Aspects of Sporinite Chemistry

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Abstract. With the recent advent of the ability to separate coal into maceral concentrates of high purity, the individual constituents of coal can now be analyzed separately, without their mutual interference, giving a much better understanding of the macromolecular structure of coal. The sporinites from two Pennsylvanian age coal samples (Illinois Basin, U.S.A.) were studied, one from a vitrinite-rich high-volatile bituminous coal, the other from a liptinite-rich high-volatile bituminous coal of slightly higher rank. Sporinites were isolated from each coal by density gradient centrifugation. The sporinite of the vitrinite-rich coal was compared chemically and petrographically with the parent coal and with the sporinite of the liptinite-rich coal. The fluorescence spectrum of the sporinite from the liptinite-rich coal is shifted to the red end of the spectrum, which may be accounted for by the somewhat higher rank of the sample and/or by differences in the original assemblage of spores. The lack of chemical differences between the extracts of the sporinite and its whole coal reinforce the concept of bitumen as an homogeneous mobile phase pervading the coal. Thus, extract chemistry seems an unsuitable technique for distinguishing between macerals from the same coal. Hopane and sterane distributions in the sporinite and parent coal pyrolyzates are very similar, but the two materials can be readily distinguished by the distribution of tetracyclic diterpanes of the phyllocladane type, which are biological marker compounds derived from higher plant material. Overall, the sporinite is considerably more paraffinic in character and has a greater preponderance of straight-chain alkane moieties than the coal as a whole. In the case of the vitrinite-rich coal, the whole-coal structure appears significantly more polyaromatic than the sporinite. The distributions of thiophenic compounds differ in the pyrolyzates of the two materials. The sporinite from the liptinite-rich coal is even less polycondensed than the sporinite from the vitrinite-rich sample. The chemical and petrographic differences of the two sporinites probably reflect the different assemblages of spores in the original peats and their different diagenetic histories.

Key words - sporinite, spectral fluorescence, organic geochemistry, maceral separation, pyrolysis

INTRODUCTION

The complex macromolecular structure of coal is still incompletely understood. Advances in the geochemical characterization of coal are essential in order to achieve the most effective and environmentally sound utilization of this vast resource. With the recent advent of the ability to separate coal into maceral concentrates of high purity, the individual constituents of coal can now be analyzed one by one, without their mutual interference,

greatly increasing the resolution of chemical detail. This paper focuses on a single coal maceral, sporinite.

The earliest work on characterizing individual macerals relied on samples in which the target macerals were naturally in high concentration, thus eliminating the need for extensive sample preparation. In recent years, with the increasing availability of high purity maceral concentrates separated by density gradient centrifugation, more thorough work has become possible. Once maceral concentrates were obtained, a wide variety of analytical approaches were attempted (Winans and Crelling, 1984; Crelling, 1989). Rapid, high-temperature pyrolysis (as py-GC, py-GCMS and py-MS) has been widely employed in maceral analysis (Larter and Douglas, 1980; van Graas et al., 1980; Allan and Larter, 1983; Meuzelaar et al., 1984; Senftle et al., 1986; Nip et al. 1988, 1989). Oxidative degradation techniques have also proven useful, both in whole-coal and kerogen analysis (Vitorovic, 1980; Hayatsu et al., 1982) and, more recently, for maceral concentrate work (Choi et al., 1988). Palmer et al. (1990) used oxidative degradation techniques specifically to identify organic sulfur forms in coal and a variety of pure macerals. Other techniques, such as chromatographic analysis of solvent extracts (Allan and Larter, 1983), FTIR (Dyrkacz et al., 1984) and solid-state NMR (Wilson et al., 1984), have also been applied to maceral studies. Hayatsu et al. (1988) characterized natural and synthetic sporinites by py-GCMS, chemical degradation techniques, solid-state NMR and FTIR. The two materials were both shown to be highly cross-linked aliphatic polymers, with minor aromatic and phenolic structures.

For the present study, we have taken two coals from the same basin, of approximately the same geologic age. The coals are different lithotypes, however. One is a paper coal (liptinite-rich), while the other is a more typical humic coal, rich in vitrinite, although with an exceptionally high organic sulfur content. Thus, the two coals record two very different depositional environments and post-depositional histories, which should be reflected in their chemical composition. We wished to compare the chemistry of the sporinite with that of its parent coal and to compare the chemical character of sporinites from the two different coals. We have performed chromatographic analyses on (1) solvent extracts, (2) products of slow, confined pyrolysis and (3) mild oxidative degradation products.

METHODS

Samples

Two samples were used in this study: sample SIU- 637J, which is a paper coal from the Roaring Creek Mine, Brazil Block Seam, Parke County, Indiana, U.S.A. and sample SIU-1386, which is the Illinois Basin Coal Sample Program Sample No. 1, taken from the Herrin No. 6 seam in west central Illinois, U.S.A. Both samples are Pennsylvanian in age.

Ultimate analysis and organic petrology

Ultimate analysis was performed on a Carlo Erba 1106 CHN analyzer and a Leco SC132 sulfur determinator. Results are reported on a dry, ash-free basis. Petrographic preparations were made following standard procedures. For reflected light microscopy, samples were examined with both white and blue light illumination according to standard methods. Reported fluorescence spectral data are the average of 20 readings. For electron microscopy, an ETEC Autoscan SEM was employed.

Maceral separation

Since coal macerals vary in their density, they can be separated using the standard medical technique of density gradient centrifugation (DGC), in which a sample is centrifuged through a density continuum and then fractionated (Dyrkacz and Horwitz, 1982; Dyrkacz et

al., 1984). In this technique the coal sample is reduced to micron size in a fluid energy mill and then partly demineralized with HF and HCl. The demineralization is completed by "floating" the sample, i.e. centrifuging it in an aqueous solution of CsCl with a density of 1.6 g/ml. The demineralized sample is then put into a vessel that is filled with an aqueous CsCl density gradient commonly ranging from 1 to 1.6 g/ml. The vessel is then centrifuged and the particles move to the appropriate density level. At this time the largest vessel in use has a 2-L capacity, which can process a maximum sample size of 2 g of coal. After centrifugation the contents of the vessel are fractionated by pumping, then filtered, washed, dried and weighed. The density and weight of each fraction are measured and plotted. The resulting density profile accurately reflects the maceral composition of the sample. The typical DGC run can separate the coal into the three main maceral groups-liptinite, vitrinite and inertinite. Preconcentration of a desired maceral group, such as the liptinites, is achieved by selecting the density boundaries or cut points on a standard DGC profile, then centrifuging the sample in a liquid of a single density. When the resulting concentrate is then processed in a 2-g DGC run, over a limited density range, individual macerals can be separated. Crelling (1988) has shown that the liptinite fraction from the Brazil Block paper coal can be separated into cutinite, resinite and sporinite. This was confirmed petrographically by fluorescence spectral and reflectance analysis.

Analysis of solvent extracts

The coal samples, micronized and demineralized as described above, were extracted with THF in a soxhlet apparatus. The extracts were dried and separated by liquid chromatography (LC) into "saturate", "aromatic", "polar 1" and "polar 2" fractions (silica gel, with C_6H_{14}, 9:1 C_6H_{14}:CH_2Cl_2, CH_2Cl_2 and 1:1 CH_2Cl_2:CH_3OH as the respective eluants). The saturate and aromatic fractions were analyzed by GCMS with a 25 m OV-1 column, temperature programmed from 100 to 300°C at 3° /min, using a Hewlett Packard 5890A GC coupled with an HP 5970B mass selective detector run in selected ion-monitoring mode.

Pyrolysis

In our earliest experiments 1 g of micronized, extracted and demineralized coal or isolated sporinite was placed in microautoclaves (steel tubes with threaded closures), which were set in a 320° C sand bath for 24 h. After cooling, the tubes were rinsed with methanol to extract the pyrolyzate. Later experiments were conducted using glass reaction vessels. Approximately 300 mg of dry sample were placed in tared 2 ml glass ampules. After weighing, the ampules were flushed with a stream of argon, sealed and placed in a Eurotherm 4303-3 tube furnace for 72 h. Temperature of 320, 340 and 380°C were used. In vitro pyrolyzates were extracted with methylene chloride in a sonicator or a soxhlet apparatus. Pyrolyzates were analyzed by LC and GCMS as described above.

Oxidative degradation

Mild oxidative degradation of the coal was accomplished by taking a 2 g sample, micronized and demineralized as described above, adding 50 ml of glacial acetic acid, followed by 20 ml of 30% H_2O_2. The mixture was heated under reflux and after I h an additional 40 ml of H_2O_2 was added dropwise to maintain the reaction. The mixture was allowed to reflux for a total of 24 h. In the case of sporinite, 0.5 g of sample was used and the amounts of reagents were scaled down accordingly. The soluble oxidation products were methylated with BF_3/CH_3OH and analyzed as methyl esters of carboxylic acids by GCMS. The GCMS conditions were as described above, except that the MS was in full-scan mode and GC was programmed from 100 to 300°C at 20° /min.

RESULTS AND DISCUSSION

Ultimate analysis

The results of the ultimate analysis are given in Table I. The Herrin and Brazil Block samples have similar carbon and nitrogen contents. However, the Brazil Block coal is considerably richer in hydrogen, with an H/C ratio of 1.20, compared to 0.91 for the Herrin coal. The Herrin sample has nearly twice the sulfur of the Brazil Block coal (4.30 compared to 2.40%) and more oxygen (12.54 vs 9.07%).

Organic petrology

The distribution of macerals in the Brazil Block and Herrin coals as determined petrographically, is given in Table 2. The Herrin coal is considerably richer in vitrinite and pseudovitrinite (82.7% total vitrinites), in contrast to 51.5% in the case of the Brazil Block. The Brazil Block sample, consistent with its description as a paper coal, is correspondingly enriched in liptinites (especially sporinite and cutinite), as well as in some inertinites. Although both coals are high-volatile bituminous, the Herrin sample is of lower rank, as it has a vitrinite reflectance of 0.42%, while the Brazil Block coal is at 0.58%. The Brazil Block sample also contains a small amount of bituminite, suggesting that some liquid generation has occurred. Its higher liptinite content is in accord with its higher H/C ratio (Table I).

The fluorescence spectra of the Herrin and Brazil Block sporinites are significantly different. The Brazil Block sporinites are distinctly "redder". The Brazil Block sample has a relatively greater intensity in the 550-700 nm range and a lower intensity in the 450-550 nm range (Fig. 1). This red shift may be accounted for by the somewhat higher rank of the Brazil Block sample and/or by differences in the original assemblage of spores, In other coals, taxonomically different spores have been noted to produce different spectra, even in the same coal sample, so a slight red shift is not necessarily due only to increase in rank. Although the coals are from the same basin and are approximately the same age, they come from sites roughly 250 km apart. Differences in the original organic matter type can thus be expected.

Maceral separation

In accord with the petrographic results, the DGC separations of both coals yield primarily vitrinite (Fig. 2). The DGC profile of the Brazil Block sample has a slightly more prominent sporinite peak and a small, but distinct cutinite peak not seen on the profile of the Herrin coal. Petrographic examination showed the Brazil Block coal to be considerably richer in these liptinite macerals {Table 2). Examinations of the DGC profiles (Fig. 2) indicated that a density cut point at 1.22 g/ml would be appropriate for a preparative centrifugation run at a single density, to further concentrate the liptinite fraction. Liptinite concentrates were thus prepared for each of the samples and subsequent high-resolution DGC yielded sporinite concentrates of high purity. The high-resolution DGC of the Brazil Block sample has been discussed previously (Nip et al., 1989), although in that case, the objective was to characterize the cutinite, not the sporinite. The sporinite of the Brazil Block sample is slightly less dense that that of the Herrin coal (Fig. 2). This is probably due to a different assemblage of spores in the parent peat, but may also be due to different responses to coalification.

Only the fractions from the centers of the DGC peaks were used in the subsequent analyses, as they are the fractions of highest purity. The fractions from the flanks of the peaks, in particular the vitrinite peak, contain multiphase particles and as such are less suitable for characterization of individual macerals. The presence of multiphase particles also accounts for the quantitative discrepancy between the petrographic and DGC results.

Table 1. Elemental analysis.

Sample name: Sample No.:	Brazil Block SIU 647J	Herrin No. 6 SIU 1386
%C	79.14	76.03
%H	7.89	5.76
%N	1.50	1.37
%O*	9.07	12.54
%S_{total}	2.40	4.30
H/C	1.20	0.91
O/C	0.08	0.12

*By difference.
Note: percentages of each element are computed on a dry, ash-free basis.

Table 2. Organic petrography. All values are reported as percentages.

Sample name: Sample No.:	Brazil Block SIU 647J	Herrin No. 6 SIU 1386
Vitrinite	44.9	62.5
Pseudovitrinite	6.6	20.2
Total vitrinite	*51.5*	*82.7*
Sporinite	13.8	2.8
Resinite	1.1	0.4
Cutinite	7.2	1.3
Fluorinite	0.2	0.4
Bituminite	3.0	0.0
Liptodetrinite	2.3	1.3
Total liptinite	*27.6*	*6.2*
Fusinite	8.3	1.4
Semifusinite	4.8	8.1
Macrinite	—	0.0
Semimacrinite	—	0.6
Micrinite	8.0	1.0
Total inertinite	*21.1*	*11.0*
Vitrinite reflectance (R_m %)	0.58	0.42

*All values reported are reported as percentages.

Fig. 1. Fluorescence spectra of sporinite from the Herrin No. 6 coal and the Brazil Block paper coal. Intensity is normalized to the maximum in each sample.
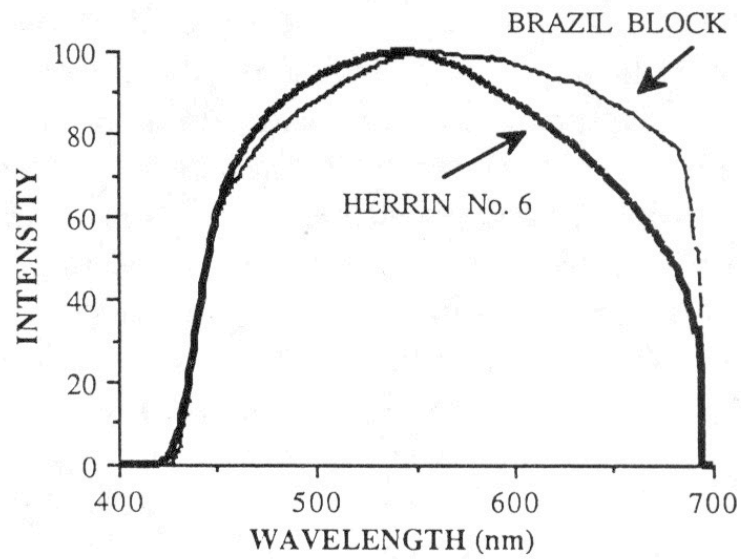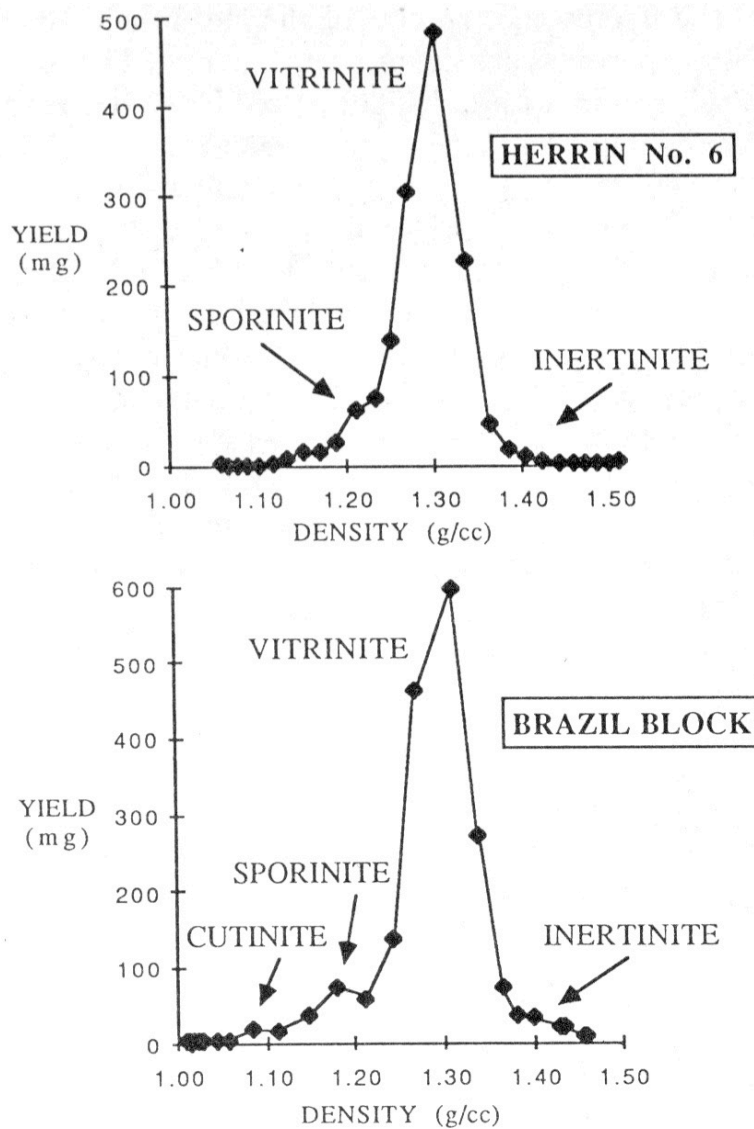

Fig. 2. DGC profiles for the Herrin No. 6 and Brazil Block coals.

The purity of the sporinite concentrates was confirmed by petrographic examination. Figure 3(a) is a photomicrograph of the Brazil Block whole coal, under blue light illumination. The yellow-fluorescing body in the center of the photograph is an intact spore, characterized by a double-walled structure with a dark zone in the center. Figure 3(b) is a photomicrograph of the concentrated sporinite, also under blue light. The intact spores are clearly visible. The identification is confirmed by the fluorescence spectra-the spectra of the sporinite in the whole coal and the isolated sporinite are statistically identical. SEM provides further evidence, as in Fig. 4, which shows the Brazil Block sporinite concentrate. Particles in the concentrate clearly exhibit sporinite morphology. In summary, the particles in fraction from the sporinite DGC peak look like and fluoresce like the sporinite in the parent coal.

Extractable organic matter

Normal alkanes of the Herrin No. 6 demineralized floated coal have a maximum at n-C_{29} and a clear odd/even predominance, as is shown in Fig. 5, which displays the results of the quantitation of n-alkanes and isoprenoids using m/z 99. The pristane/phytane ratio is high, as is the pristane/n-C_{17} ratio. Pristane is in fact the dominant peak on the m/z 99 chromatogram. The m/z 99 trace of the Herrin No. 6 sporinite extract is very similar to that of the parent coal (Fig. 5), except for the high concentration of n-C_{18}. The Brazil Block sporinite extract has its maximum n-alkane at n-$C25$ and almost no odd/even preference (Fig. 5). Its pristane/phytane and pristane/n-C_{17} ratios are also high, yet the latter is less than for the Herrin samples. n-C_{18} is also relatively enriched in the Brazil Block sample.

The predominance of n-alkanes in the n-C_{23} to n-C_{31} carbon number range and the high pristane/ phytane ratios are the hallmarks of terrestrially derived organic matter, as expected in typical coal samples (Tissot and Welte, 1984). We have found, in accord with Allan and Larter (1983), that extracts of macerals closely resemble those of the parent coals, due to a natural homogenization of the mobile phase within the coal. Thus, a comparison between extracts of macerals from the same coal is of limited usefulness. Marked differences in the extracts of the Herrin and Brazil Block sporinites (Fig. 5) most likely reflect the differences in the composition of the parent coal as a whole, rather than the sporinites in specific. The isoprenoid/n-alkane ratio of the Brazil Block sample is lower than that of the Herrin samples, reflecting the higher rank of the Brazil Block coal, corroborated by its R_m value of 0.58%, compared to $R_m = 0.45\%$ for the Herrin sample. The unusually high amounts of n-C_{18} in both sporinite extracts is believed to be a contaminant introduced during the DGC process, possibly an impurity in the surfactant.

Regarding the cyclic alkanes, the Herrin coal and sporinite extracts both have virtually identical distributions of steranes and diasteranes (m/z 217, Fig. 6), as well as phyllocladane and kaurane isomers and derivatives and hopanes. The prominent C_{29} steranes and diasteranes (Fig. 6), phyllocladanes and kauranes and C_{30} hopane are all typical of terrestrially-derived organic matter. The lack of biomarker differences between the extracts of the sporinite and its parent coal reinforce the concept of an homogeneous mobile phase pervading the coal.

Fig. 3. Photomicrographs in fluorescent light of sporinite macerals in the Brazil Block paper coal. Both frames are ≈160 μm wide. (a) A typical occurrence of sporinite in the raw coal. (b) A pair of isolated sporinite macerals as separated by DGC. Note the similarity in shape and texture of the individual. sporinite bodies to the sporinite in part (a). The very small dark particles are carbon black, added to suppress the fluorescence of the epoxy mounting medium.
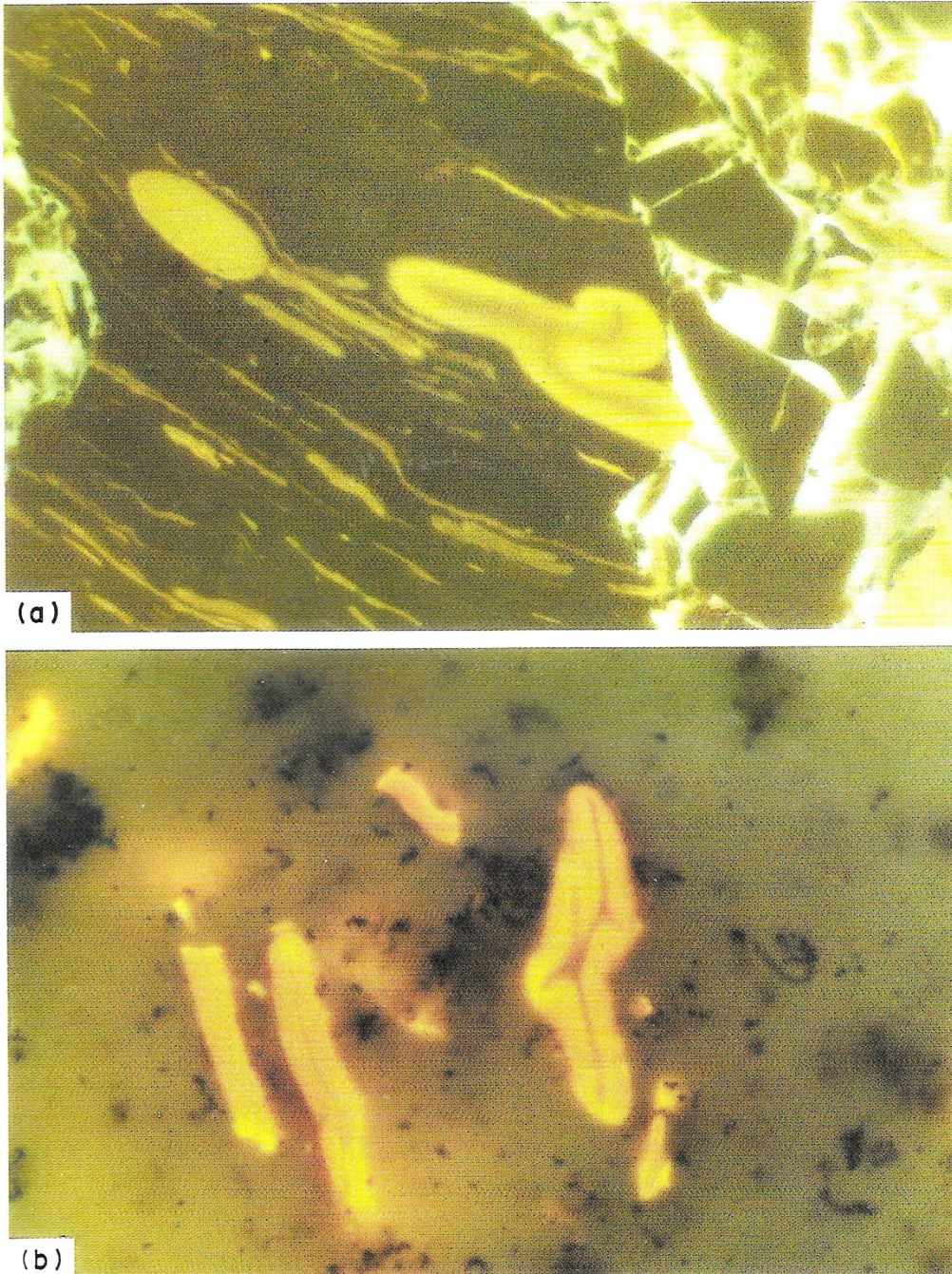
Fig. 4. SEM of sporinite macerals as separated by DGC from the Brazil Block paper coal. The field-of-view is ≈110 μm wide.

Fig. 5. Normal and isoprenoid alkane distributions in coal and sporinite extracts and pyrolyzates. Quantitations are made on m/z 99 data acquired by GCMS.
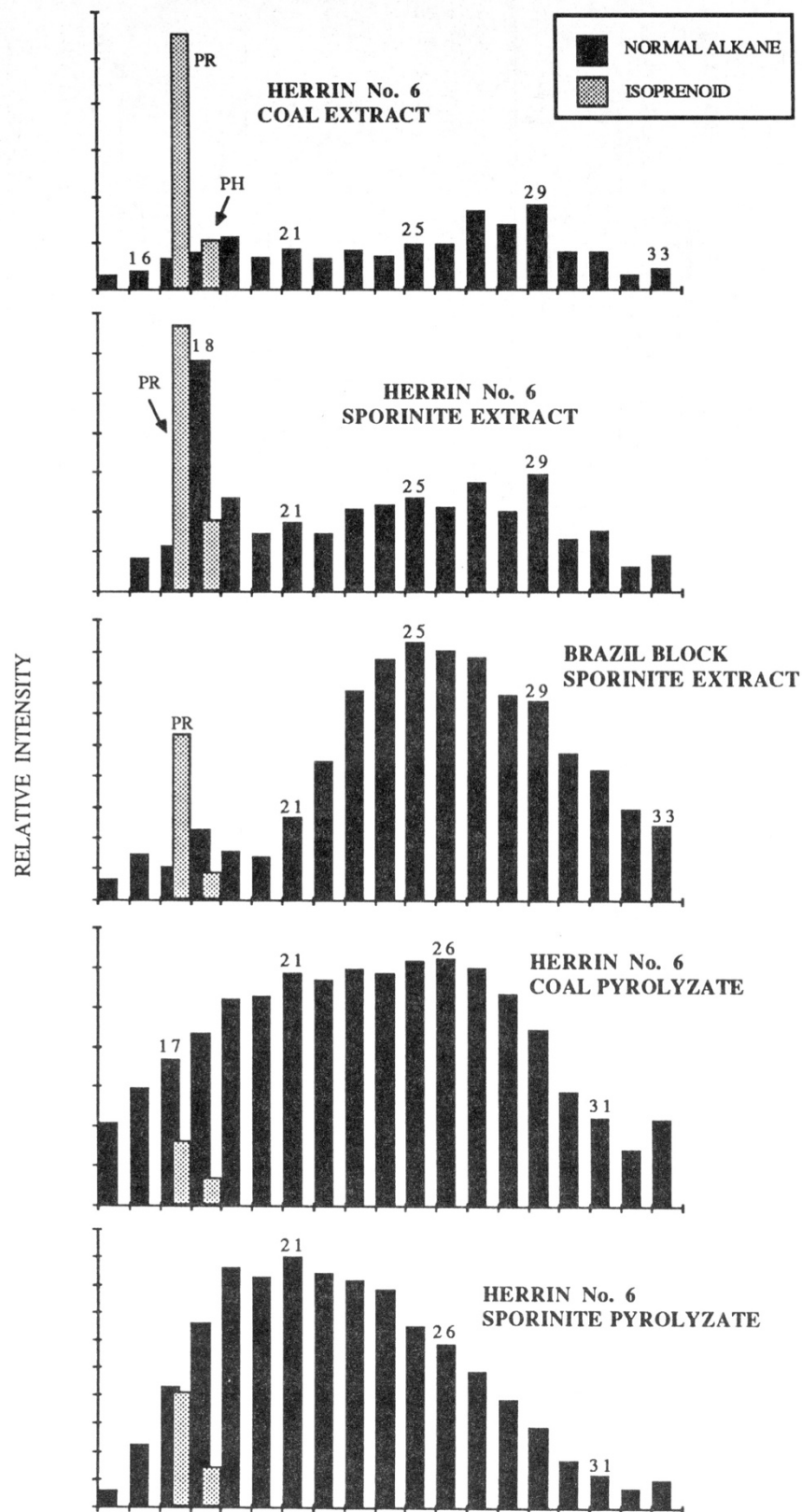
Fig. 6. Sterane distributions from the Herrin No. 6 demineralized coal and sporinite concentrate extracts. (Partial mass chromatograms using the m/z 217 ion.)
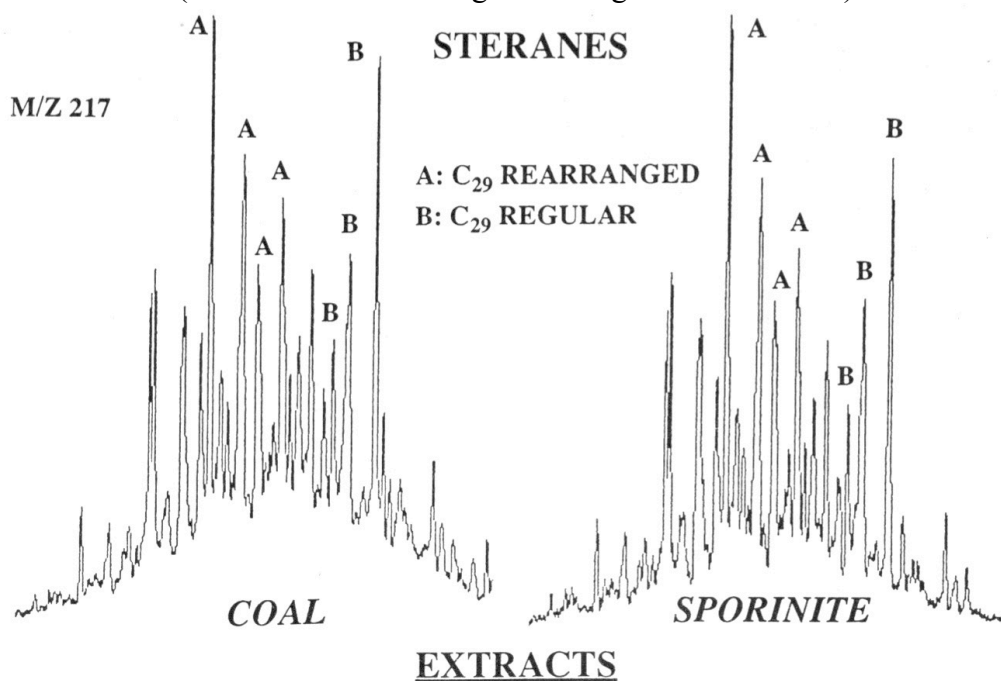

STERANES

M/Z 217

A: C_{29} REARRANGED
B: C_{29} REGULAR
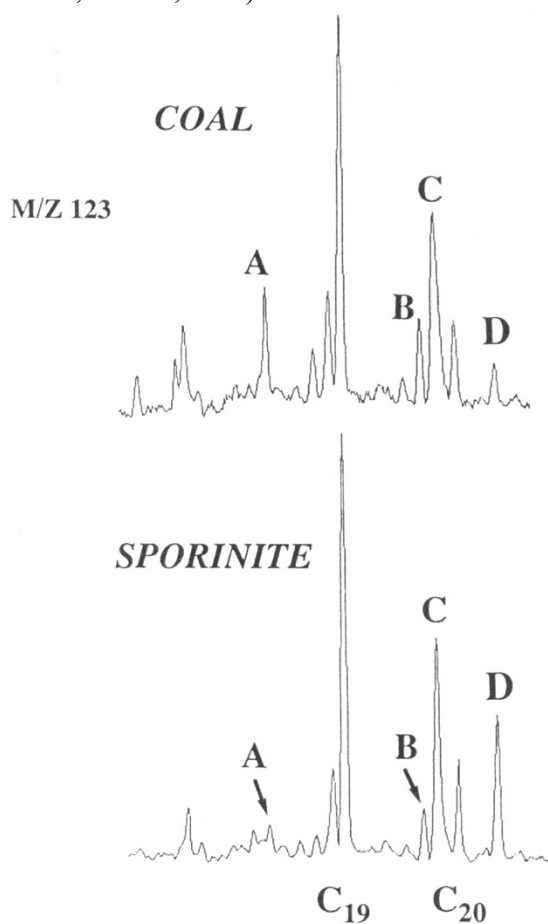
COAL   SPORINITE

EXTRACTS

Fig. 7. Partial m/z 123 mass chromatograms of the Herrin No. 6 coal and sporinite pyrolyzates. Peaks A-D are discussed in the text. Pyrolysis conditions were identical for both samples (steel microautoclaves, 320°C, 24 h).

COAL

M/Z 123

SPORINITE

C_{19} C_{20}

Comparison of sporinite and its parent coal

We have characterized the pyrolytic and oxidative degradation products of Herrin sporinite and parent coal. The samples were extracted prior to degradation, ensuring that the reaction products would be representative of the insoluble macromolecular maceral and coal structure itself.

Pyrolyzates show significant differences from the solvent extracts of the same material. For example, the Herrin sporinite pyrolyzate has a much smoother distribution of *n*-alkanes than does the corresponding sporinite extract (Fig. 5). The most prominent *n*-alkane is now n-C_{21} instead of n-C_{29} and the pristane/n-C_{17} ratio is only slightly greater than unity. There is only a slight odd/even preference and no anomalously high concentration of n-C_{18}. The pristane/ phytane ratio remains high.

Tetracyclic diterpanes of the phyllocladane type are important biomarkers in organic matter of terrestrial origin. The distribution of these compounds in the Herrin sporinite and coal pyrolyzates are shown in m/z 123 chromatograms in Fig. 7. Peak "C", a C_{20} diterpane, prominent in both the coal and sporinite, is most likely $16\alpha(H)$-phyllocladane, based on comparisons with the chromatograms and mass spectral data of Philp (1985) and Noble et al. (1985, 1986). There is considerable variation in the relative strengths of the other principal peaks on the partial chromatogram. These are as yet unidentified, but are probably isomers and derivatives of phyllocladane, kaurane or closely related compounds. In particular, the C_{20} peak "D" is much stronger in the sporinite pyrolyzate, whereas the C_{19} peak "A" and the C_{20} peak "B" are more important in the coal sample. Thus, the two materials can be readily distinguished by the distribution of tetracyclic diterpanes of the phyllocladane type, as the tetracyclic diterpanes are derived from direct high plant input, which should logically be different for different maceral types.

In addition to such distinctions on the individual compound level, there are marked differences in the relative distributions of the saturate biological markers by compound class. Figure 8 shows quantitation results on appropriate MS ions for the most prominent member of each compound class, normalized to the value for n-C_{21}. The normal alkanes, as represented by n-C_{21}, predominate in both samples, especially in the case of the sporinite. The percentage of acyclic isoprenoids, as represented by pristane, is less in the sporinite than in the coal, yet the isoprenoids are very important in both samples. The sporinite pyrolyzate contains the same relative amount of tetracyclic diterpanes (here represented by peak "C" in Fig. 7) as the coal, however, other types of polycyclic alkanes (hopanes and steranes) are relatively much less prevalent. The lower percentage of hopanes in the sporinite is especially dramatic (Fig. 8). It is interesting to note that the distribution of C_{27}-C_{35} hopanes, relative to each other, in both the coal and sporinite pyrolyzates are essentially the same, as seen by examination of m/z 191 mass chromatograms. The hopanes are the products of post-depositional bacterial activity (Moldowan et al., 1985), so it follows that all macerals of the same coal should have similar assemblages of hopanes. Also, the hopane/sterane ratio is high in both cases, as is typical for terrestrially-derived samples (Moldowan et al., 1985). It is the hopane/n-alkane ratio that distinguishes the sporinite from its parent coal (Fig. 8). Overall, the sporinite is considerably more paraffinic in character and has a greater preponderance of straight-chain alkane moieties than the coal as a whole, which is 82.7% vitrinite and pseudovitrinite.

The aromatic fractions of both pyrolyzates contain homologous series of long-chain *n*-alkylbenzenes, displayed on m/z 91 mass chromatograms (Fig. 9). The distributions of the *n*-alkylbenzenes in both samples are similar, but the chromatogram of the coal sample also exhibits a complex series of strong peaks in the 30-40 min retention time range, much less prevalent on the sporinite chromatogram, which is dominated by the straight-chain homologues. For a simple approximation of the degree of aromatization, one can compare the

relative amounts of phenanthrene, one of the predominant polyaromatic hydrocarbons in the aromatic fraction of both samples, with a prominent *n*-alkylbenzene (peak N, Fig. 9). Such a phenanthrene/*n*-alkylbenzene ratio has a value of 5 for the sporinite, in contrast to the parent coal, for which the ratio is 18. For purpose of this ratio, phenanthrene and the alkylbenzene were quantitated using m/z 178 and 91, respectively. Thus the structure of the parent coal (dominantly vitrinite) can be interpreted to be significantly more polyaromatic than the sporinite, which exhibits an aliphatic character, even in its aromatic LC fraction.

Thiophene derivatives are the most important organic sulfur compounds in the aromatic fraction of the pyrolyzates. As an example, m/z 198 mass chromatograms (Fig. 10) show the distribution of methyldibenzothiophene isomers, as well as seven additional peaks, some or all of which are possibly methylnaphthothiophene or naphthomethylthiophene isomers, based on mass spectral evidence. The relative distribution of organosulfur compounds in the sporinite is significantly different from that in the parent coal. Previously, the proportion of methyldibenzothiophene isomers has been shown to vary as coal rank increases (Leythaeuser et al., 1988). These same isomers (labeled "D" in Fig. 10) are seen here, under identical pyrolysis conditions, to vary with organic matter type.

In addition to pyrolysis, mild oxidative degradation is an effective technique for structural analysis of complex geopolymers like coal macerals (Hayatsu et al., 1982, 1988; Choi et al., 1988). Peroxyacetic acid was chosen as an oxidant because it selectively oxidizes aromatic bonds (Palmer et al., 1990). GCMS total ion chromatograms of oxidation products are shown in Fig. 11. The most prominent peaks on these chromatograms are the methyl esters of benzene polycarboxylic acids, i.e. benzene rings substituted with from two to five carboxyl groups. A benzenedicarboxylic acid is an aromatic ring that, prior to the oxidation procedure, had been attached at two sites to a larger macromolecular structure (Deno et al., 1978). The tri-substituted varieties had been attached at three sites etc. The greater the degree of substitution, the more polyaromatic the parent structure. In Fig. 11, in the case of the Herrin coal, the tetracarboxylic acids are the most prominent and the dicarboxylic are the least abundant. In contrast, the Herrin sporinite shows the di-, tri- and tetracarboxylic acids in approximately equal portions. These distributions reflect the greater polyaromatic character of the Herrin coal as a whole, as compared to its sporinite, in agreement with the pyrolysis data.

Fig. 8. Relative concentrations of representative compounds, normalized to the amount of n-C_{21} , in the saturate fraction of the Herrin No. 6 coal and sporinite pyrolyzates. Quantitations are based on GCMS data: m/z 99 (pristane and n-C_{21}), m/z 191 (hopane), m/z 123 [C_{20} terpane, which is peak "C" in Fig. 7, probably 16α(H)-phyllocladane] and m/z 217 [5α(H),14α(H),17α(H) 20R C_{29} sterane]. Pyrolysis conditions were identical for both samples (steel microautoclaves, 320°C, 24 h).
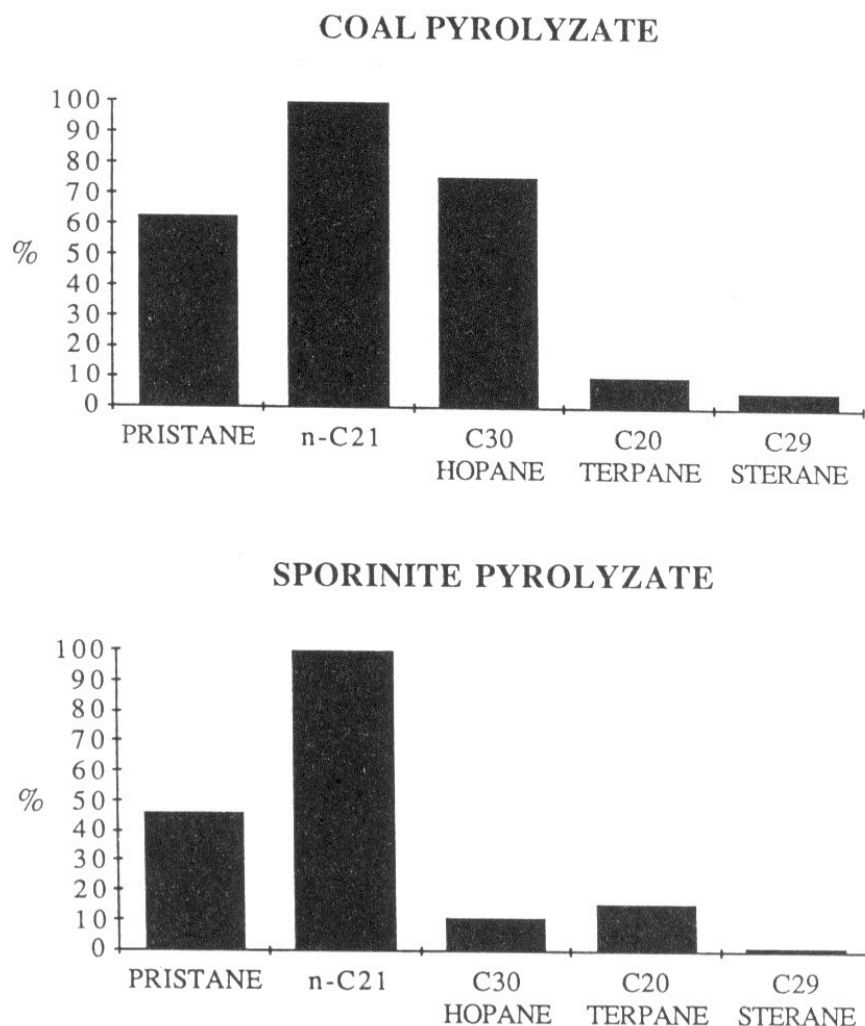
Fig. 9. m/z 91 Mass chromatograms of the aromatic fractions of Herrin No. 6 coal and sporinite pyrolyzates. Peaks labeled N are discussed in the text. Pyrolysis conditions were identical for both samples (steel microautoclaves, 320°C, 24 h).
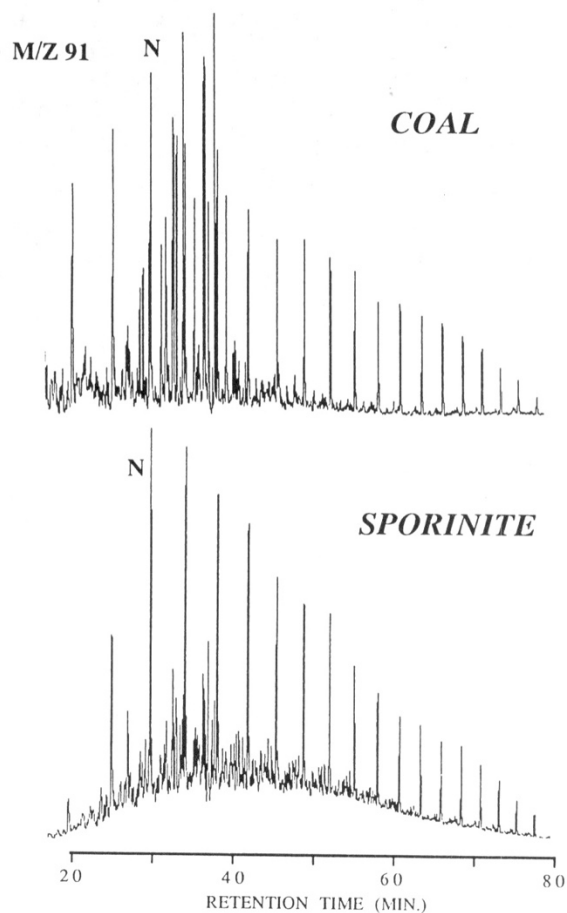

Fig. 10. Partial m /z 198 mass chromatograms of the Herrin No. 6 coal and sporinite pyrolyzates. D = methyldibenzothiophene isomers. Unlabeled peaks may be methylnaphthothiophene or naphthomethylthiophene isomers. Pyrolysis conditions were identical for both samples (steel microautoclaves, 320°C, 24 h).
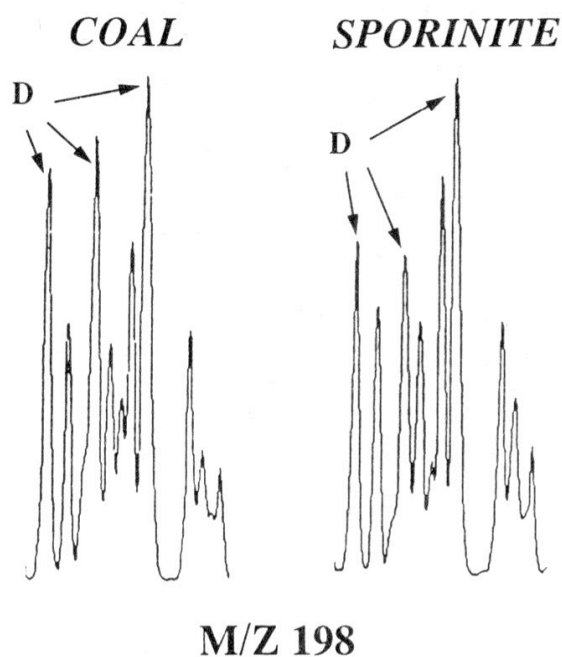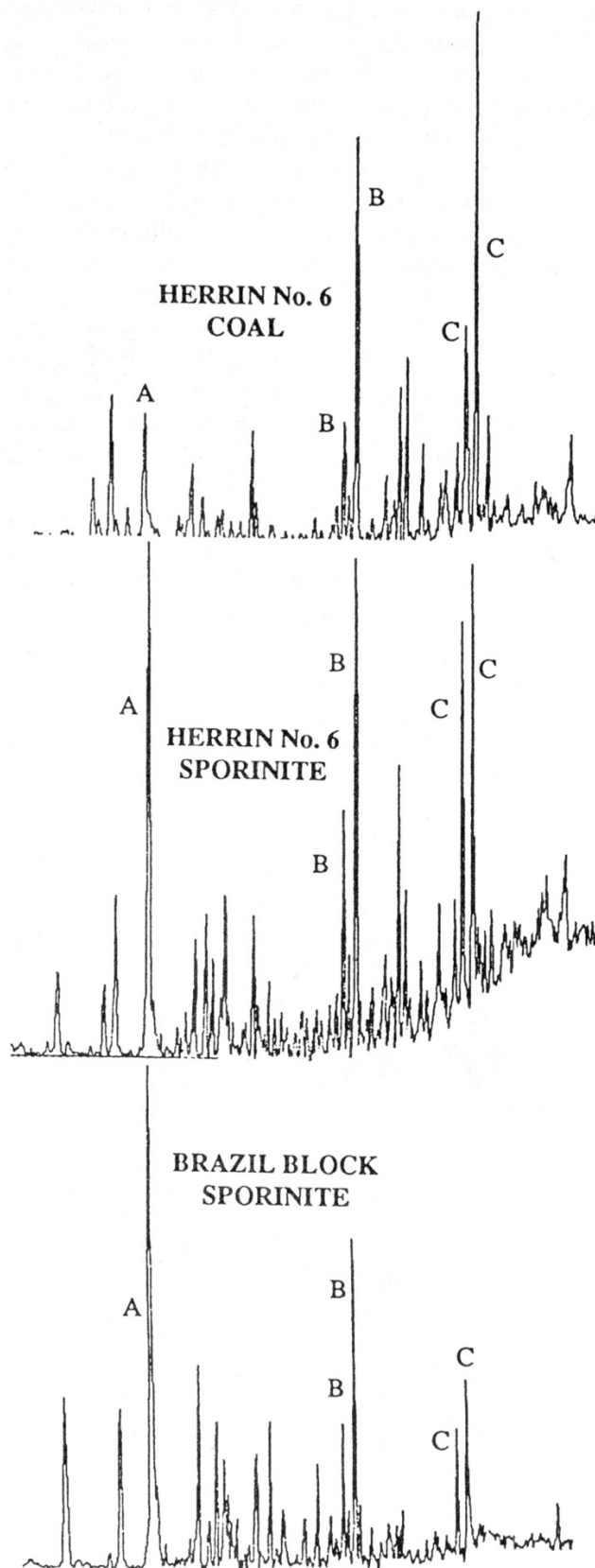
Fig. 11. Chromatograms of the total ion current from GCMS analysis of the oxidation products of the Herrin No. 6 coal and sporinite and the Brazil Block sporinite. Labeled peaks are methyl esters of the following acids: A, benzenedicarboxylic acid; B, benzenetricarboxylic acids; C, benzenetetracarboxylic acids.

Comparison of two sporinites

  The sporinites separated from the Herrin and Brazil Block coals show distinct chemical, as well as petrographic differences. The chemistry of their extracts was discussed above. The dissimilarity of the two extracts reflects the composition of the parent coals, rather than the sporinites specifically, as the extractable bitumen is mobile and free to become homogenized within the coal structure. Analysis of extracts is not a suitable technique for individual maceral characterization. Comparison of fluorescence spectra of the two sporinites does however point to significant structural differences, also discussed above.

  To unambiguously characterize the sporinites themselves, mild pyrolysis and oxidation techniques have proven useful. A series of confined (in vitro) 72 h pyrolysis experiments were run, in which the pyrolysis temperatures were varied (320-380°C). We will discuss the 320°C run for the Herrin sporinite and the 340°C run for the Brazil Block, which gave the best yields for their respective samples. The saturate fractions of these two sporinite pyrolyzates appear similar in their pristane/phytane ratios, and their hopane and sterane distributions. The Brazil Block sporinite is characterized by a more complex mixture of C_{19} and C_{20} tetracyclic diterpanes than the Herrin sporinite, as seen on the m/z 123 mass chromatograms. As these compounds are biological marker compounds derived from higher plants (Philp, 1985), such differences reflect variations in the assemblages of spores deposited in the original peats.

  The aromatic fractions of both sporinite pyrolyzates are very similar in the details of the distributions of principal compounds, e.g. phenanthrene and dibenzothiophene as well as their methyl and dimethyl homologues. *n*-Alkylbenzenes are more abundant in the Brazil Block, relative to polyaromatic hydrocarbons such as phenanthrene, indicating that it is even less polycondensed than the Herrin sporinite, already shown in turn to be less polycondensed than its parent coal, as discussed above.

  The distribution of benzenecarboxylic acids in the oxidation products shows a greater predominance of the dicarboxylic acids in the Brazil Block sporinite than in the Herrin sporinite (Fig. 11). The Brazil Block sporinite also has relatively less tetracarboxylic acids. Thus, in accord with the pyrolysis data, the Brazil Block sporinite has a less polycondensed aromatic structure than does the Herrin sporinite, even though vitrinite reflectance indicates that the Brazil Block sample is of higher rank.

CONCLUSIONS

(1) DGC is an effective technique for separation of sporinite and other macerals from coal. Once separated, the macerals can be chemically analyzed separately, without interference from other macerals, giving a much better understanding of the macromolecular structure of coal.

(2) Solvent extracts of sporinite are virtually identical with those from the parent coal. While analysis of solvent extracts is an important part of coal characterization, it is not the best means for the characterization of pure macerals.

(3) Pyrolyzates of sporinite and the parent coal show significant differences. Sporinites show a greater predominance of *n*-alkanes over branched and cyclic alkanes. Sporinites show a lesser predominance of polyaromatics over *n*-alkylbenzenes. In general, straight-chain moieties are of greater importance in the sporinite than in the parent coal.

(4) In pyrolysis work, tetracyclic diterpanes of the phyllocladane and kaurane type can be used to chemically differentiate between coal macerals, since they are derived from direct terrestrial plant input to the original peat. in contrast, hopanes, the result of post-depositional bacterial degradation, tend to be more uniformly distributed in all macerals of the same coal.

(5) Mild oxidation products of sporinite and the parent coal show significant differences, especially that the sporinite is less polycondensed than the coal. Oxidative degradation techniques are also useful in comparing sporinites from different coals.

(6) The distribution of organic sulfur compounds in sporinite differs from that of the parent coal.

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