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Geochemical Characterization of Maceral Concentrates from Herrin No. 6 Coal (Illinois Basin) and Lower Toarcian Shale Kerogen (Paris Basin)

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GEOCHEMICAL CHARACTERIZATION OF MACERAL CONCENTRATES FROM HERRIN No. 6 COAL (ILLINOIS BASIN) AND LOWER TOARCIAN SHALE KEROGEN (PARIS BASIN)

CARACTÉRISATION GÉOCHIMIQUE DES MACÉRAUX CONCENTRÉS DU CHARBON HERRIN Nº 6 (BASSIN D'ILLINOIS) ET DU KÉROGÈNE DES SCHISTES DU TOARCIEN INFÉRIEUR (BASSIN DE PARIS)

B. Artur STANKIEWICZ, Michael A. KRUGE and John C. CRELLING

Le fractionnement par centrifugation en gradient de densité (CGD) est une méthode physique de séparation des constituants de la matière organique sédimentaire. Cette technique permet la préparation des macéraux concentrés d'un même échantillon, analysables par les méthodes micro-analytiques. Les fractions CGD d'un échantillon du charbon du Bassin d'Illinois (Herrin Nº 6, Carbonifère supérieur) et du kérogène d'un schiste marin du Bassin de Paris (Toarcien inférieur) sont analysées par couplage pyrolyse-chromatographie en phase gazeuse-spectrométrie de masse (py-CG-SM), après extraction par CH_2Cl_2.

Les différences chimiques entre les fractions du charbon sont les plus faciles à reconnaître, indicatives des précurseurs biologiques très distincts. Par exemple, la liptinite ($\rho = 1,12$ g ml^{-1}) est dominée par des composés aliphatiques (n-alcènes et n-alcanes) à chaînes longues, en présence d'alkylbenzènes et d'alkylphénols. La vitrinite (1,29 g ml^{-1}) quant à elle, présente une prédominance d'alkylbenzènes et de composés phénoliques. Les hydrocarbures polyaromatiques (surtout naphtalène, phénanthrène, anthracène et leurs pseudohomologues) sont les composés majoritaires de la fusinite (1,45 g ml^{-1}). Par contre, il y a moins de variété de composés organiques dans le Toarcien. L'étude pétrographique montre que ce kérogène est principalement amorphe. Mais un pic majoritaire ($\rho = 1,18$ g ml^{-1}) à deux épaulements (1,15 et 1,23 g ml^{-1}) peut être résolu sur son profil de densité par la technique CGD multi-étapes. La différence chimique entre ces trois fractions est subtile, mais significative. Comparée aux aliphatiques, la concentration des alkylbenzènes, alkylthiophènes, alkylpyrroles et des composés phénoliques augmente avec la densité. Ceci indique probablement que cette matière organique est principalement d'origine algaire et bactérienne (en proportion variable) et partiellement séparée par CGD.

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ABSTRACT

Density gradient centrifugation (DGC) is a physical method for the separation of sedimentary organic matter into its constituents. Using DGC, it is possible to prepare maceral concentrates from a single sample, which are amenable to microanalysis. DGC fractions from a coal sample from the Illinois Basin (Herrin No. 6, Upper Carboniferous) and from the kerogen of a marine shale sample from the Paris Basin (Lower Toarcian) were analyzed by flash pyrolysis-gas chromatography/mass spectrometry, after extraction by CH_2Cl_2.

Chemical differences between the coal DGC fractions are the easiest to recognize, indicating very distinctive biological precursors. For example, the liptinite fraction ($\rho = 1.12$ g ml^{-1}) is dominated by long-chain aliphatic compounds (n-alkanes and n-alkenes), along with alkylbenzenes and alkylphenols. Vitrinite (1.29 g ml^{-1}) shows a predominance of alkylbenzenes and phenolic compounds. Polyaromatic hydrocarbons (especially naphthalene, phenanthrene, anthracene and their pseudohomologues) are major compounds in the pyrolyzate of fusinite (1.45 g ml^{-1}). In contrast, there is less variety of organic compounds in the Toarcian sample. Petrographi-

cally, this kerogen is primarily amorphous. However, a main DGC peak ($\rho = 1.18$ g ml^{-1}) with two shoulders (1.15 and 1.23 g ml^{-1}) is resolved using multi-step centrifugation. The chemical differences between these fractions are subtle but significant. Concentrations of alkylbenzenes, alkylthiophenes, alkylpyrroles and phenolic compounds increase with density, relative to the aliphatics. This indicates that this kerogen, probably of algal and bacterial origin, is partially separable by DGC.

Key words : Macerals, Coal, Upper Carboniferous, Oil Shale, Toarcian, Kerogene, Hydrocarbons, Illinois, Paris Basin.

CONTENTS

INTRODUCTION

During the past two decades, significant progress has been made in the chemical characterization of kerogen and coal. Techniques including thermal (pyrolytic) and chemical degradation have helped to simplify the complex chemical structure of kerogen. Modern analytical methods, especially gas chromatography-mass spectrometry (GC/MS), have provided the means for characterization of the degradation products. Among the conclusions drawn from these efforts was the recognition of the extraordinary chemical variety and complexity of fossil organic matter. Yet the majority of these efforts were focused on whole coal or kerogen, which in most cases are mixtures of macerals of diverse biologic origin, rather than homogeneous substances. Thus most results to date can at best be termed generalizations about the composition of kerogen and coal.

The distinctive optical properties of macerals and the diversity of their biological precursors (algae, leaf cuticles, charcoal, etc.) lead to the expectation that the various macerals must have different chemical properties as well. It is of interest to investigate such questions as which macerals are most responsible for the chemical nature of a particular coal or kerogen, whether a particular maceral such as vitrinite has a similar chemical signature in different samples, or which liptinitic macerals are the most oil-prone. The development and improvement of the separation methods like density gradient centrifugation (DGC) (DYRKACZ & HORWITZ, 1982; DYRKACZ et al., 1984; CRELLING, 1988, 1989) together with pyrolytic and chromatographic analytical methods have led to several studies on coal macerals (ALLEN & LARTER, 1983; NIP et al., 1988, 1989, 1992; LANDAIS et al., 1989, 1991; KRUGE et al., 1991; KRUGE & LANDAIS, 1992) and a better understanding of the questions mentioned above. The study of kerogen macerals has been more limited (SENFTLE et al., 1987; KRUGE et al., 1989).

The present study involves experiments on maceral separation from the classic Type II kerogen of the Paris Basin, Lower Toarcian, and Upper Carboniferous coal from the Illinois Basin. The immediate objective is the detailed chemical characterization of the macerals from the coal of an economically important seam and the kerogen of a well-known petroleum source rock, as well as a determination of the effectiveness of the DGC technique as applied to kerogen. The ultimate objective is an improved knowledge of the deposition, preservation and alteration of organic matter in sediments.

1. — METHODS

1.1. SAMPLES

A sample of fresh, non weathered, high-volatile B bituminous coal (Herrin No. 6 seam) was obtained from the Illinois Basin Coal Sample Project sample bank (Sample 101). This high-sulphur, Upper Carboniferous coal is dominated by the clarain lithotype and is bright banded with rare vitrain bands (DE MARIS & NELSON, 1990). The sample of the Lower Toarcian shale of the Paris Basin was obtained from Dr. Claude Largeau, and represents Type II kerogen moderately rich in sulphur, with a high carbonate content. The Paris Basin sample contains mostly optically amorphous organic material, partly ultralaminar alginite and partly of bacterial origin (LARGEAU et al., 1994). It was hoped that these two phases would be separable by DGC. All samples are of low maturity (pre- or very early oil window). The low levels of thermal alteration assure that the macerals still retain much of their original distinctive characteristics.

1.2. SAMPLE PREPARATION

Samples were crushed using a < – 200 mesh and extracted with excess CH_2Cl_2 in a sonicator (15 min × 8). The extraction residues were demineralized by standard techniques using 20 % HCl for 24 hr and 48 % HF for the same

time period. The Herrin coal was pulverized further in a Fluid Energy Mill in a nitrogen atmosphere, reducing vitrinite and inertinite macerals to a particle size of several µm. The liptinites are more resistant to breakage and can remain as large as 100 µm. The kerogen concentrate was treated with liquid nitrogen for 1 hour to induce fracturing in the ductile liptinitic macerals and allow for easier breakage during micronization stage. The kerogen concentrate thus prepared was reduced to micron size (85 % of the population) in a Garlock FMT mill in a nitrogen atmosphere. The small particle size permits a better separation of macerals from each other and from the non-acid digestible minerals, especially pyrite, a problem particularly acute in samples of marine origin (KRUGE et al., 1989).

1.3. DENSITY GRADIENT CENTRIFUGATION

The micronized residues were suspended in water by means of a sonicator and layered on the top of a CsCl density gradient, following published methodology (DYRKACZ & HORWITZ, 1982; DYRKACZ et al., 1984; CRELLING, 1988). The mixture was centrifuged in a Beckman J2-21M centrifuge using the zonal rotor which rotated at 10^4 rpm for one hour. The gradient was measured and the density of approximately 35 fractions was measured using a Mettler density meter. The density fractions were recovered by filtration for chemical and petrological analysis. In addition to the normal DGC processing, which covers a density range of 1.0 to 1.6 g ml^{-1}, "high resolution" separations (HRDGC) were performed, using a narrower density range (DYRKACZ et al., 1984; CRELLING, 1989; NIP et al., 1992). The HRDGC density ranges are determined from examination of the full profile and in this case, cut points for the Herrin sample were chosen at 1.25 and 1.34 g ml^{-1} and for the Toarcian at 1.3 g ml^{-1} (Fig. 1). A fresh aliquot of the kerogen was centrifuged in uniform solutions of these densities for preconcentration, then subjected to HRDGC. This permits the collection of larger quantities of the less abundant macerals than is possible by standard DGC alone and allows for improved separations.

1.4. PETROGRAPHY

White light and fluorescence microscopy was performed on whole rock and density fractions of the Paris Basin and the Illinois Basin samples. Reflectance measurements were taken to determine maturity using rotational reflectance properties of the vitrinite maceral (HOUSEKNECHT et al., 1993).

1.5. PYROLYSIS-GC/MS

Flash pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) of the density fractions was performed using a CDS 120 pyroprobe, coupled to an HP 5890 gas chromatograph with an HP 5970 Mass Selective Detector and a 25 m HP-1 column (0.2 mm i.d., film thickness 0.33 µm). Up to 2 mg of each sample was pyrolyzed in a flow of helium for 20 sec inside a platinum coil at 610 °C, as measured by a thermocouple in the sample holder. The column oven

was operated under the following program : isothermal for 5 min at 0 °C, temperature programmed at 5 °C/min up to 300 °C, and then isothermal for 15 min. The MS was operated in full scan mode (50-550 Da, 0.86 scans/sec, 70eV ionization voltage). Peaks were identified based on mass spectra and GC retention times, with reference to the U. S. National Bureau of Standards, mass spectral library and some literature (RADKE et al., 1990; DOUGLAS et al., 1991; HARTGERS et al., 1992; NIP et al., 1992; SINNINGHE DAMSTÉ et al., 1992a, 1992b, 1993). For each sample, all compounds listed in Table I were quantified, using the ions specified. Peak areas were normalized to the sum of all peaks quantified in the sample.
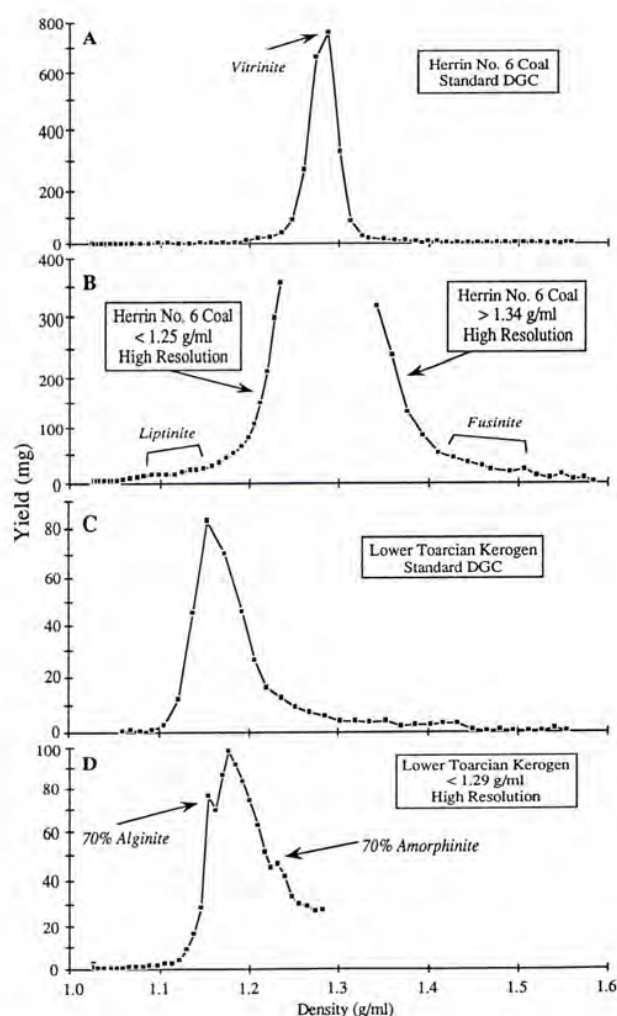

FIGURE 1

Density gradient profiles of
A) Herrin No. 6 coal, B) two Herrin No. 6 coal preconcentrates
with r < 1.25 and r > 1.34 g ml^{-1},
C) Lower Toarcian kerogen from the Paris Basin and
D) Lower Toarcian kerogen preconcentrate with r < 1.29 g ml^{-1}.

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TABLE I

Compounds and MS ions used in quantification

Compounds	MS Ions (m/z)
C_6-C_{27} n-alk-1-enes	55
C_6-C_{28} n-alkanes	57
Methylbenzene (toluene)	91 + 92
C_2-alkylbenzenes (incl. xylenes)	91 + 106
C_3-alkylbenzenes	105 + 120
Naphthalene	128
Methylnaphthalenes	141 + 142
C_2-alkylnaphthalenes	141 + 156
C_3-alkylnaphthalenes	155 + 170
Indene	115 + 116
Methylindenes	115 + 130
C_2-alkylindenes	129 + 144
Phenanthrene & anthracene	178
Methylphenanthrenes & methylanthracenes	191 + 192
C_2-alkylphenanthrenes & alkylanthracenes	191 + 206
Pyrene & fluoranthene	202
Methylpyrenes & methylfluoranthenes	216
C_2-alkylpyrenes & alkylfluoranthenes	230
Phenol	94
Methylphenols (cresols)	107 + 108
C_2-alkylphenols	107 + 122
Methylthiophenes	97 + 98
C_2-alkylthiophenes	97 + 112
C_3-alkylthiophenes	111 + 126
Methylpyrroles	80 + 81
C_2-alkylpyrroles	94 + 95

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TABLE II

Maceral composition of the Herrin No. 6 coal sample

Maceral	Volume %
Vitrinite	88.6
Total Inertinite	5.2
Fusinite	3.7
Semifusinite	0.9
Micrinite	0.6
Total Liptinite	6.2
Sporinite	2.1
Cutinite	2.9
Resinite	1.2

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ml^{-1}, which is a mixture of the amorphinite (60 %) and alginite (40 %), a shoulder at 1.15 g ml^{-1} (Pl. 2, fig. C) mainly composed of alginite (70 %) and a shoulder at 1.23 g ml^{-1} (Pl. 2, fig. D), which is mostly amorphinite (70 %) mixed with particles of alginite. Petrographic examination of a higher density fraction (1.28 g ml^{-1}) revealed a similar predominance of the amorphous matter (80 %) over alginite. HRDGC provided better, but not complete, separation of the amorphous material from the alginite, which suggests that organic matter present in the sample contains both well-preserved algal bodies and algal material which has undergone various degrees of bacterial degradation. Vitrinite reflectance measurements indicate that the Paris Basin kerogen has an $R_o$max = 0.40 % and Herrin No. 6 coal has an $R_o$max = 0.42 %, so both samples are at *ca.* the same low level of thermal alteration.

2 — RESULTS

2.1. ORGANIC PETROGRAPHY

The Herrin coal sample is primarily composed of vitrinite (Table II). Standard GDC was adequate for the preparation of a high purity vitrinite concentrate. The main peak at 1.29 g ml^{-1} is dominated (97 %) by vitrinite with very minor liptinitic contamination (Fig. 1A and Pl. 1, fig. A). HRDGC was employed to isolate the minor macerals. The HRDGC fraction between 1.42 and 1.5 g ml^{-1} contains inertinite, mostly fusinite and semifusinite with only traces of vitrinite (Pl. 1, fig. B). In the liptinite density range (1.0-1.2 g ml^{-1}) no distinct peaks of the particular macerals were detected. Careful observation shows that no satisfactory separation of the single liptinite macerals was obtained in this sample, even with HRDGC (Fig. 1B). However the part of the profile between 1.09 and 1.15 g ml^{-1} represents a clean liptinite concentrate (Pl. 1, fig. C and D) containing mixed cutinite (40 %), resinite (35 %) and sporinite (20 %) with minor vitrinite (5 %). HRDGC could not provide further separation of those macerals, probably due to the low overall amount of those macerals in the coal (7 %).

The dominant maceral in the Paris Basin kerogen is brownish-fluorescing amorphinite (Pl. 2, fig. A and B) with minor (10 %) yellow-fluorescing telalginite (*Tasmanites* and rare Dinoflagellates). The Toarcian kerogen has a main peak at 1.16 g ml^{-1} on the standard DGC profile, which is a mixture of amorphinite (60 %) and the alginite (40 %). The HRDGC profile of the preconcentrated (ρ < 1.30 g ml^{-1}) kerogen treated with liquid nitrogen shows a main peak at 1.18 g

2.2. ORGANIC GEOCHEMISTRY

2.2.1. General characteristics

Total ion current chromatograms of the three main density fractions of the Herrin No. 6 coal (liptinite, vitrinite and fusinite) provide a general overview of their chemical characteristics (Fig. 2). Pyrolyzates of these fractions reveal major contributions of n-alk-1-enes, n-alkanes, alkylbenzenes, alkylthiophenes, alkylphenols, alkylnaphthalenes and alkylphenanthrenes in different proportions depending on maceral type. The liptinite sample (a mixture of cutinite, resinite and sporinite) exhibits a predominance of the C_7-C_{31} n-alkenes and n-alkanes over aromatic compounds, as recognized in previous studies (NIP *et al.*, 1989, 1992). Alkylthiophenes are also important, as the parent coal is rich in sulphur. The vitrinite pyrolyzate is strikingly different, with C_0-C_2 alkylphenols as dominant compounds along with C_1-C_3 alkylbenzenes and C_0-C_2 alkylnaphthalenes, in accord with results obtained for other vitrinites by SENFTLE & LARTER (1987) and NIP *et al.* (1992). The highly aromatic nature of the fusinite pyrolyzate is indicated by the dominance of polyaromatic hydrocarbons such as C_0-C_3 alkylnaphthalenes and C_0-C_2 alkylphenanthrenes and alkylanthracenes. The C_1-C_3 alkylbenzene series are still abundant but phenols are less important. Concentrations of aliphatics are very low.

The Toarcian kerogen is dominated by amorphous organic matter with minor telalginite. As discussed above, the best HRDGC separation that was achieved produced two
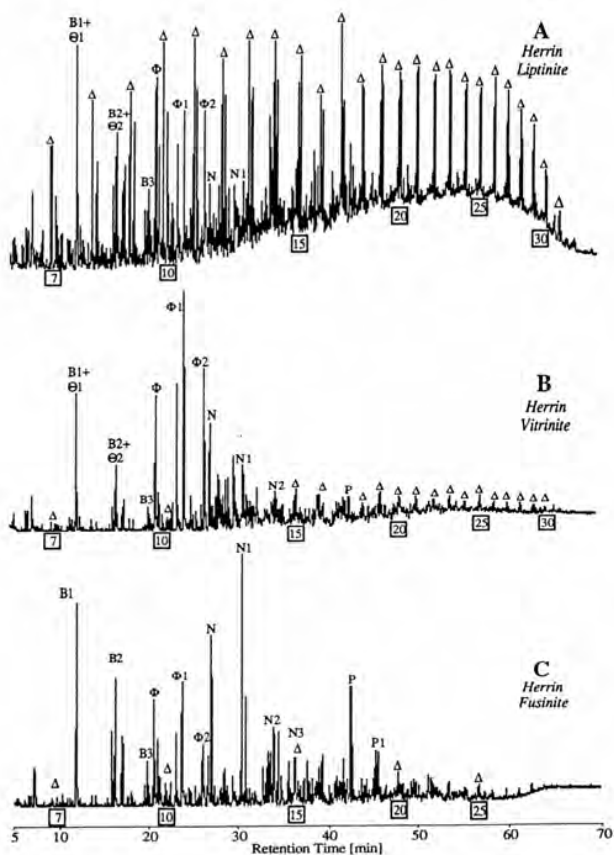
FIGURE 2

Total ion current of the pyrolyzates of the maceral fractions separated by DGC from the Herrin No. 6 coal. Key for the peaks – Bn : alkylbenzenes, Φn : (alkyl)phenols, Θn : (alkyl)thiophenes, Nn : (alkyl)naphthalenes, Φn : (alkyl)phenanthrenes, where "n" indicates the extent of alkyl substitution (0 : none, 1 : methyl, 2 : dimethyl or ethyl, etc.). Δ-pairs of n-alk-1-enes and n-alkanes. Number below chromatograms indicate the carbon number of the alkene/alkane pairs.
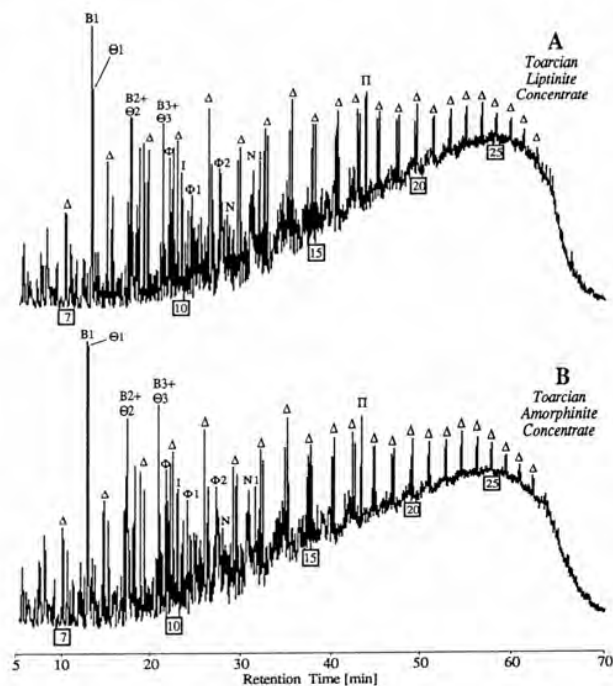

FIGURE 3

Total ion current of the pyrolyzates of the maceral fractions separated by DGC from the Toarcian Paris Basin kerogen : A) alginite concentrate, B) amorphinite concentrate. Key for the peaks – I : indene, Π : prist-1-ene. Other peaks as in Fig. 2.

maceral concentrates, one with 70 % alginite, the other 70 % amorphinite, visible as shoulders on the main DGC peak (Fig. 1D). Py-GC/MS analysis indicates that these two concentrates are chemically similar (Fig. 3), even though they are petrographically distinct. The n-alk-1-enes and n-alkanes from C_7 to C_{29} are the major constituents of the pyrolyzates, along with the C_1-C_3 alkylbenzenes and alkylthiophenes. However, the latter compounds are noticeably more abundant in the heavier fraction (Fig. 3B). Details of these subtle but significant differences are more evident in the quantification results, discussed below.

2.2.2. Aliphatic hydrocarbons

The n-alkane and n-alkene distributions for the pyrolyzates are more clearly seen on the m/z 55+57 mass chromatograms than on the total ion current traces. The liptinite fraction from the Illinois coal has a series from C_6 to C_{31} with a relatively high abundance of the long chain members

(Fig. 4A). This feature is also apparent in the vitrinite pyrolyzate. In contrast, the Toarcian kerogen aliphatics also extend from C_6 to C_{31}, but the concentration of individual homologues decreases with increasing carbon number (Fig. 4B). The apparent low abundance of the C_6-C_8 aliphatics is an artifact of the analytical conditions. The percentage of the aliphatic compounds decreases from liptinite to vitrinite to fusinite for the coal fractions (Fig. 5). The Toarcian alginite concentrate is somewhat more aliphatic than the amorphinite concentrate, but the coal liptinite is even more so.

2.2.3. Alkylbenzenes

The distribution of the C_1-C_3 alkylbenzenes is similar in all the investigated coal fractions, in which toluene is the most abundant in the series, coeluting m- and p-xylenes form the dominant C_2 peak and 1, 2, 4-trimethylbenzene is the major C_3 isomer (Fig. 6A). However, the overall relative abundance of the benzene group increases from liptinite to fusinite (Fig. 7). Toluene is still the major alkylbenzene peak in the Toarcian amorphinite concentrate, but the relative abundances of o-xylene, 1-ethyl-2-methylbenzene and 1,2,3-trimethylbenzene are greater than in the coal (Fig. 6B). There is a small relative increase in alkylbenzene content from the alginite to the amorphinite concentrates (Fig. 7). Coincidentally, the relative alkylbenzene concentrations of the Toarcian samples are close to that of the Herrin fusinite (Fig. 7).
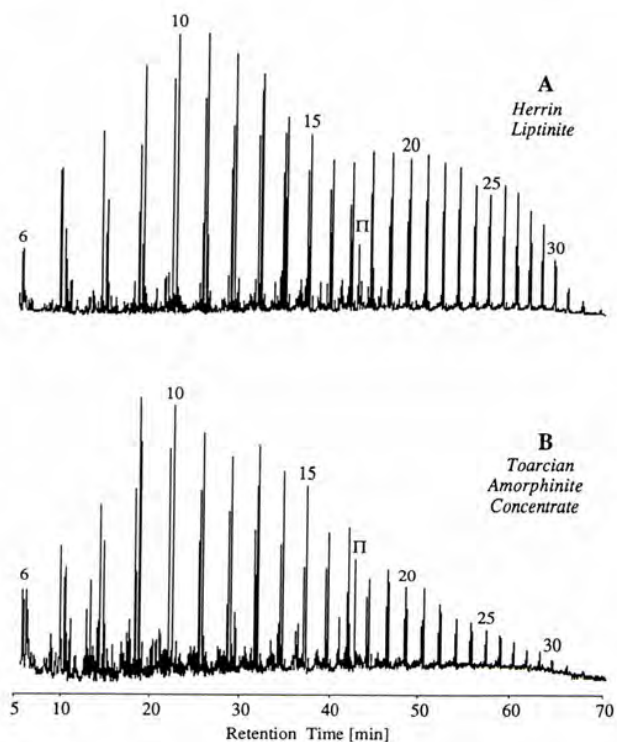
FIGURE 4

Summed mass chromatogram (m/z 55 + 57) illustrating
the distribution of the n-alk-1-enes and n-alkanes in the
A) liptinite fraction of the Herrin No. 6 coal and
B) amorphinite of the Toarcian kerogen.
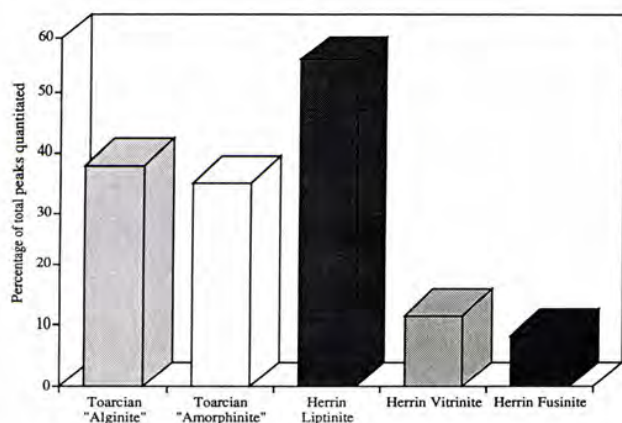Numerals are carbon numbers, Π : prist-1-ene.

FIGURE 6

Composite mass chromatograms of m/z 91 + 92, 91 + 106,
and 105 + 120 showing distribution of the C_1-C_3 alkylbenzenes in
A) Herrin vitrinite and B) Toarcian kerogen. Key – a : toluene,
b : ethylbenzene, c : m + p-xylene, d : o-xylene,
e : 1-ethyl-3-methylbenzene, f : 1-ethyl-4-methylbenzene,
g : 1,3,5-trimethylbenzene, h : 1-ethyl-2-methylbenzene,
i : 1,2,4-trimethylbenzene, j : 1,2,3-trimethylbenzene.
Chromatograms are normalized to peak "a".

FIGURE 5

Relative concentrations of aliphatics (n-alkenes + n-alkanes)
present in the Toarcian and Herrin DGC fractions,
as a percentage of total peaks quantitated.
See Tab. I for a complete list of peaks quantified
for use in these calculations.

FIGURE 7

Relative concentrations of the principal families of aromatic
hydrocarbons present in the Toarcian and Herrin DGC fractions,
as a percentage of total peaks quantified. See Tab. I for a
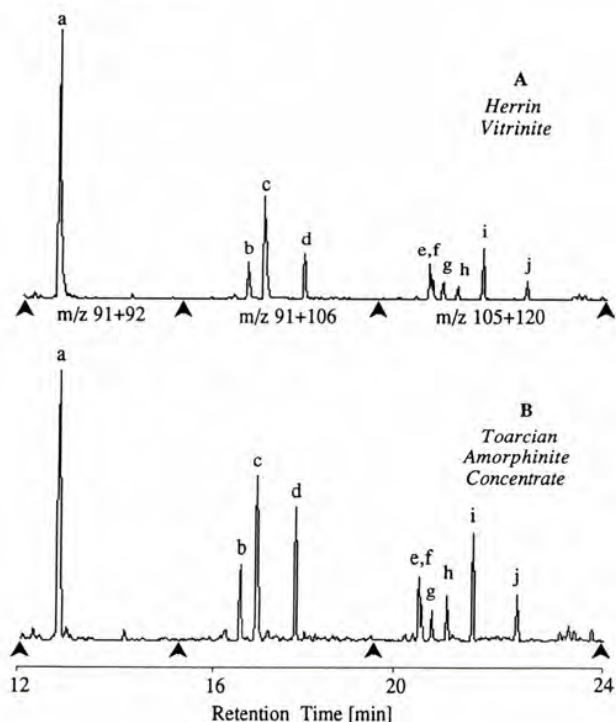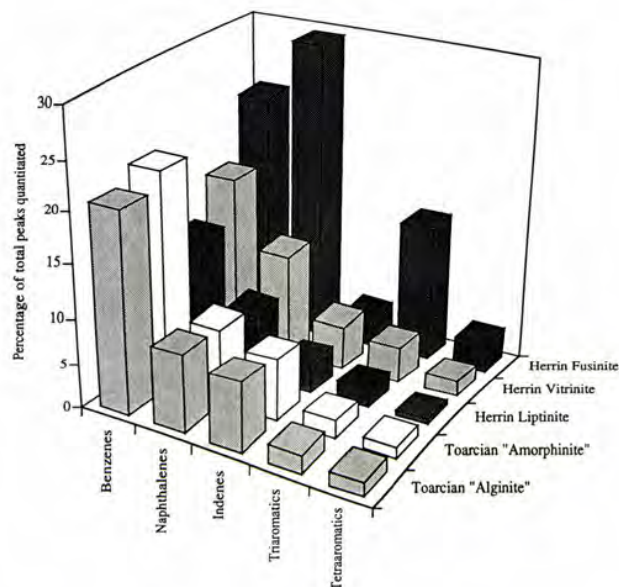complete list of peaks quantitated for use in these calculations.

2.2.4. Polyaromatic hydrocarbons

The naphthalenes are the most abundant of the polynuclear aromatic hydrocarbons present in the coal and kerogen macerals. Figure 8 shows the distributions of C_3-alkylnaphthalenes in the liptinite, vitrinite and amorphinite concentrate pyrolyzates. The liptinite has a strong predominance of 1,2,5-trimethylnaphthalene, whereas in the vitrinite the 1,6,7- / 1,2,6- and 1,4,6- / 1,3,5- coeluting trimethyl isomers are dominant. The relative abundance of the C_0-C_3 naphthalenes increases from liptinite to vitrinite to fusinite, and in the latter fraction they are the major components (Fig. 2 and 7). The Toarcian amorphinite concentrate is dominated by 1,4,6- / 1,3,5- and 1,3,6-trimethylnaphthalenes (Fig. 8C). Ethylmethylnaphthalenes are also important C_3 isomers. 1,2,5-trimethylnaphthalene, which is characteristically prominant in the coal liptinite, is relatively unimportant in the kerogen.
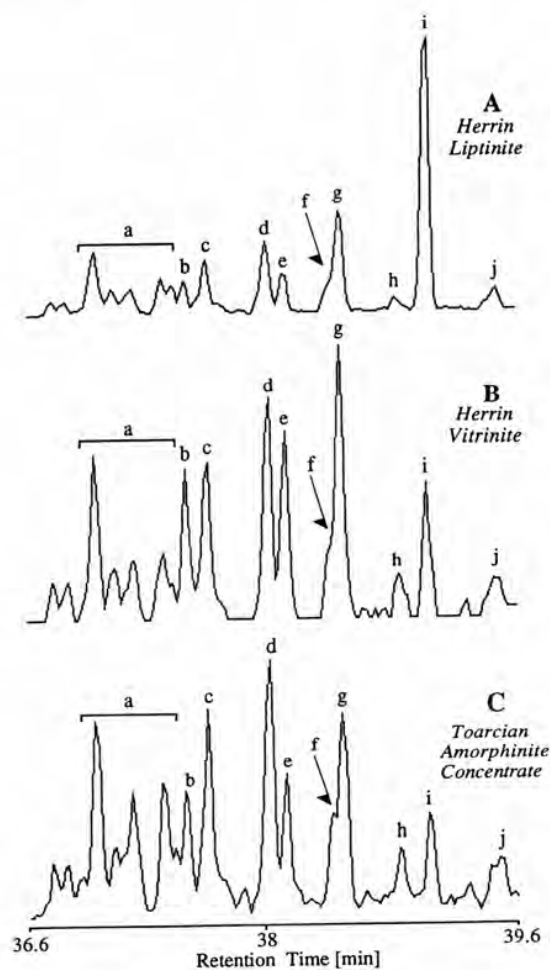
Triaromatic hydrocarbons form the second major group of polyaromatics in the maceral pyrolyzates. Figure 9 shows the distributions of the 11 resolvable C_2-alkylphenanthrene and alkylanthracene peaks. 1,7-dimethylphenanthrene is by far the dominant peak in the Herrin liptinite (peak "i", Fig. 9A). It is also strong in the vitrinite, along with dimethylanthracenes and 2,6- and coeluting 1,3- / 2,10- / 3,9- / 3,10- and 1,6- / 2,9-dimethylphenanthrenes (peaks "g" and "h", Fig. 9B). The latter two coelution peaks predominate in the Toarcian amorphinite kerogen (Fig. 9C). C_0-C_2 triaromatics are the most important in fusinite (Fig. 7).

Together with the naphthalene group, the C_0-C_2 alkylindenes are among the most important aromatic hydrocarbons in the Toarcian kerogen fractions, whereas for the coal macerals, they are relatively minor components, especially in the case of fusinite (Fig. 7). Tetraaromatic hydrocarbons (C_0-C_2 alkylpyrenes and alkylfluoranthenes) present in the

FIGURE 8

Summed mass chromatograms (m/z 155 + 170) illustrating the distribution of the C_3-alkylnaphthalenes in A) Herrin liptinite, B) Herrin vitrinite and C) Toarcian kerogen. Key to peaks : a : EMN, b : 1,3,7-TMN, c : 1,3,6-TMN, d : 1,4,6-TMN + 1,3,5-TMN, e : 2,3,6-TMN, f : 1,2,7-TMN, g : 1,6,7-TMN + 1,2,6-TMN, h : 1,2,4-TMN, i : 1,2,5-TMN, j : 1,2,3-TMN, where "EMN" represents undifferentiated ethylmethylnaphthalenes and "TMN" is trimethylnaphthalene.

FIGURE 9

Summed mass chromatograms (m/z 191 + 206) illustrating the distribution of the C_3-alkylphenanthrenes and anthracenes in A) Herrin liptinite, B) Herrin vitrinite and C) Toarcian kerogen. Key – a : EP, b : EP, c : 3,6-DMP, d : 2,6-DMP, e : 2,7-DMP, f : dimethylanthracene, g : 1,3 + 2,10 + 3,9 + 3,10-DMP, h : 1,6 + 2,9-DMP, i : 1,7-DMP, j : 2,3 + 1,9 + 4,9-DMP, k : 1,8-DMP, where "EP" is ethylphenanthrene and "DMP" is dimethylphenanthrene.

coal macerals occur in a pattern similar to that of the tria-romatics, where we can observe an increase in the relative abundance from liptinite to vitrinite to fusinite (Fig. 7). Overall, the Toarcian maceral concentrates cannot be differentiated by their contents of di-, tri- and tetraaromatic hydrocarbons (Fig. 7). It is worth noting that the kerogen fractions are overall more aromatic than the coal liptinite.

2.2.5. Heterocompounds

The distribution of C_1- and C_2-alkylthiophenes in the Herrin liptinite resembles that in the Toarcian kerogen fractions, with a predominance of the 2-methyl-, 2-ethyl-, and 2,5-dimethylthiophenes (Fig. 10A and C), i.e., those with unbranched carbon chain backbones. Branched carbon chain isomers (3-methyl-, 2,4-dimethyl- and 2,3-dimethyl-) are mor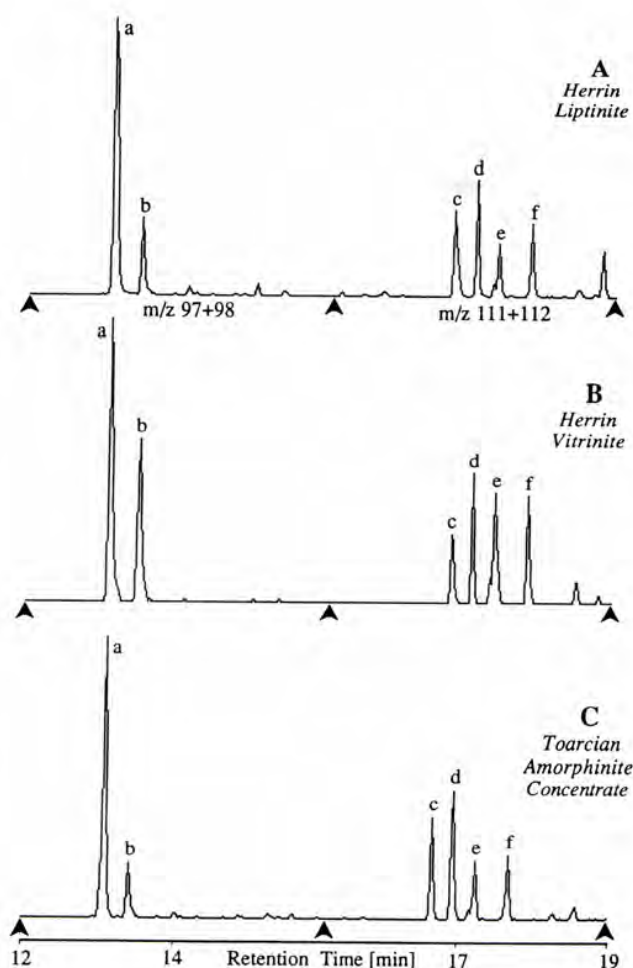e important in the Herrin vitrinite (Fig. 10B). The overall abundance of the thiophenes is the highest in vitrinite and lowest in fusinite for Herrin No. 6 coal, whereas in the Toarcian samples, the thiophene content is higher in the amorphinite concentrate than in the alginite-rich fraction (Fig. 11).

Figure 12 shows the distribution of the C_2-alkylphenols in the representative coal and kerogen fractions. In each sample 2,4-dimethylphenol is the dominant isomer. In the coal vitrinite, peak "e" is also prominent, probably due to the presence of the 3,5-dimethyl isomer (Fig. 12B). In the amorphinite concentrate, isomers with two adjacent methyl groups (2,3- and 3,4-dimethyl) are also important (Fig. 12C). Phenols are by far the most important class of compounds in the vitrinite, accounting for 45% of all peaks quantified, and they are also major components of the Herrin liptinite and fusinite (Fig. 2 and 11). While the phenols are in low abundance in the Toarcian fractions, the amorphinite concentrate shows significant enrichment of them (Fig. 11).

The Toarcian kerogen samples all exhibit the presence of the C_1- and C_2- alkylpyrroles, as shown by the representative chromatogram in Figure 13. As in the case of the phenol group, the pyrroles are minor compounds, but show interesting trends, increasing in concentration as the percentage of amorphinite increases (Fig. 11). Pyrroles are not detected in any of the Herrin samples.

FIGURE 10

Composite mass chromatograms of m/z 97 + 98 and 111 + 112 showing distribution of the C_1 and C_2-alkylthiophenes in A) Herrin liptinite, B) Herrin vitrinite and C) Toarcian kerogen. Key – a : 2-methylthiophene, b : 3-methylthiophene, c : 2-ethylthiophene, d : 2,5-DMT, e : 2,4-DMT, f : 2,3-DMT, where "DMT" is dimethylthiophene.
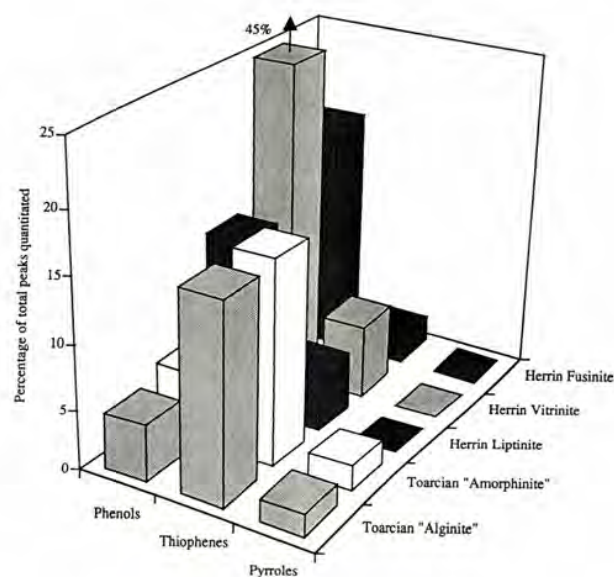

FIGURE 11

Relative concentrations of the principal families of heterocompounds present in the Toarcian and Herrin DGC fractions, as a percentage of total peaks quantified. See Tab. I for a complete list of peaks quantitated for use in these calculations. Note : values for alkylpyrroles for the Herrin coal macerals are 0%.

A
Herrin
Liptinite

B
Herrin
Vitrinite

C
Toarcian
Amorphinite
Concentrate

26.2   Retention Time [min]   28.2

FIGURE 12

Summed mass chromatograms (m/z 107 + 122) revealing distributions of C_2-alkylphenols in A) Herrin liptinite, B)Herrin vitrinite and C) Toarcian kerogen. Key — a : 2-ethylphenol, b : 2,4-DMΦ, c : 2,5-DMΦ, d : 4-ethylphenol, e : 3-ethylphenol + 3,5-DMΦ, f : 2,3-DMΦ, g : 3,4-DMΦ, where "DMΦ" is dimethylphenol.

15.5   Retention Time [min]   20

FIGURE 13

Composite mass chromatogram of m/z 80 and 94 showing the distribution of C_1 and C_2-alkylpyrroles in the pyrolyzate of the amorphinite from the Toarcian kerogen. Key — a : 2-methylpyrrole, b : 3-methylpyrrole, c : 2,5-dimethylpyrrole, d : 2,4-dimethylpyrrole, e : 2,3-dimethylpyrrole, f : 3,4-dimethylpyrrole.

3. — DISCUSSION

3.1 CHEMICAL DIFFERENTIATION OF THE HERRIN No. 6 COAL MACERALS

In comparing the internal distribution of the Herrin No. 6 maceral pyrolyzates, we observe distinct chemical differences between maceral types. The liptinite shows a strongly aliphatic character, with the predominance of n-alkenes and n-alkanes, which reflects the character of the macerals' biological precursors (leaf cuticles, resin and spores). The vitrinite pyrolyzate is dominated by alkylphenols which are the demethoxylation products of the guaiacyl and syringyl components of its lignin precursors (STOUT et al., 1988). Polyaromatic hydrocarbons are the major components in fusinite, due to the combustion processes involved in forming the precursors of this maceral (STACH et al., 1982). Aliphatic contents decrease and aromaticity increases markedly from liptinite to fusinite, as shown in particular by the di- and triaromatics (Fig. 7). The dominance of the 1,2,5-trimethyl isomer among the C_3-alkylnaphthalenes in liptinite (Fig. 8A) may indicate diagenetic derivation from hopanoids (DE LAS HERAS et al., 1991), which are relatively abundant in the liptinite pyrolyzate.

The Herrin sample is a representative of the high-sulphur coal mined extensively in Illinois and burned to generate electric power, unfortunately producing acid rain in the process. The thiophenic nature of much of the organic sulphur in the whole Herrin No. 6 coal has been recognized (SINNINGHE DAMSTÉ & DE LEEUW, 1992). It is interesting to note that organic sulphur is preferentially concentrated in the liptinite and vitrinite fractions, whereas the fusinite is relatively low in sulphur (KRUGE & PALMER, 1993), a fact reflected in the thiophene concentrations for these macerals (Fig. 11). These observations support the model of SINNINGHE DAMSTÉ et al. (1989), in which sulphur is incorporated into aliphatic moieties during diagenesis. It is apparent that, even for the same coal sample, the various maceral precursors have different capacities for diagenetic sulphurization, fusinite (extremely poor in aliphatics) being the least capable. The internal distribution of thiophenes also varies among the coal macerals (Fig. 10). The liptinite pyrolyzate show a predominance of alkylthiophenes with linear carbon backbones, indicative of the greater availability of straight-chain hydrocarbon moieties. Interestingly, vitrinite exhibits more branched carbon chain alkylthiophenes, perhaps reflecting the scarcity of straight-chain alkyl functions in its lignin precursors. One of these branched carbon chain isomers (2,4-dimethylthiophene) has been recognized as a coal marker (SINNINGHE DAMSTÉ et al., 1989). These data suggest that the vitrinite in coal is most responsible for this.

As mentioned at the outset, even high resolution DGC was incapable of cleanly separating the three main liptinite macerals (cutinite, resinite and sporinite) for this particular coal (Pl. 1), which is a typical Illinois basin mine sample. This is due to the low concentration of liptinite and to the failure of the micronization procedure for the ductile liptinite macerals. The treatment of pulverized coal with liquid nitrogen prior to micronization should be tried in the future, as it has been proven to be successful in reducing liptinite particles to micron size in the Toarcian kerogen sample.

The total ion chromatogram of the Herrin mixed liptinite (Fig. 2A) does not clearly show the characteristics for single macerals as described by NIP et al. (1989) for an Illinois
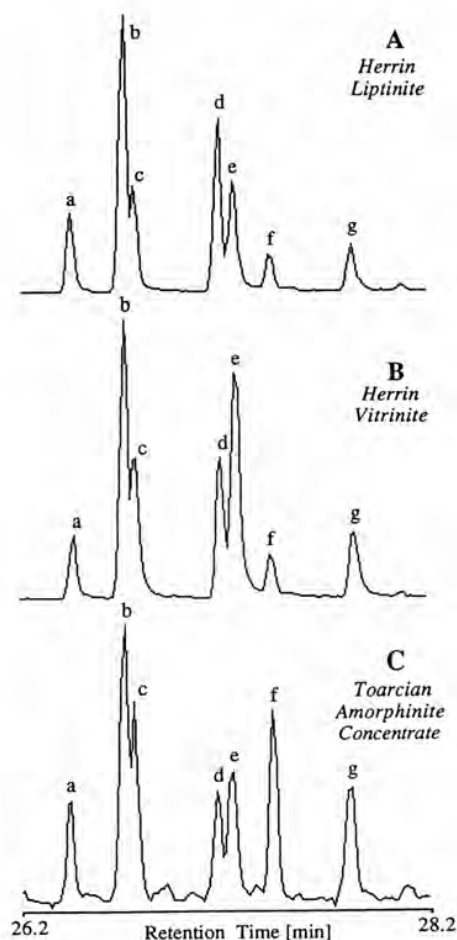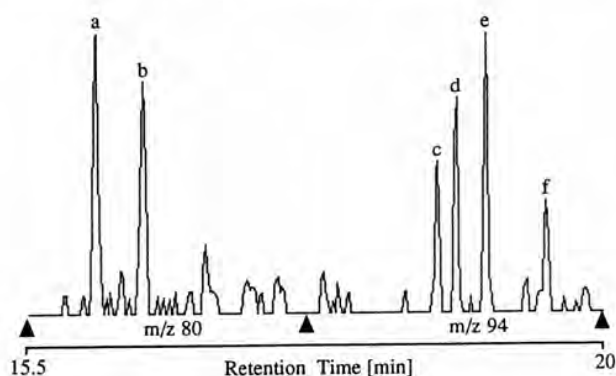
Basin coal unusually rich in cutinite and by NIP et al. (1992) for sporinite. These authors concluded that cutinite in particular is the most aliphatic, whereas alkylbenzenes may be contributed principally by sporinite. While we are not able to confirm or refute those observations, we can detect chemical evidence for resinite contributions. The prominent 1,7-dimethylphenanthrene (Fig. 9A) and 1,6-dimethylnaphthalene seen in the Herrin liptinite are considered to be resin signatures (VAN ARSEN et al., 1991), consistent with the high (40%) resinite content of this fraction. Both of these compounds are not important in the other fractions.

Density differences between the coal macerals may be explained in the simplest chemical terms by reference to their elemental composition, recalling the atomic weights of the most abundant isotopes (^{1}H, ^{12}C, ^{14}N, ^{16}O and ^{32}S). The liptinite fraction is the most enriched in hydrogen (atomic H/C = 1.25) and is the least dense. As the H/C ratio decreases from liptinite to vitrinite (H/C = 0.87), density increases correspondingly. Incorporation of heteroatoms will also further increase density, as in the case of vitrinite with its high O/C ratio of 0.20, compared to 0.12 for the liptinite (KRUGE & PALMER, 1993).

3.2. CHEMICAL DIFFERENTIATION OF THE DGC FRACTIONS OF THE TOARCIAN KEROGEN

Unlike the Herrin coal macerals, the Toarcian kerogen DGC fractions do not exhibit profound chemical differences, as is obvious from a comparison of Figures 2 and 3. This is in spite of the fact that the Toarcian fractions are petrographically distinct (Pl. 2). However, a detailed examination of the py-GC/MS data reveals subtle but significant differences between the alginite-rich ($\rho = 1.15$ g ml^{-1}) and amorphinite-rich (1.23 g ml^{-1}) fractions. These differences are not apparent in the distributions of isomers or homologues, such as the n-alkane or alkylnaphthalene series, but in the relative quantities of the compound classes taken together. Thus, with increasing density we see less aliphatics, but more alkylbenzenes and heterocompounds (Fig. 5, 7 and 11). As with the coal macerals, this may be explained in the simplest chemical terms as a reduction in density due to greater H content or an increase in density caused by greater N, O and S incorporation.

The distribution of nitrogen compounds is of special interest. We observed the presence of the C$_1$ and C$_2$-alkylpyrroles (Fig. 13) in both samples, with a significant increase in relative amount of these compounds going from the alginite-dominated to amorphinite-dominated fractions (Fig. 11). According to LARGEAU et al. (1990), who investigated several lacustrine oil shales, the three general types of morphology recognized in kerogen are : 1) selectively preserved algal material from resistant chlorophycean outer cell walls, petrographically recognizable as telalginite or lamalginite, 2) ultralaminar structures from microalgae, optically amorphous but resolvable with a transmission electron microscope and 3) truly amorphous material from bacteria. Our observations and those of LARGEAU et al., 1994 indicate that all three forms are present in the Toarcian kerogen. DERENNE et al. (1991) found relatively more nitrogen compounds (specifically alkylnitriles) in organic matter of bacterial origin. We did not detect alkylnitriles in the Toarcian kerogen, but we did recognize other nitrogen compounds (alkylpyrroles), the relative concentration of which is significantly greater in the amorphinite-dominated DGC fraction. SINNINGHE DAMSTÉ et al. (1992a) suggest that

alkylpyrroles are the pyrolysis products of tetrapyrrole pigments. However, based on the observation of the Paris Basin kerogen, we propose an alternative origin for pyrroles as products of bacterial activity.

The higher phenol content of the amorphinite concentrate may indicate a slightly greater oxidation of some of the constituents in the fraction, which may have occurred during sedimentation. Alternatively, the phenols could be the signature of the small amount of vitrinite petrographically detected in the fraction. The amorphinite concentrate shows a slight overall enrichment in alkylthiophenes as well, which may also be the imprint of increased bacterial activity during deposition.

The lack of profound chemical differences between the two maceral concentrates, as well as the difficulty in obtaining a clean separation of the amorphinite from alginite, suggests the following scenario. There was an original deposition of algal material, now preserved as telalginite and ultralaminar alginite. Post depositional bacterial alteration of the algal material varied in degree from slight to intensive, forming a continuum, rather than distinct phases. It would be of interest to examine the fractions with the transmission electron microscope, to assess the relative contribution of ultralaminar alginite to each one.

A potential source of error, especially in marine kerogen samples, may arise from incomplete demineralization. Micron-size pyrite framboids are particularly troublesome, as they are authigenic phases often growing in intimate contact with the organic matter. Traces of pyrite entrained with flakes of kerogen will distort the density profile (KRUGE et al., 1989). Therefore, great care must be taken in the preparation of kerogens for DGC. Petrographic examination of the Toarcian fractions indicates that pyrite contamination is not a significant problem in this case.

3.3. COMPARISON OF TERRESTRIAL LIPTINITE AND MARINE KEROGEN

Since the Herrin and Toarcian samples are both at roughly the same low thermal maturity level, it is possible to compare them directly and ascribe any differences or similarities exclusively to the organic matter type. The coal liptinite and kerogen have completely different biological precursors : terrestrial cutins, resins and spores vs algal and bacterial debris. Therefore, it is to be expected that they would have very distinct chemical signatures. Indeed, we observe that while both are highly aliphatic, the coal liptinite is much more so (Fig. 5). On this basis, the coal liptinite, if taken in isolation, would be more "oil-prone" than any of the phases separable from the Toarcian kerogen. The marine sample is significantly more aromatic than the terrestrial liptinite, as evidenced by concentrations of all classes of aromatic hydrocarbons except the phenanthrenes (Fig. 7). This may be due to the greater abundance of bacterial organic matter in the marine depositional environment.

A comparison of the heterocompound contents in the two organic matter types is also of interest. Somewhat ironically, the coal liptinite (as well as the other coal macerals) has significantly lower thiophene contents than the marine kerogen (Fig. 11), even though the Herrin sample is considered to be a "high-sulphur" coal. The incorporation of sulphur into coal is believed to result from marine transgression over the peat deposit and subsequent percolation of sulphate-rich sea water through the peat (CHOU, 1990). In contrast,

marine organic matter is exposed to high concentrations of sulphate throughout its depositional and diagenetic history, providing greater opportunity for sulphur incorporation. The enrichment of the Herrin liptinite fraction in alkylphenols (Fig. 11) is at least partially due to the vitrinite contamination (5 %) of this fraction, as phenols are the dominant molecular markers seen in vitrinite pyrolyzates. It is also likely that there are phenol precursor structures in the liptinites themselves, particularly the resinite. We did not detect alkylpyrroles in the coal, which could reflect a low porphyrin content and/or a lack of the bacterial activity responsible for fixing nitrogen in marine kerogens.

4 — CONCLUSIONS

1. The DGC method provided good separation of the dominant fraction in Herrin No. 6 coal (vitrinite), which is a typical Upper Carboniferous coal from the Illinois Basin. While a high purity liptinite concentrate can be isolated from the coal, even high resolution DGC cannot separate the liptinite macerals (cutinite, sporinite, resinite) from one another in this sample, which may be the result of its low overall liptinite content (7 %) or large particle size due to incomplete micronization.

2. The intensive experiments to separate alginite from amorphinite in the Toarcian kerogen, including minimalization of the particle size (ca. 1 μm) by inducing fracturing of the ductile components with liquid nitrogen, produced a partial separation, gave us DGC fractions enriched in algal and amorphous material.

3. The three investigated DGC fractions from the Herrin No. 6 coal have markedly different pyrolyzates. Liptinite is highly aliphatic, vitrinite is phenolic and fusinite is characteristically aromatic, with high concentrations of alkylbenzenes, naphthalenes and phenanthrenes.

4. While petrographically distinct, the two investigated DGC fractions from the Toarcian Paris Basin kerogen are chemically similar overall. However, there are significant relative increases in aromatic and heterocompound concentrations in the amorphinite over the alginite concentrate, as well as corresponding decreases in aliphatics. This is compatible with the formation of amorphous organic matter through variable degrees of bacterial degradation of algal debris.

5. The coal liptinite and marine kerogen are both highly aliphatic, however the marine sample is enriched in alkylbenzenes and other aromatic hydrocarbons, alkylthiophenes and alkylpyrroles, while the terrestrial liptinite fraction is more phenolic. If taken in isolation, the coal liptinite would actually be the more "oil-prone" phase.

Acknowledgements

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PLATE **1**

Photomicrographs in reflected light of density fractions from Herrin No. 6 coal
(Illinois Basin, Upper Carboniferous).

Fig. A. — Vitrinite (white light).

B. — Fusinite (white light).

C. — Liptinites (cutinite and resinite, in blue light).

D. — Liptinites (cutinite, sporinite and resinite, in blue light).
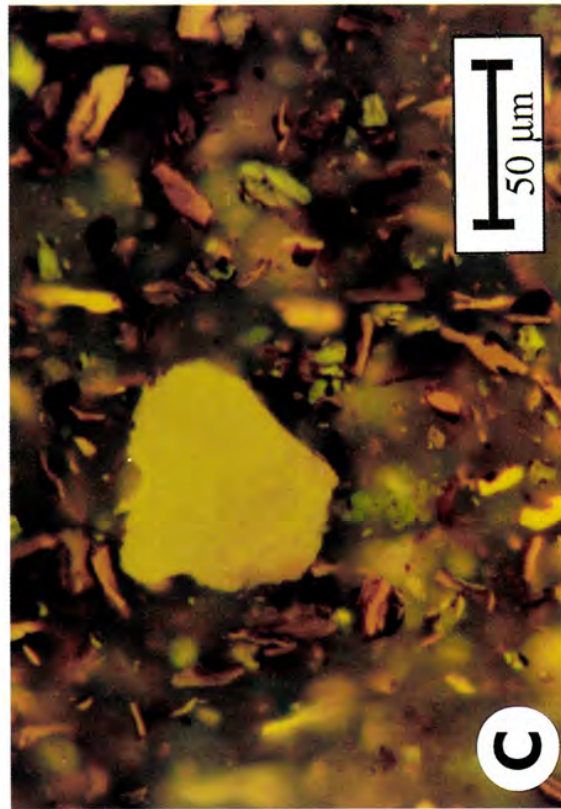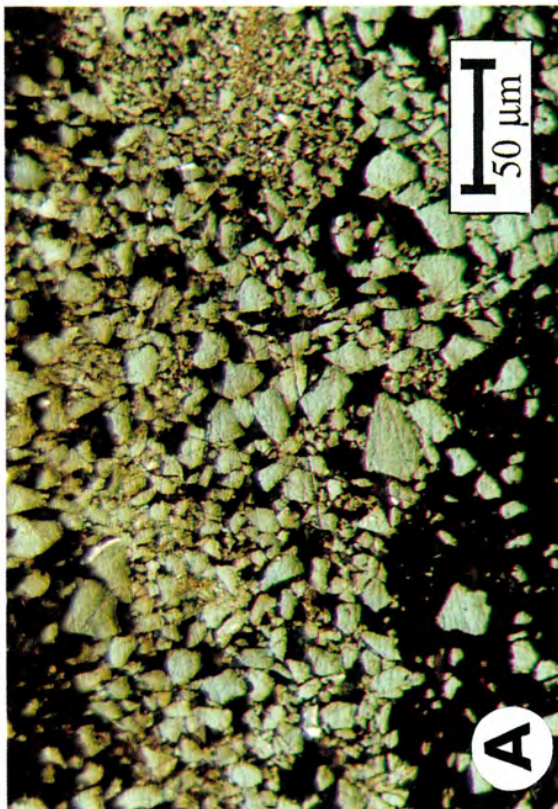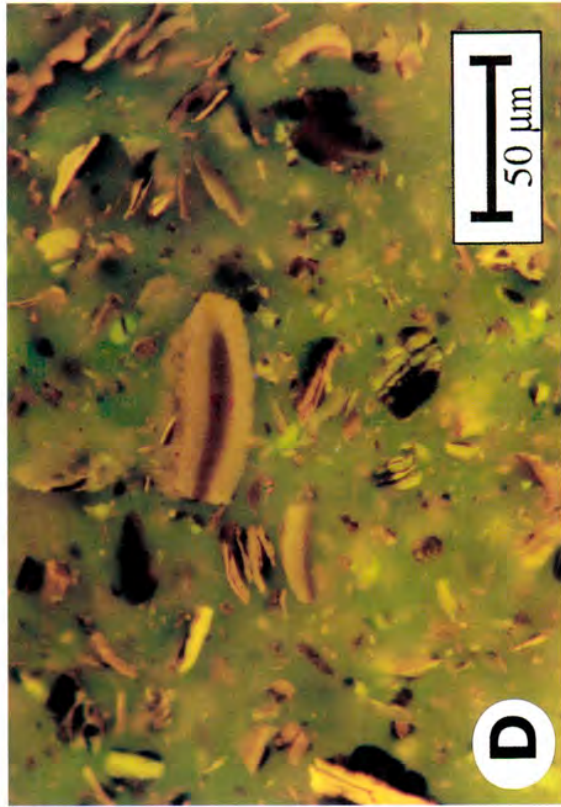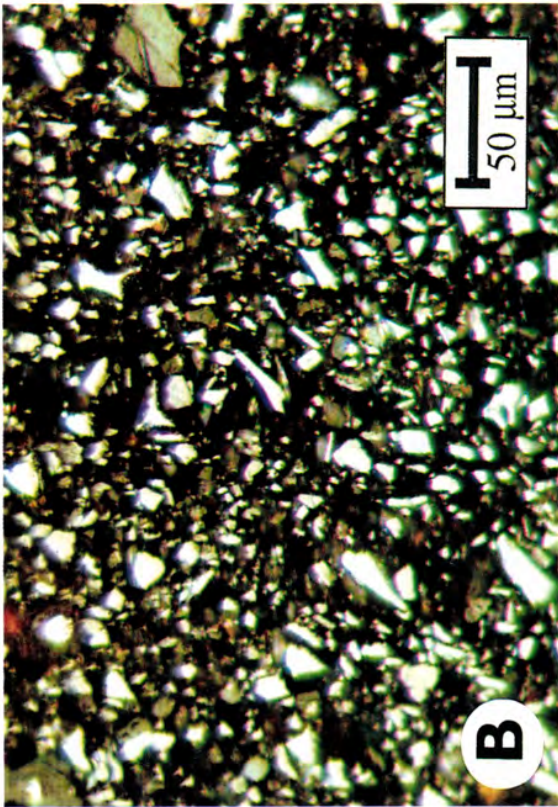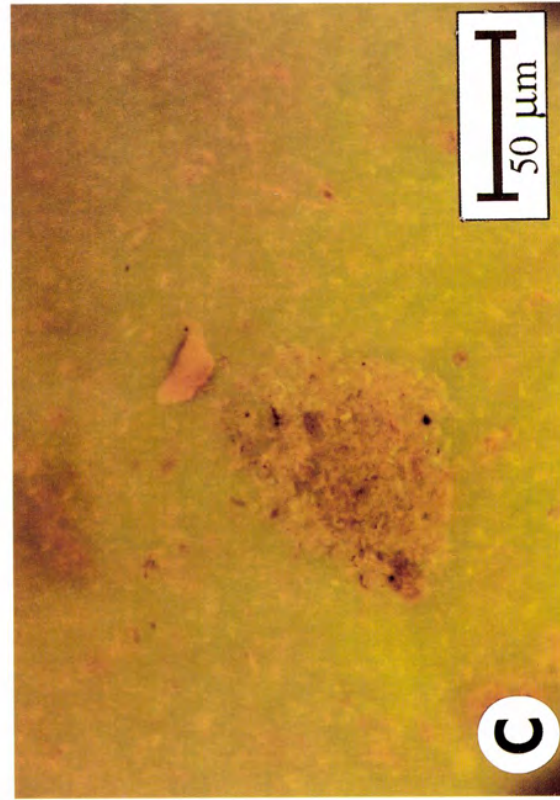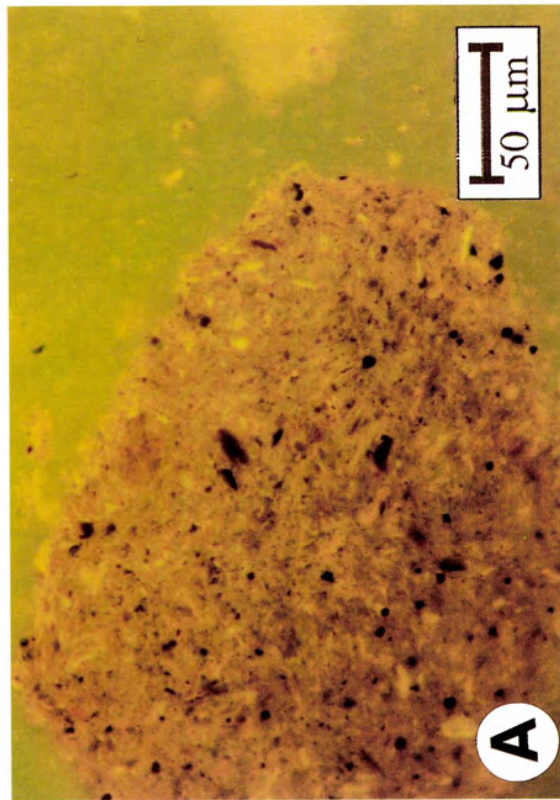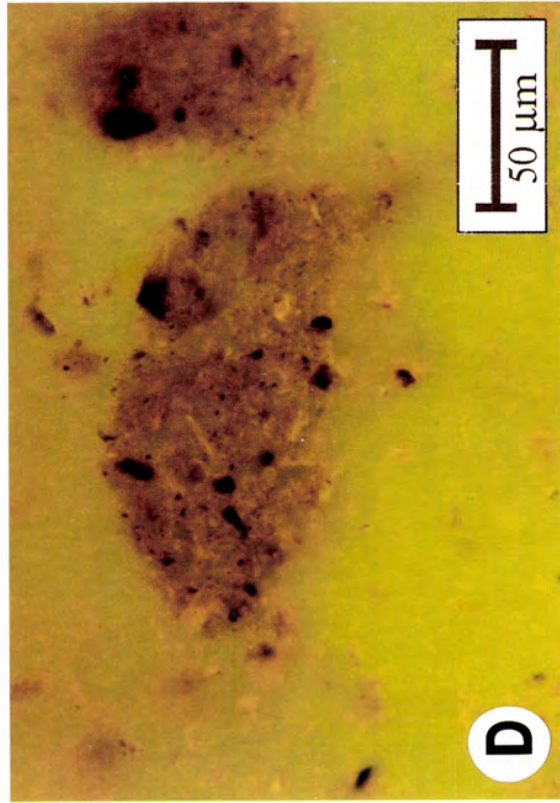
PLATE **2**

Photomicrographs in reflected blue light of kerogen and its density fractions
from the Lower Toarcian shale of the Paris Basin.

Fig. A. — Whole kerogen.

    B. — Whole kerogen (note *Tasmanites*).

    C. — 1.15 g ml^{-1} density fraction, predominantly yellow-fluorescing alginite.

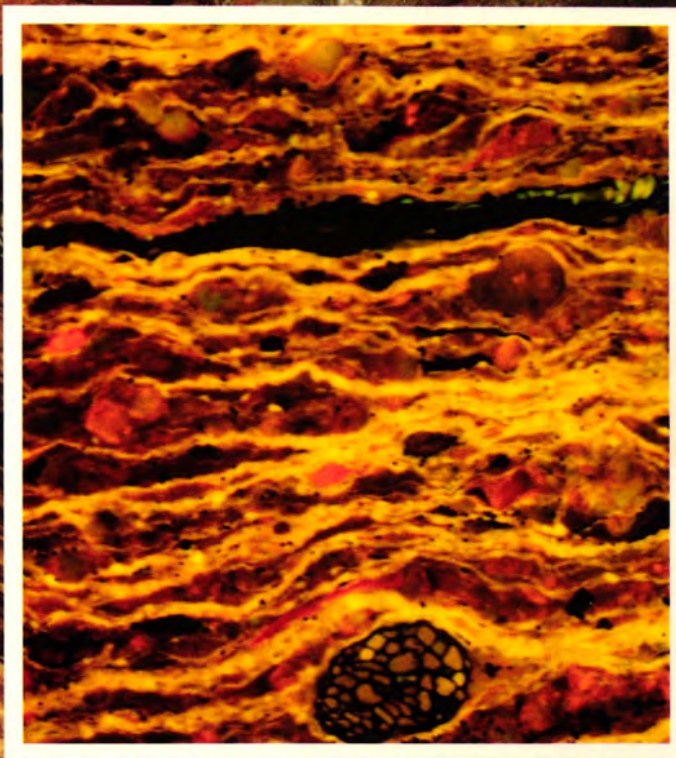   D. — 1.23 g ml^{-1} density fraction, predominantly brown-fluorescing amorphinite.

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