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Geochemical appraisal of Stefanets Member (Etropole Formation) from the eastern part of the West Forebalkan, Bulgaria

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The study presents a geochemical appraisal of key well core samples from Stefanets Member (Etropole Fm.), from the eastern part of the West Forebalkan, Bulgaria. Extractable organic matter, i.e. "free" and "bound" bitumens, was characterized by geochemical methods. Biomarkers were tracked, quantified and correlated. Parameters calculated on the base of *n*-alkanes, regular isoprenoids, hopanes, steranes and aromatic hydrocarbon distributions have determined organic matter as "mature" – early to late mature. The plots of the ratios Pr/nC_{17} *vs.* Ph/nC_{18} in a diagram were situated on the demarking line for Type II to mixed Type II/III kerogen. The magnitudes of Pr/Ph ratios < 1.0 have argued for reductive conditions in the depositional palaeoenvironment. There were proofs for hydrocarbons expelling and their total lack in "free" bitumen of the "late mature" sample. All calculated biomarker parameters have indicated that hopanes and steranes have attained their epimer equilibria. According to S29αα S/(S+R) vs. H31αβ S/(S+R) correlation one of the studied samples has been located in the "oil widow" area. Methyl phenanthrene index (MPI-3) has confirmed high samples maturity as the calculated values were in the range of 2.0-5.3.

Results have demonstrated very good agreement between Rock Eval data, biomarker assemblages and set of calculated parameters.

Keywords: West Forebalkan, Stefanets Member, biomarker assemblage, maturity

INTRODUCTION

In the process of petroleum exploration it is imperative to define the source rocks of the basins and to assess their hydrocarbon generative potentials. Therefore, methods of organic geochemistry, i.e. Rock Eval and GC/MS, are commonly applied. In previous papers [1,2] an attempt has been made to evaluate by geochemical proxies the generative potential of Middle Jurassic Stefanets Member (Etropole Fm.) from the Central South Moesian platform margin. The present study was a continuation of our attempts to characterize Stefanets Member by geochemical methods and exploring near area – the eastern part of the West Forebalkan, Forebalkan unit (Fig. 1) [3]. The size of the area is about 240 km^2 between Iskar River to the east and Ogosta River to the northwest. Lower and Middle Jurassic series are not completely developed everywhere in the study area, but among them predominates the terrigenous-carbonate succession. Extractable portions of initial ("free bitumen) and demineralized ("bound" bitumen) samples were under consideration. A broad range of homologue series were quantitatively interpreted, i.e. linear, branched and cyclic alkanes, as well as a set of polycyclic aromatic hydrocarbons (PAHs). The biomarker assemblages allowed characterization of palaeoenvironmental conditions of deposition and assessment of the generative potentials of the Stefanets Member (Etropole Fm.) from the eastern part of the West Forebalkan, Bulgaria.

Materials and methods

Six wells, located in the land of villages Galatin and Golyamo Peshtene were investigated in details. Ten well-core samples from Middle Jurassic Stefanets Member (Etropole Fm.), in depths from 1956.6 to 3866.5 m, were selected and analyzed. They are representative for the shallow part of the Early-Middle Jurassic paleo basin. Two of them (St-2 and St-7) were chosen as key samples for the area of study, because of their maturity in a range of "oil window". All geochemical parameters for the samples are given in the complex Table 1. The same protocol for "free" and "bound" bitumen isolation, fractionation and characterization as in the previous study [2] was kept.

The last generation Rock Eval 6 equipment was used for the evaluation of the organic matter and hydrocarbon generative potential. The GC-MS distributions and quantitative peaks interpretations gave us ground to calculate the following biomarker parameters: (i) CPI [4], Pr/Ph [5],

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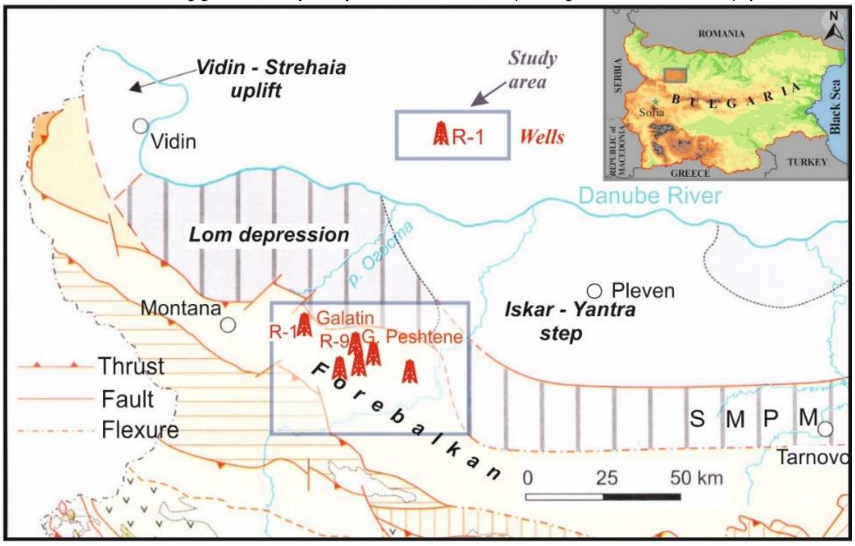

Fig. 1. Tectonic scheme of Central and North West Bulgaria with the location of the study area (after [3])

Pr/nC17 *vs.* Ph/nC18 [6] and Paq [7] all for linear n-alkanes; (ii) biomarker ratios, i.e. hopanes, moretanes, steranes and diasteranes ratios [8] for cyclic alkanes; and (iii) methylphenanthrene index (MPI-3) [9] for aromatic hydrocarbons (PAHs).

RESULTS AND DISCUSSION

Major Rock Eval indices, yields of bitumens and their fractional compositions are shown in Table 1A. Extracted amounts were relatively low and this has reflected in high losses during fractionations. Better results were obtained only for the "free" bitumen of sample St-7, namely higher portion of oils compared to the sum of polar constituents (resins+asphaltenes) and reasonable loss of ~ 11 rel. %. The quantity of organic matter demonstrates its current condition after all transformations that have been carried out throughout the lithogenesis. TOC (wt. %) of the key samples shows fair to good hydrocarbon potential. T_{max} values characterize the maturity of the evaluated source rocks as early mature to late mature, according to the widely accepted scale [10].

Separations of n-alkanes are illustrated as histograms in Fig. 2. Therein are shown distributions of three samples as in "free" bitumen of sample St-2 n-alkanes were practically absent. Determined amounts of linear alkanes and geochemical parameters are summed in Table 1B. Herein only peculiarities will be denoted, namely absence of n-alkanes in St-2 "free" bitumen and a huge amount in the "bound" bitumen, 3304 μg/g TOC (Table 1B). The total lack of the shorter homologues (nC$_{15}$-nC$_{20}$) could be an indication that all low-molecular hydrocarbons have been expelled during organic matter transformation. This argument is supported by the value of S_2 lower than 2.5 mg HC/g rock and relatively high maturity of sample St-2.

n-Alkanes distributions of sample St-7 in Fig. 2 demonstrate some differences noticeable in the calculated values for ALC, TAR and P_{aq} parameter in Table 1B. In "bound" bitumens shorter members have decreased and ALC and TAR values have increased, giving a proof that attached alkanes were preferably of terrestrial origin. Regular isoprenoids were present only in sample St-7 (Table 1B). The cross plots of the ratios in a diagram Pr/nC$_{17}$ *vs.* Ph/nC$_{18}$ are situated on the demarking line for kerogen Type II and mixed Type II/III (Fig. 3). For comparison, the positions of the previously studied samples from the Stefanets Member (Etropole Fm.) from the Central South Moesian platform margin are indicated as well [2]. A certain similarity in the depositional environment for all samples studied is depicted, namely, deposition in reductive environment of mixed Type II/III toward Type II kerogen. The magnitudes of Pr/Ph ratios < 1.0 have also argued for reductive conditions in the depositional palaeoenvironment (Table 1B).

In their study of sedimentary input of submerged/floating fresh water aquatic macrophytes Ficken *et al.* [7] proposed the P_{aq} ratio to discriminate macrophytes and emergent terrestrial plants. It was able to distinguish macrophytes from terrestrial plants from the other supply. The following P_{aq} ranges have been proposed: 0.01-0.23 for terrestrial plant wax, whereas magnitudes in the range 0.48-0.94 were associated with submerged/floating species of macrophytes. P_{aq} values in Table 1B revealed mixed n-alkane supply, more precisely, from higher plant/macrophyte wax and algal or bacterial contributions.

Table 1. Complex geochemical characteristics of samples from the Stefanets Member (Etropole Fm.) from the eastern part of the West Forebalkan: A. Rock Eval and bitumen data; B. Content of *n*-alkanes, distribution and geochemical parameters; C. Geochemical parameters based on hopanes and steranes distributions

A.

Sample	Rock Eval data							Bitumen						
	TOC	T_{max}	S_1	S_2	S_3	HI	OI	Abbreviation	Yield		Fractional composition, %			
									%	mg/gTOC	Oils	Resins	Asph.	Loss
St-2	1.235	456.5	0.03	0.23	0.31	18.5	25							
								"free"	0.02	18.4	16.1	21	32.3	30.6
								"bound"	0.11	86.3	22.5	17.4	36	24.1
St-7	0.71	440	0.045	0.38	0.42	53.5	59							
								"free"	0.05	68.5	65.2	14.3	9.1	11.4
								"bound"	0.09	57.6	11.9	24.6	33.3	30.2

B.

Sample	Bitumen	*n*-Alkanes content			Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	Distribution, rel.%			CPI[(1)]	ALC[(2)]	TAR[(3)]	Paq[(4)]
		[µg]	[µg/gTOC]	Total				short-	mid-	long-				
St-2														
	"free"	-	-	3304	-	-	-	-	-	-	-	-	-	-
	"bound"	1255.5	3304		-	-	-	0	10.8	89.2	1.05	29.5	-	0.27
St-7														
	"free"	47.4	216.5	278.6	0.89	0.23	0.27	42.9	32.1	25	1.19	22.2	0.67	0.65
	"bound"	13.6	62.1		0.76	0.39	0.33	11.3	15.3	73.4	1.26	27.5	8.14	0.23

C.

Sample	Bitumen	Hopane ratios					Sterane ratios		
		Ts/Tm	Hopane Ratio[(5)]	Moretane Ratio[(6)]	H31αβ S/(S+R)	H32αβ S/(S+R)	S29ααS(S+R)[(7)]	Diasterane Ratio[(8)]	S29 ββ/(αα+ββ)[(9)]
St-7									
	"free"	1.29	0.63	0.16	0.56	0.57	0.52	0.61	0.37
	"bound"	1.32	0.68	0.14	0.58	0.58	n.d.	n.d.	n.d.

[(1)]CPI - Carbon Preference Index; CPI = $\sum(C_{23} \div C_{31})_{odd} + \sum(C_{25} \div C_{33})_{odd}/2\sum(C_{24} \div C_{32})_{even;}$ [(2)]ALC - "average" length of carbon = S(Cn x n)/∑(Cn); n - carbon number; C_n - relative content; [(3)]TAR (**T**errestrial to **A**quatic **R**atio) = $\Sigma(nC_{27}+nC_{29}+nC_{31})/\Sigma(nC_{15}+nC_{17}+nC_{19})/$ [(4)]P_{aq} (Ratio of aquatic to terrestrial input) = $(nC_{23} + nC_{25})/(nC_{23}+ nC_{25} + nC_{29} + nC_{31})$; Ts - 18α(H)22,29,30-Trisnorneohopane; Tm - 17α(H)22,29,30-Trisnorhopane; [(5)]Hopane ratio = H29αβ/H30αβ; [(6)]Moretane ratio = H30βα/H30αβ; [(7)]Sterane S/(S+R) ratio = S29ααS/(S+R); [(8)]Diasterane ratio = Dia27βαS/(S+R); [(9)]Sterane ratio = S29 ββ/(αα+ββ)

Emergent and submerged/floating plants should have contributed to kerogen formation.

Hopanes and steranes distributions were tracked only in sample St-7. As was already mentioned above, *n*-alkanes and cyclic alkanes were practically absent in sample St-2. This peculiarity was explained by the sample late maturity and possibility of hydrocarbons expelling. In Table 1C are shown geochemical parameters for sample St-7 calculated on the base on steranes and hopanes GC-MS distributions [8]. All hopanes signatures pointed to advanced sample maturity: (i) prevalence of Ts over Tm hopane, with Ts/Tm ratio ~ 1.3; (ii) epimer ratios for hopanes 22S/22R attested that the equilibrium has been attained, i.e. homohopane index H31αβ S/(S+R) of 0.56-0.58 and almost the same magnitude for H32αβ S/(S+R) of 0.57-0.58 were determined. Hence, based on this parameter the sample St-7 was mature, as for mature samples H31αβ S/(S+R) was in the range of 0.57-0.62 [8]; (iii) there were low amounts of moretanes (moretane ratio H30βα/H30αβ 0.14-0.16), and a total lack of "bio" hopanes.

Data for steranes distribution for sample St-7 "free" bitumen are shown in Table 1C. The signature was strongly dominated by diasteranes. Recent studies have proved that maturation has tolerated steranes rearrangement to diasteranes. Respectively, the high value for the diasterane ratio 0.61 (Table 1C) attested high St-7 maturity. Some amounts of rearranged and regular steranes at a certain extent have co-eluted and it was not advisable to be correlated in a ternary diagram. However, data for sample St-7, steranes ratios S29αα S/(S+R) and homohopanes H31αβ S/(S+R) (Table 1) were correlated and therein sample was located in the "oil window". Both samples studied were characterized by the presence of PAHs with 3-5 aromatic rings, i.e. condensed (phenanthrene, chrysene, pyrene, etc.) or coupled (phenyl-naphthyl and binaphthyl). Naphthalene and its alkylated homologues were absent, probably lost during separation and fractionation procedures due to their high volatility. Phenanthrene was the maximizing PAH in the mixture. Its methylated homologues were well recognizable (Fig. 4).

For their application as biomarkers Radke and Welte [9] have developed the methyl phenathrene index (MPI). It is based on the distribution of the 2-, 3-, (9+4)- and 1-methyl phenanthrenes (Fig. 4). Principally during maturation their proportions have shown a progressive change. The maturity increase has resulted in the increase in 2- and 3-methyl phenanthrenes (thermodynamically more stable isomers at higher temperatures).

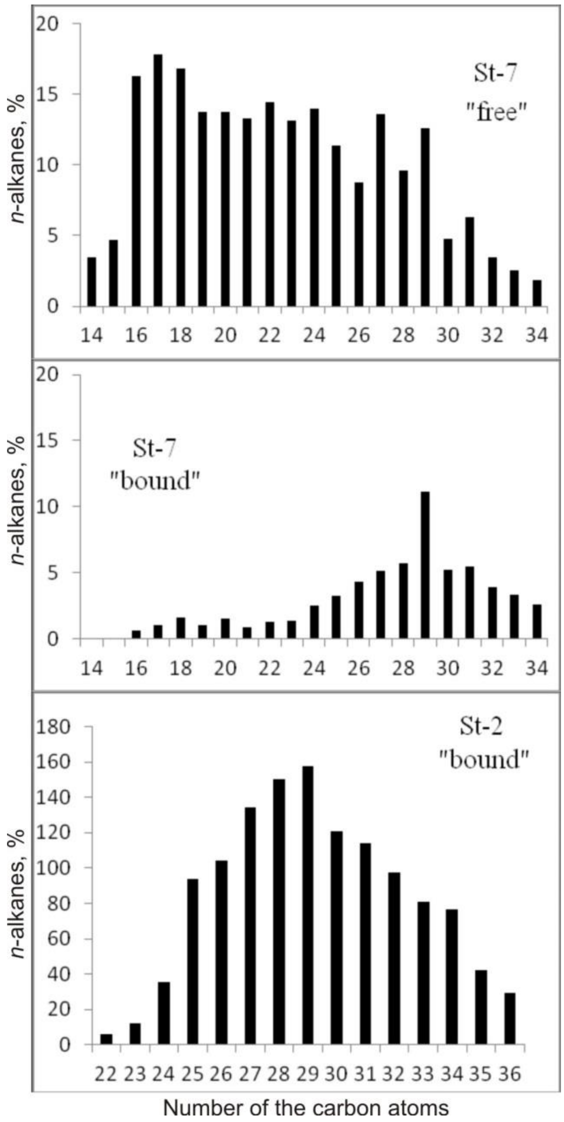

Fig. 2. Histograms of *n*-alkanes distributions

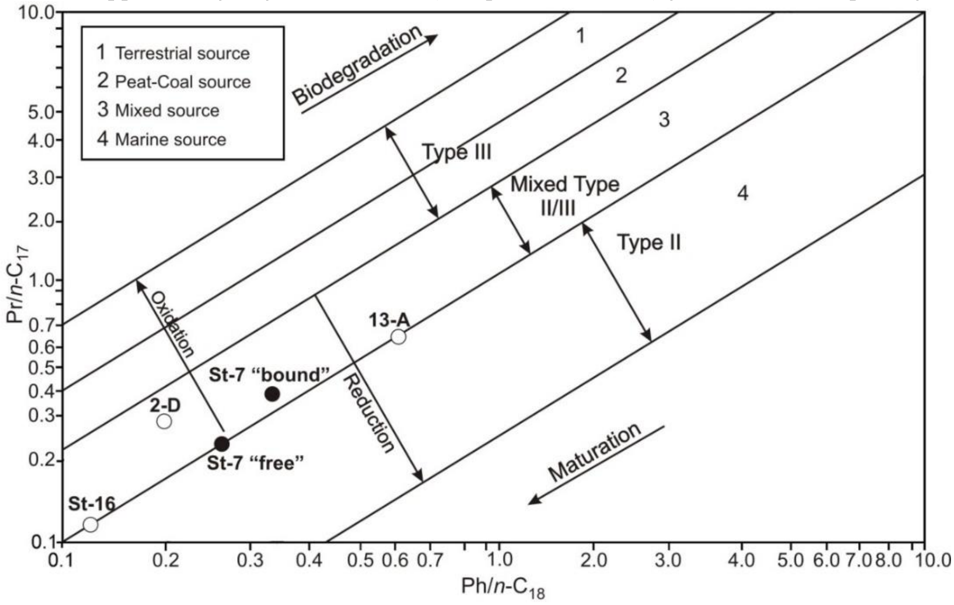

Fig. 3. Cross-plots Pr/nC_{17} *vs.* Ph/nC_{18} (positions of the previously studied samples [2] are also indicated in white dots)

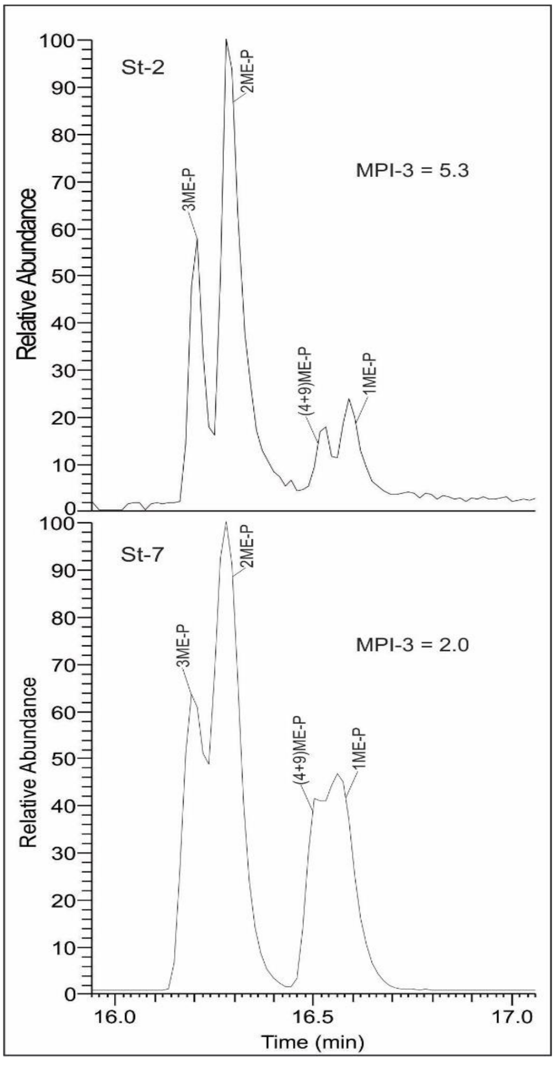

Fig. 4. Distributions of methyl phenanthrenes in samples according to SIM *m/z* 192 methyl phenanthrene index MPI-3 = Σ (2-MeP + 3-MeP)/Σ (4+9-MeP + 1MeP)

Respectively, higher values for MPI should be expected for the more mature samples. For the samples studied MPI-3 increases from 2.0 for St-2 to 5.3 for the "over mature" St-2. This result was in a very good agreement with the Rock Eval data as for St-2 was determined T_{max} 456.5 ºC - "late mature".

CONCLUSIONS

Geochemical study of two core samples from Stefanets Member (Etropole Fm.) from the eastern part of the West Forebalkan, Bulgaria has revealed the following peculiarities: (i) good quantity of organic matter according TOC (wt. %); (ii) "free" bitumen was practically absent in St-2 sample, a hint for hydrocarbons migration (or expelling) during maturation; (iii) isoprenoids correlation gave ground to assume deposition in reductive palaeoenvironment of Type II to mixed Type II/III kerogen. The magnitudes of Pr/Ph ratios < 1.0 have also indicated reductive conditions in the palaeoenvironment; (iv) all biomarker parameters calculated on the base of hopanes, steranes and PAHs distributions have argued for relatively high maturity; (v) if figure the sterane S29αα S/(S+R) *vs.* homohopanes H31αβ S/(S+R) in a cross-plot diagram one of the studied samples is positioned in the "oil window" and for both samples could be assigned "fair to good" hydrocarbon generative potential.

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