Molecular Characterization of Flash Pyrolysates of Two Carboniferous Coals and Their Constituting Maceral Fractions

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Two high-volatile bituminous Upper Carboniferous coals from the Argonne Premium Coal Set and their constituting liptinite, vitrinite, and inertinite fractions, obtained by density gradient centrifugation (DGC), were characterized by Curie point pyrolysis–gas chromatography–mass spectrometry. A detailed analysis of the pyrolysis products was performed to relate individual macerals to their (plant-derived) precursors. Liptinite fractions were found to be mainly composed of sporinite, the diagenetic product of sporopollenin. Its aliphatic character was reflected in its pyrolysate by the abundance and characteristic distribution of n-alk-1-enes and n-alkanes showing maxima at C_{11} and C_{25}. Moreover, a selective enrichment of aromatic components derived from linear carbon skeletons *via* cyclization and aromatization of functionalized, linear precursors was observed. In the sulfur-rich Illinois No. 6 coal, the addition of abiotic inorganic sulfur species to functional groups was reflected by a selective enrichment of organic sulfur compounds in the liptinite maceral. Diagenetically altered lignin derived from gymnospermous wood is the most likely precursor for vitrinite, the major constituent of both coals. Flash pyrolysates of vitrinite fractions were dominated by alkylbenzenes and alkylphenols. Inertinite fractions exhibited relatively high amounts of (poly)aromatic pyrolysis products. Thermal extraction experiments revealed that these components were mainly present as such adsorbed to or entrapped in the pore system of the maceral matrix.

Introduction

Coal consists of a complex, heterogeneous mixture of higher-plant-derived organic material which has undergone chemical changes related to depositional environment and diagenetic history.[1] Because of their high stability, resistant parts of higher plant material, such as spores, pollen, cuticles, bark, and resin-like secretions, have not been recycled completely in the biosphere and remain in the geosphere, where they became important constituents of coals. These constituents can also be distinguished microscopically by petrographic studies and are defined as macerals. They account for virtually all organic matter in coals. Three types are distinguished: liptinite, vitrinite, and inertinite. Individual maceral fractions can be obtained in two ways. The first is by hand picking of naturally-enriched maceral concentrates. This method is limited to easily

recognizable species, *e.g.*, vitrinite in vitrains and fusinites in fusains. The second is by density separation methods, especially isopycnic density gradient centrifugation (DGC), to separate the macerals.[2-4] The latter method has been successfully applied to obtain petrographically pure maceral fractions from heterogeneous coal samples.[5-10] Individual macerals were observed to

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be characterized by distinct chemical properties such as hydrogen content, heteratom content, and aromaticity, consistent with their different physical behavior.[12]

Analysis of coals and their constituting maceral fractions by FTIR and solid-state ^{13}C NMR provides overall information concerning aliphatic and aromatic moieties present and their diagenetic changes.[13,14] A more detailed molecular characterization, however, cannot be achieved by these spectroscopic techniques. Curie-point pyrolysis in combination with gas chromatography (Py-GC) and with gas chromatography–mass spectrometry (Py-GC/MS) have been applied successfully to assess the distinct chemical composition of petrographically pure density fractions of coals.[9-11] Recent work concerning the identification of complex mixtures of hydrocarbons using authentic standards has contributed significantly to our knowledge of various compound classes in pyrolysates.[16-19] This work can provide "chemical fingerprints" for petrographically pure density fractions on a detailed molecular level. This paper describes the molecular characterization of flash pyrolysates of two Upper Carboniferous coals from the Illinois No. 6 and Lewiston-Stockton seam, and their constituting maceral fractions obtained by density gradient separation using Py-GC and Py-GC/MS. Euramerican Upper Carboniferous coal-forming floras were dominated by five kinds of tropical to subtropical trees: lycopods, tree ferns, calamites, seed ferns, and cordaites.[19] The lycophytes were generally small, short-living trees with a determinate growth, producing large amounts of bark (*i.e.* periderm) but little secondary xylem or true wood. These lycopod trees were growing in peat swamps with a low taxonomic diversity. This is indicated by the existence of plant banks which, over large areas, consist of small numbers of the same type of plants. Periderm, the most abundant tissue type produced by arborescent lycophytes, is generally considered as the main contributor to the biomass of Lower and Middle Pennsylvanian coals.[20] Wood was a relatively minor component of the biomass except in swamps with abundant cordaites or calamites.[19] In the Western Interior Coal Region, marine transgressions have been identified with possible brackish influences on cordaitean-rich swamps, diminishing eastward to *Diaphorodendron* (lycophyte) communities in the Illinois Basin. The Illinois No. 6 and Lewiston-Stockton coals, taken from the Argonne Premium Coal Set,[21] were selected for this study because of their specific chemical and physical properties. The Illinois No. 6 coal is a typical

Table 1. Elemental Analysis (wt %) of Coals Used in This Study[a]

coal	C	H	N	O[b]	S$_{tot.}$	ash[c]	H/C
Illinois No. 6, demin	76.2	5.4	1.5	11.8	5.1	3.87	0.85
Lewiston-Stockton, demin	80.1	5.0	1.5	12.6	0.82	0.35	0.75

[a] Weight percent daf. [b] By difference. [c] On dry weight basis.

high-sulfur coal and the Lewiston-Stockton coal was selected for its high liptinite and inertinite content. The aim of this study is to examine in detail the molecular differences between the density fractions as revealed by flash pyrolysis, to relate specific products to their macromolecular precursor, and to study the diagenetic processes which have altered them.

Experimental Section

Samples. The Illinois No. 6 (APCS 3) and Lewiston-Stockton (APCS 7) coals used for this study were obtained from the Argonne Premium Coal Sample Program.[21] Both coals are of high-volatile bituminous rank and are of Upper Carboniferous (Middle Pennsylvanian) age (*ca.* 300 Ma).[22] The coal samples were mined, stored, and processed under an inert atmosphere as free of oxygen as possible to prevent oxidation. Prior to analysis, both coals were fluid energy mill ground operated with high-pressure nitrogen and demineralized by standard procedures using HCl and HF.[23] Petrographic and analytical data for the two coals are listed in Tables 1 and 2. Coal separations were achieved by density gradient centrifugation (DGC) as previously reported by Dyrkacz and Bloomquist.[3,4] This was performed using a JCF-Z zonal rotor and a Beckman J-21C high-speed centrifuge. The separation medium was CsCl/Brij-35. The collected density fractions were filtered and washed with water, hot water (~80 °C), and finally with ethanol. The fractions were dried at 65 °C in a vacuum oven overnight, weighed and stored under argon. The density profiles (Figure 1, outer graphs) were obtained by the weight of the isolated density fractions (42 in total for both coals). Petrographic analyses of whole coals and density fractions were performed in both blue and white light (1000 counts, 500 per mount) to determine their liptinite, vitrinite, and inertinite maceral content. These data were also plotted in the density profiles (Figure 1, outer graphs) and show the contribution of the individual macerals to the density fractions obtained. Density fractions from both coals, which consisted petrographically of pure liptinite, vitrinite, or inertinite, were selected for chemical characterization by Py-GC and Py-GC/MS. Petrographic and elemental data of these fractions are summarized in Table 3.

Curie Point Pyrolysis–Gas Chromatography (Py-GC). Flash pyrolysis experiments were performed using a FOM-4LX Curie point pyrolysis unit[24] directly connected to the injector of a Hewlett Packard 5890 Series II gas chromatograph. Samples were pressed on flattened ferromagnetic wires (iron/nickel alloy; Curie temperature 610 °C) as described by Venema and Veurink.[25] The on-line flash pyrolysis experiment was performed by inductive heating of the wire and kept at its final temperature for 10 s using a high-frequency generator (Fischer, Model 9425). Separation of the pyrolysis products was achieved by a fused silica column (25m × 0.32 mm i.d.) coated with CP Sil-5 (film thickness 0.45 μm). Helium was

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Table 2. Petrographic Analysis Data (vol %) of Coals[a]

coal	density (g/cm³)	R_0[b]	Sp.	Cut.	Res.	Bit.	Vit.	S-Fus.	Fus.	Ind.	Mi.
Illinois No. 6	1.280	0.46	3.5	0.0	0.6	0.4	90.4	2.8	1.0	1.1	0.2
Lewiston-Stockton	1.277	0.89	10.2	0.3	1.0	0.0	72.8	10.9	1.9	1.7	1.1

[a] Sp. = sporinite; Cut. = cutinite; Res. = resinite; Bit. = bituminite; Vit. = vitrinite; S-Fus. = semifusinite; Fus. = fusinite; Ind. = inertodetrinite; Mi. = micrinite. Analyses performed in both blue light and white light. Results for two samples, 500 counts each. [b] Mean maximum vitrinite reflectance.
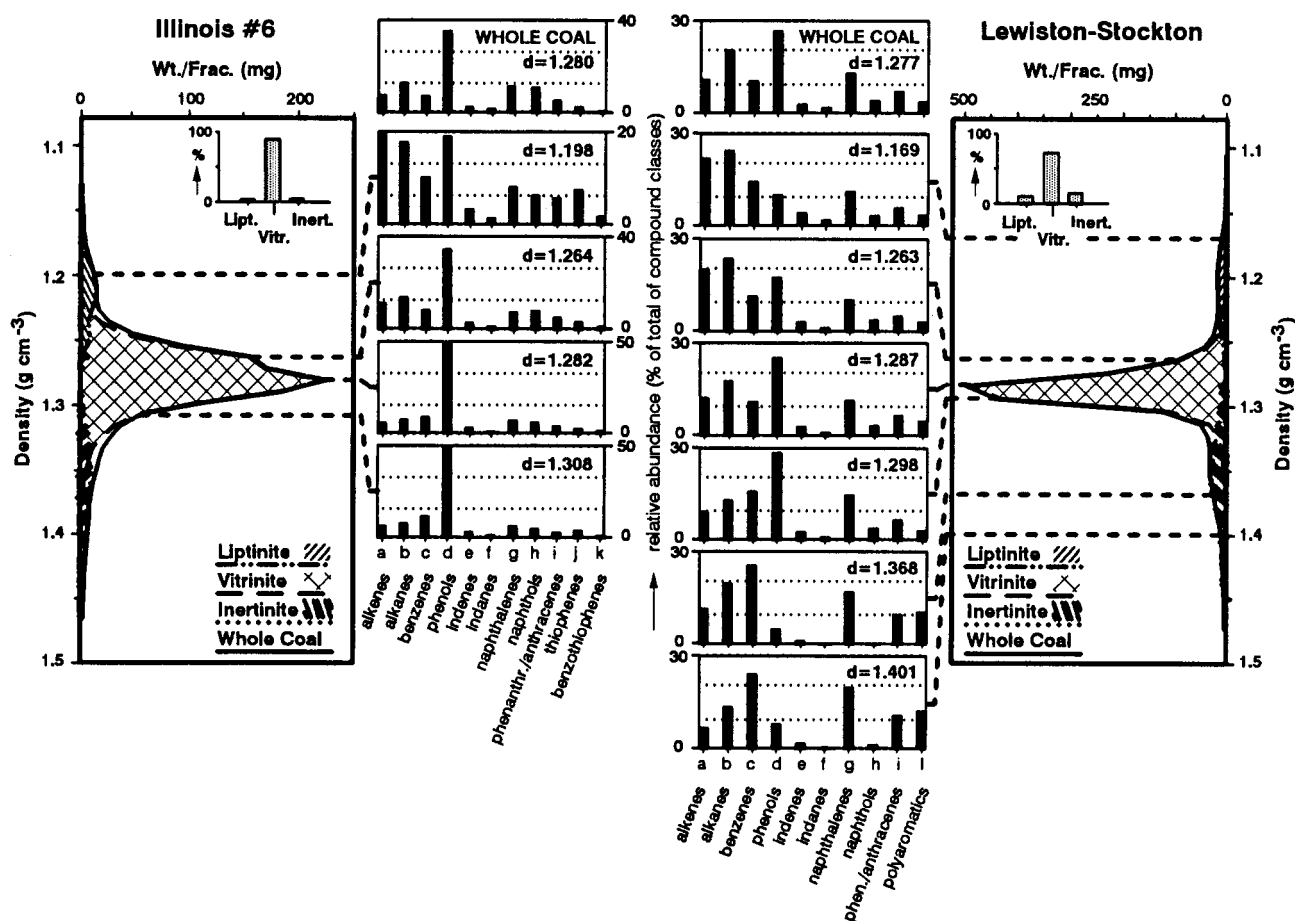
Figure 1. Density profiles and maceral distributions of Illinois No. 6 and Lewiston-Stockton coals (outer graphs). Inset bar graphs show the concentration of maceral groups in the original coal. Normalized bar plots (inner graphs) show the overall distribution of most prominent compound classes in flash pyrolysates (Curie temperature 610 °C) of the whole coals and their liptinite, vitrinite, and inertinite fractions. Selected maceral fractions are indicated in density profiles of both coals. Key: a = n-alk-1-enes and monounsaturated acyclic isoprenoids; b = n-alkanes and saturated acyclic isoprenoids; c = alkylbenzenes; d = alkylphenols; e = alkylindenes; f = alkylindanes, g = alkylnaphthalenes; h = alkylnaphthols; i = alkylphenanthrenes/anthracenes; j = alkylthiophenes; k = alkylbenzo[b]thiophenes; l = polyaromatics (alkylfluorenes/phenalenes, alkylpyrenes/benzofluorenes, alkylchrysenes/benzanthracenes, alkylbenzopyrenes/benzofluoranthenes.

used as carrier gas. The oven was programmed from 0 °C (5 min) to 320 °C (10 min) at a rate of 3 °C/min.

Curie Point Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC/MS). Curie point Py-GC/MS analysis was performed using the same conditions as described by Py-GC, using a similar Curie point device and gas chromatograph connected to a magnetic sector mass spectrometer (VG-70S; operating conditions: cycle time 1.8 s; resolution 1000; mass range 50–900). Relative amounts of the major compound classes in the pyrolysates (Table 4) were determined by integrating the individual peak areas from reconstructed summed mass chromatograms using characteristic m/z values (Table 4). These mass fragments, though the major ions, represent only part of the total mass spectrum. Moreover, the percentage of their contribution is also dependent on the compound class analyzed. The summed peak areas of each compound class, therefore, were multiplied by a correction factor (Table 4). This correction factor was calculated from mass spectra of authentic standards (NBS/Wiley library of mass spectra), selected as being representative for each

compound class. The correction factors were obtained from these spectra by taking the inverse of the percentages of the total ion current of the relevant m/z values and multiplying it by 100. Peak identifications were made by comparison of mass spectral data and retention times with those of authentic standards and published data.[15-18,26-28]

Results and Discussion

The coal samples for this study were taken from the Argonne Premium Coal Set.[21] These coals have well-characterized bulk-chemical and physical properties and were mined, stored, and processed under an inert

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Table 3. Petrographic (vol %) and Elemental (wt %)[a] Analysis Data of Selected Density Fractions

density (g/cm^3)[b]	petrography			elemental analysis				
	Lip.[c]	Vit.	Inert.[d]	C	H	N	O + S + ash[e]	H/C
Illinois No. 6 (APCS 3)								
1.198	96.5	3.5	0	76.1	6.74	1.11	16.1	1.06
1.264	0	98.5	1.5	75.6	5.71	1.45	17.2	0.91
1.282	0	100	0	74.0	5.49	1.45	19.1	0.89
1.308	0	96.5	3.5	75.0	5.46	1.43	18.1	0.87
Lewiston-Stockton (APCS 7)								
1.169	93.5	6.5	0	82.2	7.11	0.88	9.8	1.04
1.263	4	96	0	80.3	5.39	1.61	12.7	0.81
1.287	0	98.5	1.5	80.2	5.07	1.60	13.1	0.76
1.298	0	98.5	1.5	80.5	4.96	1.55	13.0	0.73
1.368	0	7	93	84.0	3.97	1.26	10.8	0.57
1.401	0	1	99	84.3	3.71	1.26	10.7	0.53

[a] Weight percent daf. [b] The densities are the values recorded when half the fraction volume was collected. The density range for a fraction varies from ±0.004 to ±0.006 g cm^{-3}. [c] Total of sporinite, cutinite, resinite, and bituminite. [d] Total of semifusinite, fusinite, inertodetrinite, and mictinite. [e] By difference.

atmosphere to prevent oxidation and/or chemical alterations of the original coal sample. The Illinois No. 6 coal (APCS 3) is a typical high-sulfur coal with low amounts of liptinite and vitrinite macerals. The coal from the Lewiston-Stockton seam (APCS 7) is of higher rank and has relatively high sporinite and inertinite contents. Figure 1 (outer graphs) shows the density profiles of both coals. It is evident that vitrinite is the most dominant maceral in both coals. Petrographic analysis of the individual density fractions revealed a maceral overlap between vitrinite and liptinite at lower densities, and overlap of vitrinite and inertinite at higher densities. These overlaps are considered to arise either through inefficient maceral liberation in the comminution stage, or by natural density variations in different maceral group particles.[3,4] Petrographically pure liptinite, vitrinite, and inertinite fractions from both coals were selected for molecular characterization by Py-GC and Py-GC/MS. Their petrographic and elemental data are summarized in Table 3.

Pyrolysis experiments were performed on nonextracted coal samples. Thermal extraction experiments (Curie temperature 358 °C) of the coal samples revealed that the major compound classes generated (aliphatics, alkylbenzenes, alkylphenols, organic sulfur compounds) at 610 °C are derived mainly or exclusively from macromolecularly-bound precursors. Alkylnaphthalenes and higher polycyclic aromatic compounds, however, were found to be mainly evaporative products. Similar compound distributions were encountered in polycyclic aromatic fractions of pyridine extracts of these coals.[21] Exhaustive extraction with conventional solvents (methanol, dichloromethane, pyridine) has proved, however, ineffective to remove all "free" hydrocarbons, which are either adsorbed or entrapped in the pore system of the coal particles.[29] Consequently, components detected in the pyrolysis experiments performed at 610 °C can, at least partly, be ascribed to the presence of low-molecular-weight substances in the coal samples evaporating under the conditions used.

Figure 2 shows the total ion currents (TIC) of the pyrolysates of the two whole coals and selected density fractions of these coals. The pyrolysates are characterized by the presence of alkylphenols, alkylbenzenes, alkylindenes, alkylindanes, alkylnaphthalenes, alkylnaphthols, alkylanthracenes/-phenanthrenes, polyaromatic components, isoprenoid hydrocarbons, and homologous series of n-alkanes and n-alk-1-enes. Nitrogen-containing compounds (pyrroles) were found to be very low in abundance or absent. Alkylthiophenes and -benzo[b]thiophenes are present in flash pyrolysates of the Illinois No. 6 coal and its density fractions, in accordance with its high-sulfur content (Tables 1 and 3). Clear differences in the compositions of the pyrolysates of the liptinite, vitrinite, and inertinite fractions (Figure 2) were observed. Phenol and alkylphenols are the most prominent aromatic pyrolysis products of both coal samples and can account for up to 50% of the total pyrolysate of the vitrinite concentrates. The flash pyrolysates of the whole coals resemble those of the vitrinite concentrates. This is in concordance with the fact that vitrinite is the most abundant maceral fraction of both coals. Homologous series of n-alkanes and n-alk-1-enes, ranging from C$_5$ to C$_{35}$, dominate the pyrolysates of the isolated liptinite fractions. Other aromatic pyrolysis products which account for the numerous peaks present in the pyrolysates are alkylbenzenes, indenes, indanes, naphthols, and polyaromatic compounds. They can account for up to 80% of the total pyrolysates of the inertinite fractions. Relative amounts of the most important pyrolysis products in the pyrolysates of both the coal samples and their liptinite, vitrinite, and inertinite concentrates are represented in Figure 1 (inner graphs) by normalized histograms. Quantification of various compound classes in the flash pyrolysates was performed by integrating the discrete peaks from summed mass chromatograms of specific m/z values (Table 4), taking into account different response factors for different compound classes. Therefore, the total peak areas of each compound class obtained were multiplied by a correction factor (Table 4). Identifications were based on mass spectral and retention time data which were compared to those of model compounds and of literature data. As a result, "chemical fingerprints" of the density fractions that consists of petrographically pure macerals were obtained by normalizing the concentrations to the total peak area for all compound classes investigated (Figure 1, inner graphs).

Alkylphenols. Phenol and its alkyl-substituted homologues are the major pyrolysis products of both coals and their density fractions, except for the inertinite density fractions in which their occurrence is relatively low (Figure 2). The relatively higher abundance of phenols in vitrinite fractions with a higher density ("pseudovitrinite") has also been observed by Nip et al.[10] Vitrinite, the dominant maceral of both coals, is generally considered to be diagenetically altered lignin, the most abundant constituent of wood in vascular plants.[1] Polysaccharide pyrolysis products and 2-methoxy- and

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Table 4. Characteristic *m/z* Values and Correction Factors Used To Calculate the Relative Abundances and Internal Distribution Patterns of Various Compound Classes in Pyrolysates of Whole Coals and Density Fractions

| compound classes	characteristic fragments	corr factor
C_7 to C_{30} *n*-alkanes	55 + 57	2.9
C_7 to C_{30} *n*-alkenes	55 + 57	4.9
C_0 to C_4 alkylbenzenes	78 + 91 + 92 + 105 + 106 + 119 + 120 + 133 + 134	a
C_0 to C_2 alkylphenols	94 + 107 + 108 + 121 + 122	2.2
C_0 to C_2 alkylindenes	115 + 116 + 129 + 130 + 143 + 144	1.8
C_0 to C_2 alkylindanes	117 + 118 + 131 + 132 + 145 + 146	1.9
C_0 to C_3 alkylnaphthalenes	128 + 141 + 142 + 155 + 156 + 169 + 170	1.8
C_0 to C_2 alkylnaphtols	144 + 157 + 158 + 171 + 172	2.4
C_0 to C_2 alkylanthracenes/alkylphenanthrenes	178 + 191 + 192 + 205 + 206	2.6
C_0 to C_4 alkylthiophenes	84 + 97 + 98 + 111 + 112 + 125 + 126 + 139 + 140	1.5
C_0 to C_2 alkylbenzo[*b*]thiophenes	134 + 147 + 148 + 161 + 162	1.6
polyaromatics		
C_0 to C_1 alkylfluorenes/alkylphenalenes	166 + 179 + 180 + 193 + 194	2.1
C_0 to C_1 alkylpyrenes/alkylbenzofluorenes	202 + 215 + 216 + 229 + 230	1.9
C_0 to C_1 alkylchrysenes/alkylbenzanthracenes	228 + 241 + 242 + 255 + 256	2.2
C_0 to C_1 alkylbenzopyrenes/alkylbenzofluoranthenes	252 + 265 + 266	2.5

a Relative abundances of alkylbenzenes were determined as described by Hartgers *et al.* (1992).
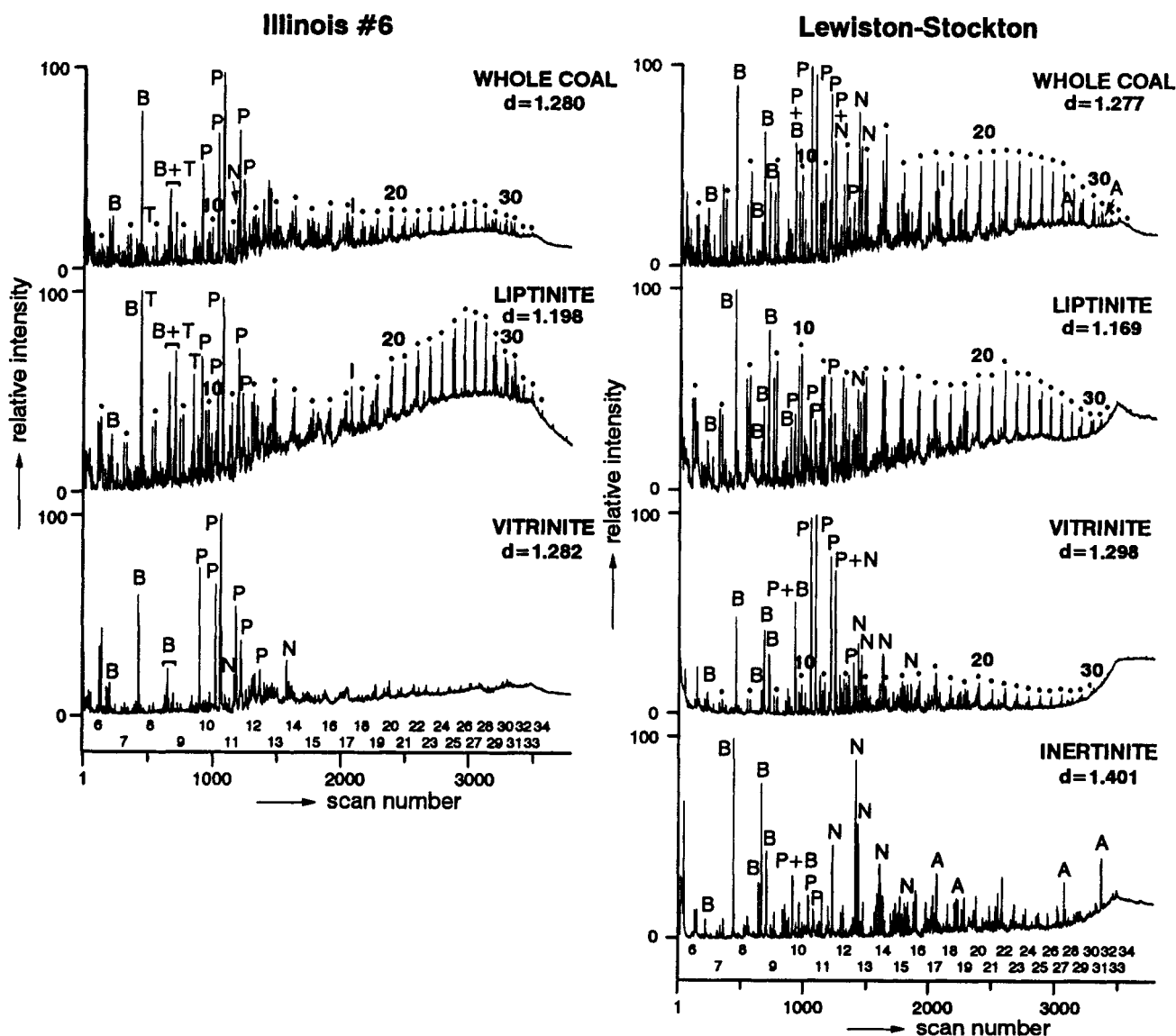
Figure 2. Py-GC/MS traces (Curie temperature 610 °C) of Illinois No. 6 and Lewiston-Stockton coals and their liptinite, vitrinite, and inertinite fractions. *n*-Alkanes are indicated by filled circles. Small numbers along the *x*-axis indicate total numbers of carbon atoms of *n*-alkane/*n*-alk-1-ene doublets. Key: B = (alkyl)benzenes; T = (alkyl)thiophenes; P = (alkyl)phenols; N = (alkyl)naphthalenes; A = polyaromatics; I = monounsaturated acyclic isoprenoids.

2,6-dimethoxyphenols, indicative markers of native lignin-cellulose,[30-32] however, were absent in the flash pyrolysates of the vitrinite density fractions. Phenolic pyrolysis products in pyrolysates of more mature Late

Carboniferous coals are supposed to be derived for the greater part from gymnospermous woody tissues (*e.g.* cordaites or calamites[19]), which, after burial, have undergone a selective decomposition of the cellulose and
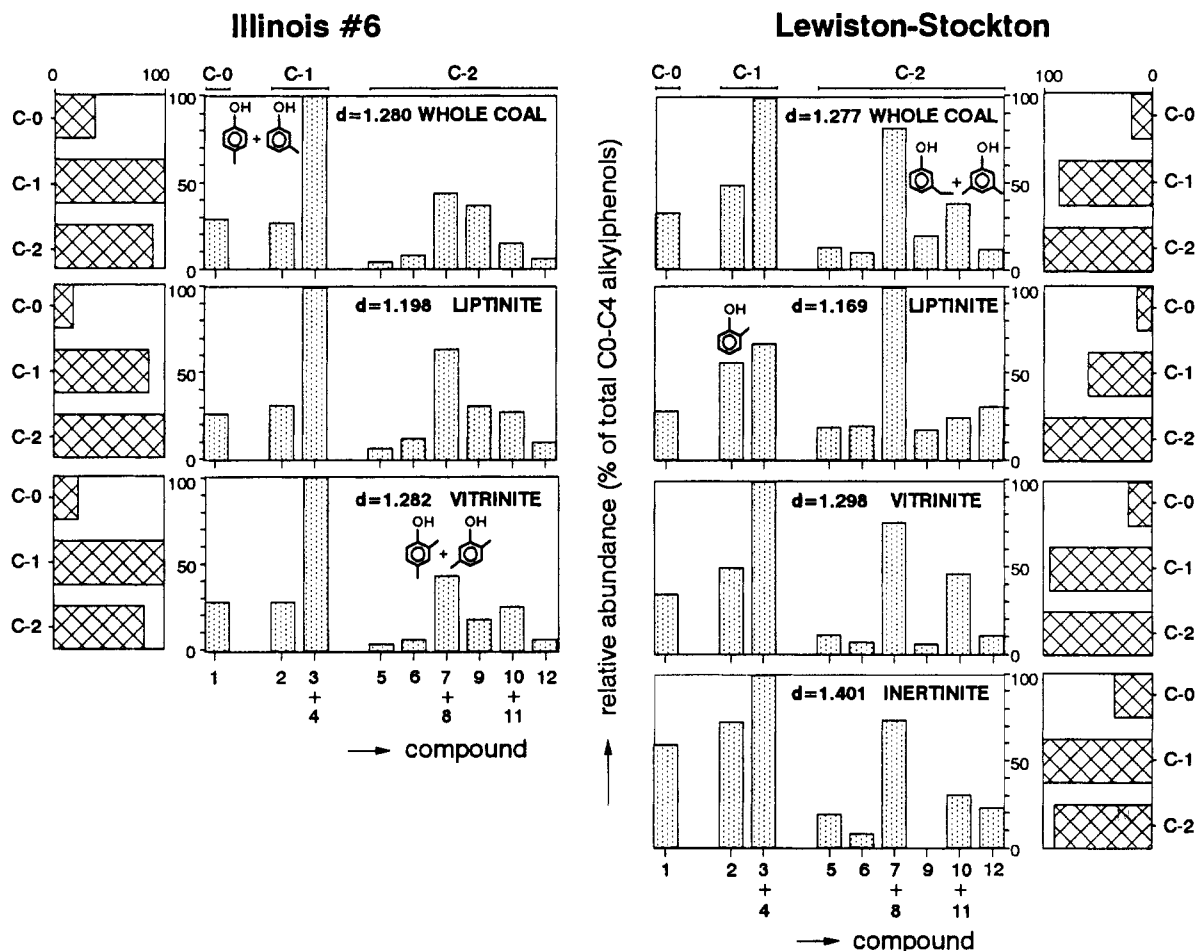
Figure 3. Bar plots showing the carbon number distributions of alkylphenols (outer bar graphs) and the internal distributions of the individual isomers (inner bar graphs) generated upon flash pyrolysis (Curie temperature 610 °C) of Illinois No. 6 and Lewiston-Stockton coals and their liptinite, vitrinite, and inertinite fractions. Peak intensities were normalized to the highest peak present in each distribution pattern. Numbers refer to compounds listed in Table 5.

hemicellulose fractions by microorganisms, leaving a relatively resistant, though modified, lignin-type biomacromolecule.[33] This is substantiated by a combined microscopic and chemical study of native and fossil outer seed coats (testae), revealing major transformations of the original lignin-cellulose constituent, involving demethoxylation reactions of the guiacyl and syringyl monomeric units of the original lignin biopolymer.[34] The preferential and relatively rapid loss of carbohydrates was also monitored by ^{13}C NMR.[35]

Analysis of the internal distribution patterns of alkylphenols in pyrolysates of the coal samples and their constituting maceral fractions revealed no significant variations within one coal sample (Figure 3), suggesting that a common precursor for these pyrolysis products is dispersed through all density fractions. Phenol and the three cresol isomers, 2-, 3-, and 4-methylphenol, are the most abundant pyrolysis products. It should be noted that two pairs of C_2 alkylphenols exhibit almost identical retention and mass spectral data and are, therefore, represented by their summed amounts (components **7** and **8**, and **10** and **11**).[17] In a few cases,

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Table 5. Alkylphenols Identified in Flash Pyrolysates[a]

1	phenol	**7**	2,4-dimethylphenol
2	2-methylphenol	**8**	2,5-dimethylphenol
3	4-methylphenol	**9**	4-ethylphenol
4	3-methylphenol	**10**	3-ethylphenol
5	2,6-dimethylphenol	**11**	3,5-dimethylphenol
6	2-ethylphenol	**12**	2,3-dimethylphenol

[a] Numbers refer to Figure 3.

however, it was observed that 2,4-dimethylphenol and 3,5-dimethylphenol were the dominant isomers present. Similar distribution patterns of phenolic compounds have also been reported in pyrolysates of coalified gymnospermous wood,[13] the major vitrinite precursor of many North American coals. The C_2 alkylphenol cluster was found to be dominated by 2,4-dimethyl- and 4-ethylphenol (components **7** and **9**). A structural model for lignin-derived vitrinite, primarily composed of guiacyl structural units, has been proposed to account for the phenol distribution pattern observed.[13] The native lignin, primarily composed of guiacyl units, was proposed to undergo chemical transformations upon increasing coalification, involving condensation of phenols to diaryl ethers and cyclization of alkyl side chains to form naphthalene structures. It can be assumed that the differences in internal distributions of compound classes as observed between the two coals are related to their different stages of coalification as reflected by their measured vitrinite reflectances (Table 2). Recent studies of native and fossil outer seed coats (testae)

revealed similar chemical changes of lignin.[34] Since the exact pathways of these transformations and the factors controlling them are not clearly known, a straightforward interpretation of the origin and distribution of (alkyl)phenols in pyrolysates of lignites and more mature coals cannot be made.

Tannins, ubiquitously occurring in higher plants and some algae, possess a substantial preservation potential in barks isolated from brown coals.[36,37] These polyphenolic compounds, therefore, can also act as a possible source of alkylphenols in coal pyrolysates. Recently, a new macromolecule from *Botryococcus braunii* race A was reported that contains phenolic moieties.[38] The contribution of these specific macromolecules to the coal samples studied is considered low, since 5-n-alkyl-1,3-benzenediol moieties, conspicuous features of this biopolymer, were absent in the coal pyrolysates. Phenols have also been reported to be an integrated part of sporopollenin.[39,40] Specific pyrolysis products of this oxygenated aromatic part of sporopollenin, like benzaldehyde and acetophenone, were only detected in trace amounts in pyrolysates of the coals and their density fractions. In conclusion, diagenetically altered lignin is believed to be the most feasible precursor for the alkylphenols found in flash pyrolysates of the North American Illinois No. 6 and Lewiston-Stockton coals.

Aliphatic Pyrolysis Products. Aliphatic pyrolysis products are present in all density fractions of both coals, yet their relative amounts are varying (*cf.* Figure 1). Aliphatic constituents appear to be enriched in liptinite fractions, as revealed by relatively high amounts of n-alkanes and n-alk-1-enes in the pyrolysates. Petrographic analyses reveal that the liptinite macerals of both coals consist for the greater part of sporinite (Table 2). A high contribution of "sporopollenins" to these density fractions, therefore, is anticipated. This resistant biopolymer, the structural constituent of the outer walls of spores and pollen from vascular plants (exines), has been the subject of many chemical studies. Based on the products found upon chemical degradation, the building blocks of sporopollenin were proposed to be carotenoids and/or carotenoid esters.[40] However, de Leeuw and Largeau[33] have argued that this assumption is probably wrong and that the carotenoids found were due to an improper purification of sporopollenin. More recent studies suggest the presence of at least two chemically distinct types of sporopollenin.[39,41-43] One type is mainly aliphatic in nature, while the other type is built up of oxygenated aromatic components. Studies on isolated and purified sporopollenins of fossilized water fern spores[44] demonstrated that the aliphatic type is selectively enriched during diagenesis and upon
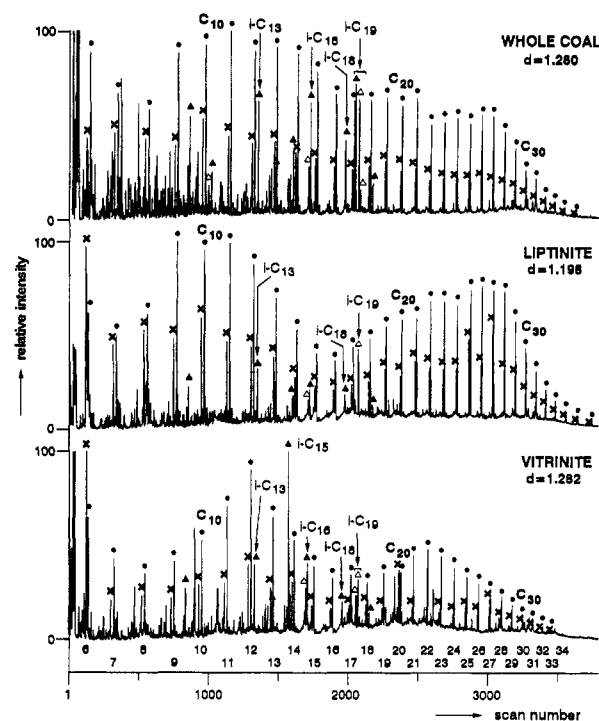
Figure 4. Summed mass chromatograms of m/z 55 + 57 showing the internal distribution of n-alkanes, n-alk-1-enes, and isoprenoid hydrocarbons in pyrolysates of Illinois No. 6 coal and its liptinite and vitrinite fractions. Key: (●) n-alkanes; (×) n-alk-1-enes; (▲) saturated acyclic isoprenoids; (△) monounsaturated acyclic isoprenoids. C_{10} refers to dec-1-ene and decane; i-C_{19} refers to pristenes.

oxidation. This observation seems to be in agreement with the more aliphatic nature of sporinite in coal,[45] the presumed diagenetic product of sporopollenin. A similar phenomenon was observed for weathered coal samples; aliphatic constituents derived from cutan were found to be selectively enriched upon degradation.[46]

Figure 4 shows the summed mass chromatograms of m/z 55 + 57, which reveal the internal distribution patterns of the n-alkanes and n-alk-1-enes in the flash pyrolysates of the Illinois No. 6 coal, and its liptinite and vitrinite fractions. A bimodal distribution can be discerned in the liptinite pyrolysate showing maxima at C_{11} and C_{25}. Similar distribution patterns of n-alkanes and n-alk-1-enes have previously been observed in pyrolysates of fossil microscope massulae and megaspores[44] and some Spanish coals.[47] A common origin from sporopollenin is proposed, supported by the mere fact that highly aliphatic macromolecules from plant remains have shown a high preservation potential upon diagenesis.[48]

Native lignin does not contain long-chain aliphatic moieties.[35] The presence of aliphatic pyrolysis products in the pyrolysates of vitrinite fractions seems to con-

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tradict this observation. As suggested before,[10,49] it is assumed that during coalification aliphatic macromolecules partly disintegrate. Migration of the released low-molecular-weight hydrocarbons is supposed to account for the different distribution of n-alkanes and n-alk-1-enes in the pyrolysates of vitrinite fractions, which show a shift toward hydrocarbons with lower carbon numbers as compared to liptinite fractions (Figure 4). Furthermore, the greater prominence of n-alkanes and n-alk-1-enes in the pyrolysate of the vitrinite fraction of the Lewiston-Stockton coal as compared to the Illinois No. 6 coal (Figure 2) is likely the result of a higher coalification stage of this coal, as reflected by its higher vitrinite reflectance (Table 2). Incorporation of long-chain lipids *via* sulfur linkages ("natural vulcanization") may be an alternative or additional pathway by which aliphatic constituents can be incorporated into the vitrinite fraction of the Illinois No. 6 coal. In line with these observations, n-alkanes produced from coals and coal-bearing strata are assumed to originate from highly aliphatic macromolecules in defined plant tissues, which contribute mainly to the liptinite macerals.[20]

Acyclic isoprenoid hydrocarbons, ranging from C_9 to C_{20}, are relatively important pyrolysis products of the whole coals and their liptinite and vitrinite fractions. Their relative abundances, revealed by the summed mass chromatograms of m/z 55 + 57 (Figure 4), show a relative enrichment in vitrinite fractions. Based on the results of heating experiments of α-tocopherol,[50] prist-1-ene and prist-2-ene are thought to be derived from a thermal breakdown of macromolecularly-bound tocopherols.[51,52] The origin of acyclic isoprenoid hydrocarbons with lower carbon numbers is, however, not completely understood. Flash pyrolysis experiments of tegmens (inner layer of seed coats)[53] generated, apart from prist-1-ene and prist-2-ene as the main degradation products, a whole series of lower acyclic isoprenoids dominated by the C_{10}, C_{16}, and C_{18} compounds. Macromolecularly-bound tocopheryl units, therefore, are proposed as likely precursors for isoprenoid hydrocarbons with lower carbon numbers.

Alkylbenzenes and Alkylnaphthalenes. Alkylbenzenes are prominent pyrolysis products of both coals and are encountered in the pyrolysates of all density fractions (Figure 2). Alkylbenzenes are known to become more prominent pyrolysis products relative to alkylphenols in high-volatile bituminous coals as compared to subbituminous wood samples.[54] Defunctionalization of oxygen-containing aromatic moieties and cyclization of lignin-derived precursors upon increasing coalification have been proposed to lead to the formation of alkylbenzene and alkylnaphthalene moieties in coal samples.[13]

These processes, leading to the formation of uniform precursor moieties, can presumably account for the

similar profiles of the C_0–C_4 alkylbenzenes and the C_0–C_3 alkylnaphthalenes in pyrolysates of the vitrinite fractions of both coals (Figures 5 and 6) and, likewise, of the whole coals. Flash pyrolysates of the liptinite fractions show a relatively higher abundance of so-called "linear" isomers (dark-colored bars) superimposed on this "constant" distribution. Linear alkylbenzenes are thought to be formed *via* cyclization and subsequent aromatization reactions of linear precursors, leading to the formation of monosubtituted or 1,2-disubstituted alkylcyclohexanes and -benzenes.[55,56] It is proposed that the long, unbranched carbon chains originally present in the native sporopollenin have undergone these transformations to a certain extent during early diagenesis, which is reflected in the higher abundance of linear pyrolysis products of the liptinite fractions. Linear alkylbenzenes have been reported to be predominantly present in pyrolysates of kerogens consisting of selectively preserved aliphatic biopolymers derived from the cell walls of the fossilized algae *Gloeocapsomorpha prisca* and *Botryococcus braunii*.[18,57] Linear alkylnaphthalenes, in this respect, can be considered to result from an additional cyclization reaction and subsequent aromatization of the second cyclohexyl ring. Alkylation of benzene or toluene, either upon diagenesis or during pyrolysis, is deemed unlikely in the formation of alkylbenzenes, since the *meta* and *para* isomers are not significantly enriched in the liptinite pyrolysates.

The alkylbenzene distribution patterns in the pyrolysate of the Illinois No. 6 and Lewiston-Stockton coals show a close resemblance to alkylbenzene distributions in pyrolysates of other coals from different geographical locations and geological ages, such as the Arang coal (Tertiary) and Beulah Zap coal (Upper Paleocene).[58] Coal pyrolysates are characterized by a relatively stronger abundance of 1,2,4-trimethylbenzene and its pseudohomologues 2-ethyl-1,4-dimethylbenzene, 1-ethyl-1,2,4-dimethylbenzene, and 1-ethyl-3,4-dimethylbenzene (compounds **19**, **29**, **30**, and **31**; Figure 5). In addition, 1-ethyl-3-methyl- and 1-methyl-3-propylbenzene (compounds **9** and **22**) appear to be enhanced. The latter compounds are supposed to be related to the altered lignin macromolecule, which possesses ether-bound 1,3-dialkylated phenolic moieties.[13] If pyrolysis would induce cleavage of the diphenyl ether bonds, then such a cleavage would produce both 2,4-dialkylated phenols and 1,3-dialkylated benzenes. The origin of 1,2,4-trialkylated benzenes, however, is presently unknown. Their origin might be related to cyclization and aromatization reactions of isoprenoid hydrocarbons involving 1,2- and 1,4-methylshifts. The occurrence of 1-methyl-4-isopropylbenzene (*p*-cymene, **19**) in flash pyrolysates of coals is considered indicative for a contribution of higher land plant material such as polysesquiterpenoids, encountered in Dammar resins and fossilized angiosperm resins.[59] Its relatively low occurrence in the pyrolysates of the coal samples studied

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Illinois #6

Lewiston-Stockton
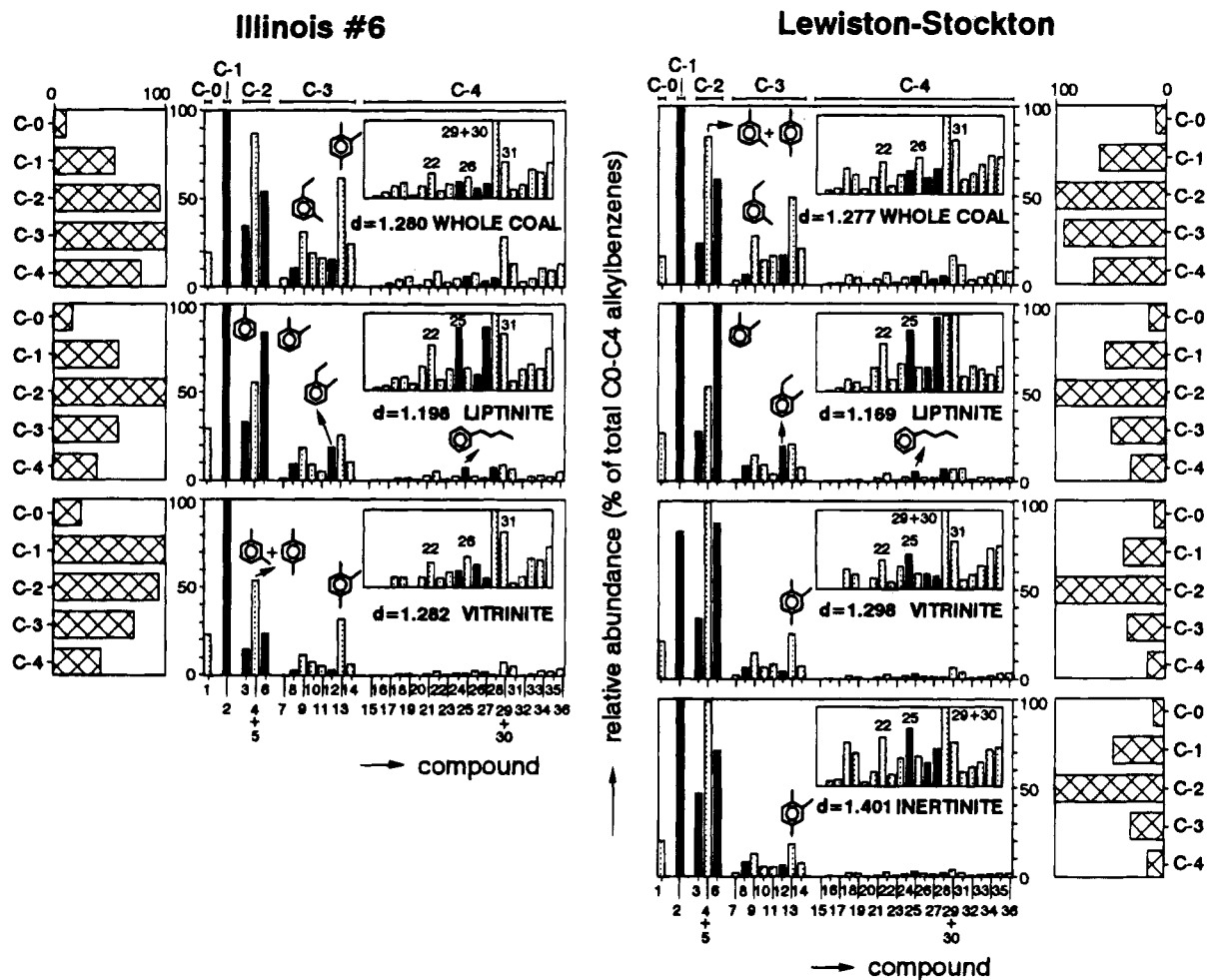
Figure 5. Bar plots showing the carbon number distributions of benzene, toluene, and C_2 to C_4 alkylbenzenes (outer bar graphs) and the internal distributions of the individual isomers (inner bar graphs) generated upon flash pyrolysis (Curie temperature 610 °C) of Illinois No. 6 and Lewiston-Stockton coals and their liptinite, vitrinite, and inertinite fractions. Dark-colored bars indicate components with a linear carbon skeleton. Peak intensities were normalized to the highest peak present in each distribution pattern. Insets show the C_4 alkylbenzene distributions normalized to the most abundant isomer. Numbers refer to compounds listed in Table 6.

Table 6. Alkylbenzenes Identified in Flash Pyrolysates[a]

1 benzene	19 1-methyl-4-isopropylbenzene
2 toluene	20 1-methyl-2-isopropylbenzene
3 ethylbenzene	21 1,3-diethylbenzene
4 *m*-xylene	22 1-methyl-3-propylbenzene
5 *p*-xylene	23 1-methyl-4-propylbenzene
6 *o*-xylene	24 1,4-diethylbenzene
7 isopropylbenzene	25 *n*-butylbenzene
8 *n*-propylbenzene	26 1-ethyl-3,5-dimethylbenzene
9 1-ethyl-3-methylbenzene	27 1,2-diethylbenzene
10 1-ethyl-4-methylbenzene	28 1-methyl-2-propylbenzene
11 1,3,5-trimethylbenzene	29 2-ethyl-1,4-dimethylbenzene
12 1-ethyl-2-methylbenzene	30 1-ethyl-2,4-dimethylbenzene
13 1,2,4-trimethylbenzene	31 1-ethyl-3,4-dimethylbenzene
14 1,2,3-trimethylbenzene	32 2-ethyl-1,3-dimethylbenzene
15 *tert.*-butylbenzene	33 1-ethyl-2,3-dimethylbenzene
16 isobutylbenzene	34 1,2,4,5-tetramethylbenzene
17 *sec.*-butylbenzene	35 1,2,3,5-tetramethylbenzene
18 1-methyl-3-isopropylbenzene	36 1,2,3,4-tetramethylbenzene

[a] Numbers refer to Figure 5.

seems to be in agreement with their petrographic analyses, showing a low contribution of resinite.

Alkylthiophenes and Alkylbenzo[*b*]thiophenes. Alkylthiophenes and -benzo[*b*]thiophenes were only found in pyrolysates of the Illinois No. 6 coal, consistent with its high organic sulfur content (Table 1). Quantitatively, organic sulfur compounds were found to be selectively enriched in pyrolysates of the liptinite frac-

tion (compound classes **j** and **k**, Figure 1). Their absence in the thermal extract (using a Curie temperature of 358 °C) of the Illinois No. 6 coal[60] demonstrates that these components are not present as free compounds in the coal matrix and are, therefore, generated upon pyrolysis. Based on molecular studies on the origin, nature, and fate of organic sulfur compounds in sediments and oils,[61,62] their occurrence is thought to result from inter- and intramolecular reactions of inorganic sulfur species (H_2S, polysulfides) with functionalized lipids during the early stages of diagenesis (*i.e.* peat stage) leading to the formation of organic mono- and polysulfides and alkylthiophenes.[61] A study of organic sulfur constituents in coal[60] revealed that alkylbenzo[*b*]thiophenes can be considered as diagenetic products formed upon increasing coalification *via* cyclization and subsequent aromatization of thiophenes.

The internal distributions of the C_0-C_3 alkylthiophenes and C_0-C_2 alkylbenzo[*b*]thiophenes are shown

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Illinois #6

Lewiston-Stockton
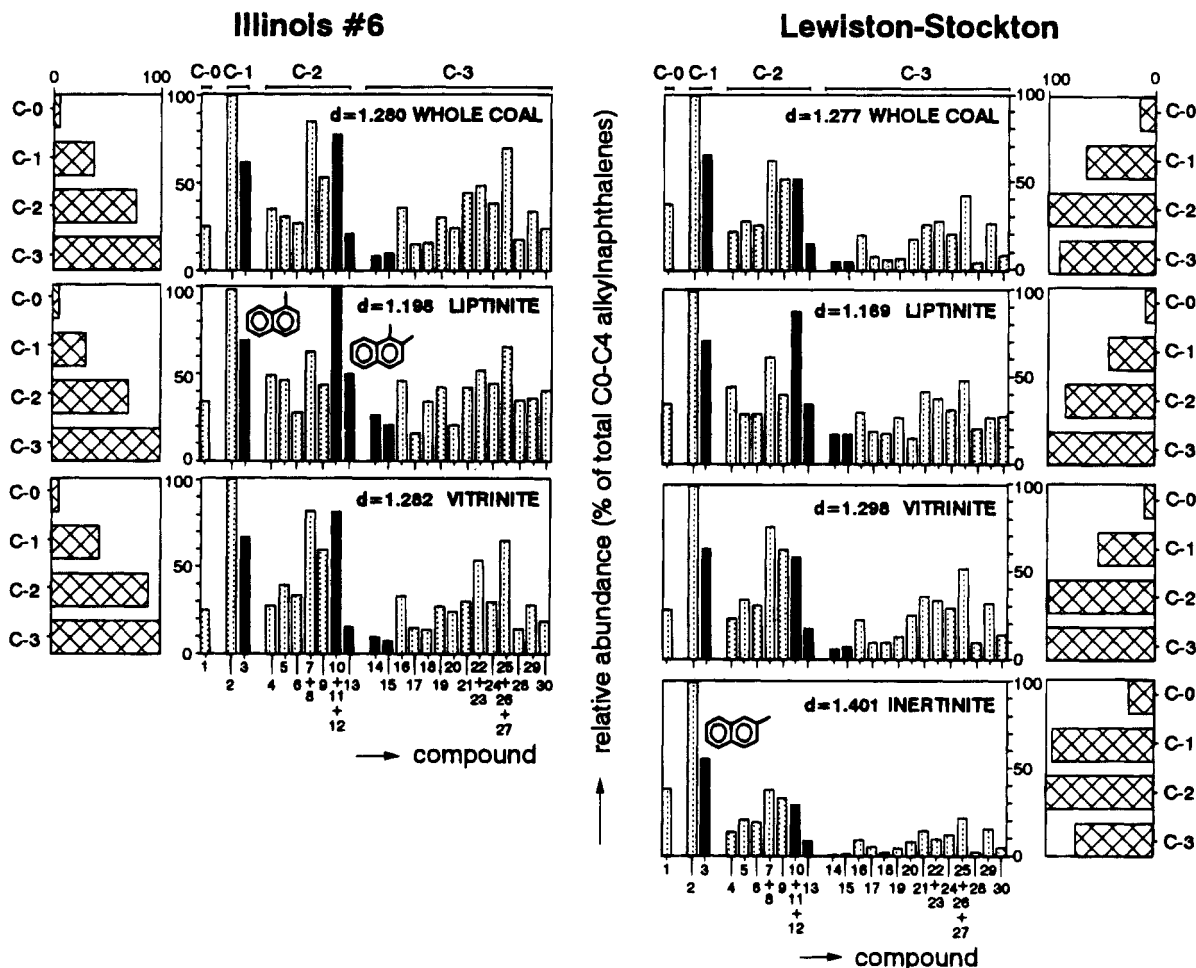
Figure 6. Bar plots showing the carbon number distributions of naphthalene and C_1 to C_3 alkylnaphthalenes (outer bar graphs) and the internal distributions of the individual isomers (inner bar graphs) generated upon flash pyrolysis (Curie temperature 610 °C) of Illinois No. 6 and Lewiston-Stockton coals and their liptinite, vitrinite, and inertinite fractions. Dark-colored bars indicate components with a linear carbon skeleton (for discussion see text). Peak intensities were normalized to the highest peak present in each distribution pattern. Numbers refer to compounds listed in Table 7.

Table 7. Alkylnaphthalenes Identified in Flash Pyrolysates[a]

|			
1	naphthalene	16	ethylmethylnaphthalene(s)
2	2-methylnaphthalene	17	ethylmethylnaphthalene(s)
3	1-methylnaphthalene	18	ethylmethylnaphthalene(s)
4	2-ethylnaphthalene	19	ethylmethylnaphthalenes
5	2,6-dimethylnaphthalene	20	1,3,7-trimethylnaphthalene
6	2,7-dimethylnaphthalene	21	1,3,6-trimethylnaphthalene
7	1,3-dimethylnaphthalene	22	1,4,6-trimethylnaphthalene
8	1,7-dimethylnaphthalene	23	1,3,5-trimethylnaphthalene
9	1,6-dimethylnaphthalene	24	2,3,6-trimethylnaphthalene
10	1,4-dimethylnaphthalene	25	1,2,7-trimethylnaphthalene
11	2,3-dimethylnaphthalene	26	1,6,7-trimethylnaphthalene
12	1,5-dimethylnaphthalene	27	1,2,6-trimethylnaphthalene
13	1,2-dimethylnaphthalene	28	1,2,4-trimethylnaphthalene
14	2-propylnaphthalene	29	1,2,5-trimethylnaphthalene
15	1-propylnaphthalene	30	1,2,3-trimethylnaphthalene

[a] Numbers refer to Figure 6.

in Figure 7. Similar to the alkylbenzenes and -naphthalenes, a general distribution pattern is observed in the pyrolysates, superimposed by components with linear carbon skeletons in the pyrolysate of the liptinite fraction (indicated by dark-colored bars). The biological precursor of these linear compounds is supposed to be similar to that of linear alkylbenzenes. Instead of cyclization, inorganic sulfur species have reacted to the double bond initially present in the sporopollenin biopolymer. A study of the distributions of sulfur-containing pyrolysis products showed that pyrolysates of Type III

kerogens (coals) are characterized by higher relative abundances of thiophenes with isoprenoid and branched skeletons.[63] Reactions of sulfur with lignin was proposed to account for the greater prominence of aromatized and branched carbon skeletons in the coal matrix, yielding 2,4-dimethylthiophene (compound f) and 2-ethyl-4-methylthiophene (compound 1) as the characteristic pyrolysis products. The occurrence of alkylthiophenes with isoprenoid skeletons, such as 2,3,5-trimethylthiophene (compound f) and 5-ethyl-2,3-dimethylthiophene (compound v), is characteristic for marine-derived Type II-S kerogens. Their relatively high abundance in the pyrolysates of the Illinois No. 6 coal seems to coincide with the presence of 1,2,4-trialkyl-benzenes, for which isoprenoidal skeletons are proposed as the common precursor.

Polyaromatics. Figure 8 shows the distribution patterns of the C_0 to C_2 alkylphenanthrenes and -anthracenes in the pyrolysates of both coal samples. Thermal extraction experiments (Curie point pyrolysis at 358 °C) reveal that these compounds are mainly derived from evaporation from the coal matrix. Relative amounts of higher condensed polyaromtic compounds, alkylfluorenes/phenalenes, alkylpyrenes/-benzofluorenes,

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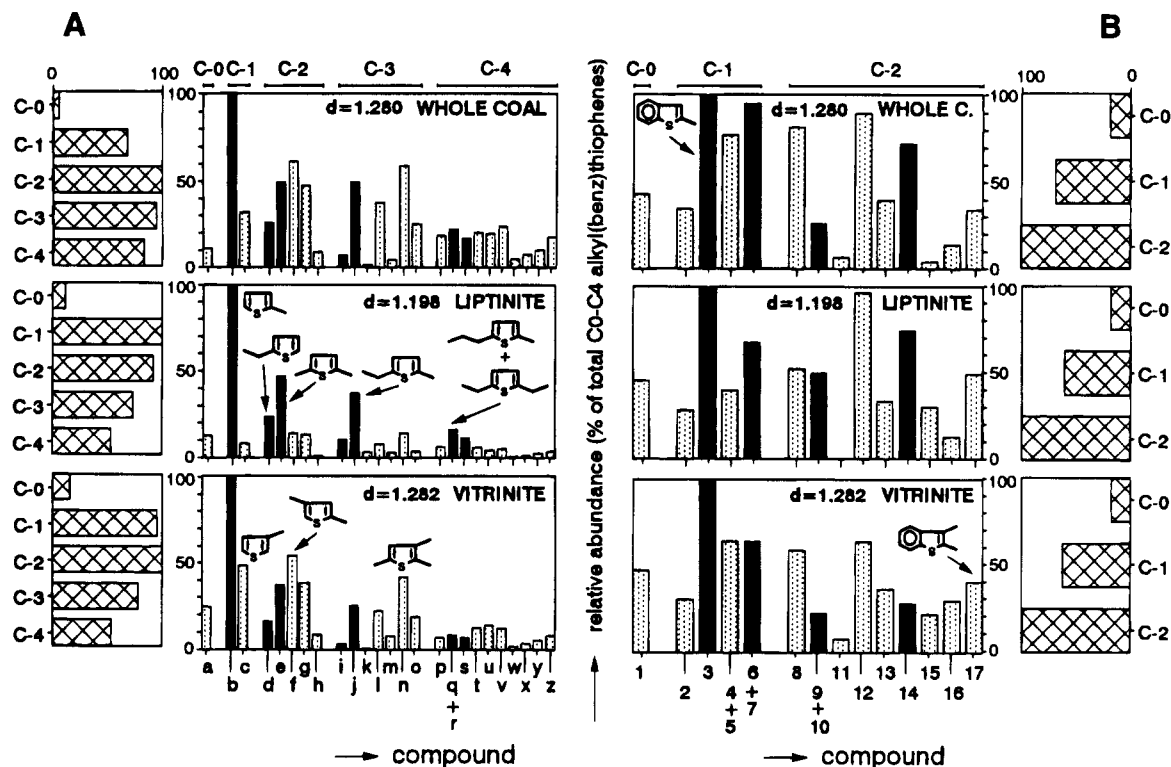
Figure 7. Bar plots showing the carbon number distributions of (A) C_0 to C_4 alkylthiophenes and (B) C_0 to C_2 benzo[b]thiophenes (outer bar graphs) and the internal distributions of the individual isomers (inner bar graphs) generated upon flash pyrolysis (Curie temperature 610 °C) of Illinois No. 6 coal and its liptinite and vitrinite fractions. Dark-colored bars indicate components with a linear carbon skeleton. Peak intensities were normalized to the highest peak present in each distribution pattern. Letters and numbers refer to compounds listed in Tables 8 and 9.

Table 8. Alkylthiophenes Identified in Flash Pyrolysates[a]

|			
a	thiophene	n	2,3,5-trimethylthiophene
b	2-methylthiophene	o	2,3,4-trimethylthiophene
c	3-methylthiophene	p	3-isopropyl-2-methylthiophene
d	2-ethylthiophene	q	2-methyl-5-propylthiophene
e	2,5-dimethylthiophene	r	2,5-diethylthiophene
f	2,4-dimethylthiophene	s	2-butylthiophene
g	2,3-dimethylthiophene	t	2-ethyl-3,5-dimethylthiophene
h	3,4-dimethylthiophene	u	ethyldimethylthiophene
i	2-propylthiophene	v	5-ethyl-2,3-dimethylthiophene
j	2-ethyl-5-methylthiophene	w	ethyldimethylthiophene
k	2-ethyl-3-methylthiophene	x	ethyldimethylthiophene
l	2-ethyl-4-methylthiophene	y	ethyldimethylthiophene
m	3-ethyl-4-methylthiophene	z	2,3,4,5-tetramethylthiophene

[a] Numbers refer to Figure 7A.

Table 9. Alkylbenzothiophenes Identified in Flash Pyrolysates[a]

1	benzo[b]thiophene	10	4-ethylbenzo[b]thiophene
2	7-methylbenzo[b]thiophene	11	2,6-dimethylbenzo[b]thiophene
3	2-methylbenzo[b]thiophene	12	C_2-benzo[b]thiophene
4	5-methylbenzo[b]thiophene	13	C_2-benzo[b]thiophene
5	6-methylbenzo[b]thiophene	14	2,4-dimethylbenzo[b]thiophene
6	4-methylbenzo[b]thiophene	15	C_2-benzo[b]thiophene
7	3-methylbenzo[b]thiophene	16	C_2-benzo[b]thiophene
8	C_2-benzo[b]thiophene	17	2,3-dimethylbenzo[b]thiophene
9	2-ethylbenzo[b]thiophene		

[a] Numbers refer to Figure 7B.

alkylchrysenes/-benzanthracenes, and alkylbenzopyrenes/-benzofluoranthenes, were only determined in the pyrolysates of the Lewiston-Stockton coal and its maceral fractions since these compounds were only present in trace amounts in the pyrolysates of the Illinois No. 6 coat and its density fractions. Their relative amounts were low relative to the alkylphenanthrenes and -anthracenes yielded upon pyrolysis (Figure 9). Polyaro-
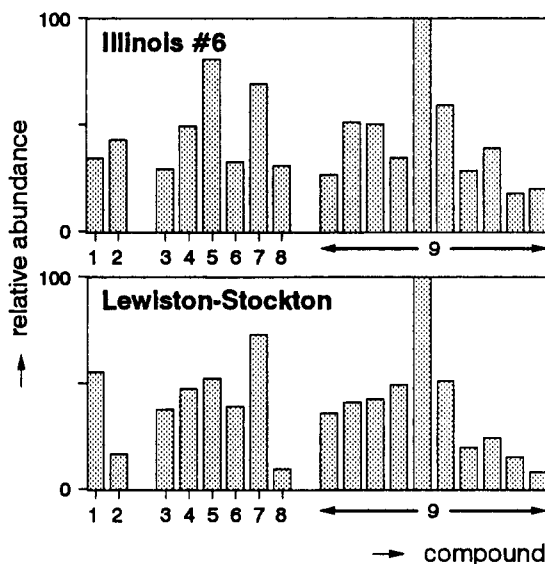

Figure 8. Bar plot showing the internal distribution patterns of alkylphenanthrenes and -anthracenes in the pyrolysates of Illinois No. 6 and Lewiston-Stockton coals. Numbers refer to compounds listed in Table 10.

Table 10. Alkylphenanthrenes/Anthracenes Identified in Flash Pyrolysates[a]

1	phenanthrene	6	1-methylphenanthrene
2	anthracene	7	9-/4-methylphenanthrene
3	3-methylphenanthrene	8	9-methylanthracene
4	2-methylphenanthrene	9	C_2-phenanthrenes/-anthracenes
5	2-methylanthracene		

[a] Numbers refer to Figure 8.

matic compounds are most prominent in inertinite concentrates. This is also reflected in the low H/C ratio's (Table 3).
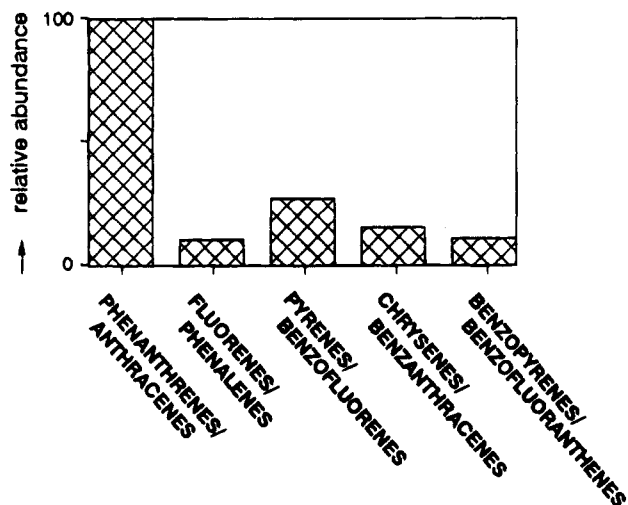
Figure 9. Bar plot showing the relative abundances of polyaromtic compounds in flash pyrolysate of Lewiston-Stockton coal. Peak intensities were normalized to the most abundant compound class present.

Based on the analysis of polyaromatic hydrocarbons in recent lake sediments, a hypothetical reaction scheme for the transformation of abietic and pimaric acids, both components of pine resin, to 1,7-dimethylphenanthrene (pimanthrene) and 1-isopropyl-7-methylphenanthrene (retene) was proposed.[64] A (partial) dealkylation of these compounds, leading to the formation of 1- and 2-methylphenanthrene, however, cannot account for the suite of isomeric compounds identified (Figure 8). Selective alkylation reactions, therefore, of α- and β-amyrin-derived pentacyclic triterpenes cannot be excluded as a (abiogenic) source for this compound class.

The major source of polyaromatic compounds in coals has been attributed to woody plant tissues, which have been modified chemically by paleofires resulting in condensed, aromatic structures.[65,66] Non- and monoalkylated forms dominate the distribution of polyaromatic pyrolysis products (*cf.* Figure 9) suggesting a high-temperature, abiogenic source. An indirect formation from biogenic precursors has been proposed, involving rapid transformations of di-, tri-, and pentacyclic triterpenoid compounds, which are major constituents of conifer resins and higher plant waxes.[64,67-70] Many of the intermediate compounds have been confirmed, giving credence to the hypothetical diagenetic changes proposed. Aromatization of α-amyrin, present in woody plants, was suggested as a possible precursor of chrysene and picene.[71] β-Amyrin, the isomeric form of α-amyrin, has been proposed as an additional precursor for hydrochrysene, which, in turn, is a likely precursor for chrysene.[72]

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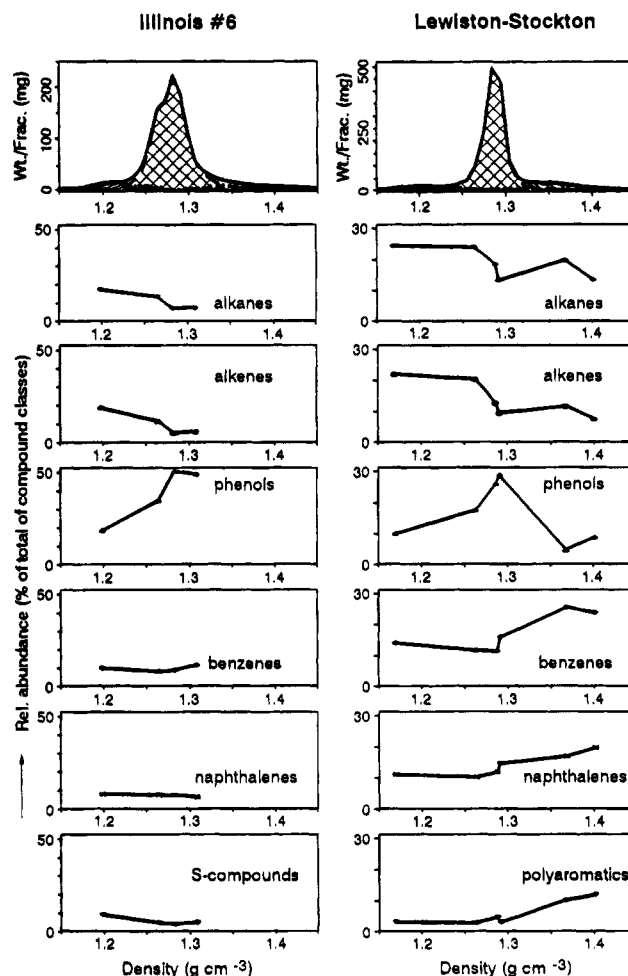
Figure 10. Relative amounts of the most abundant pyrolysis products plotted as a function of the density. Density profiles of both coals are shown at top for reference purposes.

Conclusions

A detailed molecular characterization by Py-GC/MS of petrographically pure density fractions of the Illinois No. 6 and Lewiston-Stockton coals from the Argonne Premium Coal set, obtained by density gradient centrifugation (DGC), was performed. Corresponding maceral types are characterized by similar molecular characteristics, such as gross composition and internal distributions of the most abundant compound classes present. Although no single family of pyrolysis products can be ascribed to one maceral type, a number of families of pyrolysis products show fairly large variations between the different macerals. Phenolic pyrolysis products are mainly associated with vitrinite concentrates, the main maceral of both coals. Organic sulfur-compounds are relatively enriched in pyrolysates of liptinite fractions, and the relative amounts of (poly)-aromatic compounds show an increase upon increasing density (Figure 10). Internal distributions of isoprenoid hydrocarbons, alkylphenols, and polyaromatic components show a consistent distribution pattern which appeared to be independent of the density of the fractions analyzed. Furthermore, analysis of the internal distribution patterns of alkylbenzenes, alkylnaphthalenes, alkylthiophenes, and alkylbenzo[*b*]thiophenes revealed also a general, though characteristic, distribution pattern superimposed by a larger prominence of isomers with linear carbon skeletons in the pyrolysates

of the liptinite fractions. This consistent distribution of individual compound classes is thought, therefore, to be indicative for the presence of plant-derived (macro)-molecules, which are dispersed in all density fractions without being recognized as such by petrographic analyses.

These observations indicate that, in contrast to petrographical analyses, the density fractions based on Py-GC/MS data cannot be assigned as pure macerals on a chemical basis. There might be several reasons for this. Firstly, upon coalification high-molecular-weight constituents start to disintegrate and become fluidized. As a result of their mobility, these relatively low-molecular-weight products can freely permeate the entire coal matrix. This phenomenon, becoming more important upon increasing coalification, is reflected by a less effective separation of the Lewiston-Stockton coal into its (chemically) pure maceral fractions. It is revealed by a greater prominence of n-alkanes and n-alk-1-enes in the pyrolysates of the vitrinite fractions of this coal as compared to those of the Illinois No. 6 coal, which is lower in rank. Thus, these components are not unique for one maceral type. A second possibility is the contribution of aliphatic substances from microorganisms to vitrinite precursors. The incorporation of such substances via intermolecular covalent linkages, like sulfur or oxygen bonds, hampers the complete separation of a coal into its (chemically) pure macerals. Single maceral particles, therefore, may partly be composed of petrographically unobservable species ("submacerals"). These results demonstrate that, despite their distinct chemical characteristics, macerals cannot unambiguously be assigned on a chemical basis exclusively.