

THE HISTORY AND STRUCTURE OF STANTIENITE (1)

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Abstract

Organic materials have a long history of cultural importance as gemstones. The best known such minerals are amber and jet. For almost 150 years, stantienite has been considered to be a rare structural variation of Baltic amber, which is a fossilized product of plant resins. Spectroscopic examination, however, demonstrates that the material is a variety of jet or coal, which is a fossilized product of the woody portions of plants. A Turkish material called Oltu stone or black amber has similar spectroscopic characteristics to jet and stantienite and also is a coal derivative rather than a resinous product that could be called amber.

Introduction

Following the history of a mineral can be a fascinating chemical enterprise. Amber from the Baltic Sea has been important to European culture for thousands of years. Amber is a gemstone but differs from almost all other such materials in being composed of organic constituents. It is formed from ancient plant resins, exuded millions of years ago and subjected to structural changes during the ensuing geological eras (2-8). The raw resins are composed of numerous terpenes, a class of compounds that evolved within plants to provide, *inter alia*, physical protection from the ravages of damage, disease, or drought. The original plants were either

coniferous (gymnosperms) or flowering (angiosperms). The cultural importance of Baltic amber began in the early Neolithic period (up to about 10,000 years ago). Its importance increased through Classical Egyptian, Greek, and Roman times, as trade routes developed. During the Medieval period, amber was a popular material for the construction of rosary beads. The ancient trade routes from the Baltic and North Seas to the Mediterranean Sea were known commonly as the Amber Road (9).

From prehistorical to modern times, the major European source of amber was the Samland coast in the current Kaliningrad Oblast of Russia just north of Poland. The region was reconstituted after World War II but historically was the Königsberg area of East Prussia, where up to 90% of extracted amber in the world market has been derived. By the late Middle Ages, the Baltic amber sources were controlled by the Order of Teutonic Knights. When the Protestant Reformation decreased the demand for amber rosary beads, the Order transferred control of the trade to the Koehn von Jaski merchant family of Danzig (Gdańsk today, in Poland) in 1533 (6). In 1642, the Great Elector of Prussia bought the rights from the merchants. The Prussian monopoly of the amber trade continued until 1811, when private individuals were allowed to purchase the right to collect and market amber. Amber was transported from its sources to Danzig by ship. Channels for the ships needed to be dredged, and this process created more amber sources. In 1870, the private firm of Stantien & Becker contracted with the

Prussian government for the exclusive right to mine for amber. In their first years, they harvested about 10,000 lb (4500 kg) per annum. The company's new mine in Palmnicken (today's town of Yantarny in Kaliningrad; *yantar* is the Russia word for amber or resin) enabled extraction of 450,000 lb (200,000 kg) of amber in 1875. By 1885, production was nearing a million pounds (450,000 kg), and the peak of 1.2 million pounds (550,000 kg) occurred in 1895. At this point the Prussian government reclaimed control of amber production and founded the Royal Amber Works of Königsberg (later the Preußische Bergwerks- und Hütten AG). Large scale production continued until World War I, but post-war production dropped precipitously during the 1920s and 1930s (6).

Friedrich Wilhelm Stantien (1817-1891) had businesses in the old Lithuanian towns of Klaipėda and Rumpiškės, including a fishing ship, a restaurant, and a windmill (10). From 1852, he had searched for amber in his holdings, and in 1854 he obtained the rights to deepen the shipping channel of the Curonian Lagoon and extract amber (Figure 1; Yantarny is just off the map, to the left or west, and Danzig is farther down the coast in the same direction). Moritz Becker (1830-1901) was a merchant from Danzig who joined Stantien in 1858 to establish the firm of Stantien & Becker. Continuous extraction of amber was begun in 1862 in the northern part of Juodkrantė (today in Lithuania), now known as Amber Bay. At its height, the company employed 500-600 people in three shifts, operated seven steamboats, utilized 19 steam dredgers, and built dams to keep the sea back. Stantien sold much of his holdings in 1868 for two million marks, and in 1870 the company moved its offices to Königsberg. Becker sold the firm to the state in 1899. During this time, the

fishing village of Juodkrantė became a resort. The company built the harbor, supported a school and a doctor, and even presented an organ to a new church (10). The company's name lived on as a producer of flare pistols at least until World War I.

Varieties of Baltic Amber

During the mining of amber in Juodkrantė and elsewhere, rare and unusual resinous varieties were recognized that merited scientific investigation. These materials differed from common Baltic amber in appearance and properties. Whereas Baltic amber normally has a yellowish orange appearance, a brown variety was known by the workers as *Braunharz* (brown resin) or *das Braune* (the brown), and a black variety as *Schwarzharz* (black resin) or *das Schwarze* (the black) (11). The black material, actually brownish black, was shiny, opaque, and brittle and cleaved conchoidally, as amber tends to do, whereas the brown material, actually gray-brown, was matte in appearance and rarely cleaved conchoidally.

The first scientific comparison of these varieties, vis-à-vis true Baltic amber, was reported by Pieszczyk (12) in 1880 and was abstracted the following year in the English literature. He found that the brown material dissolves in a wide variety of organic solvents, but the black material is generally insoluble. He failed to find succinic acid, which is a hallmark of Baltic amber and is reflected in its mineralogical

name of succinite (from the Latin word *succus* for juice). He determined the ash content (respectively none, 4.5%, and 3.4% for succinite, brown resin, and black resin), the specific gravity (variable, 1.126, and 1.175), the carbon content (77.73-78.96%, 67.86%, 71.02), and



Figure 1. Map of the amber-rich region on the border of Kaliningrad and Lithuania. This map is based on "Curonian Spit and Lagoon," is licensed under CC BY-SA 3.0 via Wikimedia Commons—http://commons.wikimedia.org/wiki/File:Curonian_Spit_and_Lagoon.png#mediaviewer/File:Curonian_Spit_and_Lagoon.png.

the hydrogen content (9.01-10.51%, 8.56%, 8.15%). On the basis of these differences, he concluded that the three materials are distinct minerals. He proposed the name *stantienite* for the black resin and *beckerite* for the brown resin, to honor the two men largely responsible for the expansion of amber production and trade. These minerals joined the nineteenth century proliferation of mineralogical materials related to amber: *ajkaite* (*ajkite*), *ambrite*, *burmite*, *cedarite* (*chemawinite*), *copaite*, *delatynite*, *gedanite*, *gilsonite* (*uintahite*), *glessite*, *goitschite*, *hachetite*, *jaulingite*, *jelinite*, *kochenite*, *kranzite*, *ozokerite* (*ozocerite*), *ozonite*, *rosthornite*, *rumanite*, *schraufite*, *siegburgite*, *simetite*, and *walchowite*. These terms have served primarily to identify geographical origin of the materials and were not based on any knowledge of their chemical structure. *Beckerite* and *stantienite* differ from most of these in that they were varieties found in the sands along the Baltic Sea along with *succinite* and are not geographically distinct from *succinite*.

Beck et al. (11) reexamined the case of *beckerite*, carried out critical new diagnostic experiments involving infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies, and concluded that this putative class of fossil amber is not a distinct mineral but rather contaminated *succinite*. Beck's analysis of the early literature called into question the original conclusions of Pieszczyk (12). The low proportion of succinic acid, Beck noted, was not an independent result but had been inferred from the weight of precipitated barium salts. Klebs (13) already had pointed out that there are several dark-colored Baltic resins and that Pieszczyk's single sample may not have been representative. Indeed, brown resin samples identified as *beckerite* are very heterogeneous (14). Schubert (15) concluded that the brown color of *beckerite* comes from the presence of decomposed wood and insect excrement known in German as *Frass* (from the German *fressen*, to eat). When Schubert examined the resinous portions of *beckerite*, with the exclusion of *Frass*, he found that the morphology of the resin canals was the same as present in *succinite*. He concluded that "there is no longer any justification to consider *beckerite* as a distinct resin with respect to its [botanical] origin." This conclusion falls short of saying that *beckerite* and *succinite* are structurally different. Beck and his co-workers (11) spectroscopically analyzed a dozen samples of alleged *beckerite*, most of which had come directly from Schubert, notwithstanding the 25 year hiatus between the two studies. They found that both IR and carbon-13 (^{13}C) NMR spectra showed no differences between the *beckerite* samples and control samples of *succinite*. Since the spectroscopic signals are proportional to relative amounts

of materials, the low concentrations of *Frass* compared with resin failed to provide observable signals. Moreover, the carbonyl regions of the ^{13}C NMR spectra were identical for *beckerite* and *succinite*, including the peak at δ ca. 170 indicative of the presence of succinic acid, contradicting the nineteenth century conclusions from ambiguous chemical isolation. Beck and his co-workers (11) concluded that *beckerite* is *succinite* contaminated with woody materials and insect detritus and should not be considered to be a distinct mineralogical material. The insect-altered wood (*Frass*) may not undergo the same process of fossilization as resin during geological aging.

Possibly due to its rarity, little scientific study has been carried out on *stantienite*, the other mineral described and named by Pieszczyk (12). He recognized the most defensible difference from *succinite* and *beckerite* in the latter's lack of solubility in all solvents he studied. The Expert Commission on Qualification of the International Amber Association (16), based in Gdańsk, Poland, listed and described fossil resins that accompany Baltic amber in its deposits: *gedano-succinite*, *gedanite*, Baltic *stantienite*, Bitterfeld *stantienite*, *glessite*, and *siegburgite* (which the Commission spelled "zigburgite"). This list of amber is incomplete, in that it focuses on materials found in Baltic and Bitterfeld deposits, ignoring all other European materials (as well as Asian, African, Pacific, and American) but including the very different *siegburgite*. This material, found in Germany and New Jersey (USA), is fossilized polystyrene rather than amber, which is composed of terpenoid polymers. The Bitterfeld deposits are located near the town of Bitterfeld-Wolfen in the state of Saxony-Anhalt in the former East Germany. Amber deposits have been known there since the seventeenth century but were kept secret during the Communist period, under suspicion of association with uranium deposits (17, 18). Originally assigned to the lower Miocene period (ca. 22 Mya) and then to the Oligocene (23-34 Mya), Bitterfeld amber also has been considered to be contemporaneous with Baltic amber (35-50 Mya) (19). Although the Bitterfeld coal seams are from the Miocene or Oligocene, the amber-bearing portions may have been redeposited and are more difficult to date. As a result, the Bitterfeld deposits may be considered part of the Baltic amber complex. These conclusions are based largely on the similarity of the insect inclusions in both materials and are not universally accepted. The Expert Commission (16) provides the following descriptions: "the extremely rare black *stantienite*, which produces very good sheen (the 'black amber') ... is confused with jet coal," and "other 'soft' and 'hard' black resins, occurring in somewhat greater

amounts in the Bitterfeld deposit, differing in hardness from stantienite.” Materials from both sources have been referred to as stantienite, but it is better to maintain the distinctions of Baltic stantienite and Bitterfeld stantienite, entirely on geographical considerations.

In the only modern study of stantienite, Yamamoto et al. (20) examined a single sample of Bitterfeld stantienite by gas chromatography/mass spectrometry, in conjunction with analogous examination of two succinities, two glessites, and one goitschite from Bitterfeld. Whereas the glessites contained triterpenoids characteristic of angiosperms and the succinities and the goitschite contained mono-, sesqui-, and diterpenoids characteristic of gymnospermous precursors, the stantienite produced a chromatogram predominantly of an unresolved, complex mixture of esters and diesters, indicative of waxes from higher plants. The observed carbon preference index (21) corresponded to the rank of bituminous coal. The authors did not, however, conclude that stantienite was a form of coal. Rather, they always referred to stantienite as an amber. They concluded that “peat/coal surrounding the stantienite may have contaminated the amber over geological time,” and “The resin was deposited initially in a peat layer, diagenetic changes occurred continuously at the early stages, with absorption and inclusion of leaf waxes, biopolymers and triterpenoids from the surrounding peat.” This study did not include Baltic stantienite, so any molecular differences between the Bitterfeld and Baltic materials remain to be defined.

NMR Spectra of Stantienite and Baltic Amber

Because beckerite proved to be mineralogically identical to Baltic amber, the distinct properties of stantienite suggested that further study of this variant also should be advantageous. During more than 35 years of sample acquisition, we have managed to obtain three samples of stantienite, which we now have examined by ^{13}C NMR spectra. Stantienite is insoluble in all solvents, so spectra were recorded on the bulk solid, rather on solutions, using magic angle spinning techniques (22). We compared the spectra of the three samples of stantienite with those of one sample of standard Baltic amber and two samples of jet.

1) Sample 34 of stantienite was provided in 1981 by the late Prof. Curt W. Beck (Vassar College) from his personal collection. He obtained it from the Paris Museum of Natural History, sample 100.1369, from Baltic sources.

2) Sample 1391 of stantienite from Palmnicken (now Yantarny, Kaliningrad) was originally from the collection of Prof. Jean H. Langenheim (University of California, Santa Cruz) via Laurie Gough (Polytechnic of the South Bank, London, (now London South Bank University)) and Prof. Royal H. Mapes (University of Iowa, Iowa City, now Ohio University, Athens, OH).

3) Sample 1538 of stantienite was from the collection of Mr. Teruhisa Ueno (Kyushu University, Fukuoka, Japan) in 2014. It came from the Goitzche mine, Bitterfeld, Sachsen-Anhalt, Germany.

4) Sample 1657 of Baltic amber was from Palmnicken (Yantarny), Kaliningrad, provided by the National Museum of Natural History, Washington, DC.

5) Jet sample J-10 was from Port Mulgrave, North Yorkshire, England, provided by Helen Muller, Bramhope, Leeds, England.

6) Jet sample J-14 was from Utrillas, Teruel (Aragon), Spain, provided by Ramón Requeixo-Rebón, Santiago de Compostela, Galicia, Spain.

Figure 2 contains the ^{13}C spectrum of sample 1657, Baltic amber from the Yantarny region of the Kaliningrad Oblast, taken on powdered, bulk material. The lower spectrum was recorded with normal decoupling of all hydrogen nuclei. As in all other such spectra, the dominant resonances occur in the region of saturated (aliphatic) carbon atoms, between δ 10 and 60 (23). These resonances are from CH_3 , CH_2 , and CH groups and quaternary carbon atoms. This particular pattern is repeated in all spectra of Baltic amber. In addition, weak resonances of unsaturated carbons between δ 100 and 150 are present. Characteristically, there are clear resonances from exomethylene groups ($\text{C}=\text{CH}_2$), with the unsubstituted carbon at about δ 150 and the methylene resonance at about δ 105. In addition, weak resonances occur in the carbonyl ($\text{C}=\text{O}$) region between δ 160 and 220, the peak at δ 173 being diagnostic for succinic acid. The upper spectrum was recorded with dipolar dephasing (also called interrupted decoupling). This procedure employs a delay period that allows all carbons to relax except quaternary carbons and a few rapidly moving methyl carbons. It is employed to provide a second ^{13}C fingerprint. Only two peaks remain in the saturated region. These spectra are typical for Baltic amber, which constitutes NMR amber Group C (mass spectrometric Class Ia) (24) and are very similar to the spectra of samples from the large NMR Group A (Class Ib). Both these materials derive from a similar conifer

origin. Samples from elsewhere in Europe (Romania, Sicily, France, and so on) belong to Group A. In contrast, amber from Groups B and D have an angiosperm (flowering plant) origin but have many aspects of their NMR spectra in common with Groups A and C (25, 26).

Figures 3-5 present the ^{13}C spectra for the three stan-

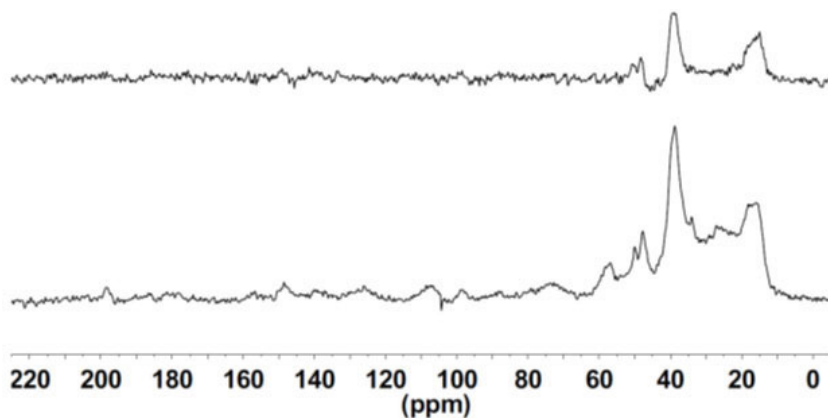


Figure 2. The ^{13}C NMR spectra of amber from the Yantarny region of the Kaliningrad Oblast, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1657).

tienite samples, which we will designate by the names of their donors, respectively Beck, Mapes, and Ueno. The Beck and Mapes samples are from the Baltic Sea and the Ueno sample from Bitterfeld, Germany. The spectrum in Figure 3 was recorded at a time when only complete decoupling was available. The other two figures contain spectra for both types of decoupling. All three spectra contain two broad peaks. The peak from saturated or aliphatic carbons has a maximum at about δ 33, with two side peaks at about δ 16 and δ 20 in all three spectra. The peak from unsaturated carbons (aromatic and possibly double bond or alkenic) contains a maximum at about δ 130. There is an additional peak at about δ 138, which is a shoulder in Figures 3 and 5 but larger in Figure 4. These peaks are from carbons with different substitution patterns. The broad peaks at about δ 80 and 180 in Figures 4 and 5 are artifacts of spinning the sample. Called spinning side bands, they appear equally spaced on either side of the main peak for highly anisotropic environments, as found with unsaturated but not saturated carbons. Figure 3 was taken at a higher spinning rate, so that they moved out of range. With dipolar dephasing (Figures 4 and 5), the saturated carbon peaks are largely reduced, and the unsaturated carbon peaks have lost much of the portion centered at δ 130, leaving predominantly the portion at δ 138. The latter

represent fully substituted unsaturated carbons (bearing no hydrogen atoms). The surviving saturated carbon resonances probably are from rapidly moving methyl groups. The important point is that the Baltic (Figures 3 and 4) and Bitterfeld (Figure 5) spectra of stantienites behave very similarly with dipolar dephasing.

These spectra differ fundamentally from the terpenoid patterns of amber, not just those of Baltic amber (Figure 2) but those of all types of amber (24). Spectra of terpenoid resins are dominated by the resonances of saturated carbons, have numerous, more defined peaks in that region, and have very weak peaks from unsaturated carbons. The spectra in Figures 3-5 of stantienite closely resemble those of coal and can be termed examples of carboniferous materials. Coal spectra contain a large, nearly undifferentiated resonance from saturated carbons and a very large resonance from unsaturated carbons. Of the coal spectra illustrated by Fyfe (22), those of lignite and subbituminous coal most closely resemble the present spectra of stantienite. Spectra of bituminous coal have stronger unsaturated than saturated peaks, spectra of anthracite lack unsaturated peaks entirely, and spectra of peat exhibit stronger saturated peaks. Resonances from phenolic carbons are found in the spectra of less matured lignite, e.g., Onakawana lignite, but are absent

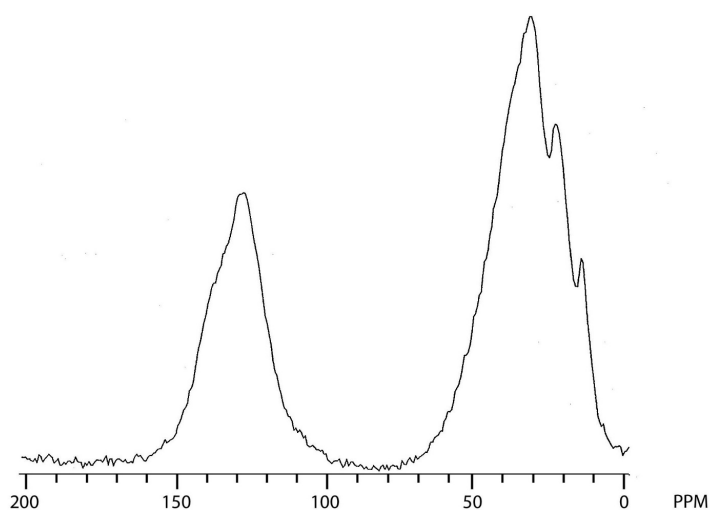


Figure 3. The ^{13}C NMR spectrum of stantienite from the Baltic Sea, donated by Curt W. Beck, with decoupling of all hydrogen nuclei (sample 34), adapted from Figure 9 of Ref. 30.

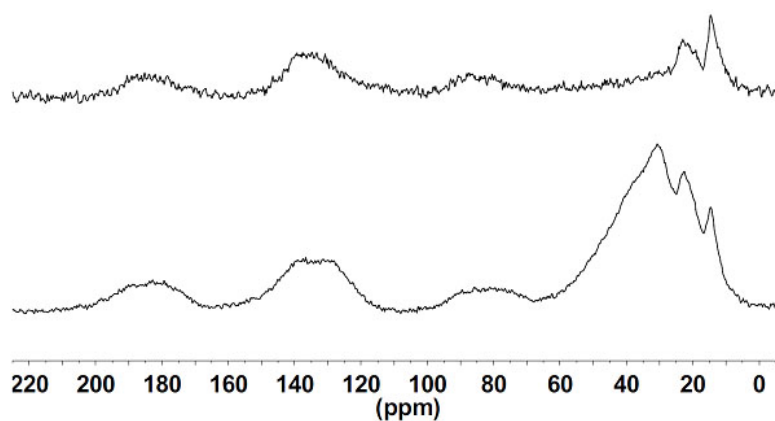


Figure 4. The ^{13}C NMR spectra of stantienite from Yantarny, Kaliningrad, donated by Royal H. Mapes, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1391).

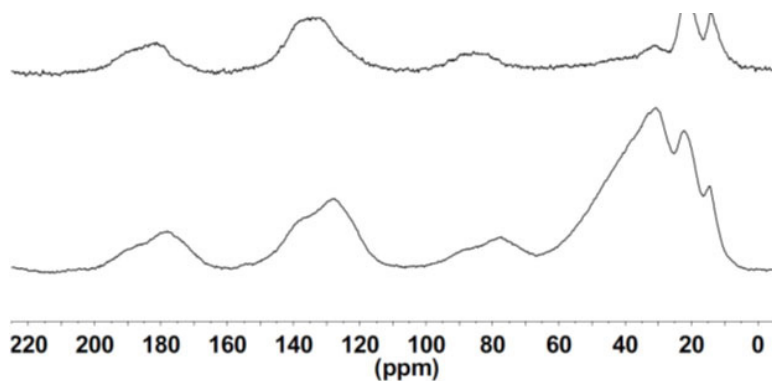


Figure 5. The ^{13}C NMR spectra of stantienite from Bitterfeld, Germany, donated by Teruhisa Ueno, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1538).

from the spectra of more matured lignite, e.g., lignite A, in Fyfe's examples. Phenolic peaks, which would occur at about δ 150, are absent in Figures 3-5. Subbituminous coal samples vary from spectra exhibiting nearly equal saturated and unsaturated peaks to spectra with much stronger unsaturated than saturated peaks. Stantienite reproducibly exhibits stronger saturated peaks, more similar to lignite. Thus we identify stantienite as a type of coal or carbonaceous material of rank most closely resembling more highly matured lignite.

Comparison with NMR Spectra of Jet

Jet, like amber, is considered to be an organic gemstone (27). Its shiny, black appearance has been appealing for jewelry and other purposes since Neolithic

times, but particularly during the Victorian period in England for mourning decoration. Jet, unlike amber but like coal, derives from woody material that has been compressed under anaerobic conditions over geological times. Lambert, Frye, and Jurkiewicz (28) inferred from the solid state ^{13}C NMR spectra of several samples that the rank of jet is between those of lignite and subbituminous coal. Figures 6 and 7 show respectively the ^{13}C spectra of jet samples from England and Spain. They illustrate typical carbonaceous spectra, with the two peaks from aromatic and aliphatic carbons. The spectrum in Figure 6 from Port Mulgrave, which is nine miles (15 km) northwest of Whitby, a famous Yorkshire source of jet, closely resembles those of stantienite in Figures 3-5. In particular, the saturated resonances in both materials exhibit the shoulder peaks at about δ 16 and 20 (compare Figures 3-5 with Figure 6). In both cases the integral of the aliphatic peak is greater than that of the aromatic peak. For the Spanish sample (Figure 7), the aromatic resonance is slightly larger than the aliphatic resonance, and the shoulder peaks on the low frequency side of the aliphatic resonance are absent. Both jet spectra exhibit a spinning side band at about δ 240. In contrast to the stantienite spectra, the jet spectra exhibit clear phenolic resonances at δ 155, a diagnostic characteristic.

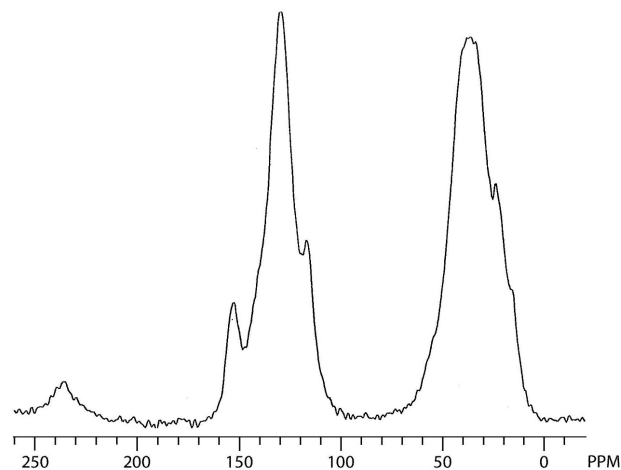


Figure 6. The ^{13}C NMR spectrum of jet from Port Mulgrave, North Yorkshire, England, donated by Helen Muller, with decoupling of all hydrogen nuclei (sample J-10).

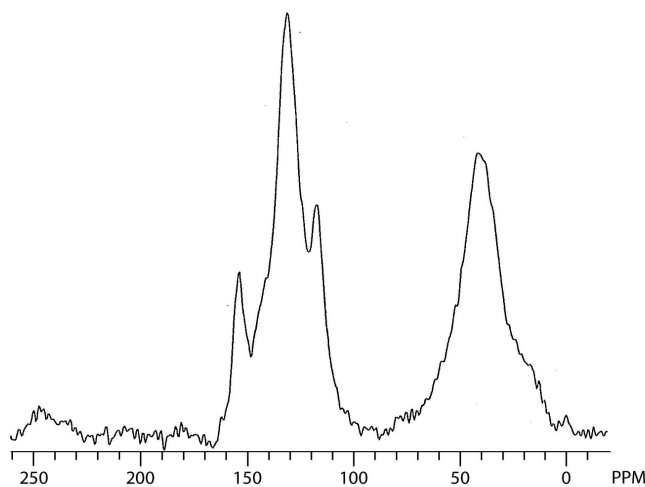


Figure 7. The ^{13}C NMR spectra of jet from Utrillas, Teruel (Aragon), Spain, donated by Ramón Requeixo-Rebón, with decoupling of all hydrogen nuclei (sample J-14), adapted from Figure 4 of Ref. 28.

Other mineraloids (noncrystalline mineral-like materials) resemble stantienite and jet, including Oltu stone from Turkey (29). Oltu stone has been found in coal mines in the Turkish province of Erzincan. Commonly called black amber, it has been worked, particularly in the Turkish city of Erzurum, for the production of jewelry and other decorative objects. We have obtained samples from two sources (Sezai Adil of Erzincan University and Serap Mutun of Abant Izzet Baysal University) and examined their carbon spectra in the solid (Figure 8). They are nearly identical to the spectra of jet in Figures 6 and 7, so that this organic gemstone, like stantienite, may be considered a variety of jet.

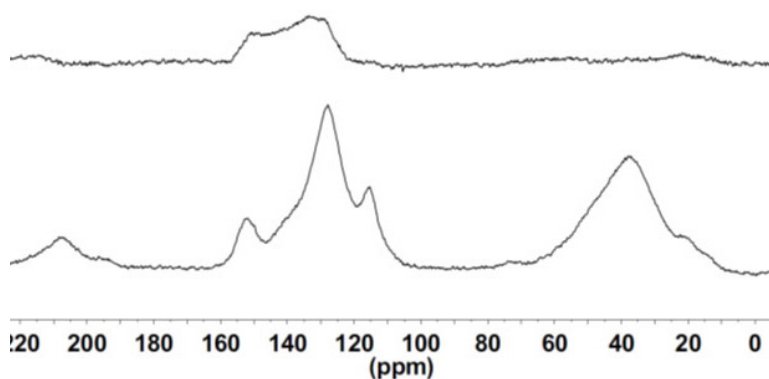


Figure 8. The ^{13}C NMR spectra of Oltu stone, donated by Sezai Adil, Erzincan University, Erzincan, Turkey, (lower) with decoupling of all hydrogen nuclei, (upper) with dipolar dephasing (sample 1666).

There is no evidence that amber degrades to a carbonaceous material. As amber matures or fossilizes (from comparison of Eocene to Cretaceous materials) (30), the saturated resonance broadens but the unsaturated region does not grow. As carbonaceous materials mature (lignite to anthracite), the unsaturated region becomes increasingly dominant. Amber in its form known as resinite is found as transparent, shiny inclusions within coal seams, the resin surviving as distinct material within the woody host during the progress of degradation.

Conclusions

The solid state ^{13}C NMR spectra of three samples of stantienite, two from the Baltic Sea and one from Bitterfeld, Germany, indicate that this mineraloid is a carbonaceous material of coal rank approximating that of mature lignite. The spectra bear no resemblance to those of amber of any variety, which are dominated by aliphatic resonances and contain very weak alkenic resonances and none from aromatic carbons. Spectra of stantienite are very similar to those of jet from England and Spain, although the latter exhibit modest phenolic resonances. Stantienite closely resembles jet in appearance and in lack of solubility. Oltu stone from Turkey also proved to be a carbonaceous, rather than a resinous material, very similar to jet.

In the mass spectral study by Yamamoto et al. (20) of Bitterfeld stantienite, the authors powdered and sonicated the single sample three times in 1:1 dichloromethane:methanol and examined both underivatized and silyl-derivatized materials by mass spectrometry. Because of the low solubility of stantienite in comparison with their other study samples, the extracts of stantienite must have represented only a minor portion of the bulk. The ^{13}C NMR method examines the entire bulk material in a powdered form. Nonetheless, Yamamoto et al. were able to draw valuable conclusions that are not in contradiction with our results. The other Baltic materials in the Yamamoto study predominantly exhibited distributions of terpenoids in their mass spectra, whereas stantienite exhibited unresolved, complex mixtures of esters, with only minor amounts of terpenoids not found in the other Baltic materials. They interpreted these results as indicative of waxes from higher plants with a carbon preference index corresponding to bituminous coal. They did not revise the structure of stantienite, however, maintaining that it is a type of amber (despite the low content of

terpenoids) that had been contaminated by surrounding peat or coal.

It is clear from the ^{13}C NMR examination of bulk, solid stantienite that it is not an amber but rather a carbonaceous material resembling lignitic coal in structure and resembling jet in structure and appearance. Oltu stone from Turkey follows the same pattern. They should not be considered varieties of amber (“black amber”) and do not merit distinct mineralogical designations.

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