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HYDROCARBON POTENTIAL OF MIDDLE JURASSIC SEDIMENTS (STEFANETS MB. OF ETROPOLE FM.) FROM THE WESTERN PART OF BALKAN OROGENIC SYSTEM, BULGARIA

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Abstract

Sediments of Stefanets Mb. (Etropole Fm.), consisting mainly of shale and siltstones, are investigated by Rock-Eval pyrolysis. The samples from the Middle Jurassic section (Bajocian in age), outcropping within the western part of the Balkan orogenic system in Bulgaria, were analyzed to study their hydrocarbon generative potential. The obtained TOC contents are in the range of 0.69–1.97 wt.%. Inorganic carbon (TIC) and total sulphur (TS) contents are low and coincide with previously published data. The values of S_1 and S_2 are between 0.01 and 0.10 (mg HC/g rock) because of the high thermal maturity level, as indicated by T_{max} values of 566—610 °C. The rocks are in the postmature stage and consequently the HI values are very low (< 10 mg HC/g TOC). The fair to good quantity, low quality, as well as the high level of thermal maturity of the organic matter, assume minor remaining gas-prone generation potential of Stefanets Mb.

Key words: Bulgaria, Balkan orogenic system, Middle-Jurassic Stefanets Mb. of Etropole Fm., Rock-Eval pyrolysis, hydrocarbon potential

Introduction. The Jurassic geodynamic evolution of Bulgarian territory is closely related to the Moesian platform, which was lately shortened and ultimately

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overprinted by the Alpine orogeny [1,2]. The southern part of the platform was affected by several compressional phases in the formation of the Balkan orogenic system. A characteristic feature of the Mesozoic sections in the Moesian platform is the almost complete coincidence of most of their lithostratigraphic units with those of the Mesozoic rocks in the Alpine fold and thrust belt [3].

The shale and clayey-carbonate sediments from the marine Lower-Middle Jurassic sequence, belonging to the southern part of the Moesian Platform, were defined to hold fair to very good hydrocarbon potential [4]. They were also considered source rocks for the discovered oil and gas-condensate fields in North Bulgaria [5,6]. Recently, core samples from the Middle Jurassic Stefanets Member (Etropole Formation), consisting mainly of shale enriched in organic matter, were an object of the detailed geochemical investigations in the Central South Moesian platform and eastern part of the Western Forebalkan [7–9]. However, the Balkan orogenic system is still underexplored in terms of its hydrocarbon potential, because of the complex geology, the lack of boreholes and contemporary geophysical data.

In the present study, the hydrocarbon potential of sediments, obtained from outcrops of Stefanets Mb. (Etropole Fm.) in the western part of Balkan orogenic system is addressed by Rock-Eval pyrolysis results (Fig. 1). The main focus is on characterization of organic matter (OM) quantity, quality and thermal maturity of the sampled sediments from the Central Balkan unit, Svoge unit and

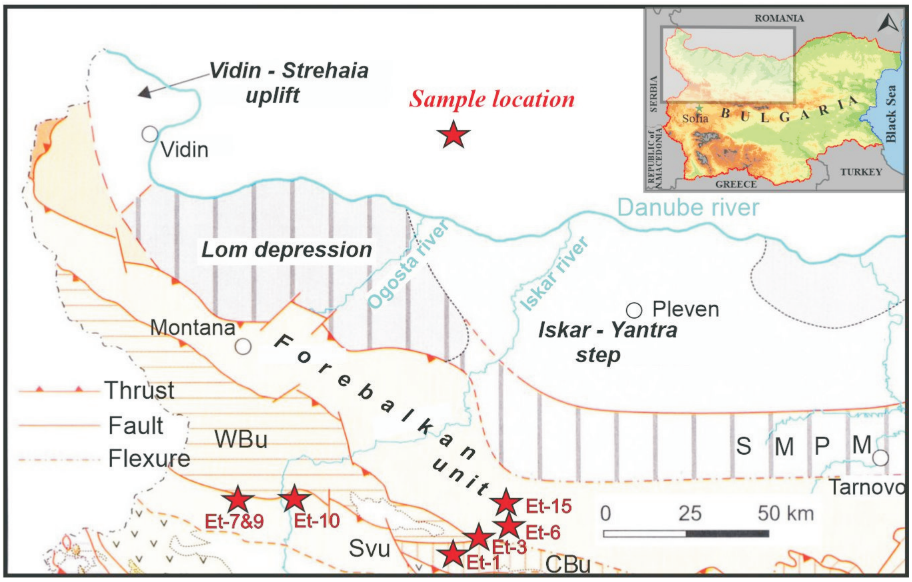

Fig. 1. Schematic tectonic map of Central and North West Bulgaria with the main tectonic units and sample locations – CBu for Central Balkan unit, WBu for West Balkan unit, Svu for Svoge unit, and SMPM for South Moesian platform margin (after [3])

Forebalkan unit. The geochemical characteristics of OM within the Lower-Middle Jurassic sequence in the Balkan orogenic system are scarce. Therefore, basic organic geochemical data of marine sediments from Stefanets Member are presented. Despite the limited number of samples, the results provide new scientific information on the OM content, maturity and hydrocarbon generation potential of the investigated rocks.

Geological settings. The Balkan orogenic system is located between the Moesian platform and the South Carpathians to the north, and the Vardar zone to the south [3] and represents a complex Late Alpine structure comprising the orogen (i.e. Balkan zone) together with its units and hinterland (the Srednogorie and Morava-Rhodope zones). The Mesozoic evolution of the Balkan Peninsula is related to the development of the northern periphery of the Tethys and the southern Eurasian margin [3]. The Balkan orogenic system is characterized by a shift from continental and shallow marine sequences formed under (semi-)arid settings (Permian – Triassic) to shallow- to deep-marine sedimentary, volcanic and volcano-sedimentary sequences formed under humid environmental settings (Jurassic – Cretaceous). The investigated Lower-Middle Jurassic sections and outcrop samples (Stefanets Mb. of Etropole Fm.) are located in the Central Balkan unit and Forebalkan unit from the Balkan zone, and Svoge unit from the Srednogorie zone (Fig. 2).

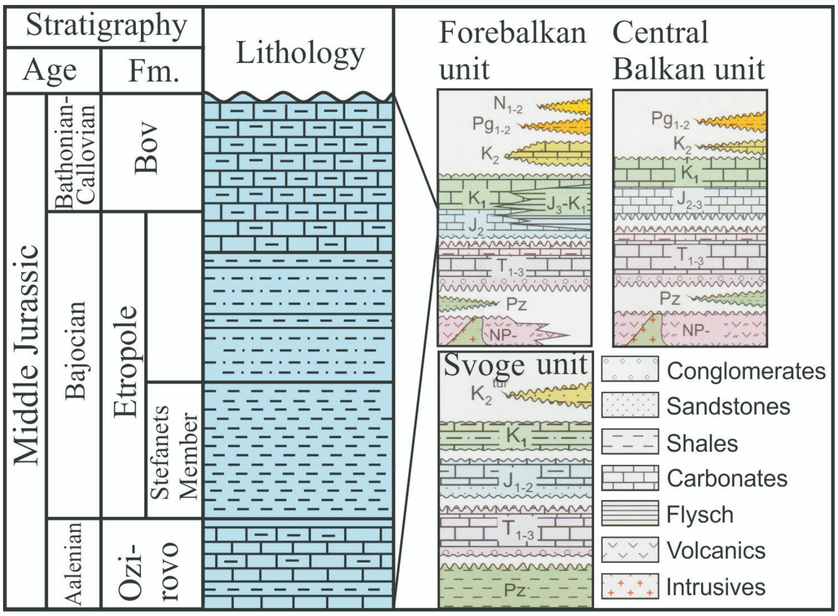

Fig. 2. Generalized column sections of tectonic units from Balkan (Balkanides) and Srednogorie zones with Middle Jurassic sediments (after [3])

The Lower-Middle Jurassic sediments are distinguished by their lithological variety and thickness in the study units (less and over 500 m, respectively). The Middle Jurassic (Aalenian-Lower Bajocian) dark grey to black (silty)shales with siderite concretions belong to the Stefanets Mb. from the lower part of Etropole Fm. and are considered to have been deposited in shallow-marine environment [10–12]. Within the Balkan zone, these sediments crop out at numerous locations, predominantly in its western part [11]. The thickness varies within a broad range, but rarely exceeds 200 m.

Material and methods. Seven Middle Jurassic samples from Stefanets Mb., Bajocian in age, were collected from outcrops (Fig. 1). They are from Lower-Middle Jurassic sections, situated in the vicinity of Etropole town (Et-1), Teteven town (Et-6), villages Lopyan (Et-3), Breze (Et-7 and Et-9), Bov (Et-10), Gradezhnitsa (Et-15), being representative for the shallow part of the Early-Middle Jurassic paleo basin [12]. The geochemical parameters of the samples are listed in Table 1.

Table 1

Rock-Eval geochemical parameters of the analyzed Stefanets Mb. outcrop samples

Sample	TIC (wt.%)	TOC (wt. %)	TS (wt.%)	T_{max} (°C)	S_1 (mg HC/g rock)	S_2	HI (mg HC/g TOC)	PI
Et-1	0.33	0.95	0.00	607	0.02	0.05	5	0.30
Et-3	0.77	1.09	0.30	604	0.02	0.09	8	0.19
Et-6	0.40	0.91	0.05	566	0.02	0.10	10	0.14
Et-7	1.12	1.97	0.22	609	0.01	0.06	3	0.14
Et-9	0.05	1.87	0.02	610	0.02	0.05	2	0.31
Et-10	5.32	0.69	0.89	605	0.02	0.05	7	0.31
Et-15	0.72	0.90	0.01	589	0.01	0.06	7	0.14

TIC = total inorganic carbon; TOC = total organic carbon; TS = total sulphur; HI = hydrogen index; PI = production index

The total carbon (TC), total organic carbon (TOC) and total sulphur (TS) contents were determined with an Eltra Helios C/S elemental analyzer on a powdered (< 250 µm) representative portion of each sample, pre-treated with concentrated phosphoric acid to remove carbonates. The amount of inorganic carbon (TIC) was calculated as a difference between TC and TOC. Rock-Eval pyrolysis [13–15] was conducted on Rock-Eval 6 instrument in the laboratory of the Montanuniversität Leoben, Austria. The contents of free hydrocarbons (S_1) and hydrocarbons obtained by pyrolysis (S_2) (mg HC/g rock) were used to calculate the Production Index ($PI = S_1/(S_1 + S_2)$) and Hydrogen Index ($HI = 100 \times S_2/TOC$) (mg HC/g TOC) [14,15]. The temperature of maximum hydrocarbon generation (T_{max}) was recorded as a maturity parameter.

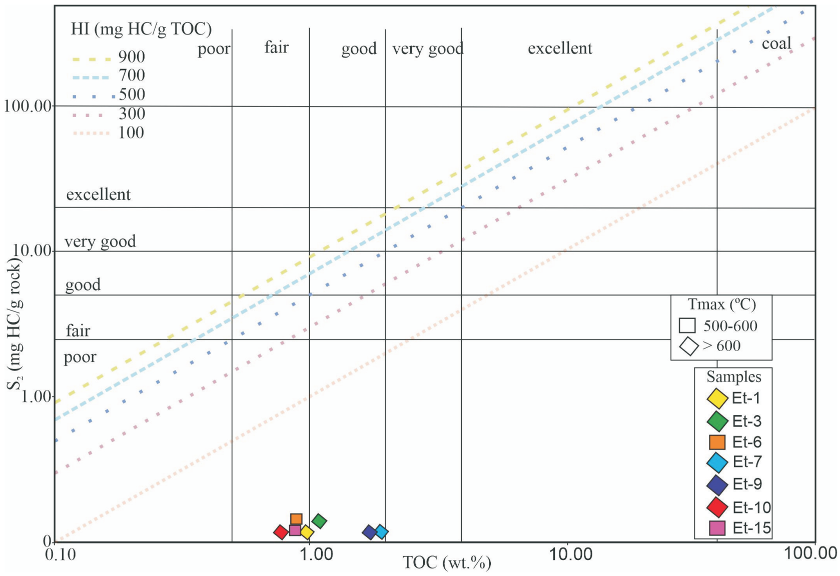

Fig. 3. Cross plot of S2 vs. TOC, displaying the hydrocarbon potential of the Stefanets Mb. samples

Results and discussion. The elemental composition and Rock-Eval parameters (TIC, TOC, TS, S_1, S_2, T_{max}, HI and PI), are listed in Table 1 and plotted in Fig. 3. The interpretation of the geochemical parameters follows the classical approach for OM evaluation – petroleum potential, kerogen type and level of thermal maturation.

The TOC contents vary in the range of 0.69–1.97 wt.% denoting a fair to good potential [16] for hydrocarbon generation (Fig. 3). Inorganic carbon (TIC) is recorded in low amounts in all samples (0.33–1.12 wt.%; Table 1). Sample Et-10 is a notable exception having the highest TIC (5.32 wt.%) and TS (0.89 wt.%). Both TOC and TIC contents fall within the range of values previously reported for Stefanets Mb. from the Moesian platform and Forebalkan [4,5,7,9].

The interpretation of the Rock-Eval results (Table 1) must comply with the reduction of TOC according to the type of kerogen and its catagenetic alternation. Losses of organic carbon in the generation and release of hydrocarbons from source rocks are significant [17,18]. All changes and reduction of the OM due to very high maturity influence also the applicability of hydrogen index (HI) in defining kerogen type.

Total sulphur contents (TS) are very low (< 0.3 wt.%; Table 1) opposite of the expectation for the considered marine depositional environment [11]. However, significant part of the sulphur might have been lost during weathering and therefore TS cannot be used as an indicator for the paleoenvironment. Sample Et-10 might represent a good example of the effect of weathering on sulphur contents.

The high TIC and TS values in that sample argue for the formation of gypsum after the preferential oxidation and removal of unstable sulphidic minerals.

Both S_1 and S_2 are very low (0.01–0.02 and 0.05–0.10 mg HC/g rock, respectively) complying with listed maturity levels of the samples (Table 1). Consequently, the calculated HI $<$ 10 mg HC/g TOC (Table 1) coupled with the high T_{max} values (566–610 °C) denote the presence of mature to over mature OM with negligible hydrocarbon generation potential in the studied outcrops of Stefanets Mb. The latter might be caused by considerable thermal alteration and exhaustion of the petroleum potential. The maturity of the sediments is higher than in the Moesian Platform and Forebalkan zone, thus arguing for significant burial of the rocks during the formation of the orogen. In that case, the very low hydrocarbon potential arises from their expulsion during the thermal increase. The residual organic matter is thus characterized by negligible generation potential of predominantly dry thermogenic gas. However, considering the very low amounts of hydrocarbons released during pyrolysis (S_2), the HI and T_{max} values should be treated with great caution and cannot be accepted as fully reliable herein.

The PI varies (0.14–0.31 mg HC/g rock), corresponding to the oil generation window [16]. The PI values underestimate the maturity level, because of the low S_1 and S_2 and cannot be considered reliable.

Conclusions. Shale and siltstone samples, representing shallow-marine Middle Jurassic sediments (Stefanets Mb. of Etropole Fm.) from the western part of the Balkan orogenic system, Bulgaria, were characterized using Rock-Eval pyrolysis. Despite the fair to good source rock quantity, according to the TOC contents, the hydrocarbon potential is limited indicated by low amounts of generated during pyrolysis S_1 and S_2.

The relationships between the inorganic and organic carbon contents reflect the paleo-environment and biological contribution during Middle Jurassic in the study area. Low sulphur contents are most likely caused by weathering affecting framboidal pyrite. Because of the high maturity of the samples the type of deposited OM in the shallow neritic part of the sedimentary basin cannot be determined.

Complex analysis of Stefanets Mb. reveals that quantity, quality and high maturity of OM assume poor remaining gas-prone generative potential.

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