A geochemical study of macerals from a Miocene lignite and an Eocene bituminous coal, Indonesia

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Abstract—Optical and chemical studies of maceral concentrates from a Miocene lignite and an Eocene high-volatile bituminous C coal from southeastern Kalimantan, Indonesia were undertaken using pyrolysis, optical, electron microprobe and FTIR techniques. Pyrolysis products of vitrinite from bituminous coal were dominated by straight-chain aliphatics and phenols. The huminite of the Miocene lignite produced mostly phenolic compounds upon pyrolysis. Differences in the pyrolysis products between the huminite and vitrinite samples reflect both maturation-related and paleobotanical differences. An undefined aliphatic source and/or bacterial biomass were the likely contributors of *n*-alkyl moieties to the vitrinite. The resinite fraction in the lignite yielded dammar-derived pyrolysis products, as well as aliphatics and phenols as the products of admixed huminite and other liptinites. The optically defined resinite-rich fraction of the bituminous coal from Kalimantan produced abundant *n*-aliphatic moieties upon pyrolysis, but only two major resin markers (cadalene and 1,6-dimethylnaphthalene). This phenomenon is likely due to the fact that Eocene resins were not dammar-related. Data from the electron microprobe and Fourier transform infrared spectrometry strongly support the results obtained by Py–GC–MS and microscopy. Copyright © 1996 Elsevier Science Ltd

Key words—vitrinite, huminite, resinite, Tertiary Indonesian coal, analytical pyrolysis-gas chromatography–mass spectrometry, Fourier Transform infrared spectrometry, maceral separation

INTRODUCTION

Most Indonesian lignites and low rank coals are liptinite-rich (averaging about 10% liptinite by volume) with low inertinite and high vitrinite (often perhydrous) contents (Hutton *et al.*, 1994) and are therefore excellent potential source rocks for oil. The debate on hydrocarbon generation and migration within coal has intensified since the early work by Brooks and Smith (1967, 1969), who proposed that certain oils originated from coals. Today it is widely accepted that some coals can indeed generate oil (e.g. Hunt, 1991). However, it is still uncertain whether such oil can be expelled from the coal structure (Landais and Monthioux, 1988; Powell and Boreham, 1994).

The coals of Indonesia and Malaysia (Java, Sumatra, Sarawak, Kalimantan) are of special interest since there are large Tertiary coal reserves in this region (e.g. Land and Jones, 1987) and chemical features of local petroleum indicate generation from terrestrial vegetation typical of the area (angiosperm plants and dammar resins) (Snowdon, 1991; Philp, 1994 and references therein). In addition, active peat bogs make the region one of the best areas to study modern coal analogs, not only for Tertiary coal-forming environments (e.g. Esterle *et al.*, 1989;

Moore and Hilbert, 1992; Staub and Esterle, 1994), but also for Carboniferous coal-bearing strata (Staub *et al.*, 1991). Critical to these efforts is the fact that the present peat-forming flora has not changed substantially since the Miocene (Demchuk and Moore, 1993; Collinson *et al.*, 1994 and references therein).

It is well-documented that the tropical angiosperm vegetation (Dipterocarpaceae) that dominated the swamp forests of Kalimantan are prolific resin producers (Collinson *et al.*, 1994). The suberins, which are associated with corkified plant cell walls (Stach *et al.*, 1975), form the maceral suberinite in Indonesian lignites. These two liptinite macerals, resinite and suberinite, although resistant to decomposition at a low maturation level, undergo major evolution in later stages of diagenesis (Stach *et al.*, 1975; Khavari Khorasani, 1987). Despite alterations, resinite is still detectable in high-volatile bituminous coals, whereas suberinite is virtually indistinguishable from vitrinite in coals of higher rank (Khavari Khorasani, 1987; Khavari Khorasani and Michelsen, 1991). The resinites in Indonesian coals have been studied extensively and it has been documented that their chemical structure is based on a polycadinene skeleton (van Aarssen *et al.*, 1990). However, samples used in most of these studies were

megascopic pieces of dammar resins or ambers (Brackman *et al.*, 1984; Anderson and Winans, 1991; Anderson *et al.*, 1992; van Aarssen and de Leeuw, 1992; van Aarssen *et al.*, 1990, 1991, 1994) rather than microscopic-size macerals. Recent geochemical studies on suberinite demonstrated its highly aliphatic character and its ability to release normal hydrocarbons, affecting the chemical nature of vitrinite (Khavari Khorasani, 1987; Tegelaar *et al.*, 1995; Khavari Khorasani and Michelsen, 1991).

In this paper we discuss the chemical characteristics of the major macerals of two Tertiary age Kalimantan coals, utilizing combined optical and chemical studies of high quality maceral concentrates isolated by density gradient centrifugation (DGC). Tertiary Indonesian coals were chosen because of the unusual perhydrous character of vitrinite, as well as high liptinite contents and suitability for the DGC procedure (Stankiewicz *et al.*, 1994). The two coals chosen permitted the comparison of the chemical signatures of macerals of different rank, derived from different floral assemblages.

METHODS

Samples

The first sample is a Miocene lignite from the Warukin Formation, southeastern Kalimantan. The second sample was an Eocene high-volatile C bituminous coal (liptinite-rich) from the Tanjung Formation, southeastern Kalimantan. Collection sites for both samples, as well as the sedimentological setting, have been previously described by Moore and Ferm (1992). The petrographic characteristics of Miocene lignites from the Warukin Formation have been published elsewhere (Moore and Hilbert, 1992; Demchuk and Moore, 1993). The Eocene coals of Kalimantan have H/C atomic ratios in a range of 0.93 to 1.12 (T. Moore, pers. commun., 1995).

Sample preparation

Approximately 50 g of each sample were crushed to 75 mm size and extracted with excess CH_2Cl_2 in a sonicator (15 min × 8). Extraction residues were demineralized using 20% HCl for 24 h and 48% HF, also for 24 h. After the samples were washed and dried, they were treated with liquid nitrogen for 1 h to induce fracturing in the ductile liptinitic macerals, which allows for easier breakage during micronization (Stankiewicz *et al.*, 1994). Coal concentrates thus prepared (42.8 g for the bituminous coal and 41 g for the lignite) were reduced to micron size in a Garlock FMT mill at 20°C in a nitrogen atmosphere (Stankiewicz *et al.*, 1994).

Density gradient centrifugation

The micronized residues (32 g for the bituminous coal and 29 g for the lignite) were suspended in water by means of an ultrasonicator and layered on the top of a CsCl density gradient, following published methodology (Dyrkacz *et al.*, 1981, 1984; Dyrkacz and Horwitz, 1982; Crelling, 1988). Analytical procedures used and operating conditions have been previously described by Stankiewicz *et al.* (1994). Density fractions were recovered by filtration for chemical and petrologic analysis. Yields of those DGC fractions examined further by chemical means varied from 200–900 mg (huminite and vitrinite) down to about 4–40 mg for the resinite-rich fractions (Stankiewicz, 1995). "High resolution" separations (HRDGC) were performed, using a narrower density range (Dyrkacz *et al.*, 1984; Crelling, 1988; Nip *et al.*, 1992). Samples for further analyses were chosen based on the examination of the DGC traces.

Petrographic observations

White light and fluorescence microscopy was performed on the whole rock and the individual density fractions. The composition of density fractions was determined using standard point counting procedure (500 points counted per pellet). Fractions which were high purity concentrates of single macerals were selected and used in subsequent chemical analyses (Table 1; Stankiewicz, 1995). The fluorescence spectra of all petrographically examined DGC fractions were taken and compared to *in situ* macerals in the raw sample (Stankiewicz, 1995).

Pyrolysis–GC–MS

Analysis of the whole Miocene lignite and six of its density fractions (1.03, 1.10, 1.26, 1.35, 1.43 and 1.55 g ml^{-1}) and the whole Eocene coal and four of its DGC fractions (1.11, 1.18, 1.27 and 1.50 g ml^{-1}) were 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). A known amount of up to 1 mg of each sample was pyrolyzed in a flow of helium for 20 s in a quartz tube heated by 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^{-1} to 300°C and then isothermal for 15 min. The MS was operated in full scan mode (50–550 daltons, 0.86 scans s^{-1}, 70 eV ionization voltage). Two of the lignite fractions (1.26 and 1.35 g ml^{-1}) were analyzed using 50 m HP-1 column (0.2 mm i.d., film thickness 0.33 μm), under the following conditions: isothermal for 5 min at 40°C, then ramped 5°C min^{-1} to 300°C and isothermally held for 20 min. Peaks were identified based on mass spectral interpretation and GC retention indices, with reference to the U.S. National Bureau of Standards mass spectral library, Wiley library, and other literature (Saiz-Jimenez and de Leeuw, 1986; Püttman and Villar, 1987; Stout *et al.*, 1988; Forster *et al.*, 1989; Radke *et al.*, 1990; van Aarssen *et al.*, 1990, 1991; Hartgers *et al.*, 1992; Nip *et al.*, 1992; Sinninghe Damsté *et al.*, 1992, 1993).

Table 1. Petrographic composition (vol.%) of the whole Kalimantan coals and selected DGC fractions

	Vitrinite or huminite†	Liptinite*						Inertinite
		Total	Cutinite	Resinite	Exsudatinite	Sporinite	Suberinite	
Eocene coal								
whole	88.2	10.0	0.6	5.2	1.4	2.2		1.8
1.11 g ml⁻¹	4.8	95.2	1.4	84.2	traces	9.6		
1.18 g ml⁻¹	38.0	62.0						
1.25 g ml⁻¹	94.8	5.0						0.2
1.27 g ml⁻¹	98.8	0.8	0.4					
Miocene lignite								
whole	87.2	11.9**	0.2	4.8	0.4	1.2	4.2	1.6
1.10 g ml⁻¹	21.8	78.2§						
1.26 g ml⁻¹	42.0	58.0						
1.35 g ml⁻¹	69.0	31.0						
1.43 g ml⁻¹	96.2	3.8						
1.50 g ml⁻¹	98.3	1.7						
1.55 g ml⁻¹	98.4	1.6						

†Vitrinite in Eocene bituminous coal, huminite in Miocene lignite.
*Specific liptinite macerals not determinable for most density fractions.
**Liptodetrinite accounts for 0.9% of the whole coal. §The majority of liptinite in this fraction is resinite.

Electron microprobe

Four (1.10, 1.35, 1.43 and 1.55 g ml⁻¹) of the lignite and three (1.11, 1.18 and 1.27 g ml⁻¹) of the bituminous coal DGC fractions were made into polished blocks according to standard coal preparation techniques (Bustin et al., 1985) and these polished blocks were sputter-coated with a carbon layer 0.023 mm thick. A Cameca SX-50 electron microprobe with the PAP matrix correction routine (Pouchou and Pichoir, 1991) was used to analyze major and minor elements in vitrinite; a PC2 (NiC) pseudocrystal was used for analyzing the light elements (carbon and oxygen). The physical conditions of the analyses were as follows: an accelerating voltage of 10 kV, a beam current of 10 nA, and a beam size of 5 μm (Bustin et al., 1993). Anthracite, magnesite, and barite were used as carbon, oxygen, and sulfur standards, respectively. Iron, Si, Al and Ca contents also were determined, with fayalite as a standard for iron, and anorthite as a standard for aluminum, silicon and calcium. For each DGC fraction, a minimum of five analyses were obtained.

Micro-FTIR

Functional groups were determined from FTIR spectra collected using a Nicolet 710 micro-FTIR spectrometer equipped with a NICPLAN microscope. A 35X IR objective was used. All spectra were obtained in reflectance mode at a resolution of 4 cm⁻¹, 128 scans were co-added for a single area analyzed (a ratio to a background of 128 scans was calculated) with the Kramers–Kronig transformation applied. Area size was 20 × 20 μm, except for the Eocene 1.11 g ml⁻¹ fraction, for which an area of 5 × 4 μm was analyzed due to small particles size. The FOCAS program was used in spectra deconvolution and in the calculation of areas under selected peaks. Bands were assigned according to Painter et al. (1981) and Wang and Griffith (1985).

RESULTS AND DISCUSSION

Organic petrography

Lignite. Huminite was the major maceral group in the lignite and accounted for 86.5% by volume (Table 1). It also included phlobaphinite (4.8%) associated with suberinite. Liptinites accounted for 11.9% and were dominated by resinite (5.0%), suberinite (4.2%) and liptodetrinite (0.9%). The main inertinite maceral was sclerotinite, volumetrically comprising 1.6% of the raw sample.

The lowest density fraction analyzed in this study was 1.10 g ml⁻¹. The identification of the micronized macerals in this fraction was often difficult due to their lack of distinct shape and very small particle size. However the high magnification (500 ×) used in optical analysis and the specific density range

Table 2. Peak identifications for Figs 1–8

Symbol	Compound name
Bn	(alkyl)benzenes
In	(alkyl)indenes
Nn	(alkyl)naphthalenes
Φn	(alkyl)phenols
Xn	dihydroxybenzenes
Γn	guaiacols
A	C₁₅-cadinene with m.w. 200
B	C₁₅-cadinene with m.w. 202
C	cadalene
D	C₁₅-cadinene with m.w. 204
E	C₁₅-cadinene with m.w. 206
C₃₀	dimers-bicadinenes with m.w. 400–410
*	n-alk-1-ene
+	n-alkane
Δ	pairs of n-alk-1-enes and n-alkanes
Pr	prist-1-ene
Å	fatty acids
HÅ	hexadecanoic acid
i	isoprenoids
PT	pentacyclic triterpenoids
#	contaminants
N	naphthalene
MN	methylnaphthalene
DMN	dimethylnaphthalene
TMN	trimethylnaphthalene
TEMN	tetramethylnaphthalene

"n" indicates the extent of alkyl substitution (0: none, 1: methyl, 2: dimethyl or ethyl, etc.).The number before alkylnaphthalene isomer abbreviations indicates the position of the methyl groups.
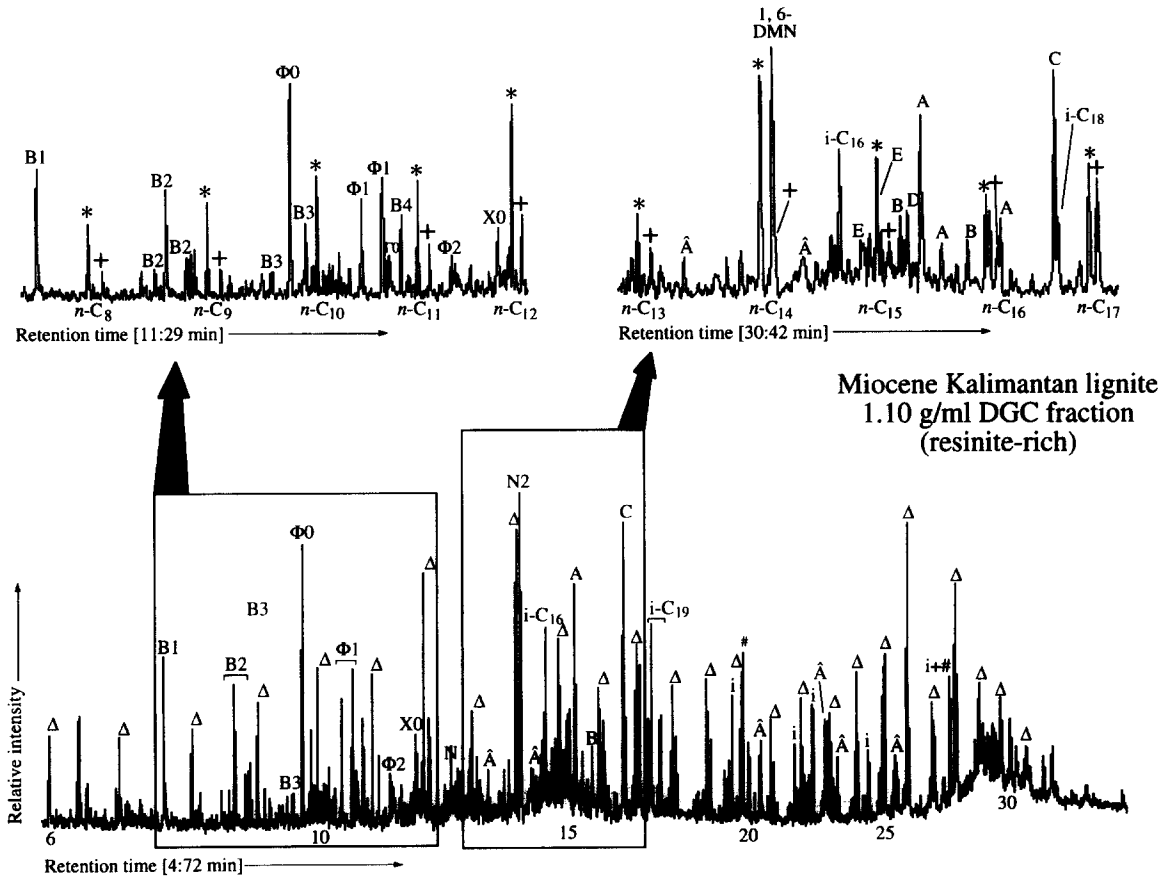
Fig. 1. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the resinite-rich fraction (1.10 g ml⁻¹) from the Miocene lignite. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.

reported in several earlier studies (Murchison and Jones, 1964; Dyrkacz *et al.*, 1984; Nip *et al.*, 1988, 1992) allowed us to conclude that the 1.10 g ml⁻¹ fraction was composed mainly of the resinite, with slight contamination by other liptinites and of fluorescing huminite maceral, perhaps phlobaphinite (Table 1). The two fractions of intermediate density at 1.26 and 1.35 g ml⁻¹ were mixed liptinites and huminite. Suberinite, sporinite and liptodetrinite fragments were the dominant liptinites in the 1.26 g ml⁻¹ fraction. The 1.43 and 1.55 g ml⁻¹ fractions were found to be "clean" huminite, suitable for further investigation (Table 1). The broad peak on a DGC profile in the huminite region was due to a heterogeneity within the huminite maceral group (Stankiewicz *et al.*, 1994).

High-volatile C bituminous coal. The high-volatile C bituminous coal was dominated by vitrinite (88.2%) and resinite (5.2%). The least dense fraction studied (1.11 g ml⁻¹) was dominated by yellow-fluorescing resinite with only minor sporinite, cutinite and exsudatinite (Table 1). The fraction at 1.18 g ml⁻¹ represented mixed liptinites (mainly sporinite) and vitrinites. The DGC fraction at 1.27 g ml⁻¹

contained high purity vitrinite and was only slightly contaminated by liptinites (0.8%). Inertinite was of minor importance and was represented mainly by sclerotinite. The fluorescence spectra of the DGC fractions investigated and other details were discussed by Stankiewicz *et al.* (1994). In summary, the petrographic characteristics of the lignite and bituminous coal samples from Kalimantan showed that both were dominated by huminite/vitrinite group macerals and had low amounts of inertinites. The Eocene vitrinite was largely derived from palm- and fern-dominated flora, whereas the Miocene huminite was mainly dicotyledonous in origin (Moore and Ferm, 1992; Demchuk and Moore, 1993). Resinite accounted for 5.2 and 5.0% of the samples, respectively (Table 1). The fluorescence spectra of the resinite-rich fractions were compared with these of the well-defined resinites in the raw samples and with other resinites spectra (Crelling *et al.*, 1989). Aside from the presence of huminite (the vitrinite precursor) in the lignite instead of vitrinite itself, the main difference in gross maceral composition between the samples was that the lignite had suberinite associated with phlobaphinite.

Pyrolysis–GC–MS

Lignite. The pyrolyzate of the resinite-rich 1.10 g ml^{-1} fraction was dominated by C_6–C_{32} n-alk-1-enes/n-alkanes pairs, together with very strong 1,6-dimethylnaphthalene, cadalene and other cadinene monomers with molecular weights of 200–206 Da (Fig. 1). These cyclic compounds are typical of southeast Asian dammar resin pyrolyzates (van Aarssen et al., 1990). The C_1–C_3 alkylbenzenes, phenol and C_1–C_2 alkylphenols were also prominent, attributable at least in part to the sporinite and minor huminite in the fraction. Other lignin-derived markers, guaiacol and dihydroxybenzenes, typical of peats and low rank coals (Saiz-Jimenez and de Leeuw, 1986; Hatcher et al., 1988; Stout and Boon, 1994) were also present, however they were minor components. Several isoprenoidal compounds were also detected, as were a number of carboxylic acids, the presence of which is intriguing, considering that the samples were extracted several times during the preparation procedure. The distinct hump in the n-C_{29} region was attributed to C_{30} cadinene dimers (van Aarssen et al., 1990), as well as pentacyclic triterpenoids of the oleanane family. The relative abundance of the cadinene-derived resin biomarkers was seen only in the 1.10 g ml^{-1} fraction, strongly

supporting petrographic findings that this DGC fraction was resinite-rich. The presence of aromatic and aliphatic pyrolysis products resulted from admixed liptinites and low density huminite material.

Fractions of 1.26 and 1.35 g ml^{-1} showed a transitional character between resinite and huminite, consistent with the petrographic findings. Both fractions had moderately abundant straight-chain aliphatics, as well as phenolic markers typical of huminite/vitrinite macerals. Compared to the 1.10 g ml^{-1} fraction, there was a marked decrease in the relative abundance of the resin markers, especially those with molecular weights of 200, 202, 204 and 206 Da, which were weak in the 1.26 g ml^{-1} fraction and not detected at all in the 1.35 g ml^{-1}. There was an increase in the relative abundance of the C_{16}–C_{20} and higher isoprenoidal compounds in these fractions.

The pyrolyzate of the huminite fraction of 1.43 g ml^{-1} showed a distinct decrease in n-alkene/n-alkane pairs, leaving the C_1–C_3 alkylbenzenes, phenol and C_1–C_2 alkylphenols as the major components. Guaiacol and dihydroxybenzenes were also relatively abundant pyrolysis products. Isoprenoids became more abundant than straight-chain hydrocarbons (Fig. 2).
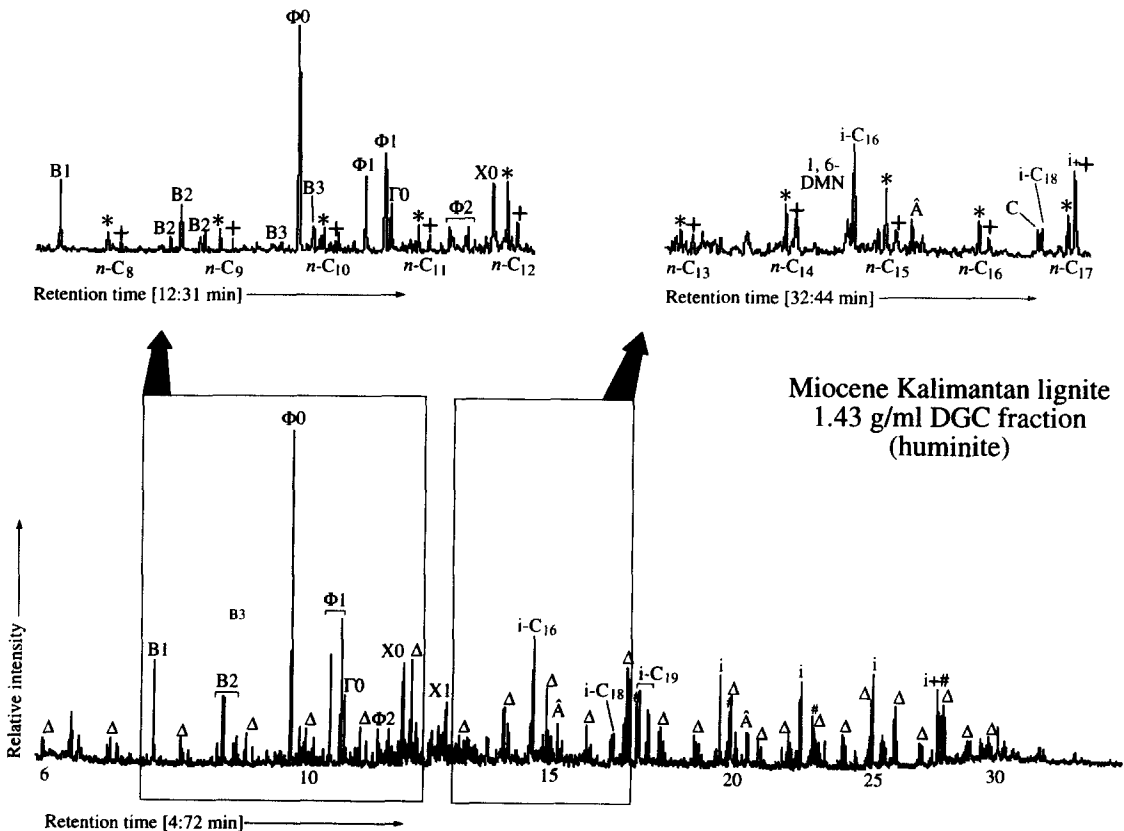

Miocene Kalimantan lignite 1.43 g/ml DGC fraction (huminite)

Fig. 2. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the huminite fraction (1.43 g ml^{-1}) from the Miocene lignite. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.
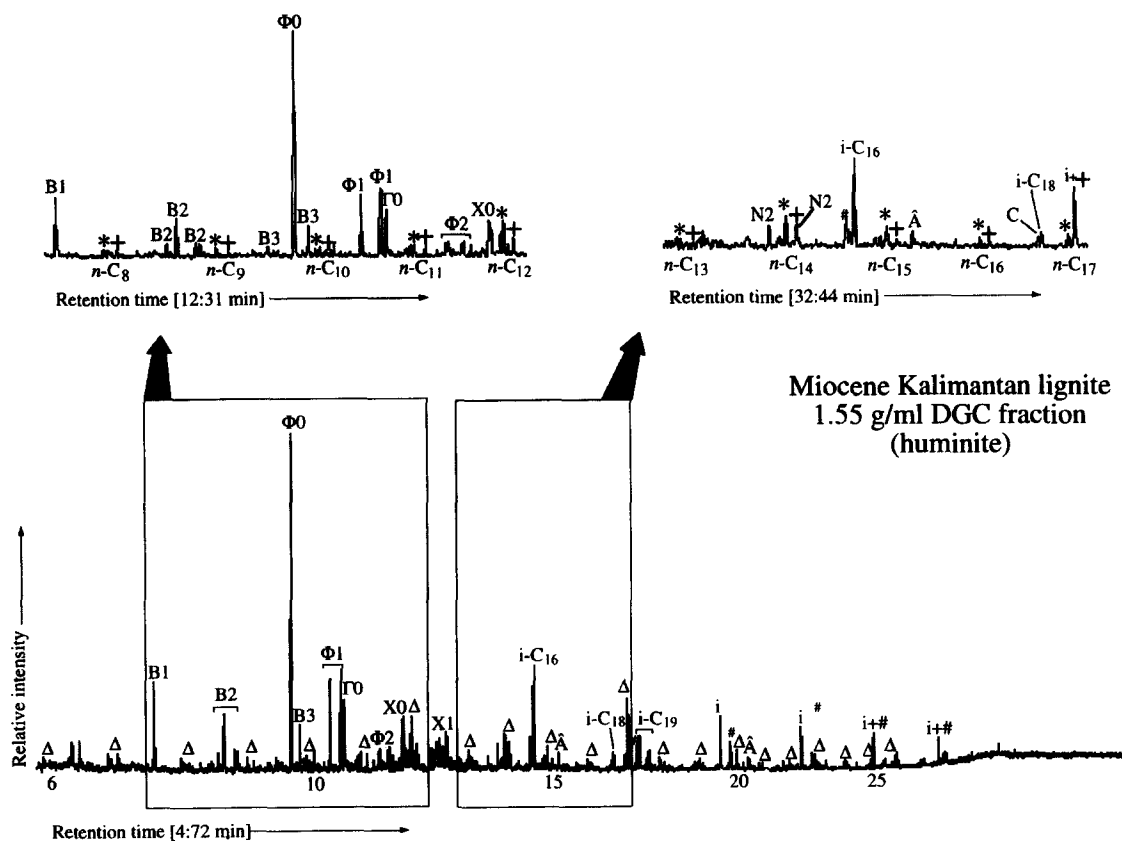
Fig. 3. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the huminite fraction (1.55 g ml^{-1}) from the Miocene lignite. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.

The most dense fraction (1.55 g ml^{-1}), like the 1.43 g ml^{-1} one, presented an example in which lignin-derived markers dominated over aliphatics in its pyrolyzate. Normal hydrocarbons were more difficult to detect, whereas guaiacol and the dihydroxybenzenes were more prominent than in the pyrolyzates of the lighter fractions (Fig. 3). 1,6-Dimethylnaphthalene and cadalene were the only resin markers present, and then only as very minor components. The prominent isoprenoids' peaks were virtually the only important aliphatic compounds in the n-C_{14} to n-C_{30} region of the pyrogram.

The pyrogram of the whole lignite (Fig. 4A) most closely resembled those of the huminite fractions (strong alkylbenzenes, phenol, alkylphenols and dihydroxybenzenes). However, the very pronounced 1,6-dimethylnaphthalene and cadalene peaks indicated a strong resinite influence, and a suite of C_6-C_{35} n-alk-1-enes and n-alkanes indicated contributions from other aliphatic-rich liptinite macerals (Table 1). The interesting phenomenon of an even predominance among n-alk-1-enes (C_{26} and C_{28}) was reported from studies on other lignites and peatified woods (Zhang *et al.*, 1993 and references therein). Tocopherols and pentacyclic terpanes were also present in the pyrolysis products of the raw lignite.

High-volatile C bituminous coal. Two DGC fractions used in the study were chemically distinct from each other. The pyrolyzate of the resinite-rich fraction at 1.11 g ml^{-1} was of a strongly aliphatic nature (n-alk-1-enes and n-alkanes from C_6 to C_{34} with a maximum at around n-C_{27}), which is normally interpreted as typical of terrestrial plant waxes (e.g. Nip *et al.*, 1988, 1989). The C_0-C_3 alkylbenzenes and C_0-C_2 alkylphenols were minor compounds, as were the hopanes (Fig. 5). The major compound eluting before n-C_{17} was cadalene, a characteristic resinite biomarker. However, it must be noted that the presence of the cadalene plus abundant aliphatics may indicate a non-dammar source for these pyrolysis products.

The 1.27 g ml^{-1} fraction's pyrolyzate was dominated by series of C_6-C_{34} n-alk-1-enes/n-alkanes, C_0-C_3 alkylphenols, C_0-C_3 alkylbenzenes, C_0-C_1 dihydroxybenzenes and C_1-C_3 alkylnaphthalenes (Fig. 6). Compared to the pyrogram of the 1.11 g ml^{-1} fraction, the relative abundance of the aliphatics decreased, while alkylphenols, dihydroxybenzenes and alkylbenzenes increased substantially, indicating the highly vitrinitic character of the fraction. The pyrogram of the vitrinite resembled that of the whole coal, which showed a strong influence of
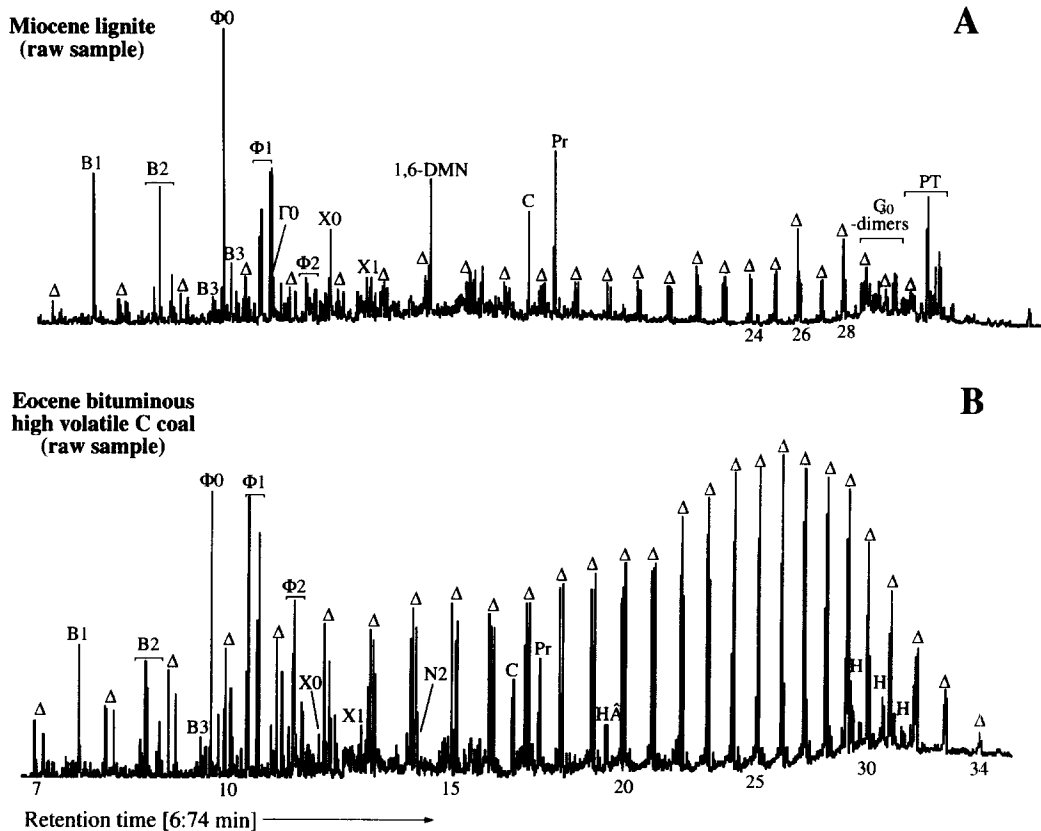
Fig. 4. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the (A) whole Miocene lignite and (B) whole Eocene high-volatile C bituminous coal. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.

the dominant maceral (vitrinite) on the overall coal chemistry (Fig. 4B). Cadalene was the only classical resin marker seen in the pyrogram of the whole coal.

A very important difference between the two DGC fractions was apparent in the distribution of naphthalene and C_1-C_4 alkylnaphthalenes (Figs 5 and 6). In the 1.11 g ml^{-1} fraction, the resin markers 1,6-dimethylnaphthalene and cadalene were clearly predominant. In the 1.27 g ml^{-1} fraction (vitrinite), methylnaphthalenes were the most abundant, the relative concentration of the resin markers decreased, and 1,2,7- and 1,2,5-trimethylnaphthalenes, together with 1,2,5,6-tetramethylnaphthalene (attributed to the degradation of β-amyrin by Püttman and Villar, 1987), were strongly pronounced (Fig. 6).

Elemental composition and FTIR

Lignite. The fraction at 1.10 g ml^{-1} was characterized by the highest carbon content of all the fractions (85.8%), whereas in the other fractions carbon content did not exceed 70%. Its oxygen content of 8.4% (Table 3) was much lower than that of any other fraction. The abundance of these two elements made this fraction unique in the lignite sample, consistent with the petrographic and pyrolytic findings that this fraction represented a

distinctive maceral group. Sulfur content was low (0.15%) and comparable to other fractions. Elements such as Fe, Ca, Si, Al, were insignificant.

FTIR spectra of this fraction revealed very strong aliphatic stretching bands in 2800–3000 cm^{-1} region, with CH_3 (2851 cm^{-1}) being subordinate to CH_2 (2924 cm^{-1}), but clearly shown as a shoulder (Fig. 7). A CH_2 band at 1455 cm^{-1} was also prominent, indicating a substantial content of aliphatic structures. The aromatic carbon band at 1612 cm^{-1} was also strong. Carboxyl/carbonyl groups were detected at around 1711 cm^{-1}. The 700–900 cm^{-1} aromatic out-of-plane region showed a distinct band at 832 cm^{-1}, assigned to long chain aliphatics, whereas aromatic bands in this region were almost undetectable. All these observations suggested that this fraction contains liptinite, which is consistent with the petrographic evidence.

The fraction of 1.35 g ml^{-1} had 67.2% carbon and about 20% oxygen. These values were close to those from two denser fractions (1.43 and 1.55), however a trend of increasing O/C atomic ratio values with increasing density was evident (Table 3). Other elements analyzed were insignificant, although Fe concentration in this and denser fractions was much higher that in the lightest one (0.65% as opposed to 0.01% in the 1.10 g ml^{-1}). Functional group
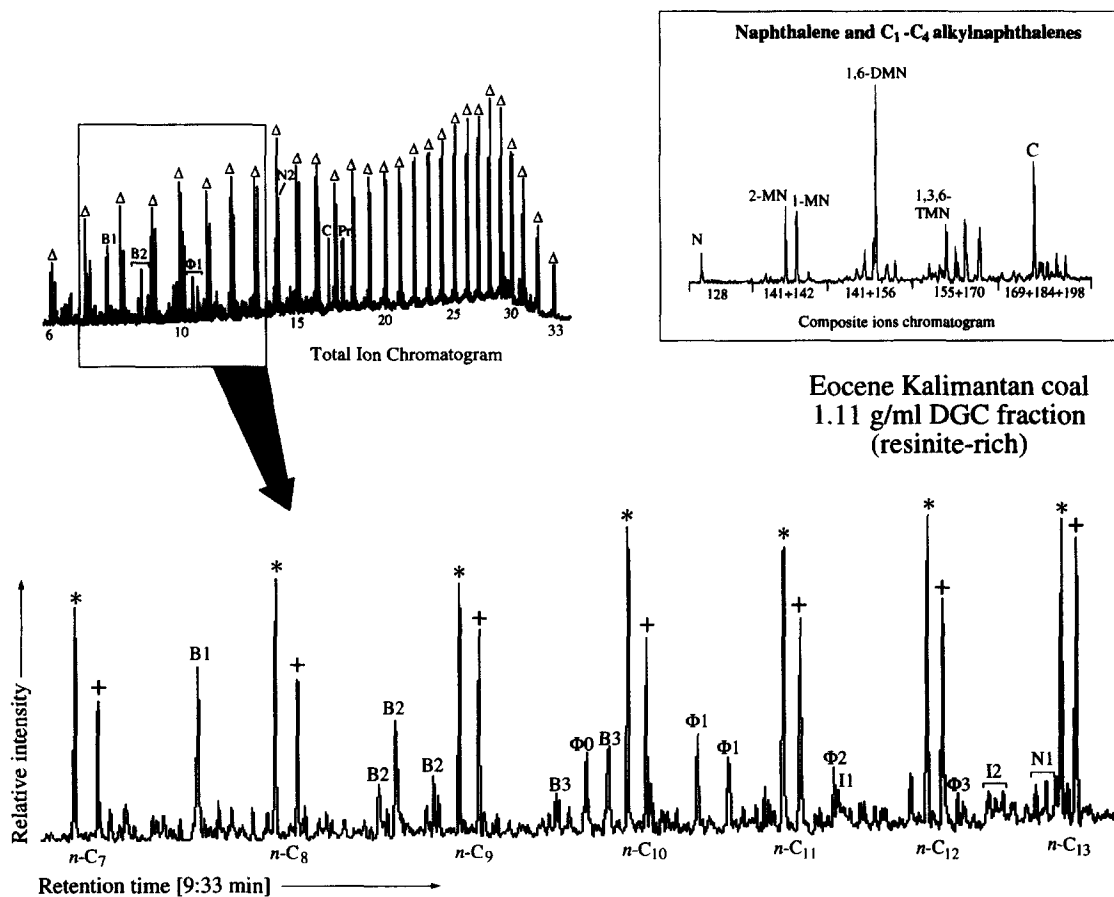
Fig. 5. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the resinite-rich fraction (1.11 g ml⁻¹) from the Eocene high-volatile C bituminous coal. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.

distribution, in general, was similar to the resinite-rich fraction and the only distinct difference was a much lower absorbance of aliphatic stretching bands in the 2800–3000 cm⁻¹ region (Fig. 7). Also, the aromatic carbon band was more prominent than in 1.10 g ml⁻¹ fraction. This indicated a lower abundance of aliphatic CH_2 and CH_3 groups and higher aromaticity in the 1.35 g ml⁻¹ fraction.

The 1.43 g ml⁻¹ DGC fraction was similar to the 1.35 fraction, both in elemental distribution and FTIR spectra. Mean carbon content (66.8) was slightly lower and oxygen content was slightly higher (20.7%) than for the 1.35 fraction. This suggested that these two fractions contained mixtures of macerals, and only the proportions of the major components were different. The most distinct difference between this and the 1.35 g ml⁻¹ fraction was a slightly suppressed aliphatic signature in the 1.43 fraction, which indicated lower concentrations of CH_2 and CH_3 groups (Fig. 7).

The most dense (1.55 g ml⁻¹) fraction had the lowest (59.2%) carbon content and highest oxygen content (24.9%). In terms of functional group distribution, this fraction differed substantially from

all other fractions. The bands representing aliphatic stretching modes were insignificant and the aliphatic band at 1448 cm⁻¹ was also less distinct. The aromatic carbon band at 1620 cm⁻¹ was dominant. The FTIR signature clearly showed that this fraction had the highest aromaticity (Fig. 7) and its spectrum resembled very closely those of huminite in lignite (Mastalerz and Bustin, 1993a, 1993b).

High-volatile C bituminous coal. In general, the elemental compositions of all three bituminous coal fractions were similar, with atomic O/C varying only from 0.145 to 0.148. The S/C ratios were very low (0.0005–0.0014) but did show an increase with increasing density (Table 3).

The fraction at 1.11 g ml⁻¹ was of very small particle size and it was difficult to obtain good quality FTIR spectra. The spectrum presented in Fig. 8 did show very low aromaticity, with aliphatic stretching modes in the 2800–3000 cm⁻¹ as the most significant bands. Even though the FTIR spectrum was of poorer quality than all other fractions, its characteristics did not leave any doubt that this fraction represented liptinitic material. FTIR spectra from the mixed liptinite/vitrinite fraction at 1.18 g ml⁻¹
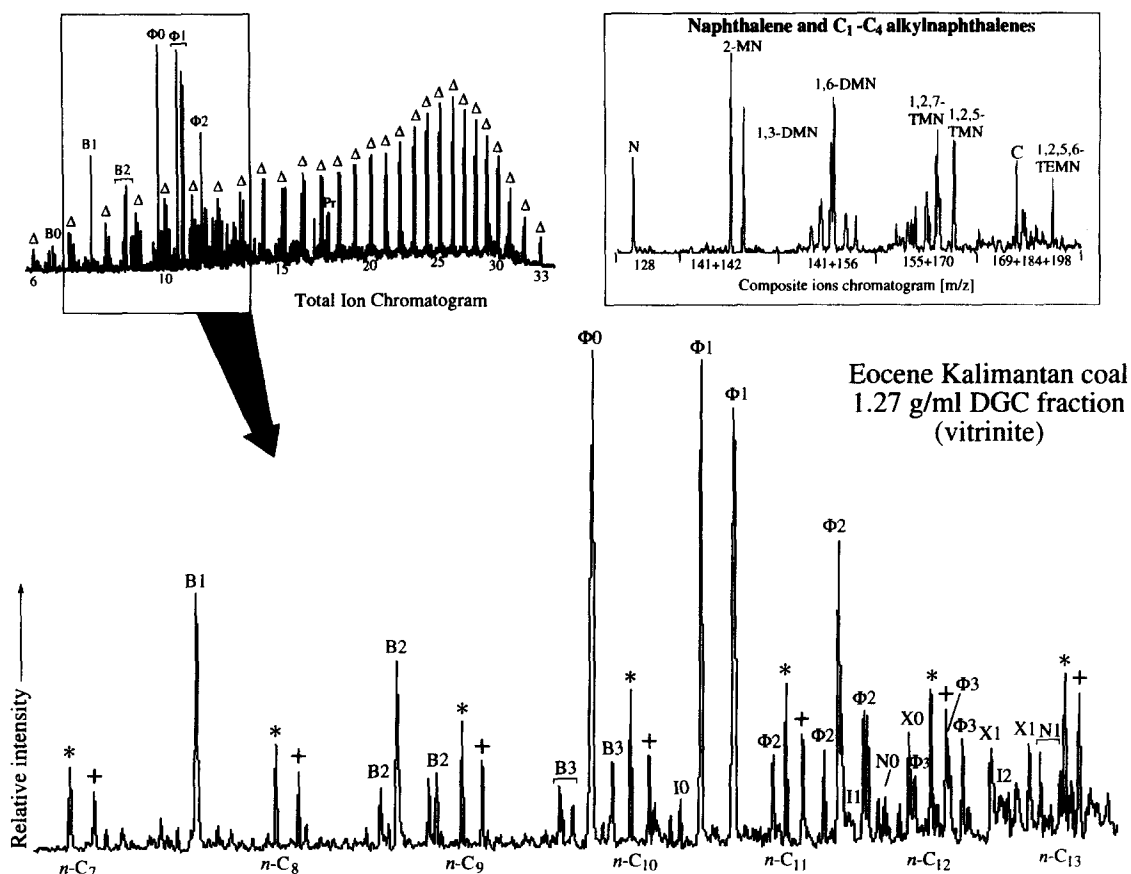
Fig. 6. Total ion current of the pyrolyzates (610°C for 20 s, 25 m HP-1 column) of the vitrinite fraction (1.27 g ml^{-1}) from the Eocene high-volatile C bituminous coal. See Table 2 for peak identifications. Numbers below chromatograms indicate the carbon number in alkene/alkane series.

revealed very strong aliphatic stretching bands in the 2800–3000 cm^{-1} region, related to CH_2 (Fig. 8). The CH_3 band was almost undetectable without curve deconvolution. The CH_2 band at 1455 cm^{-1} was prominent, as was the aromatic carbon band at 1698 cm^{-1}. Carboxyl/carbonyl groups showed as small shoulders at around 1618 cm^{-1}. These FTIR characteristics were consistent with a predominately liptinitic composition, in accord with the petro-graphic analysis.

FTIR spectra revealed distinct differences between the 1.27 g ml^{-1} and the 1.18 g ml^{-1} fraction. The most striking difference was much less abundant CH_2 and CH_3 groups in the 1.27 g ml^{-1} DGC fraction, indicating higher aromaticity (Fig. 8). This fraction also did not show oxygenated groups at 1600–1800 cm^{-1}. These characteristics suggested that vitrinitic material was dominant in this fraction, although it was clearly also very aliphatic, in agreement with the petrographic and pyrolytic data.

Table 3. Elemental composition of the Miocene lignite and Eocene coal maceral fractions obtained by electron microprobe. Percentages are averages for each element in each DGC fraction; n = number of particles analyzed for each fraction. Hydrogen and nitrogen not determinable by this method

Element	Miocene lignite DGC fractions				Eocene coal DGC fractions		
	1.10 g ml^{-1}	1.35 g ml^{-1}	1.43 g ml^{-1}	1.55 g ml^{-1}	1.11 g ml^{-1}	1.18 g ml^{-1}	1.27 g ml^{-1}
C (%)	85.765	67.183	66.822	59.221	79.126	77.999	77.230
O (%)	8.679	20.151	20.738	24.943	15.277	14.990	15.255
S (%)	0.147	0.153	0.133	0.172	0.096	0.190	0.279
Si (%)	0.146	0.045	0.021	0.016	0.046	0.035	0.028
Al (%)	0.099	0.070	0.105	0.125	0.152	0.061	1.027
Fe (%)	0.012	0.650	0.490	0.415	0.037	0.091	0.011
Ca (%)	0.014	0.170	0.290	0.900	0.003	0.007	0.013
Total (%)*	94.861	88.424	88.599	85.792	94.737	93.373	93.844
n	7	5	5	5	5	5	5
O/C	0.076	0.227	0.234	0.316	0.148	0.145	0.148
S/C	0.0006	0.0009	0.0007	0.0011	0.0005	0.0009	0.0014

*The total of all measured elements is less than 100% due to lack of detection of the H and N (limitation of the method).
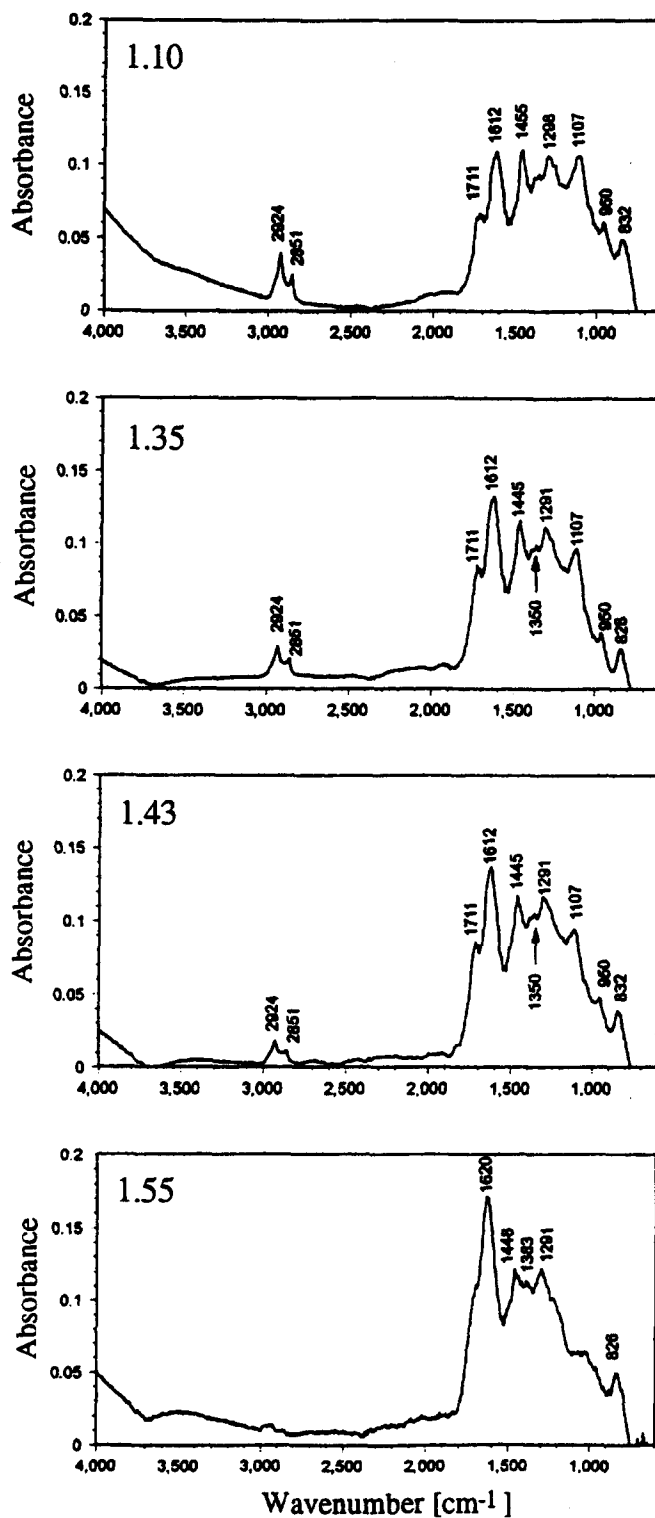
Fig. 7. FTIR spectra of the Miocene lignite DGC fractions. Note decreasing intensity of aliphatic stretching modes in the 2800–3000 cm^{-1} region from the 1.10–1.55 g ml^{-1} fractions.

Huminite/vitrinite

Both the whole bituminous coal from Kalimantan and its constituent vitrinite were distinctly H-rich, as indicated by the high concentration of normal hydrocarbons in their pyrolyzates and the prominence of aliphatic bands in the FTIR spectra. In contrast, neither the whole lignite nor its huminite-rich density

fractions showed a perhydrous character. This can be partially explained by differences in the starting material between these two coals. On the paleobotanical level, the primary organic matter of the two samples was significantly different. The bituminous coal was formed mostly from degraded palm and fern flora, while the lignite was mainly dicotyledonous in origin, with less degradation. However, the extent of the competing influences of thermal maturation and initial botanical composition cannot be unambiguously resolved without further analysis.

Aliphatic compounds were present in the pyrolyzate of the huminite concentrate in the form of an important series of long chain isoprenoids (Fig. 2). In fact, the importance of the isoprenoids increased with increasing density in the pyrolyzates of the fractions

isolated from the lignite. The proposed derivation of these compounds from macromolecularly-bound tocopherols (Goossens et al., 1984; van Bergen et al., 1993; Hartgers et al., 1994) could be valid for the Kalimantan lignite, for which tocopherols were detectable pyrolysis products in the whole coal sample. However, the presence of isoprenoids with carbon numbers greater than 20 was puzzling and requires further investigation, as the longer chain length would preclude origin from a tocopherol. In any event, straight-chain compounds were not major components of the huminite pyrolyzate.

In contrast, the vitrinite of the bituminous coal produced abundant normal hydrocarbons upon pyrolysis (Fig. 6). The strong aliphatic nature of this vitrinite, marked by the presence of the n-alk-1-enes/
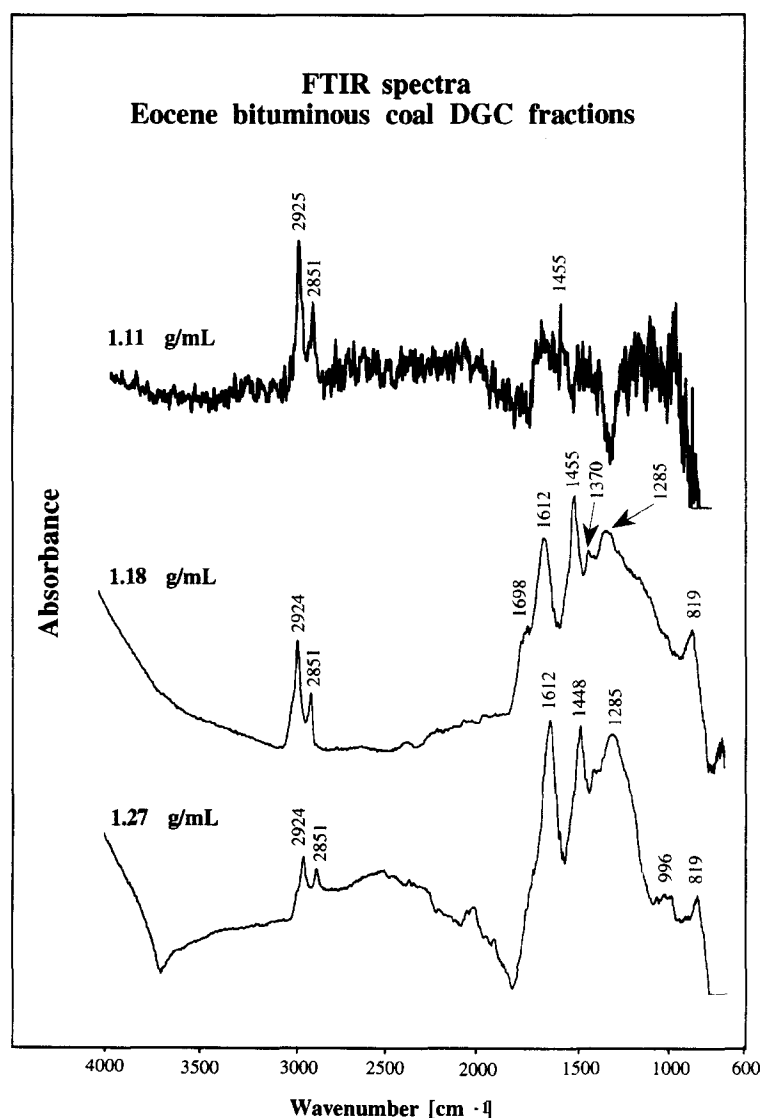

Fig. 8. FTIR spectra of Eocene high-volatile C bituminous coal. Note distinct differences in intensity of aliphatic stretching modes 2800–3000 cm⁻¹ region between fractions, stronger aromatic carbon 1612 cm⁻¹ band in the 1.27 g ml⁻¹ fraction and highly aliphatic character of the 1.11 g ml⁻¹ fraction. (The poor signal/noise ratio results from the very small size of the analyzed area. See text.)

n-alkanes in the pyrolyzate, is intriguing. It is difficult to speculate on the source or possible processes leading to the formation of (optically-defined) vitrinite rich in *n*-alkyl moieties. The only pyrolysis products of the 1.27 g ml⁻¹ fraction, which can be explained as typically vitrinite-derived are (alkyl)phenols and (alkyl)benzenes. There have been several reports published proposing sources of aliphatic (bituminous) material as possible contributors to the other coal macerals (Teichmüller, 1982; Khavari Khorasani, 1987; Stout, 1994), however none of them provided a definitive model explaining this phenomenon. Mechanisms proposed to explain enrichment of vitrinite in substances not derived from lignin, such as impregnation of woody material by resin before burial, have been recently suggested by Suarez-Ruiz *et al.* (1994). However if this latter mechanism were operating, one would expect to find biomarker compounds typical of resins (1,6-dimethylnaphthalene and cadalene) to be abundant in the vitrinite pyrolyzates, which was not the case.

An alternative cause for abundant aliphatics in the vitrinite could be a microbial contribution to the lignin matrix (Hartgers *et al.*, 1994). This could indeed have been a contributing factor, since bacterial markers (hopanoids) were detected in the bituminous coal's vitrinite pyrolyzate. The monocot angiosperm (palm) precursors of this coal are known to be especially susceptible to microbial decay (Moore and Ferm, 1992). This hypothesis could be tested by artificial maturation experiments on degraded, monocot-dominated peats.

Resinite

Another interesting problem related to macerals was that the resinite-rich fraction isolated from the Eocene bituminous coal sample was dominated by C₆–C₃₄ *n*-alk-1-enes and *n*-alkanes, whereas Indonesian resins are known to produce compounds with a cadinene-type skeleton almost exclusively (e.g. van Aarssen *et al.*, 1990). Looking at the pyrogram of the resinite-rich fraction from the bituminous coal (Fig. 5), one may say that it has a typical cutinite signature (e.g., Nip *et al.*, 1989). However, cutinite comprised only 0.6% of the coal sample and 1.4% of the DGC fraction and it is unlikely that this maceral could be the direct source of straight-chain aliphatics in this fraction. The sporinite present in this fraction (9.6%) was also unlikely to be a major source of these strong aliphatics, as this maceral is known to be more aromatic in nature than the almost purely aliphatic cutinite (Kruge *et al.*, 1991; Nip *et al.*, 1992; Collinson *et al.*, 1994; Han, 1995). Exsudatinite might be the source of these abundant straight-chain aliphatics, but it seems rather improbable since this maceral was detected only in trace amounts. Taking into account the fact that the dominant maceral in the 1.11 g ml⁻¹ DGC fraction was resinite (84.2%), it seemed logical that the overall chemical signature of the fraction must come from this maceral.

One possible explanation could be that the resins in the Eocene coals (mainly of palm and fern origin) are not dammar-related and thus do not produce cadinene-type compounds upon pyrolysis. This would in turn suggest a non-dammar source for cadalene. Thus macerals optically defined as resinites in these coals do not possess the classical resin pyrolytic signatures. A similar phenomenon has been reported for the optically defined resinous material from the Carboniferous coals, which possess a highly aliphatic character, producing predominantly straight-chain alkenes/alkanes upon pyrolysis (e.g. Nip *et al.*, 1988, 1992; Collinson *et al.*, 1994). Some other studies also reported an unexpected aliphatic character in the resinites of bituminous coals (Khavari Khorasani and Murchison, 1988). One of the important reasons why most of the published studies on resinite have not reported an aliphatic nature for the maceral was that most of them have been performed on resins and ambers younger than Eocene (Grantham and Douglas, 1980; Brackman *et al.*, 1984; Wilson *et al.*, 1984; Senftle and Larter, 1988; Anderson and Winans, 1991; Anderson *et al.*, 1992; van Aarssen *et al.*, 1990, 1991; van Aarssen and de Leeuw, 1992; Meuzelaar *et al.*, 1991).

In the pyrolyzate of the resinite-rich fraction of the lignite, most of the dammar-type markers described by van Aarssen *et al.* (1990) were present (Fig. 1). The presence of the *n*-alk-1-enes and *n*-alkanes in this pyrolyzate was attributed to the traces of admixed exsudatinite, suberinite and liptodetrinite, whereas distinct phenols and alkylbenzenes could be the result of sporinite or huminite contamination or be derived from minor lignin present in other liptinite precursors. It is important to mention that phenols might be also derived from resinous material (Crelling *et al.*, 1991). In contrast, only two classical resin marker compounds were detected in the resin-rich fraction of the bituminous coal sample, suggesting that the resinite in this particular Eocene coal does not have a polycadinene structure.

SUMMARY AND CONCLUSIONS

1. For the first time, a combination of petrographic, Py–GC–MS, FTIR and electron microprobe techniques has been applied for detailed characterization of the maceral concentrates separated by DGC from Indonesian coals.

2. The DGC technique allowed for the isolation of the dominant macerals in both samples: huminite in the lignite, and vitrinite in the high-volatile C bituminous coal. The minor resinite macerals present in both samples were partially isolated.

3. The chemical differences revealed by Py–GC–MS, FTIR and the electron microprobe between resinite-rich and huminite DGC fractions are more strongly pronounced in the lignite, as compared with the analogous maceral fractions in the bituminous coal.

4. The pyrograms of the resinite-rich concentrate from lignite showed the characteristic cadinene-type resin biomarkers among other pyrolysis products. The only prominent, known resin biomarkers in the resinite-rich fraction of the bituminous coal were 1,6-dimethylnaphthalene and cadalene, which might be of non-dammar origin.

5. The pyrolyzates of the lignite's huminite exhibited the typical highly phenolic signature of lignin-derived material, with only minor aliphatic compounds. In contrast, the vitrinite from the bituminous coal was dominated by C_6–C_{34} normal hydrocarbons, in addition to abundant phenolic compounds.

6. The aliphatic character of the vitrinite of the bituminous coal tends to implicate the original floral assemblage and possible microbial material as only logical contributors of n-alkyl moieties to these coals, since they were lacking other common sources of aliphatics, such as alginite and cutinite.

7. The unexpectedly aliphatic nature of the resinite fraction from the bituminous coal indicated that this optically-defined Eocene resinite does not possess the classical (dammar-derived) polycadinene structure. This implies that the resins found in this Eocene coal sample were chemically and botanically different from the Miocene and younger dammars.

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