

## Geochemical appraisal of hydrocarbon generative potential of Bulgarian part from the Thrace Basin: II. Cyclic biomarkers

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*Dedicated to Acad. Bogdan Kurtev on the occasion of his 100<sup>th</sup> birth anniversary*

Assemblages of cyclic components in bitumens help to verify some assumption based of linear structures interpretation and supply relevant information for the generative potential of the region and palaeoenvironment of deposition. Hopanes and steranes determine immature Type III to mixed Type II/III kerogen for the Bulgarian part of the Thrace Basin. The view for Type III kerogen is additionally supported by the signatures for triterpenoids (TTs) abundance. In bitumen fractions monounsaturated, aromatized, C-3 functionalised or partly destructed TTs are identified. All these components unequivocally attest angiosperm taxa contribution to the palaeoenvironment. Consistent with the composition of the products from TTs destruction or aromatization it is assumed that oleanane type TTs strongly prevail ursane/lupane structures. Saturated diterpenoids were practically absent in bitumen extracts. Cross-plots of Pr/Ph vs. C<sub>29</sub>/C<sub>27</sub> regular steranes attest deposition in anoxic/sub-oxic environment. Positions of samples in the diagram confirm the assumption for mixed type of OM (algae/bacteria and from land plants). Plots of steranes in tertiary diagram depict OM formation in open water environment (bay or estuarine) in lacustrine-fluvial/deltaic environments. A decrease in MPI-3 values with depth parallel to T<sub>max</sub> changes was observed. It might be a hint for redeposition of more mature OM. This surmise was not supported by the changes in biomarker parameters, *i.e.* T<sub>s</sub>/(T<sub>s</sub>+T<sub>m</sub>), hopane ratio, homohopane index, sterane C<sub>29</sub> ββ/(αα+ββ) and C<sub>29</sub> 20S/(20S+20R) ratios and positions in Pr/nC<sub>17</sub> vs. Ph/nC<sub>18</sub> diagram, all attesting maturity increase with depth. More samples and additional study are needed to verify this assumption. Rock Eval data and cyclic biomarker assemblages give us a confidence to denote that samples from the shale interval of the shale-marl formation in the Bulgarian territories and analogues to the Yenimuhacir group in the Turkish part of the Thrace Basin, can be regarded as "gas-prone" source rocks capable to generate biogenic gas. Although based on limited number of samples, some of them with low total organic carbon content, the current study is informative for a region where geochemical data are practically absent.

**Key words:** Thrace Basin; generative potential; cyclic biomarkers

### INTRODUCTION

The hydrocarbon accumulations in the Thrace Basin are associated with structural and stratigraphic traps in the Eocene to Oligocene clastic and carbonate reservoir rocks. Since the first discovery, numerous studies considering the source rocks from the sedimentary sequence in the Turkish part of the basin are published [1–8].

The sedimentary succession in the central part of the Thrace basin is more than 9000 m thick, while in the Bulgarian part the maximum thickness of the whole succession is around 2500 m. Nevertheless, based on their lithological and stratigraphic characteristics, the sediment formations are very well correlated [9]. In the Bulgarian part of the Basin, these rocks exhibit similar reservoir properties as in the hydrocarbon fields in Turkey.

The sandstone intervals of the shale-marl fm., is proposed to be analogue of one of the major reservoir units Oligocene Yenimuhacir group, which are characterized by porosity values between 9-25% and a permeability of 2-6mD [4]. Therefore, there are indications that the area of the Basin in the Bulgarian territory could be regarded as its NW flank and detailed evaluation of sediments as potential source rocks for future exploration activities is necessary.

Present study continues previous investigation on the linear biomarkers from the same provenance. Herein data on biomarker assemblage will be enriched with results for cyclic components with the aim to determine depositional environment from the perspective formations from the Bulgarian part of the Thrace Basin. The study will proceed with attempts to look for analogy with Turkish sequences of the basin with already proven oil/gas accumulations.

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## EXPERIMENTAL

Samples characteristics, scheme of separation and Rock Eval data were published in a previous paper dedicated to the linear structures in bitumen extracts [9]. Briefly, the following set of samples was studied: (i) core samples G1-G5 were from the shaly 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); (iii) G11 and G12 from shale rock outcrops.

GC-MS study was carried out on a Hewlett-Packard 6890 GC system plus HP 5973 MSD equipped with a HP-5 MS column (0.25 mm×30 m×0.25 μ 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 hold 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 MS with literature and library data, comparison of MS and GC retention times with those of authentic standards or interpretation of mass spectra. 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 to TOC and are presented in μg/gC<sub>org</sub>.

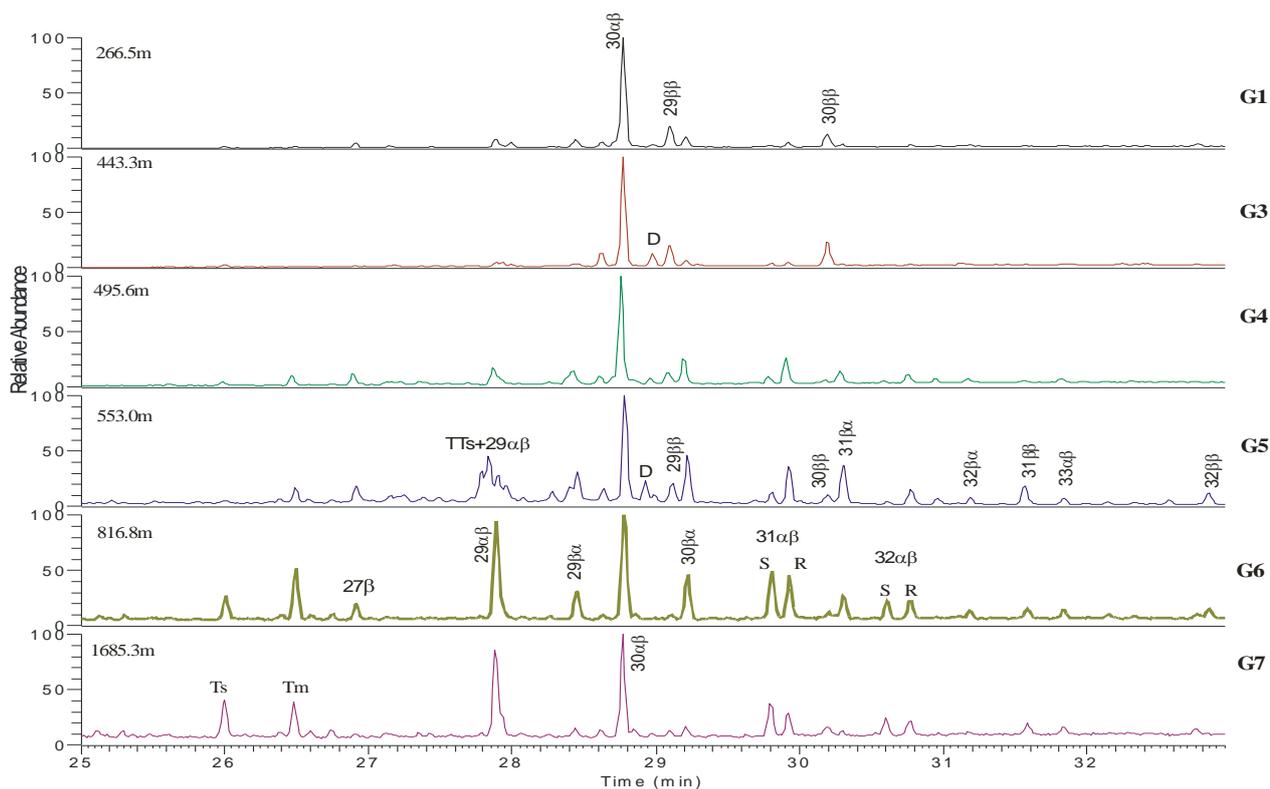
The following cyclic biomarkers were MS tracked: steranes ( $m/z$  217), diasteranes ( $m/z$  259), tri-, tetra-, pentacyclic terpanes of hopane type, benzohopanes, hopanoic acids ( $m/z$  191). Based on peak areas some biomarker parameters for hopane (H) and steranes (S) were calculated. The following ratios were determined: (i)  $T_s/(T_s+T_m)$ ; (ii)  $H_{30\alpha\beta}/H_{29\alpha\beta}$ ; (iii) S/(S+R) stereo isomers at C-22 carbon atom in homohopane  $H_{31\alpha\beta}$ ; (iv)  $\beta\beta/(\alpha\beta+\beta\alpha+\beta\beta)$  hopanes; (v) and, regular sterane S/(S+R) stereo isomers at C-20. Parameters definitions and applications are described in Peters and Moldowan [10]. Specific fragments were used for homologous and individual compounds tracking:  $m/z$  123 for diterpenoids (DTs);  $m/z$  203 and  $m/z$  218 for TTs;  $m/z$  231 for 4-Me steranes;  $m/z$  424 for 3-keto-TTs;  $m/z$  274 for products of TTs destruction and aromatization.

## RESULTS AND DISCUSSION

In the studies of fossil materials pentacyclic TTs are divided into two main groups - hopanoids (hopanes, H) and non-hopanoids [11–13]. Hopanes in Fig. 1 comprise the series  $C_{27}$ - $C_{33}$  ( $C_{28}$  absent) with their  $\alpha\beta$ ,  $\beta\alpha$  and  $\beta\beta$  isomers and some benzohopanes,  $C_{32}$ - $C_{34}$ . Hopanoids are indicators for microbial activity in the sediments. The contribution of microorganism during the diagenetic transformation of the parent OM supplies hopanes. However, some of them might be derived from lower plants like ferns [10]. Distributions of regular hopanes in Fig. 1 maximize at  $C_{30\alpha\beta}$ . Some variations with depth in hopanes parameters are obvious in Table 1 and in Fig. S1. In Fig. 1 anoxicity marker  $17\alpha(H)$ -28,30-bisnorhopane M<sup>+</sup>284 is absent, an indication that the samples were deposited in terrestrial or lacustrine environment under oxic or sub-oxic conditions [10]. This assumption contradicts a bit with correlations Pr/Ph vs.  $C_{29}/C_{27}$  regular steranes discussed later in the text where definitively anoxic conditions were depicted. Low amount of  $17\alpha(H)$ -28,30-bisnorhopane below the detection limit of GC-MS might be one possible explanation for the discrepancy. In the samples sequence G6-G9, with depth increasing tricyclic terpanes ( $C_{25}$ ,  $C_{28}$ ) have appeared. One  $17,21$ -seco-hopane,  $C_{24}$ , M<sup>+</sup>330 is detectable as well. All listed tri-/tetra terpanes are characteristic components for petroleum and petroleum source rocks [10]. For “bound” bitumens, hopanes assemblages are similar to the “free” ones, except appearance of hopanes ( $C_{27:1\alpha}$ ,  $C_{30:1\alpha\beta}$ ). They are indicators for hopanes still attached to the kerogen OM.

By  $m/z$  191 tracking in aromatics/slightly polar fractions were identified hopanoid acids (as methyl esters), maximizing at  $C_{32\beta\beta}$ , (Table 2). They are hopanes biological precursors and are common in the bitumens from immature fossils. Functionalized hopanes with carbonyl/hydroxyl group at the C-3 position are determined as well, i.e. hop-22(29)-en-3-one, M<sup>+</sup> 424,  $m/z$  189 (100%) and diplopterol M<sup>+</sup> 426. The last one is a functionalized diploptene, highly abundant in the neutrals fractions and one of the possible hopane precursors. Diploptene (peak D, in Fig. 1) is common in all hopanoid-producing bacteria and represents likely source for hopanes with <  $C_{30}$  carbon atoms.

Some biomarker parameters based of hopanes distributions are calculated and shown in Table 1. Values for  $T_s/(T_s+T_m)$  ratios for well samples are somehow dispersed, 0.21–0.53. It is known that  $T_s$  and  $T_m$  are sensitive to maturity, type of OM and



**Fig. 1.** Variations in hopanes distributions with depth increase tracked by  $m/z$  191. (Abbreviations in Table 1; TT – non-hopanoid triterpenoids; D- diploptene).

**Table 1.** Variations in hopanes distributions with depth increase tracked by  $m/z$  191.

Sample	Hopanes (H)					Steranes (S)					
	$T_s/(T_s+T_m)$ ratio	Mor/H ratio	H ratio	HomoH index	DiaS/S	$\beta\beta/(\alpha\alpha+\beta\beta)$	S/(S+R)	$\alpha\alpha$ Steranes (20R), rel.%			
								27	28	29	
"Free" bitumen											
Well	G1	-	0.09	0.08	0.1	0.4	0.27	0	36.2	20.9	42.9
	G3	-	0.05	0	0.1	n.d.	n.d.	0	n.d.	n.d.	n.d.
	G4	-	0.24	0.24	0.18	0.56	0.34	0	35	23.4	41.6
	G5	0.21	0.41	0.3	0.22	0.52	0.34	0	33.3	24.8	41.9
	G6	0.31	0.36	0.9	0.54	0.50	0.43	0.34	42.7	23.9	33.4
	G7	0.53	0	1.08	0.6	0.89	0.52	0.34	40.2	29	30.8
Outcrop	G9	0.81	0	0.75	0.63	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	G11	0.34	0.3	0.45	0.47	0.3	0.3	0.1	31	29	40
	G12	0.48	0.11	0.98	0.11	0.25	0.25	0.09	23	27	50
"Bound" bitumen											
Well	GA1	0.47	0.28	0.2	0.45	0.23	0.43	0.16	34.6	23.5	41.9
	GA3	0.56	0.08	0.12	0.48	0.4	0.22	0.07	28.8	26	45.2
	GA4	0.3	0.27	0.36	0.28	0.42	0.35	0.1	29.1	25.1	45.8
	GA5	0.28	0.38	0.39	0.3	0.45	0.32	0.1	28.3	25	46.7
	Outcrop	GA12	0.49	0.13	0.14	0.57	0.41	0.41	0.21	38	21

n.d. – not determined

$T_s$  - 18 $\alpha$ (H)22,29,30-Trisnorhopane

Moretane/Hopane ratio (Mor/H) = H30 $\beta\alpha$ /H30 $\alpha\beta$

Homohopane index (HomoH) = H31 $\alpha\beta$  S/(S+R)

Diasterane/Sterane ratio (DiaS/S) =  $\beta\alpha$ -Dia-C27(S+R)/ $\alpha\alpha$ C27(S+R)

Sterane  $\beta\beta/(\alpha\alpha+\beta\beta)$  = C29 $\beta\beta$ (S+R)/[C29 $\alpha\alpha$ (S+R) + C29 $\beta\beta$ (S+R)]

$T_m$  - 17 $\alpha$ (H)22,29,30-Trisnorhopane

Hopane ratio (H) = H29 $\alpha\beta$ /H30 $\alpha\beta$

Sterane S/(S+R) = C29 $\alpha\alpha$  S/(S+R)

**Table 2.** Compounds and homologous series identified in G5 sample, expressed in  $\mu\text{g/g}$  sample and normalized to  $\mu\text{g/g C}_{\text{org}}$ .

Series or compound classes	Bitumen							
	"Free"				"Bound"			
	Neutrals		Aromatics/Slightly polars		Neutrals		Aromatics/Slightly polars	
	$\mu\text{g/g}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g}$	$\mu\text{g/g C}_{\text{org}}$
<i>n</i> -Alkanes and isoprenoids	31.2	1351	-	-	8.2	355	-	-
<i>n</i> -Alkan-2-ones	-	-	1.92	83.1	tr.	tr.	tr.	tr.
C <sub>18</sub> <i>iso</i> -ketone	0	0	0.1	4.3	0	0	0.07	3
Diterpenoids	1.8	77.9	0	0	tr.	tr.	tr.	tr.
Polar aromatic diterpenoids	0	0	0.05	2.2	0	0	0.03	1.3
Triterpenoid (TTs)	1.9	82.3	0	0	0.25	10.8	0	0
Products of TTs destruction	1.8	77.9	0.11	4.8	0.44	19.1	0	0
Aromatized TTs	0	0	1.36	58.9	0	0	0.4	17.3
Polar TTs	0	0	0.03	1.3	0	0	0.05	2.2
Perylene	0	0	0.27	11.7	0	0	0.02	0.9
Hopanes and benzohopanes	5.2	225.2	0	0	0.62	26.8	0	0
Hopanoic acids, methyl esters	0	0	0	0	0	0	0.52	22.5
Fatty acid, methyl esters	0	0	0	0	0	0	3.96	171.5
Dicarboxylic fatty acids, dimethyl esters	0	0	0	0	0	0	0.47	20.4
Total	41.9	1814.3	3.84	166.3	9.51	411.7	5.52	239.1

samples lithology [14]. With maturation  $T_m$  is gradually transferred into  $T_s$ . In our samples set G1-G7 in parallel with the increase in burial depth the ratios  $T_s/(T_s+T_m)$  rise (Table 1 and Fig. S1), attesting increase in maturity. With increasing depth the magnitudes for hopane ratios and homohopane index also increase. Homohopane index for sample G9 is 0.63 (Table 1) and argues for a high sample maturity. In hopane distributions  $\alpha\beta$  hopanes are more prominent than  $\beta\alpha$  isomers, reflecting in varying moretane ratios, the highest calculated for OM rich samples,  $\sim 0.4$ . Hopanes distribution of G5 "free" bitumen (Fig. 1) permits determination of the relative portion of  $\beta\beta$  hopanoids ("bio"-hopanoids) from the total sum of regular hopanes. It is known that during diagenesis  $\beta\beta$  hopanoids are progressively transferred into "geo"-hopanoids ( $\alpha\beta$  and  $\beta\alpha$  epimers). The ratio "bio"/"geo" hopanes for G5 "free" bitumen is 0.16 and almost alike, 0.17, for the "bound" bitumen. The  $m/z$  191 separations in Fig. 1 and calculated parameters (Table 1) argue for immature OM comprising considerable portion of  $\beta\beta$  homologues.

Triterpenoids of non-hopanoid type are unambiguous biomarkers for angiospermous floral input, where oleananes have proven to be the most commonly cited [15]. These cyclic alkanes are identified in many oils and shales with terrestrial

source rock provenance. By tracking  $m/z$  203,  $m/z$  218 and  $M^+$  410 olean-13(18)-ene, olean-12-ene, olean-18-ene ( $\beta$ -olean-12-ene maximal) were identified. These compounds are intermediates in the classical diagenetic transformation of 3-oxygenated triterpenoids to chrysene and pyrene via the pathway proposed by Murrey *et al.* [16]. The scheme is additionally validated by the presence of C-3 functionalized oleanane/ursane type TTs with  $M^+$  424, *i.e.*  $\alpha/\beta$  amyrones (all present in the aromatic/slightly polar fractions, Table 2). Oxygenated TTs abundance is a convincing proof for the considerable terrigenous input. All compounds and homologous series identified in G5 sample, expressed in  $\mu\text{g/g}$  sample and normalized to  $\mu\text{g/g C}_{\text{org}}$ , are shown in Table 2.

In the first fractions (neutrals) were determined des-A-oleanane/ursane and their mono-/di-unsaturated homologues. Des-A-lupane,  $M^+$  330,  $m/z$  123 was in negligible content. There were several attempts to use des-A-TTs as biomarkers for paleoenvironmental reconstruction [17–19]. Commonly they have related des-A-TTs formation and accumulation to wetter climate, high water table and anaerobic environment. Respectively, such conditions might be assumed for the palaeoenvironment.

In the aromatics/slightly polar fractions products of  $\alpha/\beta$ -amyrin aromatization were depicted, *i.e.* dimethyl- ( $M^+$  310) and trimethyl ( $M^+$  324) substituted tetrahydropicenes. They are the end products of TTs destruction and aromatization [16].

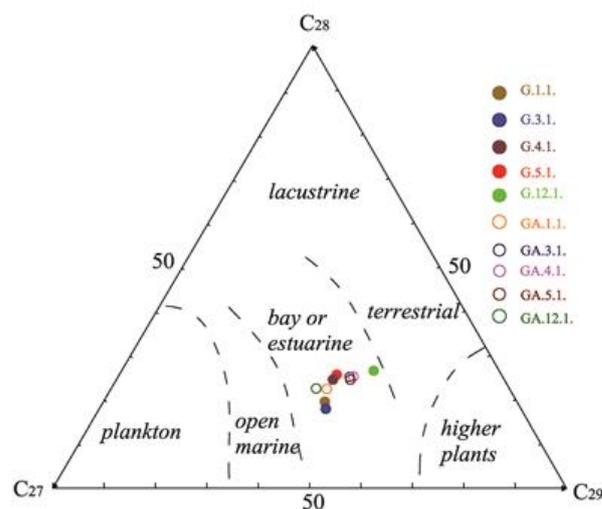
By  $M^+$  274 tracking three components were visualized: (i) with  $m/z$  218 (100%) for oleanane type TTs; (ii) with  $m/z$  259 (100%) for ursane type TTs; (iii) and, with  $m/z$  231 (100%) for lupane type TTs [20]. Ratios for the three groups were 46:3:1. Therefore, on the base of the TTs products of destruction and aromatization, oleanane type TTs seems to have been strongly predominant in the floral assemblage. Generally, TTs biomarkers do not specify palaeovegetation. They simply assign angiosperm contribution to the kerogen formation. However, studies in this field are in progress as potential TTs precursor assignment will considerably increase chemotaxonomic value of angiosperms for sedimentary environmental reconstruction [21].

No saturated DTs were detected by  $m/z$  123 tracking. Only aromatized DTs, *i.e.* simonellite and retene, were identified. These two components are the end products of diterpenoids diagenetic transformation [22–24]. Likewise DTs provide evidences for the subordinate gymnosperms presence in palaeovegetation and for advance in maturation.

Absolute amounts of the regular steranes in the studied samples are very low, which prohibits their quantitative determination. Hence, regular steranes were only qualitatively interpreted and distributions in rel. % are shown in Table 1. Signature of regular steranes in terrigenous OM is very simple: (i) dominated by  $C_{29}$  steranes; (ii) and, the ratio regular sterane/hopane is very low [25]. In a case of OM mixed input to the source rocks it is more complicated. Another feature of the regular sterane distribution is the presence of diasteranes. Recent studies have provided evidences that maturation, oxic-type environment and the catalytic role of clays tolerate rearrangement with diasteranes formation [10]. The ratios diasterane/regular sterane for the well samples were in the range 0.4–0.5 and have increased to  $\sim 0.9$  with depth, parallel with maturation (Table 1). An attempt to make a correlation with lithology has not been done.

According to the number of carbon atoms in their molecules regular steranes are grouped in  $C_{27}$ ,  $C_{28}$ ,  $C_{29}$  and distributions are plotted in Fig. 2 [26]. Commonly,  $C_{27}$  steranes are related to algal contribution while  $C_{29}$  steranes point to land plants input. This approach for steranes interpretation is

rather simplistic for general use as it is known that phytoplankton could also contribute to  $C_{29}$  sterols [27]. However, the diagram is often used for oil/source rocks correlations. The plots of samples in Fig. 2 indicate OM formation in open water environment (bay or estuarine) and imply that most likely the kerogen has been formed in lacustrine-fluvial/deltaic environments. The proportion  $C_{27}/C_{29}$  steranes varies with a depth. The algal supply, respectively the relative content of  $C_{27}$  steranes, increases with depth to  $\sim 40\%$ , while TOC rich samples (at shally intervals) are enriched in  $C_{29}$  steranes. Variations in sterane distributions for samples G1, G3 and G5 might be contributed to the changes in the sedimentary environment, namely low water table and terrigenous input. Generally, regular sterane signature confirms the assumptions based on *n*-alkane distributions [10] - mixed origin for OM, *i.e.* aquatic and terrestrial, in different proportions depending on the depth. Variations in  $C_{27}/C_{29}$  steranes ratios with depth give a picture for hydrological oscillations at different periods - arid (0.79–0.84, for shally intervals of shale-marl fm. analogue to Yenimuhacir group, Turkey) and humid ( $\sim 1.3$ , for intervals analogue of Ceylan fm., Turkey).



**Fig. 2.** Plots of steranes distributions in  $C_{27}$ ,  $C_{28}$ ,  $C_{29}$  ternary diagram after Huang and Meinschein [26].

In all samples by SIM  $m/z$  231 4-methyl steranes, *i.e.*  $C_{28}$ ,  $C_{29}$ ,  $C_{30}$ , were identified. They were interpreted as dinosteranes attesting dinoflagellates presence and microbial activity in the palaeoenvironment [10].

In samples studied polycyclic aromatic hydrocarbons (PAHs) with 2–4 condensed aromatic rings, *i.e.* naphthalene, phenanthrene (highly present), pyrene (tentatively identified) and their alkylated homologous, *i.e.*  $C_1$ – $C_4$  derivatives, were

determined. It is impossible PAHs quantification due to their low concentrations. However, it was feasible to calculate MPI-3 maturity index. It is based on distribution of methyl phenanthrene isomers. The definition, application and limits were explained by Radke *et al.* [28]. Methyl phenanthrenes ( $m/z$  192) are the most commonly found in separations and their distributions comprise peaks of 2-, 3-, 4+9-, and 1-methyl phenanthrenes. MPI-3 calculated values for well samples vary in the range 1.42–1.60, while for the outcrops samples they are in the range of 1.35–1.65. There is not an appreciable change of MPI-3 ratios with depth (1.61 to 1.43). However, a tendency for a decrease in MPI-3 values parallel to  $T_{max}$  decrease in Rock Eval parameters is recognizable [9]. It might be a hint for redeposition of more mature OM. The assumption is not supported by parameters calculated on the base of cyclic biomarkers where unequivocal proves for increase in maturation with depth were obtained (Supplementary Material 1). More samples are needed to clarify the item.

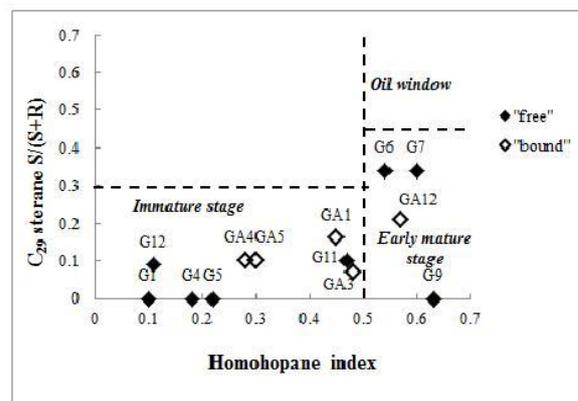
MPI-3 ratios are not calculated for “bound” bitumens as in GC-MS separations methyl phenanthrenes have overlapped with elemental sulphur. Highly substituted phenanthrenes were less abundant, except 1-Me-7-*i*-Pr-phenanthrene,  $M^+$  234, retene.

Perylene ( $11.7 \mu\text{g/gC}_{org}$ ) was present in G5 aromatic/slightly polar fraction (Table 2). Previous researches proved that its precursors could be fungi, wood-degrading fungi, terrestrial sources [29]. A diagenetic product of perylene is registered predominantly in humid, terrestrial OM rich environments.

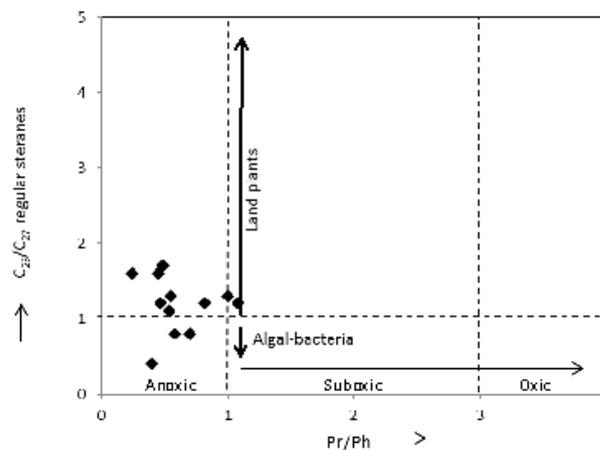
## GENERAL DISCUSSION

Data in Table 1 and Fig. S1 demonstrate that the ratio  $22S/(22S+22R)$  for  $C_{31}17\alpha(H),21\beta(H)$ -hopanes is depth dependent and from 0.10 gradually increases to 0.60, attesting that at 1685.3 m hopane epimer equilibrium is already attained. The magnitudes for sterane  $C_{29} 20S/(20S+20R)$  ratios are very low. In  $m/z$  217 track of some samples 20S epimers were virtually absent reflecting in  $S/(S+R) = 0$  (Table 1, Fig. S1). With depth increasing 20S epimer became visible and the ratio reached 0.34. The magnitudes for outcrop samples and “bound” bitumens are also low (0.07–0.21, Table 1) and argue for kerogen immature stage. Some relationship for sterane  $C_{29} \beta\beta/(\alpha\alpha+\beta\beta)$  vs. depth are recognizable as well (Fig. S1). The

values vary in the range 0.3–0.5 (Table 1), for well samples they increased with depth, attesting advance in maturation. A correlation of two maturity parameters,  $C_{29}20S/(S+R)$  for regular steranes and  $C_{31} 22S/(S+R)$  for hopanes, is shown in Fig. 3. The cross-plots unequivocally argue for kerogen immature stage. Only G6 and G7 (deeper well samples) are shifted to kerogen of “early mature stage”. None of the samples is plotted in the “oil window” area.



**Fig. 3.** Estimation of kerogen maturity by homohopane index vs.  $C_{29}$  steranes  $S/(S+R)$  ratios correlations after Peters and Moldowan [10].



**Fig. 4.** Cross-plots of  $Pr/Ph$  vs.  $C_{29}/C_{27}$  regular steranes ratios suggesting samples anoxic/sub-oxic conditions of depositions after Hakimi *et al.* [31]

Cross-plots of  $Pr/Ph$  vs.  $C_{29}/C_{27}$  regular steranes are illustrated in Fig. 4 [30, 31]. On the base of  $Pr/Ph$  ratios in the previous paper an assumption for OM deposition in anoxic/sub-oxic environment has been done [9]. Positions of samples in  $Pr/Ph$  vs.  $C_{29}/C_{27}$  regular steranes diagram (Fig. 4) confirm it. The cross-plots depict a mixed type of OM input (from algae/bacteria and from land plants) and deposition in anoxic-sub-oxic environment.

Estimates regarding the generative potential of the samples on the base of biomarkers are in a good coherency with Rock Eval data. The fractional compositions and biomarker assemblages of TOC-rich samples evaluate moderate OM contents. According to these parameters the rocks can be classified as source rocks with “fair” to “good” potential. Kerogen is defined as immature of mixed Type II/III capable to generate biogenic gas. These main conclusions fit well with the data published for the Turkish part of the Thrace Basin [3, 5–7, 32, 33]. Therein, for Thrace sediments is assumed oil/gas potential based on the data from oil/gas to source rocks correlations and basin modeling.

## CONCLUSION

The study highlights the relevance of biomarkers for source rocks and depositional environment appraisal. Assemblages of cyclic components help to verify some assumption based of linear structures interpretation and supply information for the generative potential of the region. The following observations are of particular importance: (i) Ratios sterane/hopane for TOC rich samples are very low and attest kerogen with considerable terrigenous input. Plots of regular steranes in ternary diagram depict OM formation in lacustrine-fluvial/deltaic environment in agreement with Pr/Ph ratios, 0.3–1.1. According to these geochemical data samples most likely have been deposited under oxygen-deficient, but not at completely anoxic conditions; (ii) Plots  $C_{29}20S/(S+R)$  steranes vs.  $C_{31}22S/(S+R)$  hopanes denote immature to early mature OM; (iii) Geochemical proxies determine immature mixed Type II/III kerogen with considerable supply of microbially reworked OM. Variety of TTs in sample G5, *i.e.* monounsaturated, aromatized or C-3 functionalized as ketones and alcohols, partly destructed, *etc.*, admits Type III kerogen and indicates floral supply dominated by angiosperm taxa. Based on the compositions of products from TTs destruction/aromatization, oleanane precursors preponderance over ursane/lupine structures is assumed; (iv) MPI-3 index and  $T_{max}$  values gave a hint for redeposition of more mature OM. On the other hand this surmise was not supported by the changes in biomarker parameters with depth, *i.e.*  $T_s/(T_s+T_m)$ , hopane ratio, homohopane index, sterane  $C_{29} \beta\beta/(\alpha\alpha+\beta\beta)$  and  $C_{29} 20S/(20S+20R)$  ratios and positions in Pr/nC<sub>17</sub> vs. Ph/nC<sub>18</sub> diagram. More extensive survey is required to test the validity of this assumption. Finally, for some

samples of the shaley intervals of the shale-marl Fm. a similarity with Yenimuhacir group in the Turkish part of the Thrace Basin is admitted. These successions are resolved as potential “gas-prone” source rocks capable to generate biogenic gas. However, further work on the Bulgarian part of the Basin using densely sampled Fms. is needed to confirm or reject this point.

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Electronic Supplementary Data available here. 

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## ГЕОХИМИЧНА ОЦЕНКА НА ВЪГЛЕВОДОРОД ГЕНЕРИРАЦИЯ ПОТЕНЦИАЛ НА БЪЛГАРСКАТА ЧАСТ ОТ ТРАКИЙСКИЯ БАСЕЙН: II. ЦИКЛИЧНИ БИОМАРКЕРИ

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(Резюме)

Наборът от цикличните биомаркери дава възможност да се проверят някои вече направени заключения на базата на състава и разпределението на линейните структури и предоставя допълнителна информация относно генериращия потенциал на региона и палеообстановката на отлагане. Хопаните и стераните определят керогена от българската част от Тракийския басейн като незрял от Тип III и/или от смесен Тип II/III. Представата за Тип III кероген се потвърждава и от широкото разпространение на тритерпеноиди. Във всички изследвани битуми присъстват мононенаситени, ароматни, C-3 заместени с функционални групи или частично деструктурирани производни на тритерпеноиди. Всички те са недвусмислено указание за присъствие в палеоблатото на широколистна растителност. В съгласие със състава на продукти от разграждане и ароматизация на тритерпеноиди се предполага, че олеановите структури доминират над урсанови или лупанови такива. В битумите практически липсват наситени дитерпеноиди. Зависимостта Pr/Ph vs. C<sub>29</sub>/C<sub>27</sub> стерани допуска отлагане в променяща се обстановка като позициите на пробите в диаграмата потвърждават схващането за смесен тип на органичното вещество (водорасли/бактерии и наземна растителност). Разпределенията на стераните, оформено в тройна диаграма, допуска формиране на органичното вещество в открити води (залив или устие на река) в езерна-речна или делтова обстановка. Установено бе, че стойностите за MPI-3 намаляват паралелно с тези за T<sub>max</sub>, което допуска преотлагане на по-зряло органично вещество. Това твърдение не се подкрепя от измененията на някои биомаркери с удълбочаване на пробата, а именно T<sub>s</sub>/(T<sub>s</sub>+T<sub>m</sub>), отношението на хопаните, индекса на хомохопаните, отношенията C<sub>29</sub> ββ/(αα+ββ) и C<sub>29</sub> 20S/(20S+20R), позициите в Pr/nC<sub>17</sub> vs. Ph/nC<sub>18</sub> диаграма. Всички те утвърждават повишение на зрялостта с удълбочаване. Тези експериментални данни показват, че твърдението следва да се провери с анализа на по-голям брой проби. Данните от Rock Eval и съставът на цикличните биомаркери дават основание да се допусне, че пробите от шистовия интервал на глинесто-мергелната задруга на българска територия са аналог на Йенимухачир групата от Турската част на Басейна и могат да се разглеждат като перспективни газоносни скали за продуциране на биогенен газ при залягане при подходящи термобарични условия. Независимо, че настоящото изследване е проведено с ограничен брой проби, някои от които са с ниско съдържание на общ въглерод, то дава информация за геохимичната обстановката в регион, за който практически липсват сведения.