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BIOMARKERS COMPOSITION AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) CHARACTERISTIC OF BULGARIAN COALS WITH DIFFERENT RANK AND ORIGIN

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Abstract

Biomarker composition and polycyclic aromatic hydrocarbons (PAHs) concentrations of three coal samples from Bulgarian deposits of different rank are presented. The coal samples were taken from Stanyantsi, Bourgas and Dobroudja coal basins. Gas chromatography–mass spectrometry (GC-MS) was applied to assess organic matter source and to identify and quantify PAHs in the studied samples. Coal rank was determined on the basis of vitrinite reflectance, Ro %.

The alkane patterns of the three samples are dominated by long chain n-alkanes (C_{27}-C_{31}), usually found in higher terrestrial plants rich in cuticular waxes. With increasing rank, the odd over even predominance is significantly reduced and short-chain n-alkanes are present in higher quantities. Increased pristane/phytane ratios in the Dobroudja coals are attributed to the influence of coal rank on this parameter. Based on terpenoid biomarker composition, angiosperm-dominated vegetation is concluded for the Bourgas coal whereas conifers dominated the peat-forming vegetation at Stanyantsi. Low terpenoid biomarker concentration and high contents of alkylated naphthalenes and phenanthrenes in the bituminous coal reflect the diagenetic conversion of the plant-derived terpenoid hydrocarbons to alkylated PAHs. Highest PAHs concentration was recorded in samples of higher rank (bituminous coal), and

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the lowest concentration was found in lignite samples. The examination of the PAHs composition revealed that 3 and 4 ring unsubstituted PAHs are dominant in the lignite and bituminous coal samples, whereas 4 and 5 ring PAHs predominate in subbituminous coal. We assume that the composition of PAHs in the extractable portion of coals is irrespective of the coal-forming vegetation.
Key words: organic geochemistry, biomarkers, PAHs

Introduction. Coal exploitation, transportation and combustion causes serious environmental impacts. Extensive coal combustion, for example, results in an increase in pollutants such as sulfur dioxide, nitrogen oxides, mercury, and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere [1]. The release of unburnt coal particles into the environment as a result of either the mining/transportation of coal (Pies et al. [2]) or the natural erosion of coal seams (Stout et al. [3]), is also of ecological relevance. The characteristics of coal are influenced by many different factors, like, climate, vegetation type, facies variation during peat accumulation and the extent of organic matter degradation during diagenesis. The biomarker analysis of the extractable organic matter of coal has increasingly contributed to the understanding of the palaeoenvironment in the mires and has provided clues to the botanical input involved in their formation [4]. Radke et al. [5] studied the composition of PAH in "mobile phase" of coal and argue that the concentration of PAH varies depending on coal rank. Based on a collection of 50 coal samples from 11 coal basins worldwide Laumann [6], compared and assessed variations in the concentration and composition of PAH. Bechtel at al. [7] evaluated the differences in petrography and the molecular composition of hydrocarbons from Bulgarian coal basins Bourgas and Maritza East with respect to their relationship to floral assemblage, sedimentary facies and diagenesis. The coals from Maritza East Stefanova et al. [8–10], have been investigated regarding the composition of biomarkers of hydrocarbon fractions of different lithotypes before and after desulfurization. The differences in vegetation and diagenetic changes between two lignite deposits Stanyantsi and Beli Breg have been established by Zdravkov et al. [11].

The aim of the study is to determine the biomarker composition, concentration and type of polycyclic aromatic hydrocarbons of three Bulgarian coal samples with different ranks, and to establish relationships with reflectance and the conditions of their formation.

Material and methods. Three samples of the Bulgarian deposits Stanyantsi, Bourgas and Dobroudja (Fig. 1), representing lignite, subbituminous, and bituminous coal, respectively, were investigated.

Coal rank was determined on the basis of vitrinite reflectance, Ro % (Table 1) with Leica DM RX microscope in 50 points. For microscopic investigations the samples were crushed to a maximum size of 1 mm, mounted in epoxy resin, ground and polished.

Fig. 1. Location of Stanyantsi, Bourgas and Dobroudja basins

For the determination of the molecular composition of hydrocarbons, approximately 5 g of each sample were extracted by dichloromethane for 1 h at 75 °C and a pressure of 75 bar in a Dionex ASR 200 instrument. After concentration, the extracts were dissolved in a solvent mixture of hexane:dichloromethane (80:1) and asphaltenes were subsequently separated by centrifugation. The hexane-soluble organic compounds (maltenes) were subdivided into saturated and aromatic hydrocarbons and polar components using a Köhnen–Willsch MPLC (medium pressure liquid chromatography) instrument [5]. The fractions of saturated and aromatic hydrocarbons were analyzed by a gas chromatography–mass spectrometer (GC-MS) Finnigan MAT GCQ, equipped with a DB-5MS silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness). Oven temperature was programmed from 70–300 °C with steps of 4 °C/min, followed by a isothermal period of 15 min. Helium was used as carrier gas. The device was set in electron impact mode with a scan rate of 50–650 Daltons (0.7 s/scan). Identification of biomarkers is based on retention time and comparison of mass spectra with published data. The determination of absolute concentrations of biomarkers was done using internal standards (deuterated n-tetracosane for the aliphatic fraction and 1,1'-binaphthyl for the aromatic fraction).

Results and discussion. *Petrographic characteristics (Vitrinite reflectance)*. Vitrinite reflectance values (R_0) of 0.13% for the Stanyantsi deposit, of 0.32% for Bourgas, and of 1.12% for the Dobroudja coal are consistent with the coal rank classification as lignite, subbituminous coal and bituminous coal, respectively.

Molecular composition of the hydrocarbons n-Alkanes, isoprenoids. In the low-rank coal samples, long-chain n-alkanes (n-C_{27} to n-C_{31}) predominate

Table 1

Concentration of n-alkanes, proportion of n-C_{15-19}, n-C_{21-25} and n-C_{27-31} relative to sum of n-alkanes, CPI, pristane/phytane ratio, concentration of hopanes and hop-17(21)-ene, concentration of diterpenoid and angiosperm-derived triterpenoid hydrocarbons, concentration of alkylated naphthalenes and phenantrenes, concentration of PAHs (3, 4, 5, 6- rings) in Stanyantsi, Bourgas and Dobroudja coal samples

Sample	n-alkane (ppm)	n-C_{15-19}/ n-alkane	n-C_{21-25}/ n-alkane	n-C_{27-31}/ n-alkane	CPI	Pr/Ph	Diter-penoids (ppm)	Triter-penoids (Angio-sperms) (ppm)
I St	37.93	0.01	0.13	0.71	6.58	0.96	23.40	13.25
I Bu	60.85	0.02	0.08	0.73	4.15	1.61	26.99	31.18
I Dj	57.54	0.20	0.33	0.33	1.29	3.60	10.62	4.93

Sample	Hopanes (ppm)	Hop-17(21) -ene (ppm)	Alkylated Naph. (ppm)	Alkyl-ated Phen. (ppm)	PAHs 3-ring (ppm)	PAHs 4-ring (ppm)	PAHs 5-ring (ppm)	PAHs 6-ring (ppm)
I St	5.35	4.30	0.36	0.50	0.24	0.27	0.16	0.00
I Bu	47.15	14.56	1.69	0.58	0.32	0.77	2.04	0.54
I Dj	19.47	0.00	35.99	29.16	6.42	3.92	2.36	0.17

the saturated hydrocarbon fractions (Table 1). In the Dobroudja sample medium chain (C_{21}–C_{25}) and long-chain (C_{27}–C_{31}) n-alkanes are present in equal concentrations. Values for the carbon preference index (CPI, according to Bray and Evans [12]) are higher than 1.0, reflecting a marked predominance of odd over even-numbered alkanes. Higher CPI values (up to 6.6) are found in the Stanyantsi and Bourgas coals in agreement with their lower rank. The low CPI of 1.3 found in the Dobroudja coal is consistent with the results obtained on bituminous coals (Table 1). Maximum intensities in the n-C_{27} and n-C_{29} range are reported to be characteristic for wood-dominated vegetation, whereas herbaceous vegetation and mosses result in high n-C_{31} relative intensities [13]. According to Zdravkov et al. [11] the relative proportions of n-alkanes may be used as an indication of a change in the proportions of woody (n-C_{27} and n-C_{29}) versus herbaceous vegetation (n-C_{31}). However, Herbin and Robins [14] noted that a higher concentration of the C_{31} n-alkane may indicate the participation of conifers to the peat forming vegetation. Under consideration of these results, differences in alkane distribution patterns seen in the Stanyantsi, Bourgas and Dobroudja coals may indicate changes in the relative proportion of angiosperms versus conifers in the peat-forming vegetation.

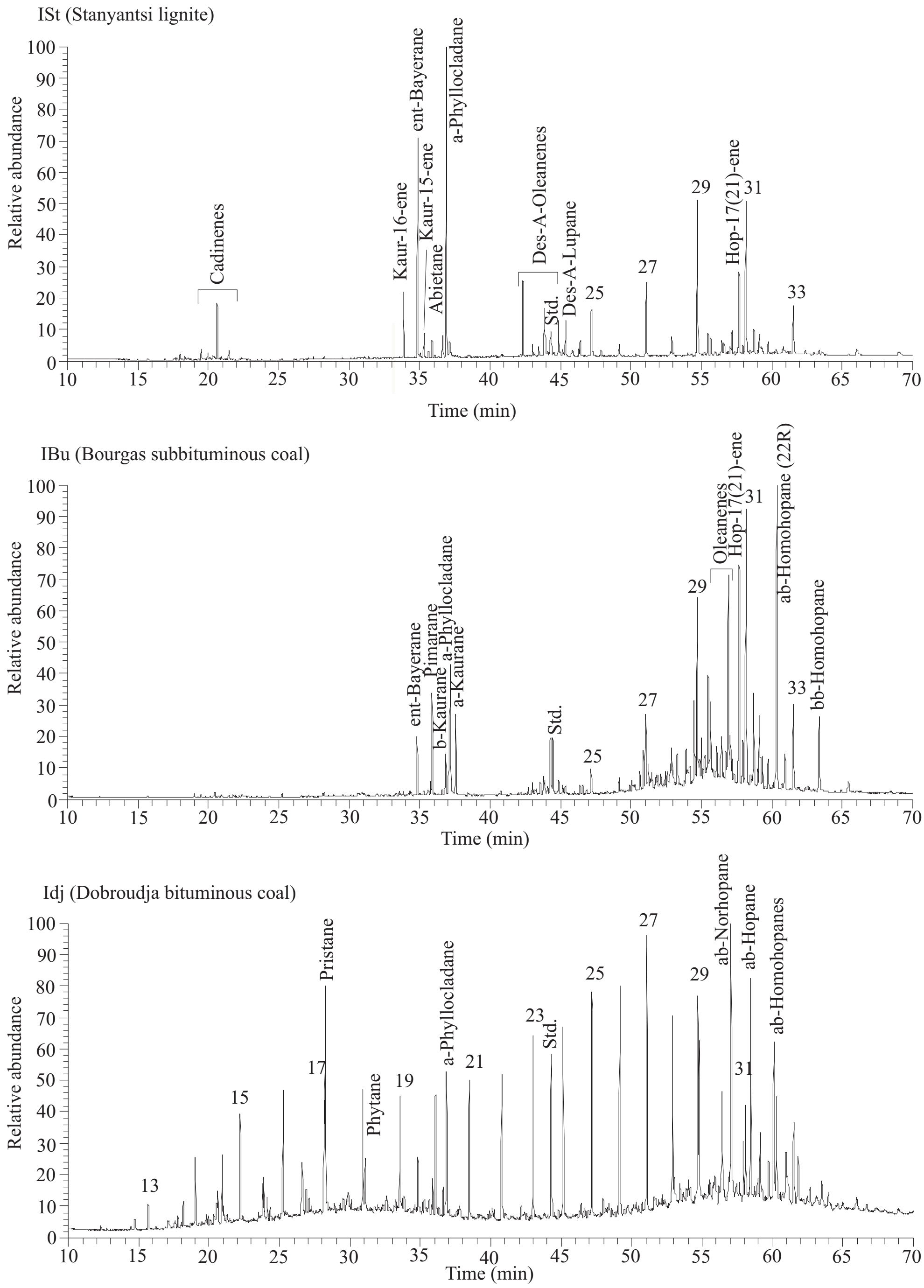

Fig. 2. Gas chromatograms (TIC) of saturated hydrocarbon fraction from Stanyantsi, Bourgas and Dobroudja coal basins. *n*-Alkanes are labelled according to carbon number. Std. = standard (deuteriated *n*-tetracosane)

Acyclic isoprenoids of the samples are represented by acyclic hydrocarbons pristane (Pr) and phytane (Ph). The ratio of Pr versus Ph has been used to evaluate the Eh potential of the depositional environment [15]. However, it has been shown that the pristane/phytane ratio is strongly influenced by the thermal maturity of the organic matter, which is related to the rapid formation of pristane with increasing maturity [16]. Immature organic matter in the Stanyantsi sample is characterized by a very low concentration of Pr and Ph, whereas coal from the Dobroudja deposit shows high contents of Pr and Ph (Fig. 2). In accordance with the proposed maturity-dependence of Pr/Ph ratios by Tissot and Welte [17], a value less than 1 is found in the Stanyantsi coal, while Pr/Ph ratios of 1.6 and 3.6 are obtained from the Bourgas and Dobroudja samples, respectively (Table 1).

Diterpenoids and triterpenoids with non-hopanoid skeleton. The diterpenoids in the samples are mainly represented by hydrocarbons with beyerane, abietane and phyllocladane type skeletal structure. The following diterpanes were identified in the non-aromatic hydrocarbon fractions: norpimarane (only in Dobroudja sample), kaurenes (only in Stanyantsi sample), beyerane, pimarane (for Bourgas and Dobroudja samples), β-phyllocladane (for Dobroudja sample), abietane and α-phyllocladane (Fig. 2). The non-hopanoid diterpane α-phyllocladane is usually found in conifers except of Pinaceae by ten Haven et al. [18] and is regarded as a typical biomarker of Araucariaceae, Cupressaceae, and Taxodiaceae. In all samples, the aromatic tri-cyclic diterpenoids dehydroabietane, simonellite and retene occur (Fig. 3). Retene is the dominant aromatic diterpenoid in the Dobroudja coal sample.

Non-hopanoid triterpenoids are present only in samples of Stanyantsi and Bourgas. Triterpenoids containing the structures typical of the oleanane, ursane, or the lupane type derivatives are considered as biomarkers for angiosperms [19]. They have been found in wood, bark and roots of recent angiosperm species [19]. The compounds identified in the saturated and aromatic hydrocarbon fractions include ring-A degraded and pentacyclic oleanane-, ursane-, and lupane-type triterpenoids (Fig. 3). From the relative amounts of di- versus angiosperm-derived triterpenoids, a conifer-dominated vegetation can be concluded for the Staniantsi deposit, whereas the Bourgas coal evolved from Angiosperm-dominated vegetation [7]. The low contents of terpenoid biomarkers characteristic for land plants found in the Dobroudja sample are related to the advanced degradation of these compounds during maturation.

Hopanoids. The non-aromatic cyclic hydrocarbons are dominated by hopanes (Fig. 2). The hopanoid patterns in the samples are characterized by the presence of $\beta\beta$ and $\alpha\beta$ type hopane from C_{27} to C_{31} in the Stanyantsi and Burgas samples and from C_{27} to C_{33} in the Dobroudja sample. C_{28} hopanes were not detected. In the samples from Stanyantsi and Bourgas, hop-17(21)-ene was detected in high amounts, consistent with the low rank of the coals. The pres-

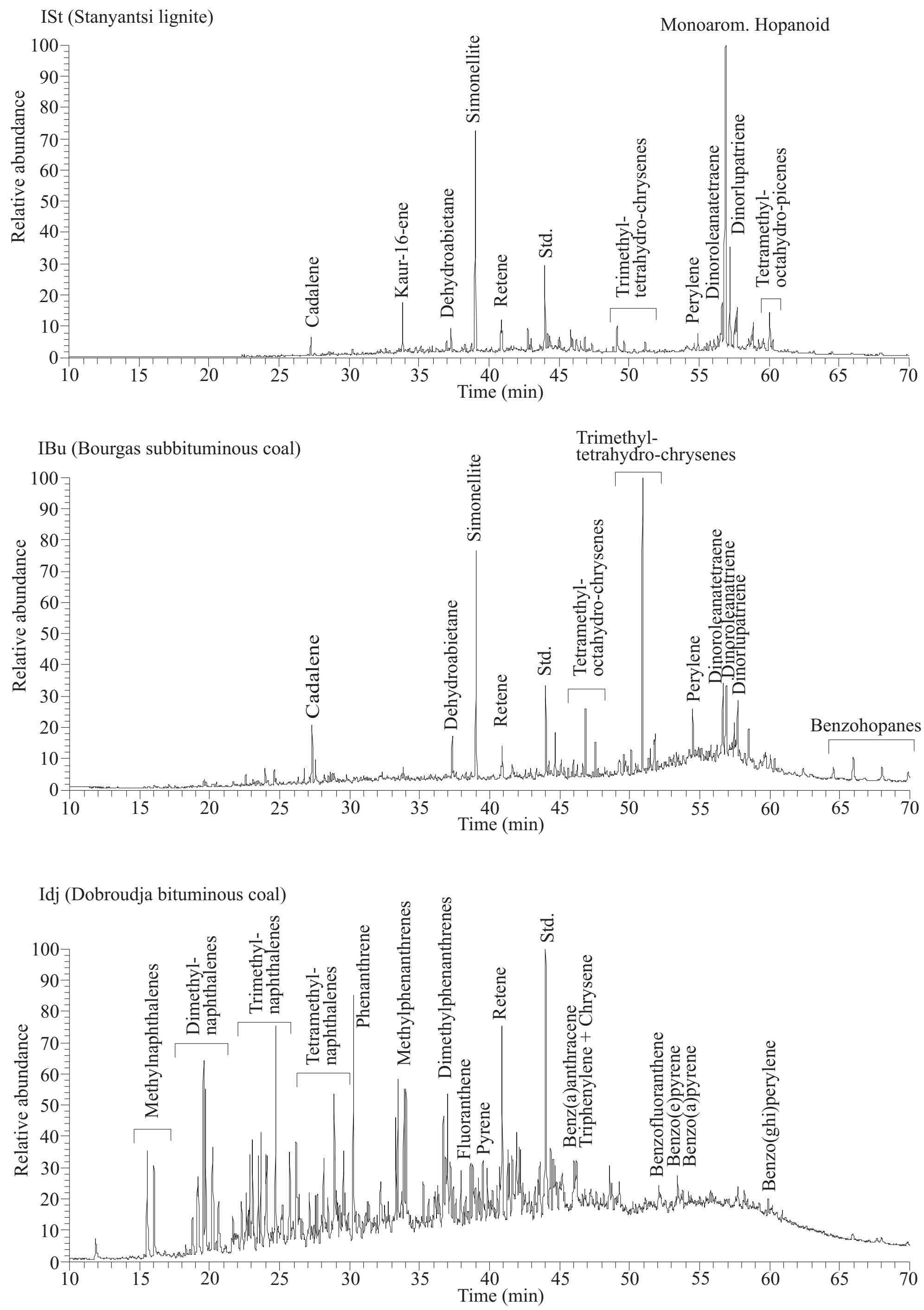

Fig. 3. Gas chromatograms (TIC) of aromatic hydrocarbon fraction from Stanyantsi, Bourgas and Dobroudja coal basins. Std., standard (1,10-binaphthyl)

ence of hopanoids indicates microbial (bacterial) activity in paleomires. Bacterial activity in peats is related to fluctuations of the (ground) water level. However, a contribution from fungi, as well as from some mosses and ferns cannot be excluded.

The predominance of hopanes with $\beta\beta$ stereo configuration in the lignite sample (Stanyantsi) is typical of immature organic matter. In the coals from Bourgas $\alpha\beta$ homohopane (22R) is present in higher concentration than $\beta\beta$ homohopane, and in the Dobroudja sample $\beta\beta$-hopanes are missing, reflecting the isomerisation of hopanoids with increasing rank.

PAH, Alkylnaphthalenes and Alkylphenantrenes. In all samples polycyclic hydrocarbons (PAHs) with two to five-membered rings are found (Table 1). Six-membered ring PAHs occur in coals from Bourgas and Dodroudja deposits (Table 1). The total concentration of these hydrocarbons is in the order: Stanyantsi < Bourgas < Dobroudja. In the coal sample from Stanyantsi phenanthrene predominates the other PAHs (0.12 ppm), whereas in Burgas perylene and benzo(a) pyrene (0.96 and 0.75 ppm) are highest. In the Dobroudja coal phenanthrene and pyrene are present in high amounts (5.37 and 1.43 ppm). The concentration of two to five-membered ring PAHs in the coals is in the same order as the total concentration. The exception is the content of six-membered rings in the Burgas coal sample, exceeding the concentration found in the Dobroudja sample.

Alkylnaphthalenes are present in highest amount in the Dobroudja coal sample (Table 1) They are only detected in very low contents in the aromatics of the Burgas and Stanyantsi samples. The presence of these compounds, has been used to identify the transformation process of pentacyclic triterpenoids to alkyl naphthalenes during degradation of OM under reducing conditions [20]. In all studied samples, methylphenanthrenes are detected, but only in the coal from Dobroudja, di- and trimethylphenanthrenes occur (Fig. 3). Perhaps these hydrocarbons are generated by fragmentation and dehydrogenation of triterpenes [20].

Conclusion. The complex geochemical study established that the coals from the three basins show differences in their chemical composition related to rank and vegetation. As a result of the different thermobaric conditions the macromolecular structure and the degree of coalification of organic matter are changed. PAHs differ in amount and number of aromatic rings, reflecting the intensity of aromatization processes. The low concentrations of the terpenoid biomarkers and the high contents of naphthalene and phenanthrene in bituminous coal are attributed to the degradation of terpenoids during diagenesis. Degradation evolved gradually from lignite to bituminous coals. The obtained data from this study supports the earlier conclusion that the concentration of PAHs is closely associated with rank of the coals.

The determined biomarkers, and relative amounts of di- versus angiosperm-derived triterpenoids show that the peat-forming vegetation of coals from Stanyantsi deposit was conifer-dominated, and from Bourgas was Angiosperm-dominated. No correlation between the composition and quantity of PAHs and type of coal-forming vegetation could be established.

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