Geochemical appraisal of hydrocarbon generative potential of Bulgarian part from the Thrace Basin: I. Linear biomarkers

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Dedicated to Acad. Bogdan Kurtev on the occasion of his 100th birth anniversary

Bulgarian part from the Thrace Basin is recognized as its NW flank. Hydrocarbon generation for some formations in the Bulgarian part, analogue to Turkish ones with already proven generative abilities, is expected. In order to assess source rocks and to foresee exploration activities in the region, eleven samples from the prospective formations, *i.e.* seven well samples and four outcrops samples, are evaluated by geochemical proxies. Extractable organic matter (OM), the so-called "free" bitumens, and extracted after demineralization ("bound" bitumens), are characterized. A broad range of biomarkers is considered. In this study linear structures, *i.e.* n-alkanes, regular isoprenoids, n-alkan-2-ones, n-alcohols, fatty acids, etc. will be considered. Rock Eval data and component analysis determine immature Type III and mixed Type II/III kerogen. n-Alkanes are dominant in all bitumen extracts. Their distributions are complex, depth dependent and give a hint for more mature OM redeposition. The cross-plots of regular isoprenoids in Pr/nC_{17} *vs.* Ph/nC_{18} diagram implies immature mixed Type II/III kerogen. Pr/Ph ratios, argue for immature OM deposited in anoxic/sub-oxic environment. The cross-plots of TOC *vs.* P_{aq} argue for at least two pools of n-alkanes: (i) short chain homologous from algal/bacterial contribution; (ii) and, mid-chain, from submerged/floating macrophytes wax. Fatty acids, nC_{12}-nC_{34} with "even" numbered dominance and changes with depth, are identified only in the "bound" bitumens. A similarity in possible origin with n-alkanes is assumed. Dicarboxylic fatty acids, nC_{18}-nC_{30}, maximizing at nC_{26}, nC_{28}, nC_{30} are recognizable as well.

Key words: Thrace Basin; oil/gas generative potential; geochemical proxies

INTRODUCTION

Thrace Basin spreads through the European part of Turkey, the most NE part of Greece and SE part of Bulgaria. It is one of the largest natural gas and oil producing basins in Turkey [1]. Generative potential of source rocks from the Turkish part of the Thrace Basin with proven potential for oil/gas generation is described [1–3].

The studied area is situated within the Early-Palaeogene Madjarovo foreland depression, which formed along the intensively faulted eastern part of the Rhodope massif [4]. Rocks of different age and compositions were outcropped on the surface of the studied area and question of interest for oil/gas exploration was the clastic rocks of the sediment sequence with Tertiary (Eocene and Oligocene) age. Information from well investigations is limited as the deepest one reaches 1754 m. In the Turkish part of the Basin these intervals with Eocene and Oligocene age are the major reservoirs for the hydrocarbon accumulations [1].

Shally intervals of the terrigenous-limestone-shale fm., and shales and mudstones of shale-marl fm. are considered the most promising seals in the reservoir systems in the Bulgarian part of the basin [5]. These intervals are further characterized by a good generative potential for hydrocarbons as well.

Current study is inspired by the renewed interest to Mezardere Fm. as a potential oil resource for hydrocarbons supply in Turkey [3]. The aim of the present investigation is to assess by geochemical proxies the hydrocarbon generative potential of samples from the perspective Fms. in the Bulgarian part of the Thrace Basin. Search for a similarity with Fms. in the Turkish part of the Basin is under special concern.

EXPERIMENTAL

Tectonic scheme of the Bulgarian part of the Thrace Basin in comparison with Turkish part and lithostratigraphy of the area under study are shown in Supplementary Material (Fig. S1).

The following set of samples was studied (Table 1): (i) core samples G1-G5 were from the shally intervals of shale-marl Fm., analogue to Yenimuhacir group in Turkey; (ii) core and outcrop

samples G6-G10 were from the rocks analogue of Ceylan Fm. (Turkey). Outcrops are commonly weathered, resulting in altered OM. Therefore, special attention was paid to collect them from fresh cuts at positions with low dips; (iii) and, sample G11, G12 with Neogene age from shale rock outcrops. All samples were crushed, grounded, sieved to < 0.25mm. Firstly, they were characterized by Rock Eval pyrolytic technique [5]. Preliminary data and parameters definition could be found in [6].

For lipids isolation about 40g of each sample were subjected to exhaustive Soxhlet extraction with chloroform. By this protocol "free" bitumens were prepared. The residue in the thimble after extraction was treated by 10% HCl for demineralization. Cl^- ions in the filter cakes were removed by copious washing. Later on they were dried at ambient temperature, grounded and transferred into thimbles for subsequent extraction with chloroform for "bound" bitumen isolation. Solvents of the highest purity were used. Extracts were concentrated at reduced pressure. The yields of bitumens, *i.e.* "free" and "bound", were calculated in wt. %. Asphaltenes in bitumens were precipitated by pouring samples solutions in a high excess of chilly *n*-hexane (1:50, v/v). Asphaltenes were filtered and dried to constant weights.

Bitumen fractional compositions were determined by column adsorption chromatography on mini-columns (10×100mm) filled with Kieselgel 60, 0.2-0.5 mm (Merck). The following eluents were used: hexane - for elution of neutrals; dichloromethane (DCM) - for aromatics and slightly polars; and acetone - for nitrogen, oxygen and sulfur containing (NOS) components. The neutrals were treated by Cu turnings for removal of elemental sulfur.

GC-MS study was carried out on a Hewlett-Packard 6890 GC system plus HP 5973 MSD equipped with a HP-5 MS column (0.25mm×30m×0.25μ film thickness) with flame ionization detector (300°C). A split/splitless capillary injector (300°C) is used in the splitless mode (valve reopened 1 min after injection). After 0.5 min isothermal period at 85°C the oven temperature was increased to 200°C at 20°/min and then to 320°C at 5°/min. The MSD was operated in the electron impact (EI) mode with energy of 70 eV and scan range from 50 to 650 Daltons. The data were acquired and processed with the HP software. Individual compounds were determined by comparison of mass spectra (MS) with literature and library data, comparison of MS and GC

retention times with those of authentic standards or interpretation of mass spectra [7, 8]. For MS spectra tracking Xcalibur software was used. MS were quantitatively interpreted by inner standards application, *i.e.* deuterated nC_{24} for the neutral fraction, and triethylbenzene for the aromatic slightly polar fraction. Amounts were normalized in μg/gC_{org}.

The distribution patterns and relative amounts of *n*-alkanes were tracked by single ion monitoring (SIM) of *m/z* 85. Based on *n*-alkanes separations carbon preference index (CPI) value was calculated [7, 9]. Some specific fragments were used for SIM tracking: *m/z* 183 for regular isoprenoids, *i.e.* pristane (Pr) and phytane (Ph); *m/z* 58 for linear alkan-2-ones; *m/z* 111 for linear alcohols; *m/z* 74 and 88 for esters of linear fatty acids (FAs).

RESULTS AND DISCUSSION

For some samples Rock Eval data in Table 1 indicate total organic carbon (TOC) above 0.5% (G1-G5, G12). For samples with TOC < 0.5% (G7, G9-G10) data for T_{max} are doubtful and are omitted. The relationship TOC *vs.* HI demonstrates linear correlation with R^2=0.755, giving us a confidence to keep TOC data for G2 and G6 in Table 1.

A tendency for decrease in T_{max} (from 437.5^{o}C to 428.5^{o}C) for the shallowest samples is recognizable. These data evoke more mature OM for the shallowest interval. Registered decrease in T_{max} is rather narrow. However it is indicative for redeposition of more mature OM and this possibility should be consider in the further appraisal by geochemical proxies.

Based on the TOC values, the samples range from "poor" to "fair" generative potential (Fig. 1A), a view supported by the Rock Eval data (Table 1). The highest TOC (2.31%) was determined for sample G5. Such magnitude is characteristic for source rocks with "good to very good" hydrocarbon generative potential as is visible in Fig. 1A, where S_1+S_2 were correlated with TOCs [10]. According to this diagram TOCs values were high for samples from the Shale-marl formation corresponding to Mezardere Fm. in the Turkish part of the Basin. On this base they were depicted as perspective and received special attention in further study.

Yields of bitumens and their fractional compositions, *i.e.* neutrals, aromatics/slightly polars, NOS and asphaltenes, are shown in Table 2. Oily fractions, first and second ones, are studied by GC/MS. Table 3 summarizes the total amounts of *n*-alkanes, normalized to TOC (μg/gC_{org}).

Table 1. Rock Eval data of samples.

| Sample		Depth (m)	Rock Eval data						
			S_1	S_2	S_3	T_{max}	TOC (%)	MINC(%)	HI
Well	G1	266.5	0.010	2.455	0.790	437.0	1.295	1.975	189.5
	G2	363.7	0.000	0.135	0.990	437.5	0.475	2.635	28.5
	G3	443.3	0.025	3.345	1.025	430.5	1.825	2.050	183.5
	G4	495.6	0.005	1.290	0.745	431.5	1.275	1.385	101.0
	G5	553.0	0.015	3.390	1.035	428.5	2.310	0.650	147.0
	G6	816.8	0.000	0.010	0.230	428.5	0.235	5.525	4.0
	G7	1685.3	0.005	0	0.115	n.d.	0.100	2.780	0
Outcrop	G9	-	0.010	0	0.330	n.d.	0.065	3.565	0
	G10	-	0.010	0	0.165	n.d.	0.035	3.185	0
	G11	-	0.000	0	0.575	n.d.	0.070	1.860	0
	G12	-	0.040	0.065	0.590	418.0	1.035	1.080	103.0

n.d. – not determined.
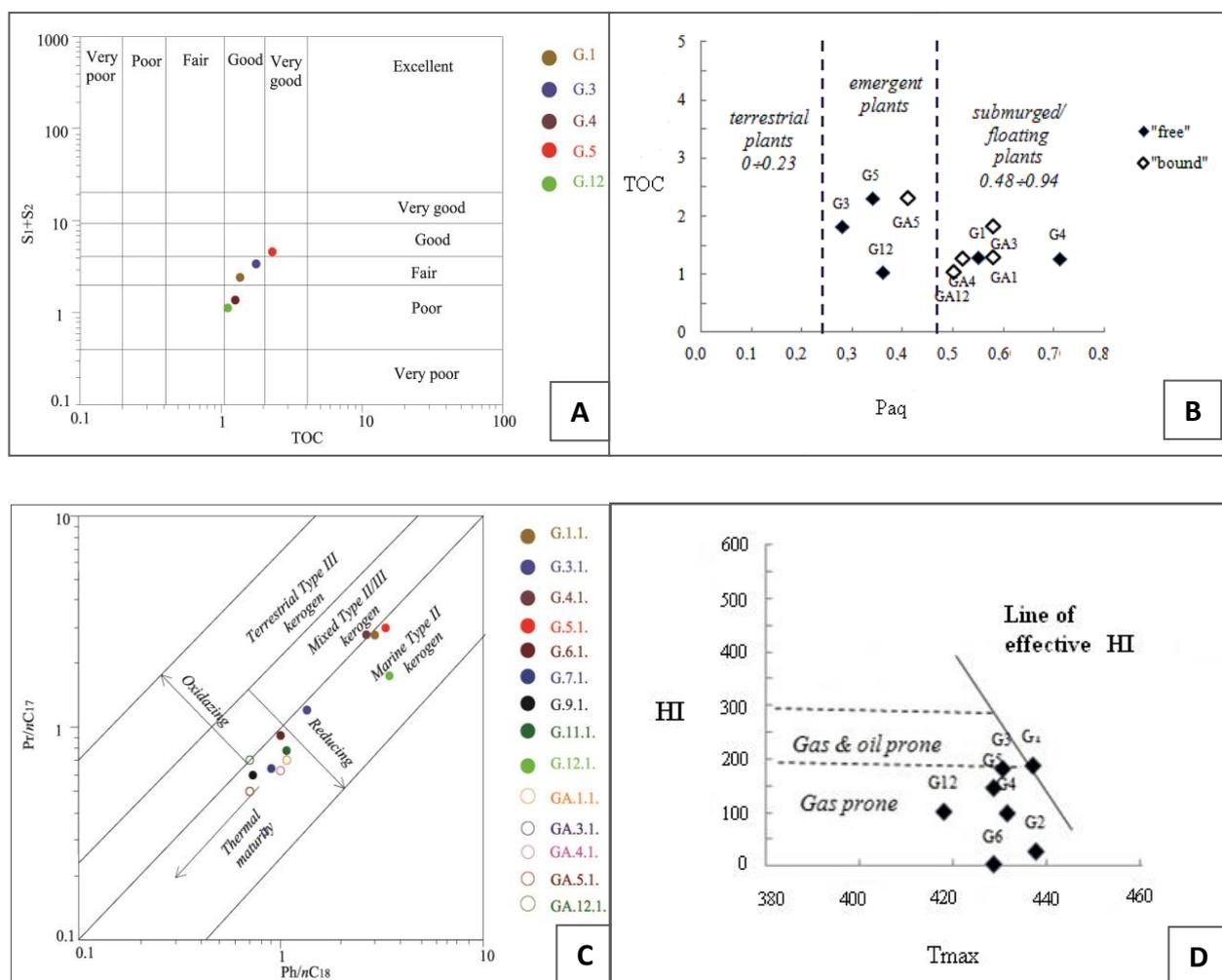
Fig. 1. Correlations of Rock Eval data and biomarker parameters. A) Plots S_1+S_2 *vs.* TOC for appraisal of generative potential; B) Relationship P_{aq} *vs.* TOC distinguishing different pools of *n*-alkanes contributions after Ficken *et al.* [11]; C) Cross-plots of Pr/nC_{17} *vs.* Ph/nC_{18} for kerogen type assignment after Hunt [15] (● – "free" bitumen; ○ – "bound" bitumen); D) Plots of HI *vs.* T_{max} highlighting the increase in HI prior to the onset of oil expulsion after Sykes and Snowdon [19].

Lipid distributions are visualised as histograms in Fig. 2. Relative amounts of short-, mid- and long- chain *n*-alkanes are presented in Table 4.

Portions of long chain homologous in "free" bitumens constitute >60% of the *n*-alkanes, except for sample G4, which is extremely enriched in short

chain members. For TOC rich samples, *i.e.* G3, G5, G12, a tentative shift of *n*-alkanes signature to mid-chain members is recognizable (Fig. 2). The trend is accompanied by a decrease in CPI values (Table 3). Lower CPI ratios might be indicative for the

subordinated incorporation of plant-wax *n*-alkanes into the "bound" bitumens.

At a certain extent *n*-alkanes distributions could assign a mixture of immature and mature OM. In fact, the *n*-alkane distributions for some samples

Table 2. Yields of bitumens and their fractional compositions, in %.

Sample		Yields (%) "Free"	Yields (%) "Bound"	Fractional composition, % "Free" bitumen Neutrals	Aromatics/ slightly polars	NSO	Asphaltenes	Losses	"Bound" bitumen Neutrals	Aromatics/ slightly polars	NSO	Asphaltenes	Losses
Well	G1	0.17	0.13	5.6	16.8	26.1	47.3	4.2	3.7	5.1	19.5	58.6	13.1
	G2	0.12	0.06	1.2	3.0	14.5	72.8	8.5	6.5	6.5	20.4	58.7	7.9
	G3	0.17	0.09	2.5	18.1	21.1	50.3	8.0	7.8	6.1	37.7	38.1	10.3
	G4	0.15	0.07	3.9	7.7	33.7	51.2	3.5	12.2	10.5	42.9	32.4	2.0
	G5	0.14	0.08	13.0	15.2	24.1	43.2	4.5	15.4	11.5	36.5	32.3	4.3
	G6	0.05	0.03	7.2	11.2	16.4	57.9	7.3	11.5	11.5	26.5	39.8	10.7
	G7	0.05	0.03	4.0	4.5	13.1	75.0	3.4	tr.	9.3	30.5	49.2	11.0
Outcrop	G9	0.03	0.04	4.8	10.6	25.2	50.0	9.4	10.1	8.0	25.4	55.8	0.7
	G10	0.08	0.03	0.3	6.4	7.8	84.3	1.2	10.6	12.6	31.7	44.2	0.9
	G11	0.06	0.05	5.6	9.7	20.9	58.8	5.0	7.1	7.1	28.4	50.6	6.8
	G12	0.11	0.06	12.9	14.4	37.1	34.7	0.9	18.8	11.9	27.3	41.5	0.5

Table 3. Amounts of *n*-alkanes in mg/g sample, regular isoprenoids in $\mu g/gC_{org}$ and CPI values.

	Sample	Σ *n*-alkanes, (mg/g)	Pr $(\mu g/gC_{org})$	Pr/nC_{17}	Ph $(\mu g/gC_{org})$	Ph/nC_{18}	Pr/Ph	CPI*
"Free" bitumen	G1	7.50	11.55	2.83	12.47	3.01	0.93	4.59
	G3	3.98	3.91	1.26	3.25	1.44	1.20	2.31
	G4	4.02	31.00	2.81	37.80	2.72	0.82	2.28
	G5	22.48	80.18	3.02	81.25	3.42	0.99	1.57
	G6	2.06	17.26	0.92	12.25	1.00	1.41	1.16
	G7	2.17	1.04	0.64	0.60	0.91	1.73	1.11
	G9	1.96	0.97	0.60	0.70	0.72	1.39	1.13
	G11	2.35	0.74	0.78	0.40	1.10	1.85	1.43
	G12	3.53	2.79	1.80	7.11	3.60	0.39	1.43
"Bound" bitumen	G1	2.36	0.85	0.72	0.40	1.16	2.13	1.26
	G3	4.54	1.14	0.33	0.27	0.83	4.22	0.98
	G4	2.79	3.70	0.63	1.66	1.00	2.23	1.19
	G5	5.87	5.02	0.50	2.46	0.71	2.04	0.95
	G12	5.63	1.05	0.69	1.96	0.69	0.54	0.90

*CPI= $\Sigma[(nC_{23} \div nC_{31})_{odd} + \Sigma(nC_{25} \div nC_{33})_{odd}]/2 \Sigma(nC_{24} \div nC_{32})_{even}$

Table 4. *n*-Alkanes distributions in TOC rich samples, in rel.% and calculated P_{aq} values.

Sample		Short-	Mid-	Long-	Short-	Mid-	Long-	"Free"	"Bound"
		n-Alkanes, in rel. %*						P_{aq} value**	
		"Free" bitumens			"Bound" bitumens				
Well	G1	9.7	28.5	61.7	12.6	41.2	46.2	0.55	0.58
	G3	15.3	23.7	61.0	18.7	52.0	29.3	0.28	0.58
	G4	53.5	32.0	14.5	15.7	41.0	43.3	0.71	0.52
	G5	16.7	22.3	61.0	5.0	28.4	66.6	0.34	0.41
Outcrop	G12	9.5	26.9	63.6	9.8	39.1	51.1	0.36	0.50

*Short chain *n*-alkanes Σ (nC_{16} -nC_{20}), Mid-chain *n*-alkanes Σ (nC_{21}-nC_{25}), Long chain *n*-alkanes Σ (nC_{26}-nC_{34}),
**P_{aq} = (nC_{23}+nC_{25})/(nC_{23}+nC_{25}+nC_{29}+nC_{31}) after Ficken *et al.*[12].
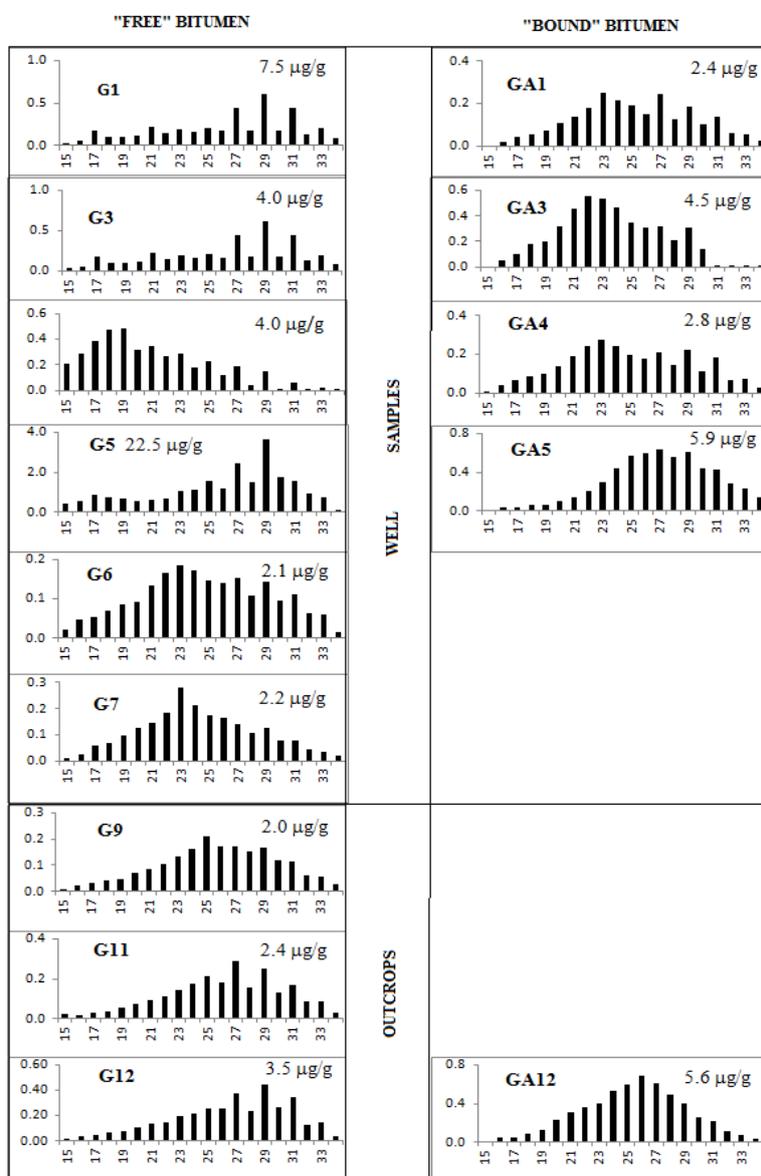

Fig. 2. Histograms of *n*-alkanes distributions (numbers correspond to carbon atoms).

strongly resemble that in oils (G4), suggesting contribution from redeposited mature OM. *n*-Alkanes distribution for sample G4 is typical for Type I kerogen. At low maturity levels even the mid-chain *n*-alkanes are characterized by odd-over-even predominance, *i.e.* high CPI. A possibility for mature OM deposition is discussed in the second part of the study devoted to the cyclic biomarkers.

Ficken *et al.* [11] have proposed P_{aq} ratio with the aim to discriminate macrophytes and emergent terrestrial plant. The proxy takes into account the fact that submerged/floating species are rich in mid-chain *n*-alkanes while higher plants are enriched in longer homologous. Respectively, the P_{aq} ratio distinguishes macrophytes of terrestrial plants from the other supply. This proxy is often used to assess the impact of hydrological changes in peat transitions from wet fen to dry periods [12]. The cross-plots of TOC *vs.* P_{aq} in Fig. 1B argue for at least two pools of *n*-alkanes [13]: (i) short chain homologous from algal/bacterial contribution; (ii) and, mid-chain, from submerged/floating macrophytes wax. According to Ficken *et al.* [11] P_{aq} values in the range of 0.01-0.23 are linked to terrestrial plant wax, whereas values in the range 0.48-0.94 are associated with submerged/floating species of macrophytes. P_{aq} values in Table 4 point to a mixed *n*-alkanes origin, namely, from higher plant/macrophyte wax and algal or bacterial contributions. Interestingly, P_{aq} values for the "free" bitumens are lower as compared to the magnitudes calculated for the "bound" bitumens. On the other hand, the lowest values are calculated for samples with the highest TOC contents. This is a hint that the increase in TOCs can be attributed to a substantial input of emergent plants to the palaeoenvironment (Fig. 2B). Relatively close values of ~0.50 are calculated for the "bound" bitumens. This evokes submerged/floating macrophytes OM input. The tendency is additionally confirmed by the data for CPI in Table 3 where systematically higher values for the "free" bitumens ratios comparing to the '"bound" ones are calculated.

The acyclic regular isoprenoids, *i.e.* Pr and Ph, are registered in all studied samples. Their amounts, together with Pr/Ph, Pr/nC_{17} and Ph/nC_{18} ratios are shown in Table 3. Ph concentrations are higher than nC_{18}, thus giving distinctively high Ph/nC_{18} ratios, especially for TOC rich samples. Ratios Ph/nC_{18} are in the range of 3.0-3.6 for the "free" bitumens, while for the "bound" bitumens total amounts of isoprenoids and calculated ratios are lower.

The Pr/Ph ratio is frequently used to assess depositional environment. However it is well known that isoprenoids/*n*-alkanes ratios generally suffer from two main problems: (i) Pr and Ph may originate not only from the phytyl side chain of chlorophyll-α, but also from tocopherols and bacterial lipids. (ii) Isoprenoids and *n*-alkanes are strongly influenced by the maturity and Pr is preferentially formed during maturation. In the meantime, *n*-alkanes experience thermal degradation and cracking, which introduces great uncertainties in calculating the ratios. Nevertheless the ratios are still often used with the proviso that the data should be considered as biased.

Pr/Ph values > 3 are attributed to OM from land plants (oxidising conditions of deposition), while values < 1.0 indicate anoxic conditions. Magnitudes in the interval 1.0-3.0 suggest intermediate conditions of deposition (sub-oxic condition) [14]. Pr/Ph ratios in Table 3 were moderate and have denoted that source rocks were deposited in sub-oxic conditions. Hunt [15] proposed to plot the ratios in the Pr/nC_{17} *vs.* Ph/nC_{18} diagram (Fig. 1C). Therein samples with high TOCs are located at the zone of immature kerogen almost on the demarking line for Type II and Type II/III kerogen. Actually such plots tolerate deposition in sub-oxic conditions and have sustained assumption based on Pr/Ph ratios. Cross-plots for "bound" bitumens in Fig. 1C were somehow dispersed, and typical for more mature Type II kerogen. These results were in agreement with the patterns of *n*-alkane distributions illustrated in Figure 2, where macrophyte contribution from submerging/floating vegetation to "bound" bitumens formation has been depicted.

According to Pr/nC_{17} *vs.* Ph/nC_{18} diagram mixed Type II/III kerogen is characteristic for high TOCs samples with "good" hydrocarbon generative potential (Fig. 1C). It comprises "gas-prone" source rocks as has been already assumed based on Rock Eval data [5]. This view is additionally strengthened by HI *vs.* T_{max} correlation, assigning "gas prone" source rocks for TOC rich samples (Fig. 1D). As far as similarity with Mezardere Fm. in the Turkish part was already assumed (Fig. S2), it was supposed that the source rocks under study will be capable to generate biogenic gas at appropriate burial and thermal palaeoenvironmental conditions of deposition.

Long-chain acyclic *n*-alkan-2-ones nC_{13}-nC_{33}, maximizing at nC_{29}, 2-nonacosanone, $M^{+}422$, were present in aromatic/slightly polars. Highly abundant

was C_{18} isoprenoid ketone, a clue for a microbial activity, as it has been supposed to be derived from the microbial degradation of phytol [16]. In all separations "odd" numbered *n*-alkan-2-ones have prevailed over the "even" numbered homologues. Distribution signatures for long-chain *n*-alkanes and *n*-alkan-2-ones were similar as both series have maximized at the long chain "odd" members. This resemblance has admitted a product-precursor relationship [14].

Thereinafter "even" carbon numbered *n*-alkanols, nC_{22}-nC_{28} (C_{max} nC_{26}) were identified, accompanied by two esters of 9-hexadecenoic acid, *i.e.* C_{34} and C_{36} ($C_{16:1}$- C_{18} and $C_{16:1}$-C_{20}). Alkyl esters were often major constituents of the natural waxes of microorganism, plants and animals [17]. Alkan-2-ones, *n*-alkanols and alkyl esters are common in the plant kingdom and attest land plants in the studied area [14, 18].

Fatty acids (FAs) were registered only in the "bound" bitumens, where they have represented significant portions of the fractions (Table 2). Their distribution covered a broad span of homologous, nC_{12}-nC_{34}, with "even" numbered dominance. FAs signatures were characterized by two maxima, at the ubiquitous nC_{16} and at long chain member, nC_{28}. Proportions of the two groups of FAs have varied. With depth the relative amount of the short chain FAs has increased and *i*-, *ai*-FAs have appeared. A similarity in possible origins with *n*-alkanes was admitted. In "bound" bitumens dicarboxylic fatty acids (di-FAs), nC_{18}-nC_{30} were identified as well. FAs distribution pattern has denoted at least two possible sources – from ester hydrolysis of diagenetically reduced cutins, suberins or of glycerides from cell membranes for the shorter members and from the hydrolysis of epicuticular waxes. FAs distribution, like in the case of *n*-alkanes, has admitted mixed kerogen origin, from higher plant/macrophyte wax and from algal or bacterial contributions.

CONCLUSION

The study of linear biomarkers in samples from the Bulgarian part of the Thrace Basin reveals the advantage of combining bulk and organic geochemical proxies for source rocks evaluation. The following observations are of special importance:

(i) *n*-Alkanes distributions are complex and give molecular evidences for variation in palaeovegetation and palaeohydrological conditions of deposition. Signatures for the "free" bitumens are characterized by long homologous dominance and high CPI values. "Bound" bitumens are enriched in mid-chain members. The cross-plots of TOC rich samples in Pr/nC_{17} *vs.* Ph/nC_{18} diagram imply immature to slightly mature Type II/III kerogen. Pr/Ph ratios argue for immature OM deposition in anoxic/sub-oxic environment. However this point should be considered rather biased inasmuch as it is possible that some regular isoprenoids are still in "bound" state. *n*-Alkanes distributions admit mixed origin, namely, from higher plant/macrophyte wax and algal or bacterial contributions. Lower P_{aq} values are denoted for the "free" bitumens comparing to the "bound" ones. This is a hint that an increase in TOCs for "free" bitumens can be attributed to emergent/terrigenous supply. Comparable P_{aq} values of 0.50 calculated for "bound" bitumens argue for submerged/floating macrophytes OM input;

(ii) Patterns of distributions for long-chain *n*-alkanes and *n*-alkan-2-ones are similar as both series maximize at the long chain "odd" member homologues. The similarity admits a product-precursor relationship. Fatty acids (FAs) with a broad span of homologous, nC_{12}-nC_{34}, and "even" numbered dominance are registered only in the "bound" bitumens. A similarity in possible origins with *n*-alkanes is evident.

The decrease in T_{max} and *n*-alkane distributions for the shallowest samples evokes more mature OM redeposition. However, the assumption needs verification by additional data and will be considered in the study of cyclic structures.

Electronic Supplementary Data available here.

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ГЕОХИМИЧНА ОЦЕНКА НА ВЪГЛЕВОДОРОД ГЕНЕРИРАЩИЯ ПОТЕНЦИАЛ НА БЪЛГАРСКАТА ЧАСТ ОТ ТРАКИЙСКИЯ БАСЕЙН: I. ЛИНЕЙНИ БИОМАРКЕРИ

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(Резюме)

Частта от Тракийския Басейн, намираща се на територията на България, се определя като негов северозападен фланг. Данните за въглеводородния потенциал на този регион за момента са ограничени. Очаква се някои формации, аналози на такива от турската част на басейна, за които са доказани добри генериращи способности за въглеводороди, да имат нефто/газоносни свойства. С цел оценка перспективността на района чрез методи на органичната геохимия, подробно са изучени 11 проби (7 сондажни и 4 разкрития). Под формата на „свободен" и „ свързан" битуми е изследвано екстрахируемото органично вещество. Чрез Rock Eval и GC-MS е изучена широка гама от органични съединения, някои от които биомаркери. В настоящето изследване обект на изучаване са линейните биомаркери: *n*-алкани, изопреноиди, мастни киселини и др. Rock Eval данните и компонентният състав определят органичното вещество като незряло от Тип III и от смесен Тип II/III. Във всички екстракти преобладават *n*-алкани. Разпределението им по дължина на алкиловата верига се променя с дълбочината на сондажа. Има и данни за преотлагане на по-зряло органично вещество. Позициите на изследваните проби в Pr/*n*C$_{17}$ *vs*. Ph/*n*C$_{18}$ диаграма определя керогена на потенциално нефто/газогенериращите скали като незрял, от смесен Тип II/III. Отношението Pr/Ph е характерно за слабо преобразувано органично вещество, отложено в редукционна и/или променяща се палеообстановка. Само в „свързаните" битуми са установени мастни киселини, *n*C$_{12}$-*n*C$_{34,}$ с преобладаващи четни хомолози и разпределение повлияно от дълбочината на залягане. За тях се предполага произход като на *n*-алканите Установени са и дикарбоксилови киселини, *n*C$_{18}$-*n*C$_{30}$, като максимални са *n*C$_{26}$, *n*C$_{28}$, *n*C$_{30}$.