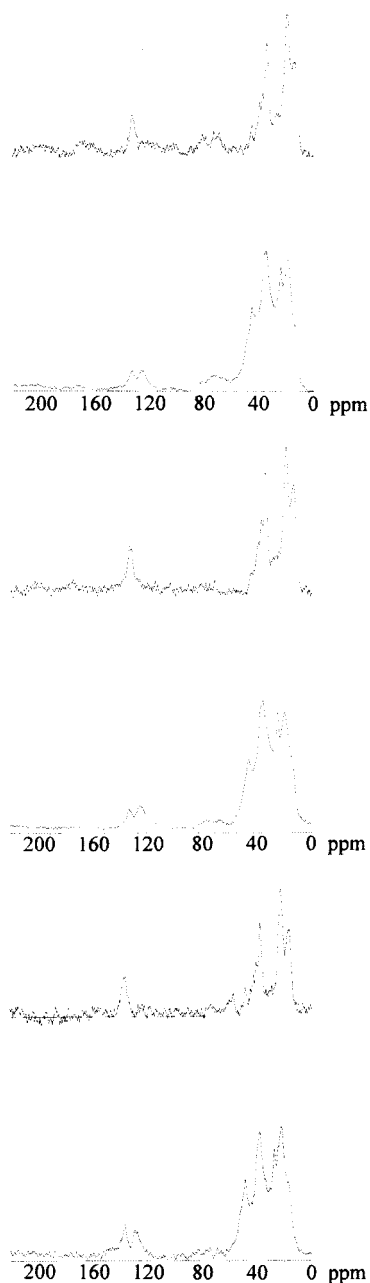

FIGURE 4. Pairs of ^{13}C spectra (with interrupted decoupling on top) of samples from Group A (see Summary). From the top, the spectra are from the Huntly Coalfield of the Waikato Coal Measures in New Zealand dating to the Late Eocene, the Magothy Formation at Beach Cliffs, Cliffwood, New Jersey, dating to the Late Cretaceous, and from the Paris and Acquitaine Basin in northwestern France dating to the Late Cretaceous.

mineralogically known as cedarite or chemawanite, Late Cretaceous),[15] Kansas (Late Cretaceous),[16] Mississippi (Late Cretaceous),[16] Greenland (Cretaceous),[16] Bavaria (unpublished), Switzerland (uncertain age),[16] Southwest Asia including Lebanon, Israel, and Jordan (Early Cretaceous),[16] and China (Liaoning province, possibly Eocene),[14] as well as New Jersey,[15] France,[16] Sakhalin,[14] New Zealand, and Australia.[13] Fossilized resins that produce these characteristic spectra thus circle the globe and presumably hark back to the single land mass of Gondwanaland.

FIGURE 5. Pairs of ^{13}C spectra (with interrupted decoupling on top) of samples from Group B (see Summary). From the top, the spectra are from the Cape Patterson Coal Mines in Australia dating to the Early Cretaceous, from the Claiborne Formation near Malvern, Arkansas, dating to the Eocene, and from the Hukong Valley of Burma with uncertain date.

European Amber

By the end of the nineteenth century, indigenous deposits of fossil resin had been found in virtually every European country, although the most famous sources from antiquity to the present have been those from the shores of the Baltic Sea. Baltic amber had been given the mineralogical term succinite (from the Latin *succus* for juice), but numerous other mineralogical classifications have arisen, including rumanite (from Romania), simetite (from Sicily), and walchowite (from Moravia). These were usually based more on locality of the source than on
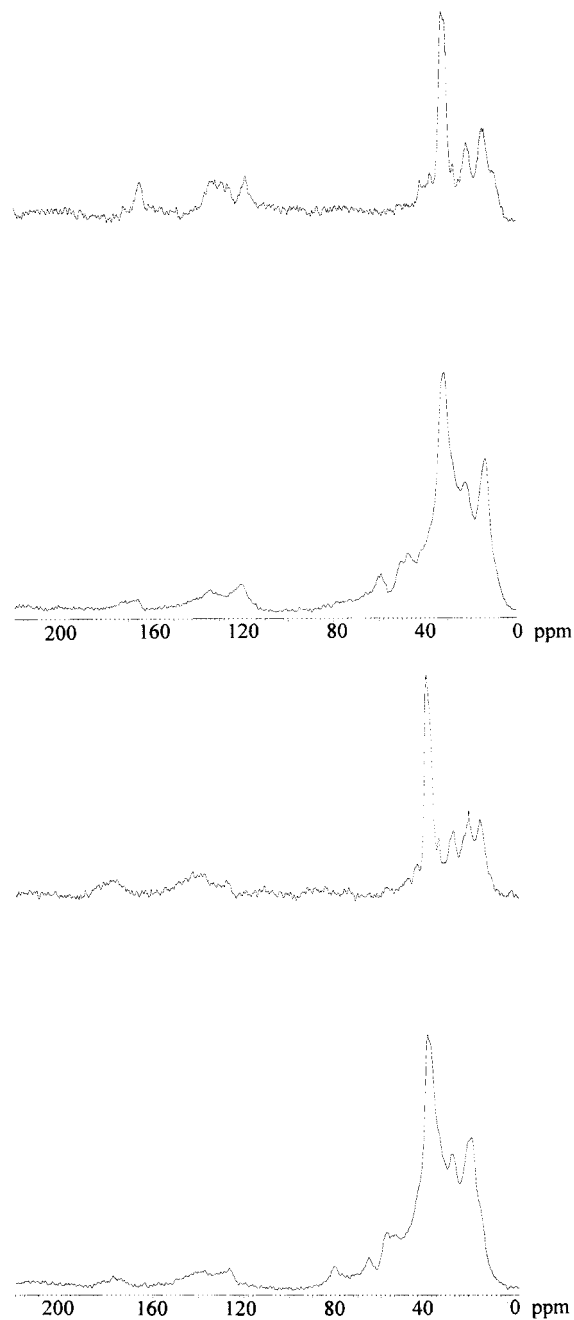

FIGURE 6. Pairs of ^{13}C spectra (with interrupted decoupling on top) of samples dating to the Tertiary Period in Europe and similar to those from Group A (see Summary). The top pair are of rumanite (from Romania, sample no. OA11-116). The bottom pair are of walchowite (from Moravia, Paris Museum of Natural History, sample no. 65.z16). The samples were provided by C. W. Beck.

chemical or physical distinctions. The presence of succinic acid sometimes was used as a chemical diagnostic for succinite.

We have already noted that Cretaceous samples from France, Switzerland, and Germany exhibit the pattern characteristic of *Agathis*-related materials found worldwide. Numerous Tertiary European samples follow a similar pattern, including those with the mineralogical designations rumanite, simetite, schraufite, walchowite, and delatynite. Figure 6 illustrates the pairs of spectra for
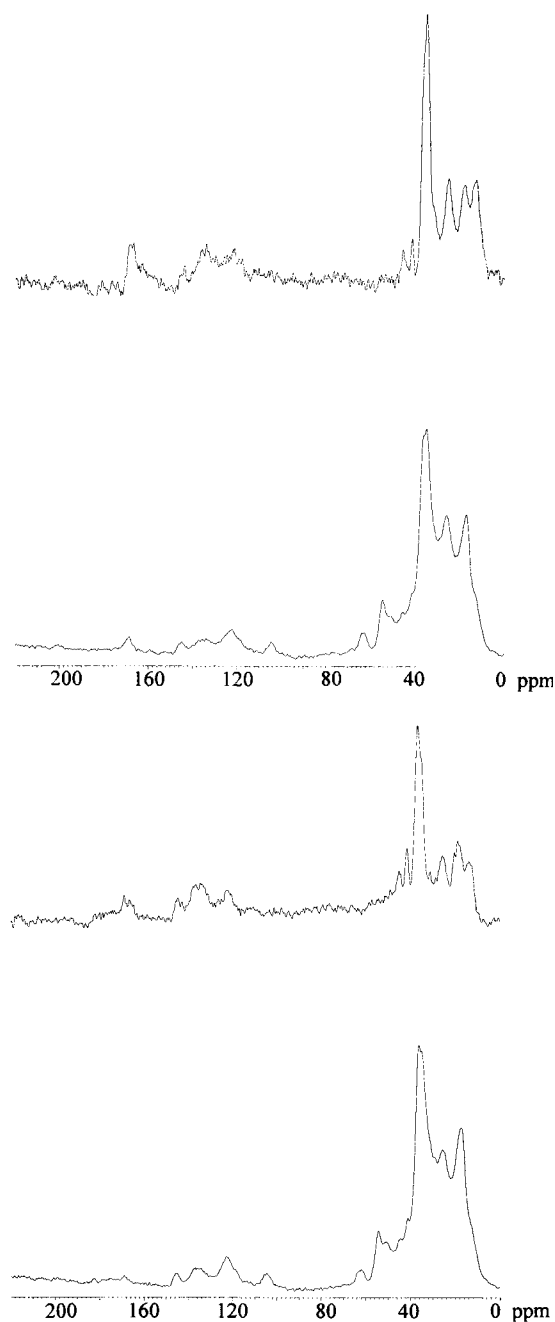
FIGURE 7. Pairs of ^{13}C spectra (with interrupted decoupling on top) of Baltic amber (Group C, see Summary). The top pair are of succinite (sample B-4 from the Geologisches Staatsinstitut Hamburg). The bottom pair are of beckerite (sample no. 2). The samples were provided by C. W. Beck.

samples of rumanite (top) and walchowite. Comparison to the spectra in Figure 4 shows few differences, except that the Cretaceous samples exhibit a sharp peak near δ 42, particularly with interrupted decoupling. The rumanite spectra practically overlay the Cretaceous spectra. It is reasonable to conclude that these samples belonged to *Agathis* or a related family.

Baltic amber, however, presents distinctive spectra, as illustrated in Figure 7 for succinite (upper pair) and beckerite. There are strong similarities to the spectra of *Agathis* in the saturated region, both with normal and

interrupted decoupling. For example, the spectrum of Baltic amber taken with interrupted decoupling (topmost spectrum in Figure 7) is essentially indistinguishable from the analogous spectra of walchowite in Figure 6 (bottom) and Late Cretaceous French resin in Figure 4 (bottom). The differences come primarily in the alkenic region of the spectra with normal decoupling, as the Baltic ambers exhibit pronounced exomethylene resonances at δ 110 and 150. This functionality is found in labdanes such as agathic acid and communic acid (which are bicyclic) but not in abietanes such as abietic acid and pimaric acid (which are tricyclic). Exomethylene resonances are found in Baltic ambers (Figure 7) and in Tertiary, fossilized *Agathis* (middle of Figure 3a), but not in any Cretaceous samples worldwide or in the European Tertiary samples. As with infrared spectroscopy,[5] the NMR spectra of Baltic amber are able to distinguish the materials from all other fossil resins.

The series of *Agathis* spectra illustrated in Figure 3a demonstrate how the exomethylene resonances disappear with time. Thus, it is possible that Baltic amber represents a less altered variety of materials from the same plant source as the Tertiary European samples with *Agathis*-like spectra. Less alteration can result either from a more recent age or from less destructive conditions during burial. Coal chemists refer to the process of alteration as maturation. An alternative explanation is that a distinct botanical variety existed in abundance around the Baltic Sea, which for example produced abietanes rather than labdanes. The ancient producer of Baltic amber is most often assigned to an extinct conifer species, *Pinites succinifera*,[5] but also has been placed in the genera *Pinus*, *Abies*, *Taxoxylum*, *Pityoxylon*, and *Picea*.

Although NMR cannot answer the question of maturation vs distinct species, it can establish the close relationship of Baltic amber to the giant *Agathis*-like family of fossil resins, and it can provide a practical distinction. Stout, Beck, and Anderson have recently made the case, based on GC/MS analysis of organic constituents, that rumanite is identical to Baltic amber but experienced more severe conditions that caused degradation.[20] Thus, Baltic amber may not represent a distinct paleobotanical source, but it gives a diagnostic NMR fingerprint and hence represents a distinct material phenomenologically.

American and African Resins

A large proportion of commercial resins sold as amber in the Americas come from the Dominican Republic on the island of Hispaniola.[21] Columbus already had noticed these materials by his second voyage to the New World. The deposits are Tertiary, with a range from 15 to 45 million years ago, and came from the extinct species *Hymenaea protera*. The spectra, as illustrated by the top pair in Figure 8 (from the mine site La Aguita), bear a close resemblance to the spectra of modern *Hymenaea courbaril*, the second pair from the top in Figure 2. The normal spectrum has strong exomethylene resonances, like Baltic
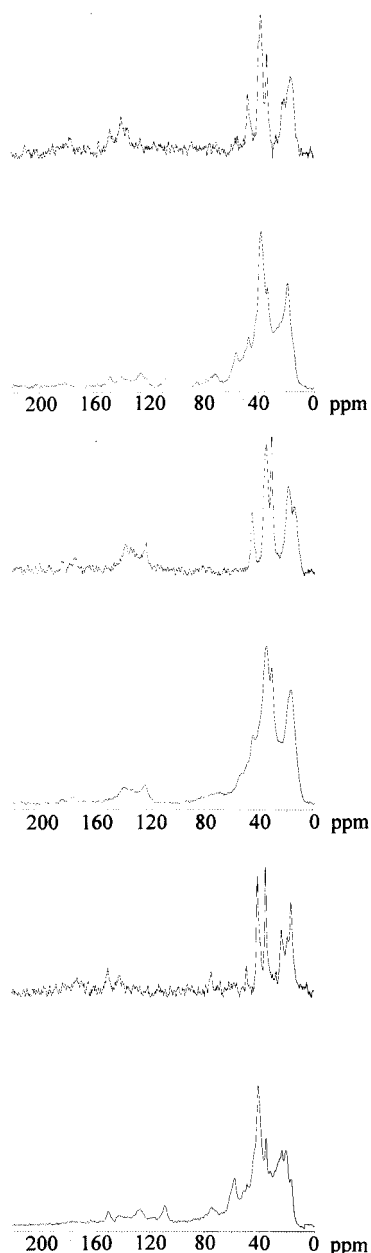
FIGURE 8. Pairs of ¹³C spectra (with interrupted decoupling on top) of American and African fossil resins (Group D, see Summary). From the top, the spectra are from the La Aguita mine in the Dominican Republic, Simojovel in the Mexican state of Chiapas, and Madagascar (sample GC12-43).

amber (Figure 7), but here resemblances to the Baltic spectra end. In particular, the saturated region of the spectrum of Dominican resin with interrupted decoupling very closely resembles the characteristic four-line pattern seen in Figure 2 for modern *Hymenaea* (note that the horizontal scales of Figures 2 and 8 are different). Resins with very similar spectra have been found in Colombia, South America.[12]

A second major source of fossil amber in the New World is the Mexican state of Chiapas,[2] particularly the sites of Simojovel and Totolapa. The paleobotanical source of this material is not clear, but floral parts found in the amber resemble *Hymenaea*. The spectra, illustrated

by the middle pair in Figure 8, are clearly distinct from those of Baltic amber and in fact are rather similar to those from the Dominican Republic, but without exomethylene resonances. It is possible that Chiapas resins represent older or more degraded forms (possibly by volcanic activity) with a similar botanical source. The saturated regions in the normal spectra compare favorably. With interrupted decoupling, the resemblances are even closer. Fossil resin from Africa shows close similarities with this group of materials. We previously published the spectrum of fossil resin from Tanzania from the Quaternary Period or the Pliocene epoch,[12] and it is very similar to that of Dominican amber. The bottom pair of spectra in Figure 8 are of resin from Madagascar. The similarities are less remarkable but still present. The angiosperm genus *Copaifera* from the Leguminosae family also is present in Africa, so that the range of spectra do not necessarily reflect *Hymenaea* as the sole source.

Summary of Groups of Fossil Resins Based on NMR

In our global survey of fossil resins, we have found four major groupings.

Group A. Found throughout the world during Cretaceous times, this group has been traced forward to the extant conifer genus *Agathis* in New Zealand and Australia. Sample spectra are given in Figure 4. It corresponds to Class Ib of Anderson et al.[7]

Group B. With widespread occurrence during Tertiary times from India across the Pacific to North America, this group has not been traced by NMR to a specific modern genus. None of the specific resins examined by NMR are found in the Anderson study, but this group may correspond to their Class II (Utah and Indonesia). Some of the members have been associated with the family Dipterocarpaceae. Sample spectra are given in Figure 5.

Group C. The famous Baltic amber group is localized in Europe to the Tertiary Period. It corresponds to Anderson's Class Ia. Sample spectra are given in Figure 7. Although no correspondence with modern genera is known, Baltic amber is presumed to have a coniferous source related to the families Pinaceae (which include pines) or Araucariaceae (which include kauri). It may have the same paleobotanical source as Group A but experienced less chemical degradation. Our phenomenological groupings are based on NMR spectra alone, and Baltic amber clearly represents a distinct class.

Group D. Derived from *Hymenaea* and possibly related to leguminous angiosperms such as *Copaifera*, this group is found in the Americas and in Africa. It corresponds to Anderson's Class Ic, and sample spectra appear in Figure 8. Thus, groupings based respectively on GC/MS and on NMR come to remarkably similar conclusions.

These groupings by no means exhaust the classes of fossil resins. Anderson et al. described at least three other

FIGURE 9. Amber bead T-150/1 from Tipu, Belize, with diameter ca. 1.5 cm. Photograph by Brian Boyle, Royal Ontario Museum.

minor classes.[7] For example, fossil polystyrene (their Class III) is found in New Jersey and has been characterized by IR, MS,[23] and NMR.[16] It is not expected, however, that there are any other major groupings to rival the four listed above.

Archaeological Comparisons

Given a source book of NMR spectra with a global basis, it should be possible to identify the provenance of fossil resins found in archaeological contexts. Beck has used IR spectra for such purposes, particularly for identifying Baltic amber.[5] The primary deterrent to a similar use for NMR is the rather large sample required, at least 30 mg, which could damage or destroy an amber object. Fortunately, amber beads are rather common, so their value in the museum context can be low.

We examined an amber-like bead that was found in Colonial-period Maya deposits from the site of Tipu in Belize (Figure 9),[24] dated to approximately 1575 A.D. It gave NMR spectra clearly characteristic of Baltic amber (Group C) rather than of materials from New World sources such as Chiapas or Hispaniola (Group D). Thus, this bead was a trade object imported presumably by the Spanish from Europe.

A similar story applies to two amber beads from Romania.[25] One had been found in the cave of Cioclovna (dated from the Bronze Age to the Iron Age) and the other at the site of Piatra Cetii (dated from the Neolithic Period to the Middle Ages). Both samples gave the characteristic NMR spectrum of Baltic amber rather than the more degraded spectrum of rumanite (Romanian amber). Despite the availability of Romanian sources of fossil resin (rumanite), both these archaeological materials had been brought in as trade objects (succinite). Romania lies along a natural north–south trade route from the Baltic to the Mediterranean Sea.

Thus, NMR provides a reliable method for the determination of provenance of archaeological fossil resins when sufficient material is available.

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