Chapter 10

Molecular Characterization of Vitrinite Maturation as Revealed by Flash Pyrolysis Methods

H. Veld[1,2], J. W. de Leeuw[3], J. S. Sinninghe Damsté[3], and W. J. J. Fermont[2]

[1]Laboratory of Paleobotany and Palynology, University of Utrecht, Heidelberglaan 2, 3584 CS Utrecht, Netherlands
[2]Geological Survey, P.O. Box 126, 6400 AC Heerlen, Netherlands
[3]Netherlands Institute for Sea Research (NIOZ), Division of Marine Biogeochemistry, P.O. Box 59, 1790 AB Den Burg, Netherlands

Curie-point pyrolysis - gas chromatography analyses were performed on four vitrinite concentrates of maturity levels from 0.96 %Rmax to 1.93 %Rmax. Analyses were carried out on "thermal extracts" obtained at a Curie-temperature of 358 °C and on pyrolysates obtained at a Curie-temperature of 770 °C. The relative concentrations of alkylphenols and alkylnaphthalenes decrease with increasing maturity. Alkylbenzenes are prominent pyrolysis products throughout the maturity interval investigated. A significant increase in the relative concentration of alkylphenanthrenes and alkylbiphenyls with increasing maturity is noted. There is a substantial similarity between the compositions of "thermal extracts" and pyrolysates. This indicates that the trends observed are mainly due to changes in frequency distributions of extractable compounds. Vitrinite reflectance measurements carried out on the unextracted and extracted concentrates revealed no significant differences with one exception. For one sample, with a maturity approximately at the transition from the "oil window" to the "gas window", solvent extraction resulted in a significantly higher reflectance value of the residue. This sample was rich in extractable n-alkanes.

A major constituent of many coals is vitrinite. The macerals of the vitrinite group are derived from plant cell wall material (woody tissue) by processes of humification. During the subsequent physico-chemical stage of coalification time and temperature are the main factors governing the transformation of organic matter. A wide variety of methods has been applied to monitor these thermally induced chemical and physical changes. The most important physical parameter to measure the degree of coalification or maturation is based on the progressive change in the capacity of macerals to reflect incident light. The

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advantage of reflectance measurements is that the relatively small measurement area allows determinations to be carried out on specific macerals. Vitrinite reflectance is by definition measured on one vitrinite maceral, i.e. telocollinite (*1, 2*). Unlike most of the other macerals telocollinite shows a relatively gradual change with increasing coalification. Many of the chemical rank parameters are obtained from bulk samples of coal. There is evidence that the values of these parameters depend on the relative proportions of the different macerals present in the coal (*3, 4*). Previous studies demonstrated that flash pyrolysis methods are very useful for the characterization of the insoluble fraction of coals, coal macerals and their precursors on a molecular level (*5 - 9*). However, these studies concentrated either on the characterization of relatively low rank coals or did not account for specific coal petrographic compositions of the studied material. To date only a few studies applied analytical pyrolysis methods on high rank coals (*7, 10*). The aim of the present study is to examine in detail the molecular changes that take place in a series of high rank vitrinite macerals as revealed by flash pyrolysis.

Material

Four vitrinite concentrates were obtained from the European Centre for Coal Specimen (SBN). The concentrates were prepared from Upper Carboniferous (Westphalian) vitrinite-rich coals from the Ruhr area in Germany by means of chemical and mechanical comminution and density flow separation techniques (*11*). The density separations were carried out using mineral density solutions to avoid contamination of organic solvents. The purity of the concentrates ranges from 93.8 to 98.0 %. The vitrinite reflectance values of the concentrates range from 0.96 to 1.93 %Rmax, which classifies the coals as high volatile bituminous A to low volatile bituminous coals. A data summary is given in Table I. More detailed information on the chemical and petrographical properties of the parent coals and of the vitrinite concentrates is given elsewhere (*12*).

Table I. Data summary of the vitrinite concentrates

Code	*Parent coals*						*Vitrinite concentrates*					
	%Ro	*SD*	*V*	*L*	*I*	*M*	*%Ro*	*SD*	*V*	*L*	*I*	*M*
312	1.07	0.04	48.2	7.4	29.4	15.0	1.02	0.05	93.8	2.2	4.0	0.0
313	1.31	0.04	69.0	0.0	10.0	21.0	1.26	0.06	98.0	0.0	2.0	0.0
314	1.63	0.06	82.4	0.0	15.0	1.6	1.64	0.10	95.8	0.4	3.8	0.0
315	1.89	0.06	65.2	0.0	32.8	2.0	1.91	0.12	96.0	0.2	3.6	0.2

%Ro = mean random vitrinite reflectance, *SD* = standard deviation, *V* = %Vitrinite, *L* = %Liptinite, *I* = %Inertinite, *M* = %Mineral matter (Data provided by the European Centre for Coal Specimen).

Methods

Vitrinite reflectance. Mean maximum vitrinite reflectance measurements (%Rmax) were carried out following standard procedures (*1, 2*). Vitrinite reflectance was measured on polished blocks of the parent coals, the unextracted and the extracted vitrinite concentrates. The different fractions of the samples have the extensions P, B and R, respectively (see Table II). Measurements were carried out under oil immersion at a wavelength of 546 nm using a Leitz MPV III microscope system.

Curie point pyrolysis - gas chromatography (Py-GC) and Curie point pyrolysis-gas chromatography - mass spectrometry (Py-GC-MS). The Py-GC analyses were performed on a Varian 3700 gas chromatograph, equipped with a FOM-3LX unit for pyrolysis (*8*). The samples were applied to a ferromagnetic wire (*13*). A Curie point high-frequency generator (Fischer, Model 9425) was used to generate the magnetic field. The ferromagnetic wires were inductively heated in 0.15 s to their Curie temperatures, 770 °C for pyrolysis and 358 °C for "thermal extraction", and were kept at their final temperature for 10 s. Separation of the pyrolysis products was achieved using a fused-silica column (25 m x 0.32 mm I.D.) coated with CP Sil-5 (film thickness 0.45 μm). Helium was used as the carrier gas. The oven was programmed from 0 °C (5 min isothermal) to 320 °C (10 min isothermal) at a rate of 3 °C/min. Ultrasonic solvent extraction of the vitrinite concentrates was executed using methanol-dichloromethane (1:1). Thermal extraction (358 ° C) as well as flash pyrolysis (770 °C) was performed on the unextracted and the solvent extracted vitrinite concentrates.

For the Py-GC-MS analyses, the same pyrolysis unit, capillary columns, carrier gas and temperature conditions of the HP 5890 Hewlett Packard gas chromatograph were used, as mentioned for the Py-GC analyses. The GC column was directly inserted into the ion source of a VG-70S mass spectrometer. Electron impact spectra were obtained at 70 eV using the following conditions: mass range *m/z* 50-900; cycle time 1.8 s.

Results

The results of the reflectance measurements are presented in Table II as the mean of 50 readings and their standard deviation. Except for sample 313 no significant differences in reflectance values were recorded between the three different sample fractions. For sample 313 the measured reflectance of the parent coal and its vitrinite concentrate are almost identical whereas the reflectance value of the extracted concentrate is 0.16 %Rmax higher, which is considered significant.

In Figures 1a-d the chromatograms of the pyrolysates of the unextracted samples are shown. The identification of the components released was by Py-GC-MS and is given in Table III.

A considerable decrease in the number of components with increasing rank, especially between the samples 313 and 314, is noted. The relative

proportions of the constituents also change with increasing rank. Figure 1a shows the partial Py-GC trace of sample 312-B. This pyrolysate is mainly characterized by the presence of alkylbenzenes, alkylphenols, alkylnaphthalenes and, to a lesser degree, by homologous series of n-alkanes and n-alk-1-enes. Sample 313-B has a similar composition although the relative abundances of the individual components differ to some extent. Both the C_2-alkylated naphthalenes as well as n-alkanes are the most dominant peaks in the pyrolysate of this sample.

Table II. Vitrinite reflectance measurements

Code	*P*		*B*		*R*	
	%Rmax	*SD*	*%Rmax*	*SD*	*%Rmax*	*SD*
312	0.98	0.06	0.96	0.04	0.96	0.05
313	1.23	0.05	1.21	0.06	1.37	0.04
314	1.66	0.05	1.59	0.07	1.64	0.05
315	1.93	0.06	1.93	0.07	1.88	0.06

P = Parent coal; B = Unextracted vitrinite concentrate; R = Extracted vitrinite concentrate; SD = Standard deviation

The pyrolysates of samples 314-B and 315-B are dominated by alkylbenzenes, alkylnaphthalenes, alkylanthracenes and alkylbiphenyls. Straight chain n-alkanes, n-alk-1-enes and alkylphenols are still present as minor constituents and differences exist in the relative proportions of the individual components. As can be deduced from Figure 1 there is a distinct maximum in the relative abundance of the n-alkanes and the C_2- and C_3-alkylated naphthalenes (Q and T) in the pyrolysate of sample 313-B, as compared to the other samples.

The chromatograms of the flash pyrolysates of the extracted vitrinite concentrates (Figures 2a-d) and their unextracted counterparts (Figures 1a-d) reveal only minor differences in composition. The main difference is a significant reduction of the relative abundance of the C_2-alkylated naphthalenes and the n-alkanes. This is most obvious in sample 313 (Figures 1b and 2b).

The chromatograms of the series of "thermally extracted" vitrinite concentrates which were previously solvent extracted show a very high signal to noise ratio due to the relative efficient removal of soluble compounds. This series is not further discussed here.

The results obtained by the "thermal extraction" at a Curie temperature of 358 °C show that the thermal extracts have a similar composition as the pyrolysates of the unextracted vitrinite concentrates (Figure 3). The proportions, however, may differ significantly. The main differences in comparison to the pyrolysates are a clear dominance of alkylnaphthalenes and a lower yield of alkylphenols and alkylbenzenes. n-Alkanes are present as

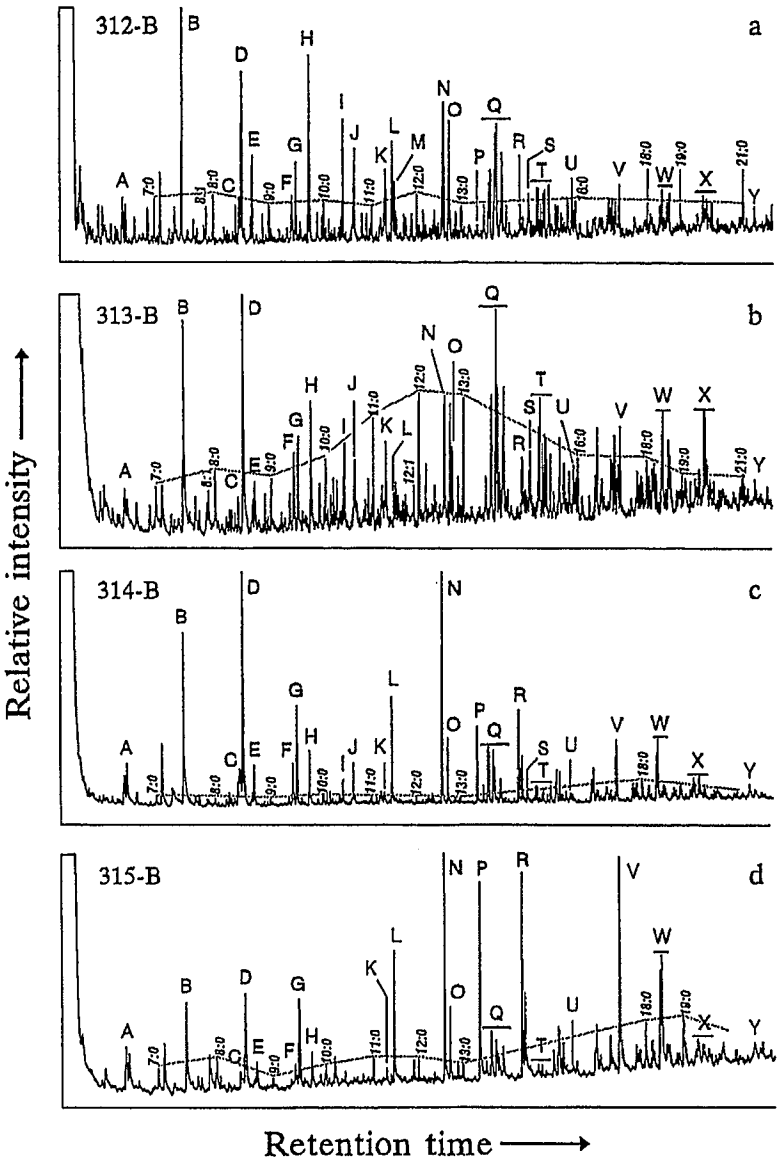

Figure 1. Partial chromatograms of the flash pyrolysates (Curie temperature 770 °C) of the unextracted vitrinite concentrates. Peak identifications are indicated in Table III. #:1 = n-alk-1-enes, #:0 = n-alkanes. Vitrinite reflectance values (%Rmax) of each sample is given in Table II. For analytical conditions, see Methods section.

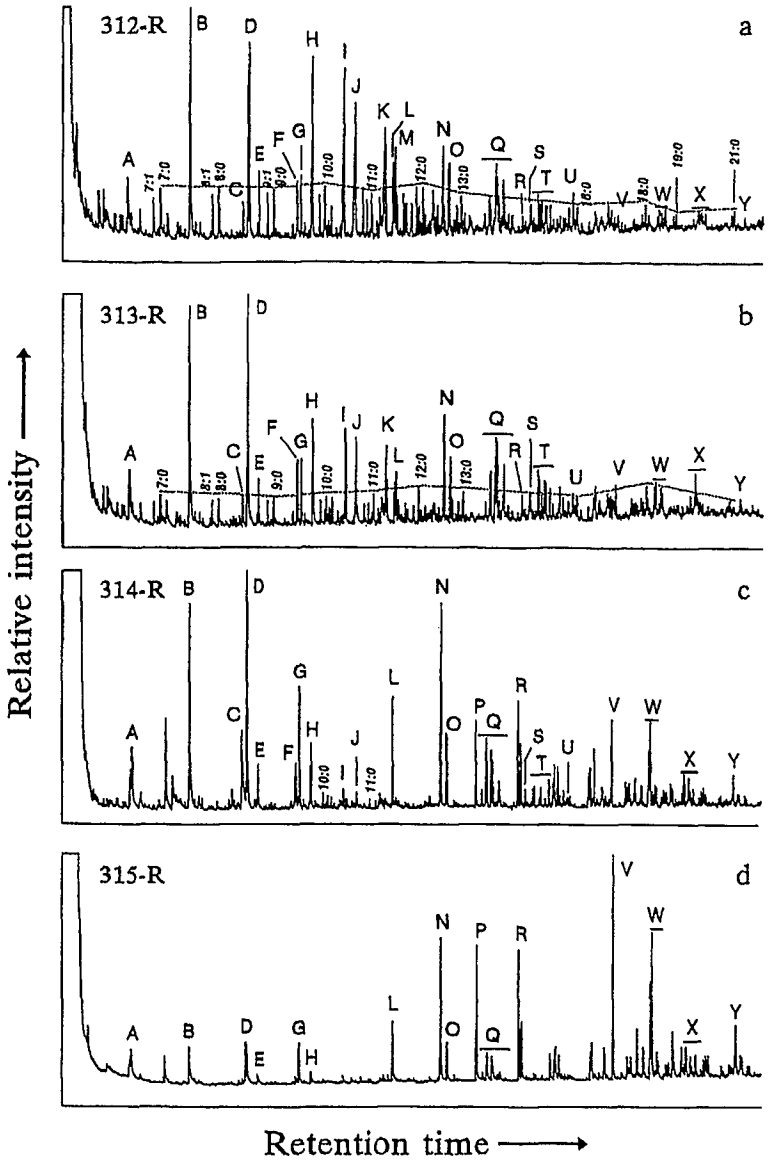

Figure 2. Partial chromatograms of the flash pyrolysates (Curie temperature 770 °C) of the extracted vitrinite concentrates. Peak identifications are indicated in Table II. #:1 = n-alk-1-enes, #:0 = n-alkanes. Vitrinite reflectance values (%Rmax) of each sample is given in Table II. For analytical conditions, see Methods section.

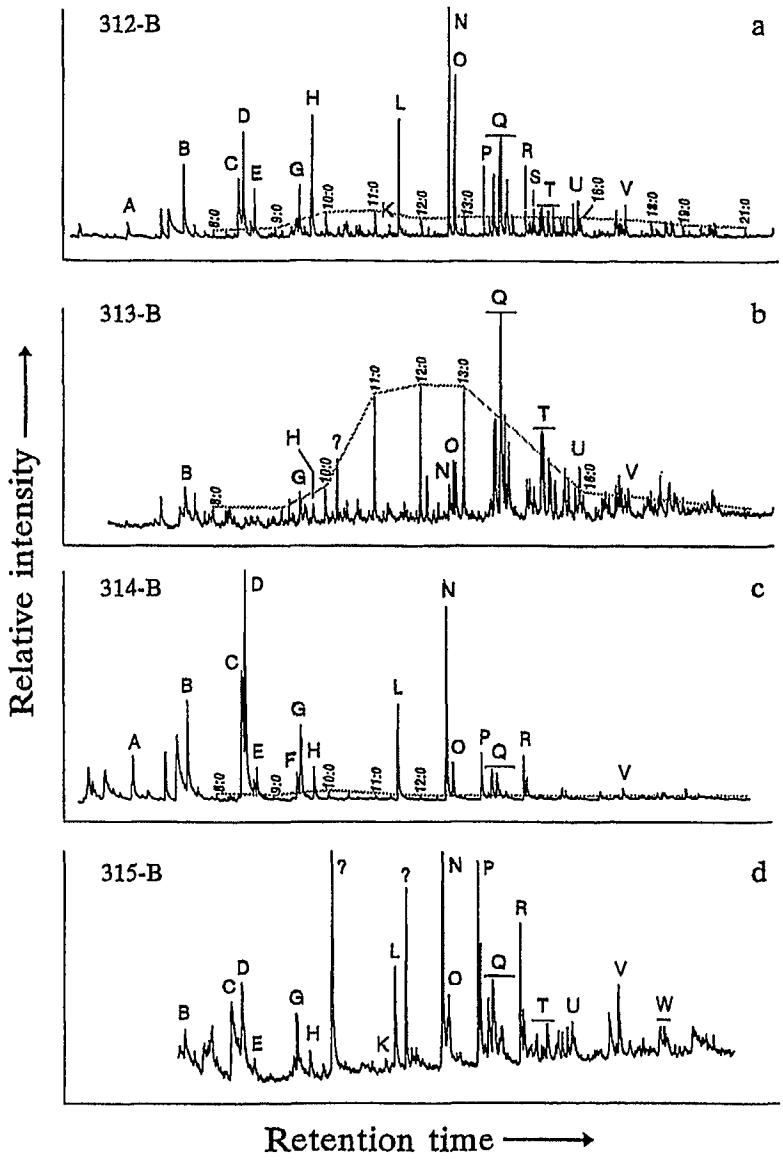

Figure 3. Partial chromatograms of the "thermal extracts" (Curie temperature 358 °C) of the unextracted vitrinite concentrates. Peak identifications are indicated in Table III. #:1 = n-alk-1-enes, #:0 = n-alkanes. For analytical conditions, see Methods section.

minor components in the thermal extracts, the n-alk-1-enes are virtually absent. As an exception the thermal extract of sample 313 is dominated by n-alkanes (Figure 3b).

A semi-quantitative analysis of the four samples is presented in Figure 4. For this figure the peak areas of most of the aromatic components identified in Table III have been calculated for both the unextracted and the extracted vitrinite concentrates. The relative proportions of the different components are normalized to the largest peak in the chromatogram. Although C_2-alkylated naphthalenes are the most dominant components in the pyrolysates of the samples 312 and 313, solvent extraction results in a distinct relative increase of alkylbenzenes and alkylphenols. The differences between the pyrolysates of the unextracted and the extracted vitrinites of the samples 314 and 315 are less distinct.

In Figure 5 a summary of the relative abundance of four classes of aromatic components present in the pyrolysates is presented as a function of maturity (vitrinite reflectance). These groups represent a summation of the components given in Table III. The most obvious trend in both the unextracted and extracted vitrinites with increasing maturity is the relative decrease of phenols. In both fractions of all samples benzenes generally constitute over 30 % of the pyrolysis products quantified. The total sum of the naphthalenes also remains high between 25 to 40 %. Furthermore, the relative abundance of phenanthrenes shows a significant increase with increasing maturity. Although not shown here biphenyls show an almost identical trend as the phenanthrenes.

Table III. Major components identified in the flash pyrolysates and the thermal extracts

	Component		*Component*
A	Benzene	M	3,5-Dimethylphenol and 3-Ethylphenol
B	Toluene		
C	Ethylbenzene	N	2-Methylnaphthalene
D	1,3 and 1,4-Dimethylbenzene	O	1-Methylnaphthalene
E	1,2-Dimethylbenzene	P	Biphenyl
F	1-Methyl-3-ethylbenzene and 1-Methyl-4-ethylbenzene	Q	C_2-Naphthalenes
		R	C_1-Biphenyls
G	1,3,5-Trimethylbenzene	S	Dibenzofuran
H	Phenol (and 1,2,4-Trimethylbenzene)	T	C_3-Naphthalenes
		U	C_1-Dibenzofurans
I	2-Methylphenol	V	Phenanthrene
J	3 and 4-Methylphenol	W	C_1-Phenanthrenes/Anthracenes
K	2,4-Dimethylphenol	X	C_2-Phenanthrenes/Anthracenes
L	Naphthalene	Y	C_1-Pyrenes

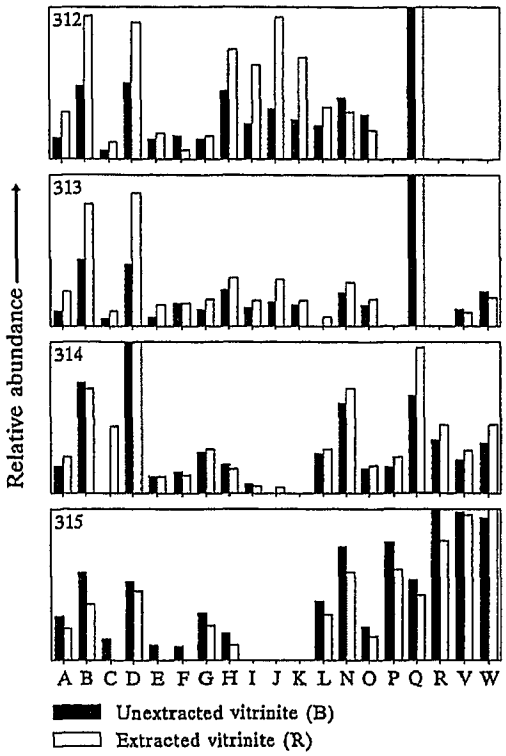

Figure 4. Semi-quantitative representation of the concentrations of the components identified in Table III for the unextracted and extracted vitrinite concentrates. Peak areas were calculated relative to the largest peak in each chromatogram.

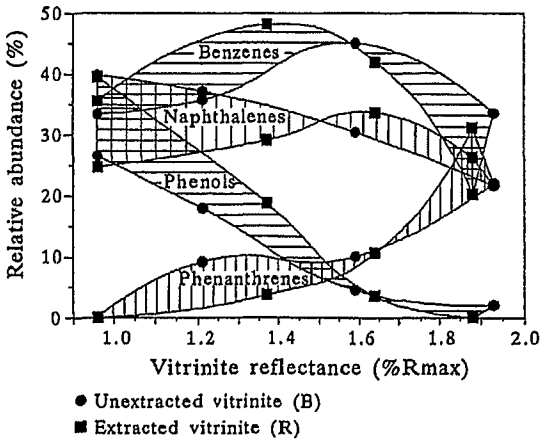

Figure 5. Schematic representation of the relative concentrations of the aromatic components as a function of maturity.

Discussion

The wide maturity range and low number of samples do not allow for a fine-tuning of the trends observed. The observed differences between samples of different rank have an exclusively semi-quantitative aspect because all the pyrolysis products identified at a reflectance value of 0.96 %Rmax are also present in the sample with a reflectance value of 1.93 %Rmax. The reduction in the yield of alkylphenols upon pyrolysis with increasing maturity has been discussed in earlier papers (*7, 14*). A similar result is obtained here. The relative abundance of the alkylbenzenes shows a rather wide scatter throughout the coalification range investigated and appears to be little affected by increasing coalification. The abundance of the alkylphenanthrenes and alkylbiphenyls clearly increases with increasing maturity. The increase in the relative yields of the n-alkanes and the C_2- and C_3-alkylnaphthalenes followed by a decrease is likely to be related to hydrocarbon generation and subsequent expulsion from the vitrinite matrix as coalification continues. The reflectance value of 1.21 %Rmax approximates the end of the bituminization range of coals which is set at a reflectance value of approximately 1.30 %Rmax (*15*). This reflectance value coincides with the transition from the oil window to the gas window and with one of the "coalification jumps" of liptinites (*15*). Because pure vitrinite concentrates were used in the present study the differential effects of maceral composition upon the character of the pyrolysis yields can be neglected. Moreover, because of their very low abundance in the parent coals, liptinite macerals are not regarded here as a possible source for the n-alkanes and alkylnaphthalenes. However, the possibility of different source materials for the vitrinites can not be excluded. The most important biopolymeric precursor of vitrinite is considered to be lignin. The different pyrolysis products of extant lignin are well-documented (e.g. *6*) and the transformation of lignin up to the subbituminous stage of coalification (0.5 - 0.6 %Rmax) is relatively well-established (*16, 17*), because the coalified tissue up to this maturity level can be morphologically related to woody cell tissue (xylem). With increasing coalification such morphological features gradually disappear. Moreover, because of the intimate association of pure telinite (cell tissue) with collinites (e.g. cell fillings) in bituminous coals the differentiation between both is extremely difficult. It has recently been demonstrated that the precursor of collinites may consist of highly aliphatic constituents which have migrated into the cell lumina (*18, 19*). Upon pyrolysis these materials yield homologous series of n-alkanes and n-alk-1-enes. Benzenes, naphthalenes, and phenanthrenes are not reported to be pyrolysis products of wood lignins (*6*). This suggests that these products are formed as a result of increasing coalification. However, recent studies on gymnospermous bark tissues, which contain lignin moieties, indicate that benzenes and naphthalenes may also be pyrolysis products of extant lignins (*20*). It is suggested (e.g. *21*) that incorporation of other components in the vitrinite matrix during early degradation (e.g. bacterial or fungal-derived) and/or coalification (impregnation by liquid hydrocarbons) is not unlikely.

The above findings support the view that the "vitrinite macromolecule" may show considerable chemical variation inherited from precursors which are not exclusively lignins. This chemical variation will to some extent also be recorded by vitrinite reflectance measurements. The results of sample 312 reveal that at identical reflectance values the chemistry of a sample may show considerable, mainly semi-quantitative, differences. This indicates that the extractable fraction has no significant influence on vitrinite reflectance values. However, for sample 313 a significant difference of 0.16 %Rmax has been recorded between the reflectance values of the unextracted and the extracted vitrinite concentrate. This sample, unlike the other three samples, is dominated by (extractable) C_2-alkylated napthalenes and n-alkanes. It thus appears that there is a relationship between the presence of these components and the vitrinite reflectance value of this sample. In several studies suppressed vitrinite reflectance values are related to higher hydrogen contents of the vitrinite (*21-24*). This is supported by the considerable higher aliphatic character of this sample as revealed by flash pyrolysis. From our study it may be concluded that the extractable fraction of aliphatic compounds present in the vitrinite matrix is capable to absorb a significant fraction of photons from an incident light beam. As a consequence the removal of this fraction results in a higher vitrinite reflectance value for the extracted vitrinite concentrate. The results are not conclusive whether this chemical differentiation is the result of early diagenetic variation or caused by hydrocarbon generation within the vitrinite maceral. Because of its position within the "oil window" it may be a combination of both factors (*25*).

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