

SPECTROSCOPIC EVIDENCE FOR THE CHEMICAL STRUCTURE OF ALGAL KEROGENS

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ABSTRACT

Two Permo-Carboniferous alginites (one sample is from Torbane Hill in Scotland and the other is from South Africa) have been examined by high-resolution ^{13}C nuclear magnetic resonance employing the techniques of magic angle spinning and cross polarization. This examination has shown that these algal kerogens have predominantly aliphatic-type structure with a relatively high proportion of polymethylene chains and concomitant low total aromatic content. The aliphatic nature of alginite is further confirmed by both ^1H nuclear magnetic resonance spectroscopy employing the magic angle spinning technique as well as Fourier transform infrared analysis. This work and other organic geochemical studies suggest that algal geologic materials tend to preserve their basic aliphatic structure after burial despite relatively extensive diagenetic evolution under mild/moderate geological conditions. This interpretation is of much interest in connection with the problems of the origin and nature of Precambrian life.

INTRODUCTION

Kerogen, commonly defined as the insoluble portion of the organic geochemical matter in sediments, has been the subject of many organic geochemical studies. Organic geochemists have characterized this geo-organic material as originating from algal and/or higher plant remnants (Welte, 1973). Of the two extremes, algal kerogens are generally considered to have an aliphatic-type structure while the structure of higher plant kerogens are more aromatic in nature (Tissot and Welte, 1978). The best known algal kerogens are the Permo-Carboniferous (ca. 280×10^6 y old) torbanites which are believed to be derived from lacustrine algae similar to the extant green-type algae *Botryococcus braunii* (Kutzing) (Blackburn and Temperley, 1936). General aspects of the geology of torbanites and the phytochemistry of their algal progenitor have been thoroughly discussed by Cane and Albion (1971).

Torbanite is interesting from the view-point of paleoenvironmental studies of the origin, evolution, and the distribution of plant life at the algal level. For organic geochemists, torbanite has a special value as a premier geochemical model for the study of the chemical structure of algal kerogens, as this particular kerogen has a simple biological and geological history. Thus, if the structure of torbanite could be systematically unravelled, new and useful information should become available on the general chemical nature of algal kerogens. However, elucidation of the details of

the structure of the kerogen has been frustrated by the nature of the material. Chemical degradation has been used by many researchers to obtain small fragments more readily amenable to analysis by techniques such as gas chromatography and mass spectrometry. However, these degradation methods have many disadvantages such as ambiguity as to whether the degradation products truly reflect the structure of the original kerogen. Infrared (IR) spectroscopy of kerogen has provided the most useful structural information to date (Rouxhet et al., 1980) but Fourier transform IR spectroscopy (FTIR) offers a number of advantages over conventional IR for the characterization of coal-like material (Painter et al., 1981).

Recently developed methods for obtaining high-resolution nuclear magnetic resonance (NMR) spectra of solids (Pines et al., 1973; Scheler et al., 1981) have been exploited very successfully in the analysis of coal and related materials (Maciel et al., 1979; Rosenberger and Rentrop, 1982; Wilson et al., 1984; Pugmire et al., 1984). ^{13}C NMR with cross polarization (CP) and magic angle sample spinning (MAS) and ^1H NMR with MAS are powerful non-destructive tools for the analysis of carbonaceous sedimentary rocks. Depending on the nature of the carbonaceous material and the concomitant resolution obtainable, a wide range of structural information can be obtained (Rosenberger and Rentrop, 1982; Wilson et al., 1984; Pugmire et al., 1984). In the complex carbonaceous sediments, the diversity of structural components leads to broad bands that frequently lack detail. However, employing multiple pulse techniques, it is possible to obtain additional structural information (Wilson et al., 1984; Pugmire et al., 1984). Although ^{13}C and ^1H NMR techniques are extremely good methods for the qualitative study of coal and related materials, there are still some uncertainties regarding the quantitative interpretation of the integrated intensities and the data must be carefully taken in order to obtain reliable data, as described by Wilson and Vassallo, (1985).

We have used ^{13}C CP/MAS and ^1H MAS to study two torbanite kerogen samples: one is from the Torbane Hill Scotland while the second is from South Africa. We report here detailed descriptions of the carbon skeletal structure.

EXPERIMENTAL

The isolation procedure was similar to that used by Saxby (1970, 1976) and Premovic (1984). Powdered rock (50 g) was extracted with benzene methanol (3:1 v/v) for 96 hours in a Soxhlet apparatus. The residue remaining in the Soxhlet thimble was treated with boiling hydrochloric acid (HCl, 4M) to remove most of the carbonates. Carbonate removal was checked by IR analysis. The insoluble residue was demineralized further by repeated treatment with boiling hydrofluoric/hydrochloric acids (HF/HCl, 22M and 0.25M, respectively). This acid mixture removes silicates (Saxby, 1970) and the removal was checked by IR analysis. The final residue is alginite. It contained only small traces of inorganic minerals, including pyrite, as confirmed by the electron microprobe analysis.

All ^{13}C NMR spectra were recorded at 25.15 MHz on a Bruker CXP-100 as previously described (Wilson et al., 1984). The 1K FIDS, acquired with a 3 ms contact time, 0.35 second recycle time and a rotor frequency of ca. 4 KHz, were zero filled to 8K before Fourier transformation. The pulse sequence employed for obtaining the dipolar dephasing (DD) spectra is described elsewhere (Alemany et al., 1983).

Proton NMR spectra were taken at 270 MHz with MAS and BR-24 (Borum and Rhim, 1979) at room temperature on a home-made NMR pulse spectrometer.

For FTIR analysis, the sample was mixed with anhydrous potassium bromide and pressed into the disc (2.5 mg/150 mg KBr) with a load of 200 MPa.

The spectra were recorded at room temperature on a Bruker ISF 113 v FTIR spectrometer.

RESULTS AND DISCUSSION

Petrographic analysis of the torbanites in question demonstrated that alginite is the major maceral present, in amounts high enough to preclude the necessity of further concentration (Dulhunty, 1939). The Scottish and South African alginite samples with relatively high carbon content, C 82.8% and 80.5%, respectively (Allan et al., 1980) would be classified as bituminous coals (Millais and Murchison, 1969) according to current standards (Petrakis and Grandy, 1980) on the basis of carbon content alone. These samples yield very low amounts of soluble organic matter (the Scottish 0.58% and South African 0.32%) (Allan et al., 1980). Cane and Albion (1973) suggested that alginite is an oxidative polymer of straight-chain alkenes of the formula $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ ($n = 15, 17$ and 19), if it is derived from the green stage of the *Botryococcus* growth cycle (Knights et al., 1970). Allan et al., (1980) analyzed the Scottish and South African alginite samples by a variety of geochemical and optical techniques. The results of this study indicate that these alginites are composed of a polymeric material which contains a relatively high proportion of straight-chain and simple branched aliphatic structures. These authors also suggested that the total aromatic content of these torbanite macerals is small on the basis of elemental and IR analyses.

Figure 1 shows a typical ^{13}C CP/MAS spectrum of a powdered alginite sample of South African torbanite. The Scottish alginite spectrum was essentially identical, Figure 1b, except that the upfield (ca 120 ppm) peak in the aromatic/alkenic region is more intensive relative to the 140 ppm peak than is noted for the South African torbanite. Because the alginite spectrum contains fine structure, a relatively detailed description of the carbon functional groups is possible. The resonances from approximately 0 to 100 ppm are due to aliphatic carbons which comprise about 88% of the total carbon present. Those in 100 to 160 ppm range are due to unsaturated carbons (alkenic and aromatic) and comprise about 9% of the total. Finally, the resonances above 160 ppm in frequency are from carbonyl groups and provide about 3% of the total integrated intensity.

Within the aliphatic region of the spectrum, the resonances from 0 to about 50 ppm arise from hydrocarbon groups while those from ~55-70 ppm would constitute alcohols and/or aliphatic ethers. The strong peak at 34 ppm is mainly from methylene groups (flanked by two other methylene groups) or from methinyl carbons in general. The shoulder at 17 ppm arises from the methyl groups. The resonance centered around 125 ppm would include the internal alkenic carbons (C-CH=CH-C) or protonated aromatic carbons. The resonance centered around 145 ppm is in the region where one would find signals arising from substituted alkenes (in vinyl or isopropenyl structures) or aromatic carbons attached to alkyl or alkenyl groups. The peak at 180 ppm represents carboxyl (acid and/or ester) groups and a resonance at 210 ppm arises from ketonic carbons.

In order to obtain additional structural information, we employed the DD technique which removes most of the methine and methylene carbons from the ^{13}C NMR CP/MAS spectrum but one still sees remnants of methyl groups (approximately 50% of methyl carbon signal will persist under the experimental conditions) and highly mobile methylene groups as well as a major remnant of the non-protonated carbons (Petrakis and Grandy, 1980). The lower trace of Figure 1 represents a DD spectrum of the South African alginite. It can be seen that about 14% of methylene/methine peak is still observed indicating a number of highly mobile methylene groups. While more work is required for verification, it is interesting to speculate that these methylene groups belong to polymethylene chains with a lower degree

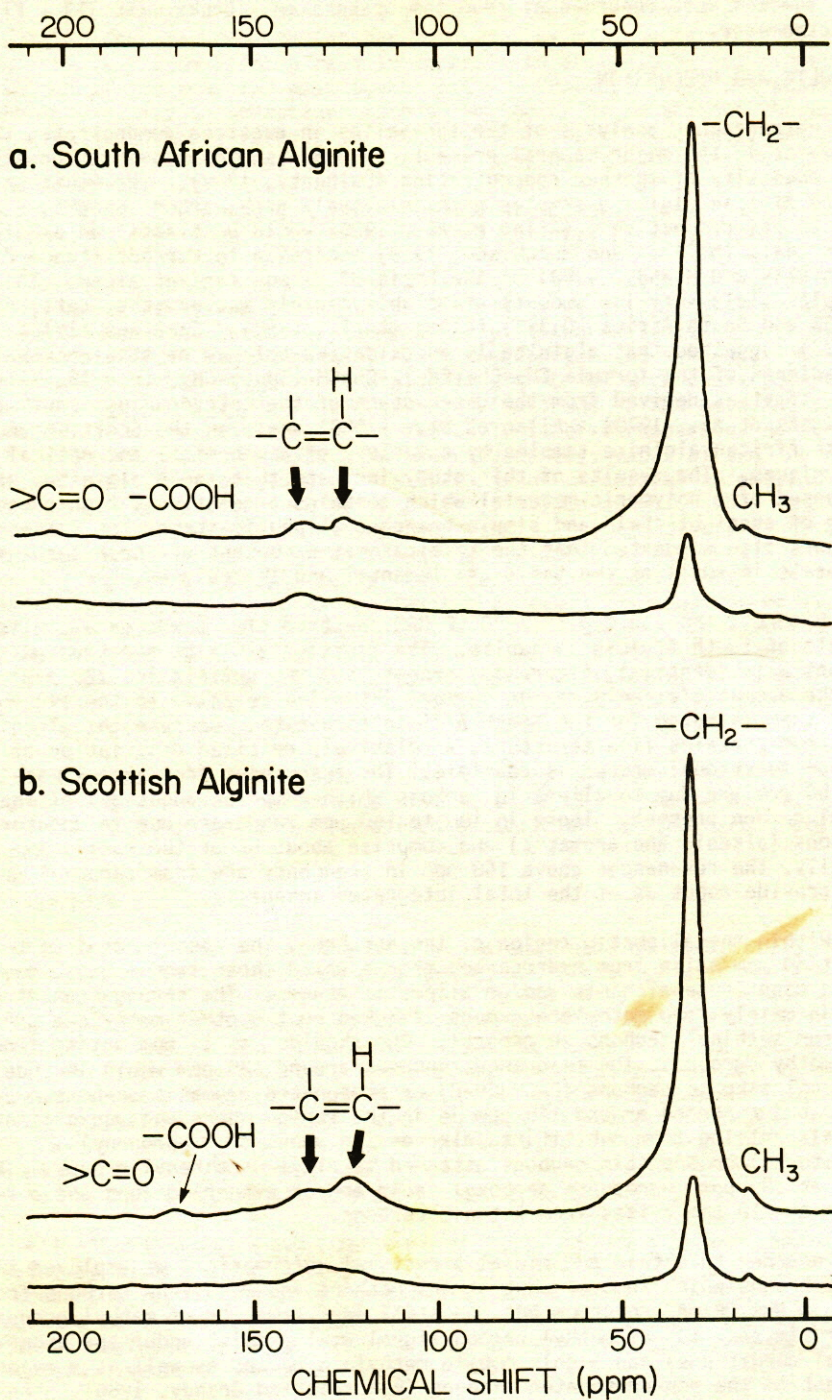


Figure 1. Carbon-13 NMR spectrum of a powdered sample of: (a) the South African alginite, and (b) the Scottish alginite. Lower trace represents DD spectra.

of order (e.g. amorphous domains within alginite) (Havens and Koenig, 1983). The fact that the 125 ppm resonance essentially vanishes implies that this signal arises, probably, from internal alkenic carbons of vinyl or isopropenyl type or protonated aromatic carbons. However, on the basis of the proton MAS work, there appears to be very little aromatic protons present and, hence, the peaks in question in the ^{13}C NMR data must arise primarily from alkenic groups. On the other hand, since DD had a small effect on resonance at 145 ppm, it is reasonable to conclude that this peak could be attributed to nonprotonated alkene carbons such as would arise at branched centers.

The ^1H NMR (BR-24/MAS) (Borum and Rhim, 1979) of a powdered alginite sample (0.5 g) of South African torbanite, Figure 2, shows a presence of a strong aliphatic proton band and an absence of aromatic proton band inferring that more than 90% of organic protons are aliphatic. The Scottish alginite has an essentially identical spectrum except it shows a weak aromatic signal.

Thus our NMR results suggest that the Scottish and South African alginites are aliphatic materials which contain relatively high proportion of polymethylene chains and rather low amounts of aromatic groups in the structures. These results give strong support to the tentative structural model proposed by Cane and Albion (1973) based on the analytical work of Knights et al. (1970) and they are in substantial agreement with the work of Allan et al. (1980).

Further evidence for aliphatic-type structure of alginites in question was seen in their FTIR spectra. All of the spectra were dominated by strong aliphatic absorption bands at $2920 \pm 1 \text{ cm}^{-1}$ and $2860 \pm 1 \text{ cm}^{-1}$, Figure 3 (the Scottish alginite), and $1460 \pm 5 \text{ cm}^{-1}$. The former two bands can be assigned to methylene groups, although there is also some contribution from methyl C-H stretching modes at these frequencies. There is no absorption band near 2960 cm^{-1} characteristic of extensive chain branching but a moderate absorption at $720 \pm 1 \text{ cm}^{-1}$ indicates a presence of polymethylene chains in alginite macromolecules.

Previous studies have demonstrated, employing the ^{13}C and ^1H (Rosenberger and Rentrop, 1982) NMR techniques, predominant aliphatic structure (>85% of the total) for both bituminous (C=84.1%) Oelsnitz boghead coal (Carboniferous, ca. 325×10^6 y old, USSR) and subbituminous (C=71.5%) Estonian kukersite (Ordovician, ca. 500×10^6 y old, USSR). Geo-organic matter of these algal coals contains as much as 90% and 80% of alginite, respectively (Rosenberger and Rentrop, 1982). Moreover, according to Monin et al. (1980) kukersite appears microscopically to be composed of *Botryococcus*-type algae similar to those found in the torbanites examined although it has a different overall chemical structure. Chemical degradation studies of subbituminous (C=75.8%) tasmanite (Permian, ca. 250×10^6 y old, Tasmania) infer its aliphatic-type structure; the major precursor of this geological material is believed to have been algae (Ishiwatari and Machihara, 1982). Our recent examination of the tasmanite kerogen using the ^{13}C and ^1H solid state NMR indicate that this geo-organic material contains mainly aliphatic-type structures (>95%) (Premovic, Michel, Rosenberger, unpublished).

Recently, we have studied kerogen of the Gunflint chert (Middle Precambrian, ca. 1.9×10^9 y old, Canada) using the FTIR and ^{13}C NMR spectroscopies (Premovic et al., 1986). The results of this investigation suggest that the Gunflint chert kerogen has predominantly aliphatic-type structure. A similar conclusion is reached for kerogen of the Paradise Creek chert (Late Precambrian, ca. 1.6×10^9 y old, Australia). These kerogens are believed to be derived from Precambrian algal and/or bacterial organisms (Smith et al., 1970). The trace quantity of soluble organic

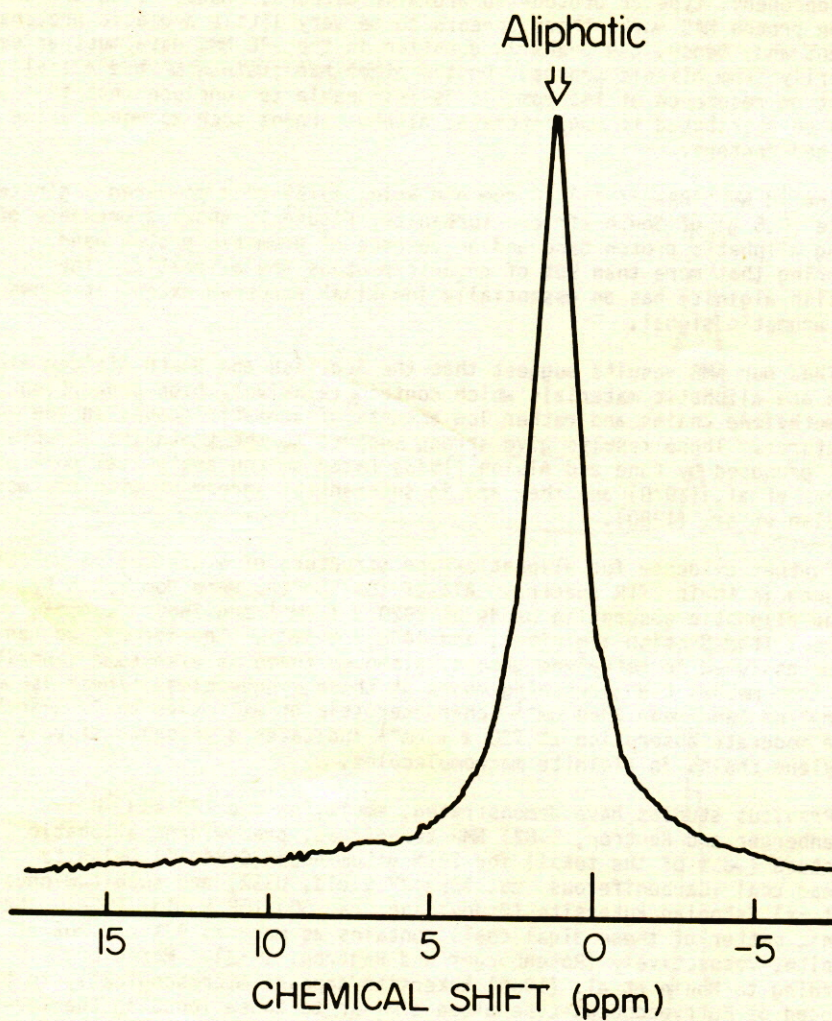


Figure 2. Hydrogen-1 NMR spectrum of a powdered sample of: the South African alginite.

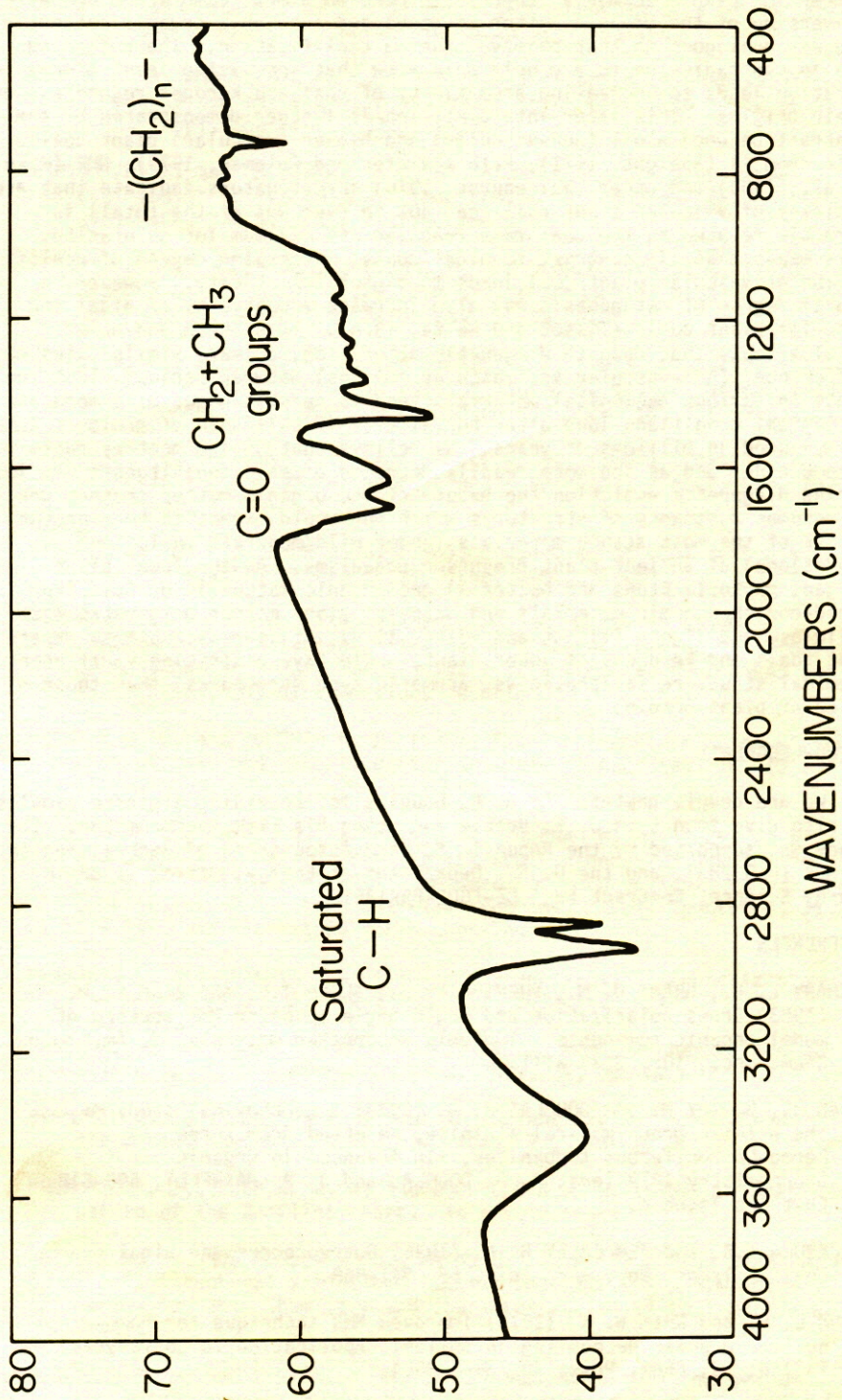


Figure 3. FTIR spectrum of a powdered sample of the Scottish alginite.

matter in these Precambrian cherts indicate an almost complete diagenetic conversion of the organic matter to gases and insoluble organic matter, a process analogous to that observed during coalification. These findings are in contradiction to a widely held view that increasing level of coalification leads to increasing aromaticity of coal and kerogen regardless of their origins. This later interpretation is further demonstrated by the contrast between algal (non-vascular) and higher (vascular) plant coals. Data from IR (Speight, 1971), FTIR (Painter and Coleman, 1979), NMR (Miknis et al., 1980) and other (Whitehurst, 1978) investigators indicate that aromaticity of vascular plant coal (ca. 40% to over 90% of the total) is directly related to the coal rank reaching its maximum for anthracite. This means that, in contrast to algal coals, increasing degree of coalification of vascular plant coal leads to higher aromaticity. However, a higher degree of catagenesis may also increase aromaticity of algal and vascular plant coals (Tissot and Welte, 1978). Thus these and other results imply that despite diagenetic alteration, primary similarities or differences (non-vascular vs. vascular origins) between various plant remnants in various geological materials tend to persist under mild/moderate geological conditions long after burial even if this span of geologic time is measured in billions of years. We believe that as sedimentary rocks become older and as the more readily degraded organic constituents are lost during diagenetic evolution the nature of geo-organic matter changes until it assumes constancy of structures which one would expect to be representative of the most stable materials (under mild/moderate geological conditions) of ancient plant precursor organisms. As the lower plant (algae, phytoplanktons and bacteria) geo-organic matter is derived from lipid-enriched humic materials and vascular plant matter originates from cellulose and lignin (Tissot and Welte, 1978), it is reasonable to expect that coals and kerogens of lower plants would have a strikingly different chemical structure (aliphatic vs. aromatic type structures) than those of vascular plant origin.

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