

Characterisation of the Lower Palaeozoic sediments in NE Bulgaria for hydrocarbon potential assessment by integrating geochemical and geophysical research data

Gergana Meracheva, Efrosima Zaneva-Dobranova, Nikolay Hristov

Faculty of Geology and Exploration, University of Mining and Geology, 1700 Sofia, Bulgaria,
e-mails: g.meracheva@gmail.com; e.zaneva@gmail.com; nk.hristov@gmail.com

(Received: 29 August 2023; accepted in revised form: 10 November 2023)

Abstract. The Lower Palaeozoic marine sediments in NE Bulgaria could be considered not only as a potential hydrocarbon source rock, but also as a potential unconventional oil and gas reservoir. Several wells have penetrated this succession composed of mudstones, shales, siltstones, minor limestones, and marls. The knowledge on the major parameters of these rocks is rather obscure and is based on scarce rock sample data, because only a limited interval was drilled by coring, while most of the section was covered only by logging. Therefore, the current study combines geological, geophysical, and geochemical methods to characterise and assess the hydrocarbon potential of this succession. In the studied samples, one of the main parameters – total organic carbon, varies between 0.5% and 2.61%, which defines the rocks as having fair to good potential. A relatively positive correlation is observed between total organic carbon content and geological depth. The Lower Devonian–Silurian sediments exhibit generally higher total organic carbon content than the other part of the section. The applied method of using well-loggings allows the identification of vertical and lateral distribution of organic matter. A good correlation was observed between the total organic carbon data yielded by the geochemical method and the different well-log calculations. The obtained data on the type of organic matter and the degree of maturity show mainly gas potential of the shale succession. Different approaches, using Rock-Eval analysis and classical methodology of vitrinite reflectance (R_o), were applied for thermal maturity evaluation. Such combination and integration of different methods provide a more detailed and wide-ranging assessment of the Lower Palaeozoic sediments, and the data received could change the prospect and exploration strategy of a potential unconventional hydrocarbon resource.

Meracheva, G., Zaneva-Dobranova, E., Hristov, N. 2024. Characterisation of the Lower Palaeozoic sediments in NE Bulgaria for hydrocarbon potential assessment by integrating geochemical and geophysical research data. *Geologica Balcanica* 53 (1), 3–18.

Keywords: Silurian shales, organic matter, maturity, NW Bulgaria.

INTRODUCTION

Decrease in hydrocarbon (HC) reserves from already discovered fields located in accessible depths and areas, as well as still huge dependence on these energy resources, determines an increase in interest in unconventional sources of energy. Lower Palaeozoic organic matter-rich facies have been identified as important HC source rocks globally (Schmok-

er, 1993; Tan *et al.*, 2013; Zou, 2017; Luo *et al.*, 2020). These sediments were mainly deposited in marine environments and were also considered as a target for unconventional shale gas fields in North America, the Arabian Peninsula, North Africa, the Taurus region of Turkey, and the Siberian Platform. In the last decade, in Central and Eastern Europe, Lower Palaeozoic, and more specifically Silurian, sediments have been actively studied in regard to

their potential as unconventional shale reservoirs (Tari *et al.*, 2012, 2014; Sliupa *et al.*, 2016; Poprawa, 2020). In their schematic palaeogeographic model of the Silurian Basin of Central and Eastern Europe, Tari *et al.* (2012, 2014) showed that basin fragments are scattered along a broad zone through Europe with a NW–SE strike. A large part of the Silurian Basin is located on the Moesian Platform, somewhat isolated from the other basin fragments presently. Whereas extensive exploration of these sediments in this basin has been carried out in Poland, Lithuania, and Ukraine, considerably less is known about the extent of the Silurian succession and its potential in the SSE part of the basin, in Romania and Bulgaria. The distribution of the Lower Palaeozoic sediments in NE Bulgaria can be concluded from the several wells that have penetrated Ordovician–Lower Devonian rocks. A small interval was drilled by coring, while most of the section was covered only by well logging. Therefore, the knowledge on the major parameters of these rocks is rather obscure and is based on scarce rock sample data. For that reason, the current study combines geological, geophysical, and geochemical data to characterise and assess the HC generation potential of this pelitic succession.

Based on studies of unconventional HC reservoirs all over the world, it has been noted that prolific petroleum systems are usually recognised by several minimal conditions, which should be met in order to assess the oil and gas potential of shale sediments (Selley, 1998; Zou, 2017). These thresholds include, but are not limited to, shale thickness, depth, total organic carbon (TOC), type and maturity of organic matter (OM), which are the most important factors for commercial gas production.

When geochemical data are unavailable or insufficient, geophysical wireline logs and interpretive techniques can be used as qualitative indicators of organic content (Petters and Cassa, 1994). These methods are most reliable within small areas where wireline response has been calibrated to geochemical data.

The objective of the current study is to describe the present geological features of the Lower Palaeozoic sediments in NE Bulgaria and to determine their organic geochemical properties. In the current research, a suite of geophysical well-logs and Rock-Eval pyrolysis were applied to obtain information on its OM content, genetic type, vertical and spatial variability. To obtain information on thermal maturity, besides Rock-Eval pyrolysis, the classical methodology of vitrinite reflectance (Ro) was also used.

GEOLOGICAL SETTING

The present-day tectonic framework of NE Bulgaria, where the research area of the current paper is located, is composed of the eastern parts of the following major structural units: Moesian Platform, Southmoesian Peri-platform, Fore-Balkan and South slope of the Dobrudzha Massif (Dabovski and Zagorchev, 2009; Fig. 1). Various palaeodynamic models have been presented over the years (*e.g.*, Nachev and Nachev, 2001; Yanev *et al.* 2005b; Dabovski and Zagorchev, 2009), according to which the main part of the territory of North Bulgaria is generally occupied by the Moesian Microplate. The sedimentary structure of the Moesian Microplate was formed during the Palaeozoic, Triassic, Jurassic–Early Cretaceous and Late Cretaceous–Palaeogene sedimentation cycles.

In NE Bulgaria, the Palaeozoic section in the base consists of a marine sediment sequence with Ordovician to Visean age, with numerous local unconformities (Fig. 2). It is covered unconformably by continental Carboniferous and Permian deposits (Yanev *et al.*, 2006). The oldest sediments drilled by wells are mostly pelitic sediments of Ordovician age, which was determined by the presence of acritarchs and probable cryptospores (Lakova and Hristov, 2018). The sediments are mudstones, dark grey and light grey shales and siltstones formed in different marine environments – from the shelf and continental slope to deepwater areas. The thickness of the Ordovician succession varies widely and reaches up to 600 m in the northern part of the area. Reconstruction of the palaeogeography is very difficult due to the significant migration of individual Palaeozoic terranes, changes in primary spatial relationships, reduction of part of the basin, and the allochthonous position of some blocks (Yanev, 2000b).

The Ordovician, Silurian and Lower Devonian rocks form a sedimentary succession which reflects a stage of strongly expressed subsidence of the territory. The succession consists mainly of dark shales, mudstones and siltstones, with minor limestones and marls, up to 2000 m thick. It is divided into six informal lithostratigraphic units and is considered (Yanev and Boncheva, 1995) as the lower part of the calcareous-terrigenous shale unit. The age of these units is proved by the presence of conodont and graptolite fauna, as well as by chitinozoans, acritarchs and spores (Steenmans and Lakova, 2004; Lakova and Hristov, 2018). Locally, thin quartzites and sandstones of possible Emsian–Eifelian age cover the Lower Devonian sequence with shales.

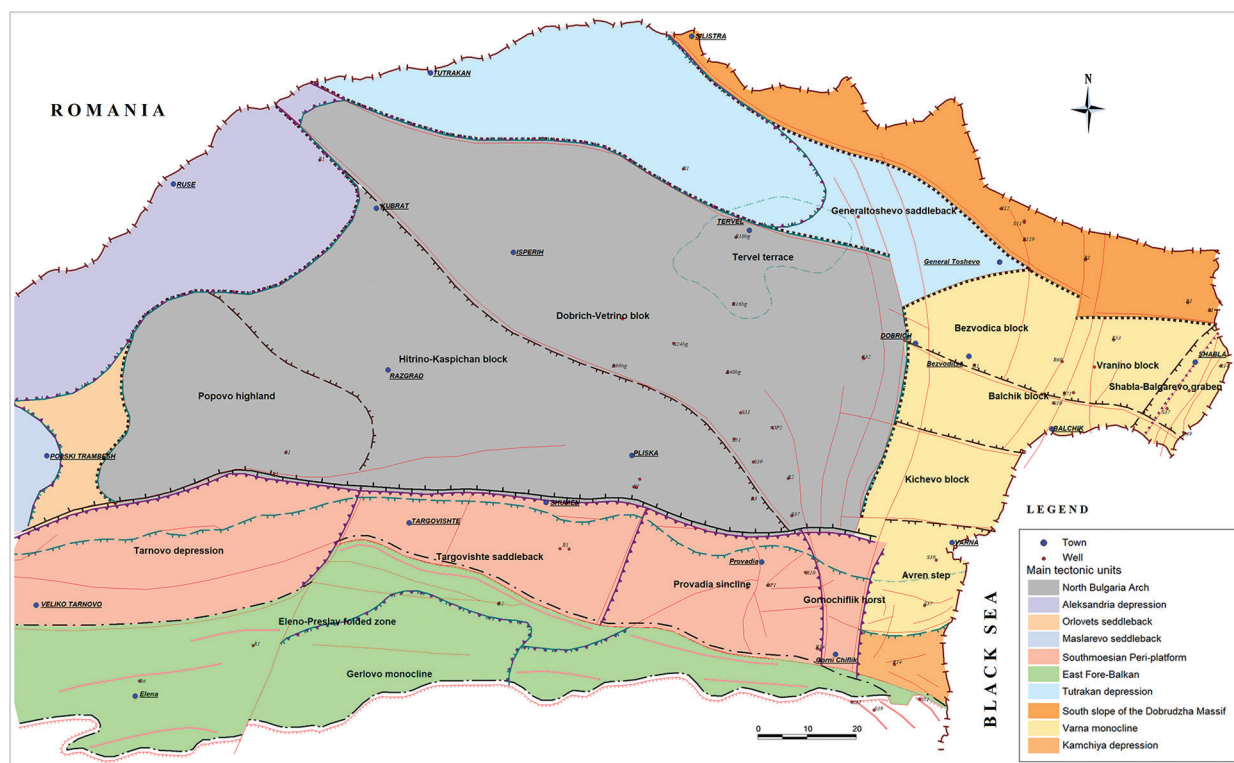


Fig. 1. Tectonic map of the studied area and location of analysed wells (after Dabovski and Zagorchev, 2009, with additions).

A stage of uplift followed, expressed in carbonate and regressive shale-terrigenous complexes. This stage took place during the Middle–Late Devonian, Carboniferous and Permian. The Middle–Upper Devonian to Visean carbonate sequence is subdivided into several lithostratigraphic units. The total thickness of carbonate platform sediments drilled is 1200–2000 m, thickening from NW to SE.

The general uplift is associated with highly developed block faulting. The tectonic activity was high, especially during the Permian. As a result of the Caledonian–Hercynian movements, some structures, such as the North Bulgarian Uplift, took shape. The present-day tectonic appearance of the Moesian Platform, with clearly expressed NW–SE direction of some major faults, as Pece-neaga–Camena, Intramoesian (Silistra–Belgun), Kubrat–Vetrino, is probably evidence for drifting processes (Tari *et al.*, 2012). According to Tari *et al.* (2012), Moesia, as a microplate, was separated from the European margin at about the end of the Middle Jurassic and started to drift towards the SE. There are no constraints on the rate of the drifting, but by the Aptian, Moesia should have reached its present-day position some 800 km to the SE from its original position.

METHODOLOGY

For an optimal HC potential analysis, an integrated multidisciplinary approach is necessary since, in practice, data availability (cores, logs, seismic data, geochemistry, geological studies) are limited (Ma, 2016). To explore the HC potential of the Lower Palaeozoic strata more systematically and comprehensively and to describe their depositional and evolutionary history, we could not limit ourselves in the analysis of the available data only in the region of NE Bulgaria. Moreover, the Lower Palaeozoic, and more specifically the Lower Devonian–Silurian, sediments have been penetrated by only a few wells. Therefore, in the present study, analysis and correlation of the information from the deep wells that penetrated Lower Palaeozoic sediments in the entire North Bulgaria was carried out. For a detailed analysis of the present geological setting, geological and geophysical data from more than 30 wells have been used and verified (Fig. 1). Next, most of the well-logs were digitized and prepared for software input. Inasmuch as some of the wells analysed during this study had been drilled at the end of the last century, the quality and thoroughness of geophysical wireline logging may vary. An integrated work-

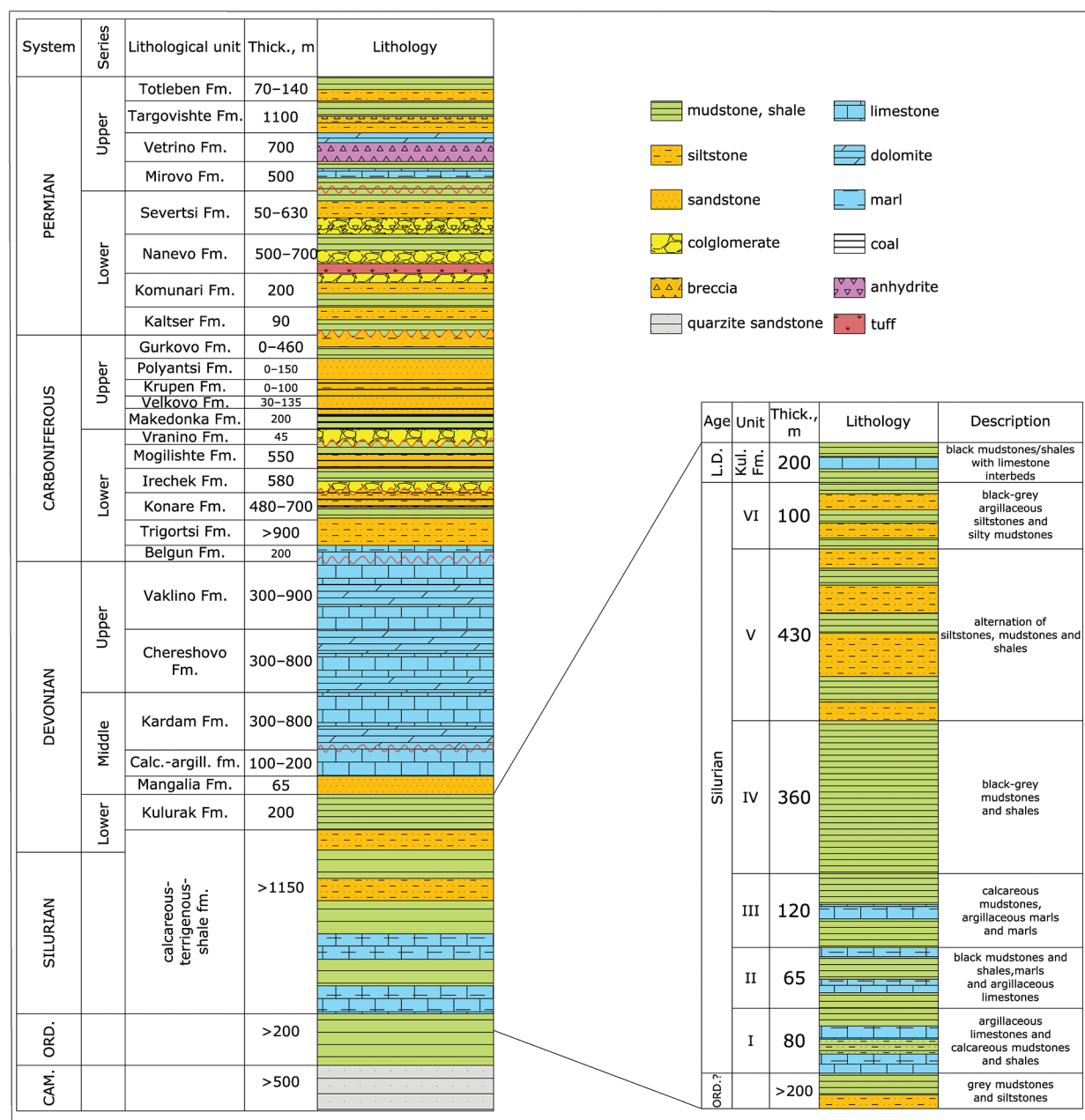


Fig. 2. Generalised lithostratigraphy of the Palaeozoic strata in NE Bulgaria (after Yanev and Boncheva, 1995, with modifications).

flow combining the different methods was carried out in the study area.

One of the key characteristics for determining the HC potential of shale sediments is TOC content. This parameter is usually obtained by laboratory tests of cores, cuttings and sidewall plugs. In order to determine the quantity of TOC in the rocks, approximately 330 samples were measured, using a Leco SC-632 instrument. In the current research, Rock-Eval analysis was performed on a total of 52

core samples collected from seven wells (OP-2 Mihalich, R-2 Vetrino, R-1 Marash, R-119 Kardam, R-120 Ograjden, R-1 Vaklino, R-1 Rogozino) in order to obtain the basic geochemical parameters. Although this method is relatively effective and accurate, it provides non-continuous measurement data only for some parts of the sediment section. Furthermore, it is also costly and time-consuming. In order to overcome these limitations, different continuous well-logging data can be applied to esti-

mate TOC along the entire geological section. The well-logs used for source rock evaluations and calculation of TOC most commonly include density, sonic, gamma ray, neutron and resistivity by using several methods (Hester *et al.*, 1990; Passey *et al.*, 1990; Schmoker, 1993).

In this research, two different techniques for TOC determination, *i.e.*, geochemical data and geophysical well-logging, were integrated to determine TOC content. The comparison of the result allows evaluation of the HC generation potential of the shales and mudstones in the entire examined Lower Palaeozoic succession.

Geochemical analysis

The samples were analysed using a model Rock-Eval 6 instrument equipped with the necessary modules to perform the full volume of tests to evaluate the source rock HC potential by pyrolysis. The application of this technique is based on the procedure (Espitalié *et al.*, 1985a, b), which was carried out in the following order: the necessary amount of rock sample (50–100 mg) was inserted into a temperature-programmed crucible in an inert atmosphere (N₂) at a temperature from 200 °C to 650 °C and subsequently in an oxygen atmosphere at a temperature above 850 °C. The following set of characteristics was measured and subsequently, the parameters were:

- S₁ – the amount of free HC in the rock, mg HC/g rock;
- S₂ – determines what amount of HC the rock could generate when exposed to suitable thermobaric conditions. The obtained results show the unrealised generation potential. These are HCs that are produced during sample heating and simulate kerogen cracking, mg HC/g rock;
- S₃ – the amount of CO₂ released during the initial phase of the analysis, mg CO₂/g rock. Based on the data of this parameter, the amount of O₂ in the studied samples was determined;
- T_{max} – temperature of maximum formation of HCs corresponding to maximum S₂. With the data obtained from this parameter, the degree of maturity of kerogen in the investigated samples was determined.

All listed parameters were used to determine TOC, petroleum potential (PP), production index (PI), hydrogen index (HI) and oxygen index (OI). Both the measured and calculated values provide a basis for

the characterisation of the OM, *i.e.*, its amount, genetic type, and degree of transformation.

Well-log analysis

For identifying organic-rich source rocks, a typical response on different conventional logs, such as gamma ray, density, resistivity and sonic logs, is generally used. The presence of OM resulted in the physical properties of gamma ray, sonic, neutron and resistivity logs, which usually show high values, while the density log reduces. The degree of maturation also plays a role. In this study, the method proposed by Passey *et al.* (1990), which is an advanced and approved (Zhao *et al.*, 2016) technique to estimate TOC, was applied. This technique is named $\Delta\log R$ and includes estimating TOC from three methods: sonic/resistivity, neutron/resistivity and density/resistivity logs. The approach is expressed in the log separation that occurs between the resistivity and the other logs, due to the presence of organic matter. In the current study case, when applying the sonic/resistivity log method, a separation between the two curves was observed along the intervals of organic-rich shales and mudstones. Previously, logs of both resistivity and sonic curves were overlaid on the same track, with the resistivity log displayed in logarithmic and the sonic in linear scale.

The mathematical expression for the calculation of this separation is shown in the following equation:

$$\Delta\log R = \log\left(\frac{R}{R_{baseline}}\right) - 0.02(\Delta t - \Delta t_{baseline}) \quad (1),$$

where $\Delta\log R$ is the separation between the two logs measured in the logarithmic resistivity cycle; R is the resistivity, Ωm ; Δt is the sonic measurement, $\mu s/ft$; $\Delta t_{baseline}$ is the sonic corresponding to $R_{baseline}$ in the lean shale interval (non-source rock).

It has been observed (Passey *et al.*, 1990) that a linear relationship exists between $\Delta\log R$ and TOC content, which is also a function of the level of organic maturity (LOM). Hence, using quantified log separation $\Delta\log R$, the TOC is calculated by the following equation:

$$TOC = \Delta\log R \times 10^{[2.297 - (0.168 \times LOM)]} \quad (2)$$

LOM is usually derived from available maturity information (*e.g.*, vitrinite reflectance – R_o , T_{max} ,

etc.). In the current study, LOM was correlated and calculated by the LOM scale comparison table suggested by Tissot and Welte (1984).

On the other hand, there are rather scarce sonic log data available for the Silurian–Lower Devonian section in most of the wells. Therefore, the application of this method, in regard to the estimation of the distribution of organic matter in mudstones and shales at this age, is rather limited. Whereas some wells were subject to gamma-ray logging, these logs are suggested (Šliaupa *et al.*, 2016; Zhao *et al.*, 2016) as an efficient tool for calculating the distribution of organic matter. In the current study for the calculation of TOC content from gamma-ray logs, the equation developed by Šliaupa *et al.* (2016) for shales from the NE part of the Silurian Basin was also applied. The equation is derived from gamma-ray log data and TOC measurements from several representative wells of the same sediment succession and can be written as:

$$TOC = \exp(0.15 \times GR) \times 0.12 \quad (3)$$

Another equation for TOC calculation is also applied, which was proposed by Schmoker (1993), who found that there was inverse correlation between TOC and formation rock density. The theoretical basis is that the organic matter density (1.03–1.10 g/cm³) in shales is significantly lower than that of the surrounding rock matrix (the density of clay skeleton is 2.30–3.10 g/cm³), resulting in a lower well-logging density of high-quality shale. For organic-rich, low-porosity and low-permeability shale, formation rock density varies with the variation of organic matter abundance. Otherwise, another factor that affects total rock density is the presence of pyrite in rocks. The deviating data points may result from the influence of abnormally high-density pyrite, which is much higher than rock mineral density.

In field exploration and development, formation rock density is usually measured by density well-logging. Therefore, the formula for calculating TOC by density well-logging is written as:

$$TOC = (a \times \rho) + b \quad (4),$$

where ρ is well-logging density, g/cm³; a and b are regional empirical factors.

Vitrinite reflectance measurements and analysis

For thermal maturity evaluation, vitrinite reflectance is the most used indicator in HC exploration

in post-Devonian rock sequences. However, due to the lack of vitrinite in pre-Devonian rocks, in order to determine the thermal maturity of Lower Palaeozoic rocks, different methods for reflectance measurements from other forms of organic materials have been proposed, which are widely used in the petroleum industry (Cole, 1994; Bertrand and Malo, 2012; Petersen *et al.*, 2013; Hartkopf-Fröder *et al.*, 2015). Hence, the reflectance of zooclasts, vitrinite-like particles and solid bitumen, $T_{\max}$, and biomarkers have been proposed to assess organic maturity in Lower Palaeozoic sediments. In some cases, in overmature sediments, $T_{\max}$ may be inaccurate and unreliable due to low S_2 , less than 0.2 mg HC/g rock (Peters, 1986; Peters and Cassa, 1994). Nevertheless, Lower Palaeozoic sediment rocks often contain bitumen and other zooclasts. Zooclasts have a clear advantage in reflectance studies due to their specific biological sources compared to that of solid bitumen and vitrinite-like particles, and thus their reflectance was naturally regarded as having a superior potential as a thermal maturity indicator. In general, in Lower Palaeozoic marine rocks, graptolites are a more widely used group for reflectance measurements than other zooclasts, and as a result, the graptolite reflectance has been applied by organic petrologists for several decades (Cole, 1994; Bertrand and Malo, 2012; Petersen, 2013; Hartkopf-Fröder *et al.*, 2015; Luo *et al.*, 2020). It is the reason to choose and apply such an approach in this research.

In the current study, a few representative shale core samples from sediments with Silurian age that contain visible graptolites on the bedding surface were chosen for reflectance measurement (Fig. 3). The samples were first cut parallel to the bedding, placed in a cold epoxy resin block, and then polished with a variety of wet and dry papers, diamond polishing compounds and colloidal silica, using a standard procedure (Taylor *et al.*, 1998). Polished blocks were prepared from representative rock pieces mounted in epoxy resin. Reflectance measurements were performed on a TIDAS MSP 200 spectrometer, attached to a Leica DM 2500P microscope with a 50× oil objective lens. The calibration was done using Spinel ($R = 0.421\%$), YAG ($R = 0.902\%$) and GGG ($R = 1.716\%$) reflectance standards.

Mean random reflectance readings were obtained on different forms of organic materials including graptolites, chitinozoans, vitrinite-like particles, and bitumen. These reflectance values were then converted to vitrinite-equivalent reflectance values, which were based on the conversion for-



Fig. 3. Core sample photograph with visible graptolites on the bedding surface of a Silurian mudstone.

mulas proposed and derived by Jacob (1989), Cole (1994), Landis and Castaño (1995), Bertrand and Malo (2012), Petersen *et al.* (2013), and Luo *et al.* (2020). A comparison of these methods and used

equations was made and the assumption of each has been considered. The results obtained are used further for determining LOM in equation (2).

RESULTS AND DISCUSSION

Geochemical interpretation of Rock-Eval data

One prerequisite for successful assessment of the HC potential of shale sediments is a sufficiently high amount of OM in these rocks, estimated by the parameter TOC (wt.%). For the examined samples from the Lower Palaeozoic sediments, the TOC content, measured by the Leco device, varies widely and depends on the age of the sediments (Fig. 4.). On the histograms illustrated in Fig. 4, it is visible that TOC content almost positively correlates with increasing geological age, except for the sediments of the Lower Carboniferous Series, which shows variable high values. Upper Devonian carbonates demonstrate generally the lowest TOC content. The sediments with Middle Devonian age are characterised by relatively lower TOC content than those with Silurian–Early Devonian age. TOC content of mudstones and shales of Silurian–Lower Devonian strata varies widely, with an average value of over 0.5%. Nevertheless, the higher average value is in these sediments, which reaches 2.61%.

In the plot TOC vs stratigraphic depth for some well-sections, it is observed that TOC content increases with depth (Fig. 5). Most of the profiles demonstrate higher TOC concentrations in the

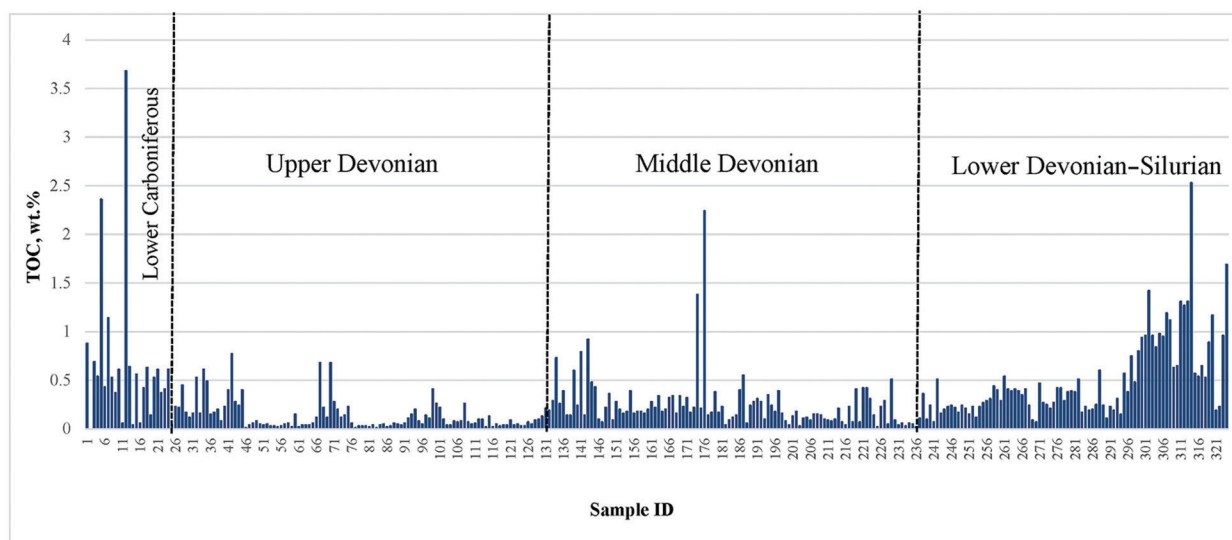


Fig. 4. Histograms of TOC content, measured by Leco device, in relation with stratigraphic age.

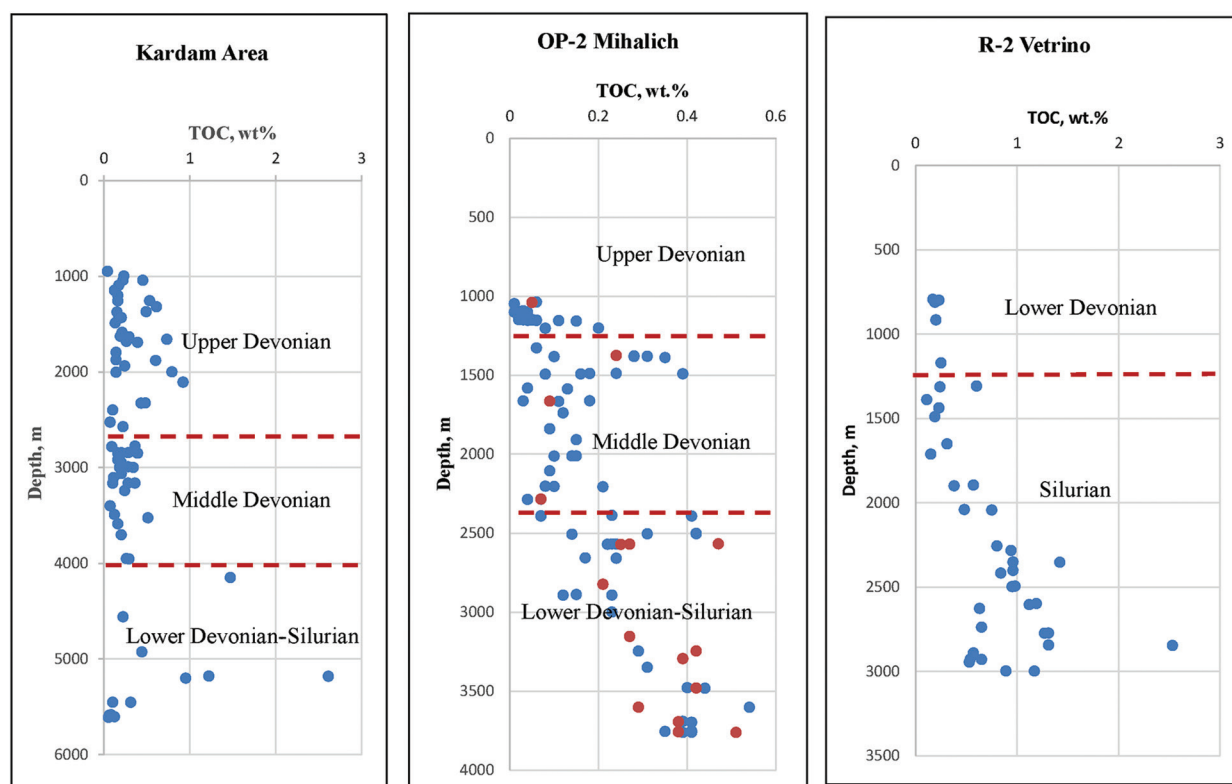


Fig. 5. TOC content versus depth for three sections studied in NE Bulgaria.

lower part, where mudstones and shales of the Silurian–Lower Devonian are present, and lower TOC concentrations in the upper part, where carbonates and/or siltstones of the Middle–Upper Devonian dominate.

The OM richness of the measured samples can thus be described as moderate, which is an important parameter for evaluating source rock in a conventional petroleum system and is a promising prerequisite for further Rock-Eval analyses.

The results from the Rock-Eval study indicate a large variability in the geochemical parameters and indices, which is observed within individual lithostratigraphic horizons and individual regions and wells (Table 1).

TOC values for the analysed samples vary broadly from traces to over 0.5% in more of the studied samples of well-core. In one of the analysed samples, the amount of TOC reaches 2.61%, which is the highest organic carbon content and was measured in shales with Silurian age. This stratum was also characterised by the highest average value of 0.6 wt.%. The average of all TOC in the analysed Middle–Upper Devonian sediments is 0.2 wt.%.

The HC contents, expressed by S_1 and S_2 , showed similar distribution and variability patterns. The contents vary from traces to 0.59 for S_1 and to 1.67 for S_2 . Most of the samples had limited HC content, only in traces.

The results obtained show that, according to the accepted classifications (Peters and Cassa, 1994), the analysed sediments can be considered as a source rock with “fair to good generating potential” (Fig. 6). This plot of TOC vs PP ($S_1 + S_2$) reveals that there are data points of the studied samples, which show the organic richness and HC potential, indicating “fair to good” source rocks and “fair to good” organic matter content. This is also indicated by further calculation from well-logs TOC content.

In the current study, the HI index in the samples from the Lower Palaeozoic section shows a considerable variation, which is similar to the TOC and HC contents. The reason is that this index is calculated from TOC and S_2 values. The HI values in some samples from the Silurian–Lower Devonian succession are above 50 mg/g, but the average values are rather low, which indicates a relatively “poor” HC potential. Nevertheless, approximately

Table 1
Core sample Rock-Eval data

Well ID	Sample area	Sample ID	Depth (m)	Age	TOC (%)	S ₁ mg/g	S ₂ mg/g	T _{max} °C	HI mg/g	OI mg/g
R-119	South slope of the Dobrudzha massif	1	1317.7	Late Devonian	0.61	0.44	1.13	441	109	2
R-119		2	2916	Middle Devonian	0.18	0.08	0.04	353	12	6
R-119		3	2995.5	Middle Devonian	0.22	0.05	0.03	379	33	5
R-119		4	3103	Early Devonian	0.11	0.07	0.04	428	80	9
R-119		5	3160	Early Devonian	0.36	0.07	0.01	453	3	3
R-1		6	3490	Middle Devonian	0.12	0.02	0.01	327	3	162
R-1		7	3950	Early Devonian	0.26	0.01	0.01	509	4	59
R-1		8	3954	Early Devonian	0.29	0.01	0.03	390	9	31
R-1		9	4148	Early Devonian	1.47	0.53	1.65	430	113	42
R-1		10	4559	Silurian	0.22	0.01	0.01	523	3	44
R-1		11	4925	Silurian	0.44	0.18	0.67	335	154	275
R-1		12	5178	Silurian	1.22	0.02	0.01	327	1	9
R-1		13	5181	Silurian	2.61	0.11	0.20	344	8	7
R-1		14	5200	Silurian	0.95	0.29	0.84	409	89	90
R-1		15	5452	Silurian–Ordovician?	0.10	0.01	0.01	335	6	126
R-1		16	5453	Silurian–Ordovician?	0.31	0.05	0.03	325	10	37
R-1		17	5583	Ordovician–Cambrian?	0.08	0.01	0.01	475	7	154
R-1		18	5588	Ordovician–Cambrian?	0.06	0.01	0.01	447	9	129
R-1		19	5604	Ordovician–Cambrian?	0.12	0.01	0.01	328	8	117
R-1		20	5610	Ordovician–Cambrian?	0.05	0.01	0.02	452	35	213
OP-2	North Bulgarian arch	21	1039.6	Late Devonian	0.05	0.01	0.06	452	46	20
OP-2		22	1374.8	Middle Devonian	0.24	0.05	0.06	461	24	4
OP-2		23	1664	Middle Devonian	0.09	0.03	0.04	425	28	11
OP-2		24	2284	Middle Devonian	0.07	0.02	0.05	439	71	14
OP-2		25	2567	Early Devonian	0.47	0.05	0.02	539	4	2
OP-2		26	2569	Early Devonian	0.27	0.02	0.04	533	22	7
OP-2		27	2571	Early Devonian	0.25	0.06	0.01	438	78	24
OP-2		28	2823.2	Early Devonian	0.21	0.01	0.05	525	71	48
OP-2		29	3153	Silurian	0.27	0.01	0.05	559	50	15
OP-2		30	3245	Silurian	0.42	0.08	0.01	435	55	12
OP-2		31	3480	Silurian	0.42	0.11	0.02	350	30	36
OP-2		32	3601.5	Silurian	0.29	0.04	0.05	409	29	45
OP-2		33	3693.3	Silurian	0.38	0.03	0.01	447	16	16
OP-2		34	3294	Silurian	0.39	0.11	0.01	447	3	18
OP-2		35	3757	Silurian	0.38	0.19	0.01	270	3	26
OP-2		36	3761	Silurian	0.51	0.08	0.06	433	12	20
R-2		40	810	Early Devonian	0.19	0.09	0.07	578	116	3
R-2		41	1436	Early Devonian	0.23	0.08	0.10	402	43	2
R-2		42	2350	Silurian	0.96	0.09	0.08	435	8	1
R-2		43	2842	Silurian	1.69	0.14	0.21	431	16	0
R-1		44	2252	Early Devonian	0.61	0.06	0.01	482	2	11
R-1	Varna monocline	45	3157.3	Early Carboniferous	0.53	0.05	0.41	446	77	0
R-1		46	3175.8	Early Carboniferous	0.61	0.07	0.47	446	77	0
R-1		47	3354.4	Early Carboniferous	0.37	0.1	0.67	450	181	0
R-1		48	3355.8	Early Carboniferous	0.41	0.19	0.87	450	212	0
R-1		37	1869.9	Middle Devonian	0.11	0.02	0.01	419	9	600
R-1		38	2191.5	Middle Devonian	0.09	0.16	0.01	436	11	467
R-1		39	3394.8	Early Devonian	0.20	0.16	0.01	411	5	405

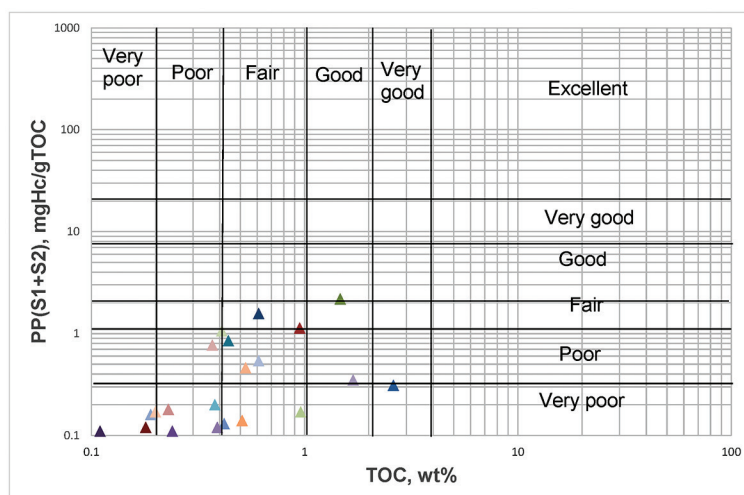


Fig. 6. Diagram presenting hydrocarbon generation potential.

30% of the samples are characterised by values above this limit.

To determine the kerogen type, the Van Krevelen diagram is used. It correlates the ratios between carbon (C), hydrogen (H) and oxygen (O). These relations are expressed respectively by the HI and OI obtained during the Rock-Eval pyrolysis on the modified pseudo-Van Krevelen diagram. When plotting the calculated values for HI and OI for many of the studied samples, it can be assumed

that in a large part of the studied rock intervals, the kerogen is type III, and in the remaining samples it is type II (Fig. 7a). The ratio TOC vs HI (Fig. 7b) shows the expected generated HCs from the study samples as mixed gas and oil, a part of the examined samples show undefined gas source generation potential, and a few samples are in the zone of fair oil source.

In order to assess the degree of maturity of the OM, the Rock-Eval T_{max} measurements were taken.

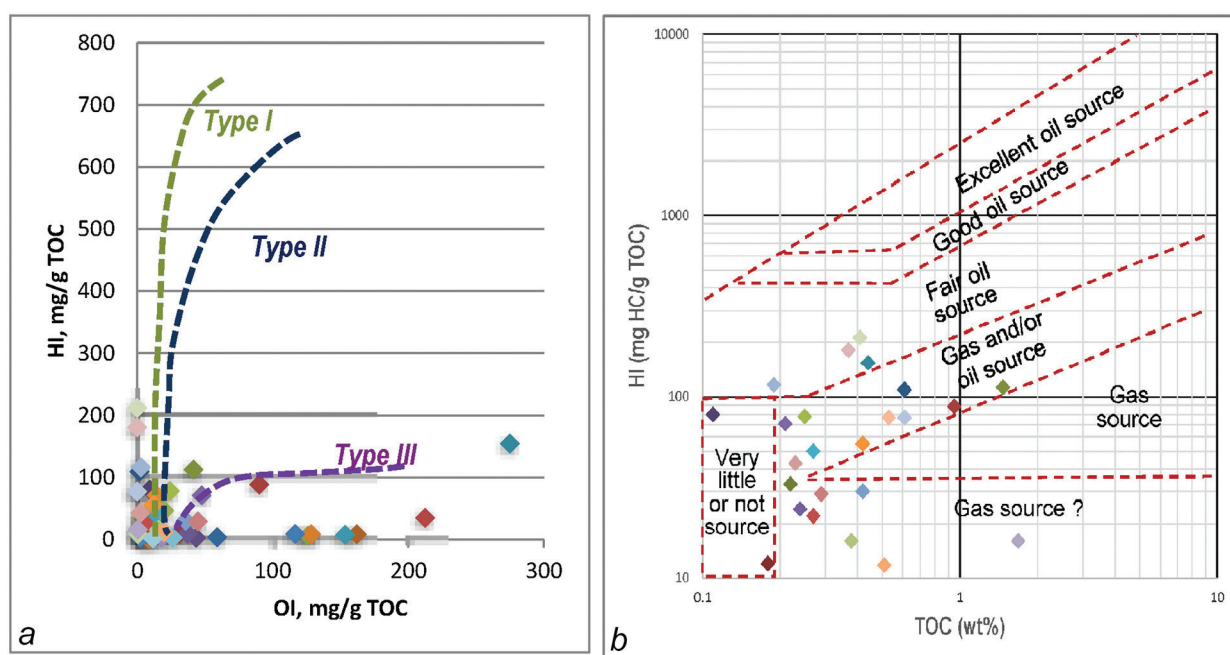


Fig. 7. Diagrams showing kerogen type on modified Van Krevelen diagram (a) and expected hydrocarbons and hydrocarbon-generation potential (b) of the Lower Palaeozoic succession.

Generally, samples with <0.2 wt.% TOC do not provide reliable $T_{\max}$ values. In a considerable part of the samples, the values of S_2 are very low and these samples may exhibit inaccurate values of $T_{\max}$ (Peters, 1986; Peters and Cassa, 1994). The measured $T_{\max}$ from Rock-Eval pyrolysis shows that most of the investigated samples are in the immature to mature stage of maturity, but the maturity does not correlate with increasing depth. This is confirmed by the plot of $T_{\max}$ vs depth (Fig. 8a). Approximately half of the $T_{\max}$ values do not exceed 435 °C, 30% of the values are in the oil window, three values show that the sediments are in the wet gas window, and four are in the overmature stage or dry gas window. This is illustrated on the plot of $T_{\max}$ vs HI, which also indicates that the kerogen type of the studied samples in sediments with Late Ordovician–Silurian–Early Devonian ages is type III, which mainly produces gas in case of maturation (Fig. 8b). It is common to compare vitrinite reflectance to $T_{\max}$ data to establish the robustness of both types of data. In order to tighten the range of the estimated thermal maturity, $T_{\max}$ values were further compared to optical reflectance measurements.

Well-log interpretation

Comparison of TOC and well-log data in gamma ray, acoustic, density and resistivity logs of the Late Ordovician–Silurian–Early Devonian interval

shows a good correlation (Fig. 9). It indicates that these curves, especially gamma-ray curve, can be used for the vertical TOC distribution patterns. This correlation presents a typical response of organic-rich shales in wireline logs according to reference values for source rock identification (Passey *et al.*, 1990), which shows that the 150 API cut-off value chosen to define source potential mudstones and shales in this contribution corresponds to TOC values of above 1%.

Since it is determined (Schmoker, 1993) that, in typical source rock, density logs are most sensitive to variations in TOC content, the most used method for calculation of TOC is by deriving it from density logs. Therefore, in the current study, this ratio is applied first. In the calculation of TOC from density log, it is observed that the calculated values are overestimated in comparison with the TOC measurement from Rock-Eval. For this reason, adjusting Schmoker method parameters is required, by using other relationships between TOC and density log. Consequently, TOC is estimated by using other equations (5), (6), (7), in which TOC is derived both from density and gamma-ray logs (Fig. 9):

$$TOC = -3.68 \times DEN + 10.08 \quad (5),$$

$$TOC = 6.48 + 0.004355 \times GR - 2.469 \times DEN \quad (6),$$

$$TOC = 6.09 + 0.00288 \times GR - 2.300 \times DEN \quad (7).$$

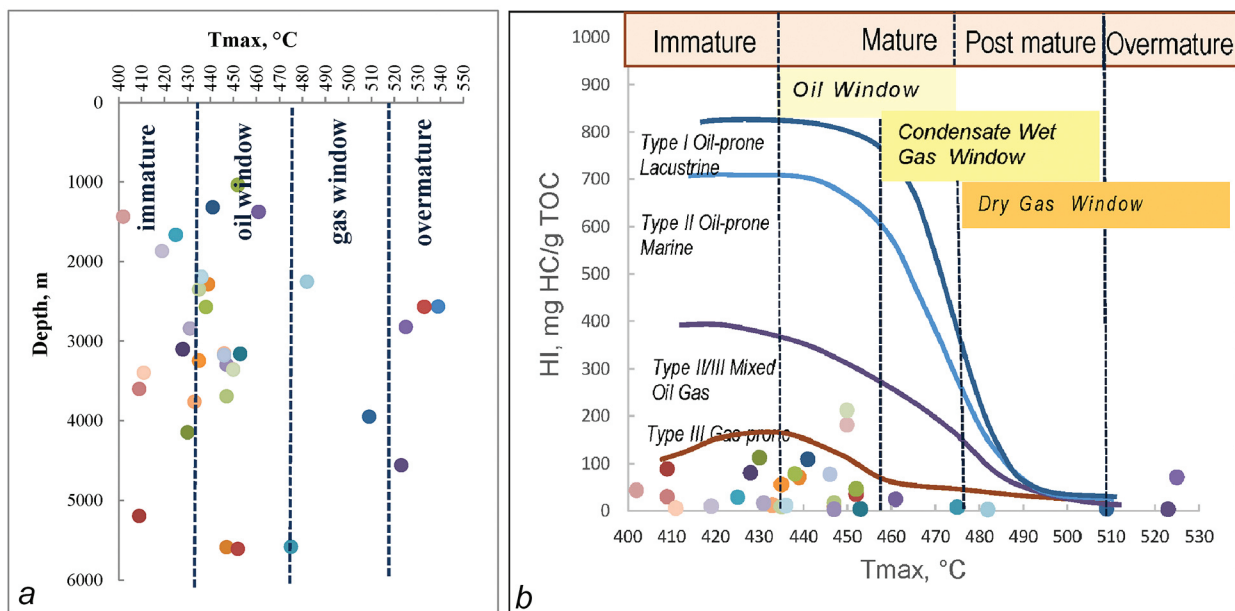


Fig. 8. Relation between thermal maturity ($T_{\max}$) and depth of the samples (a) and thermal maturity ($T_{\max}$) and HI (b).

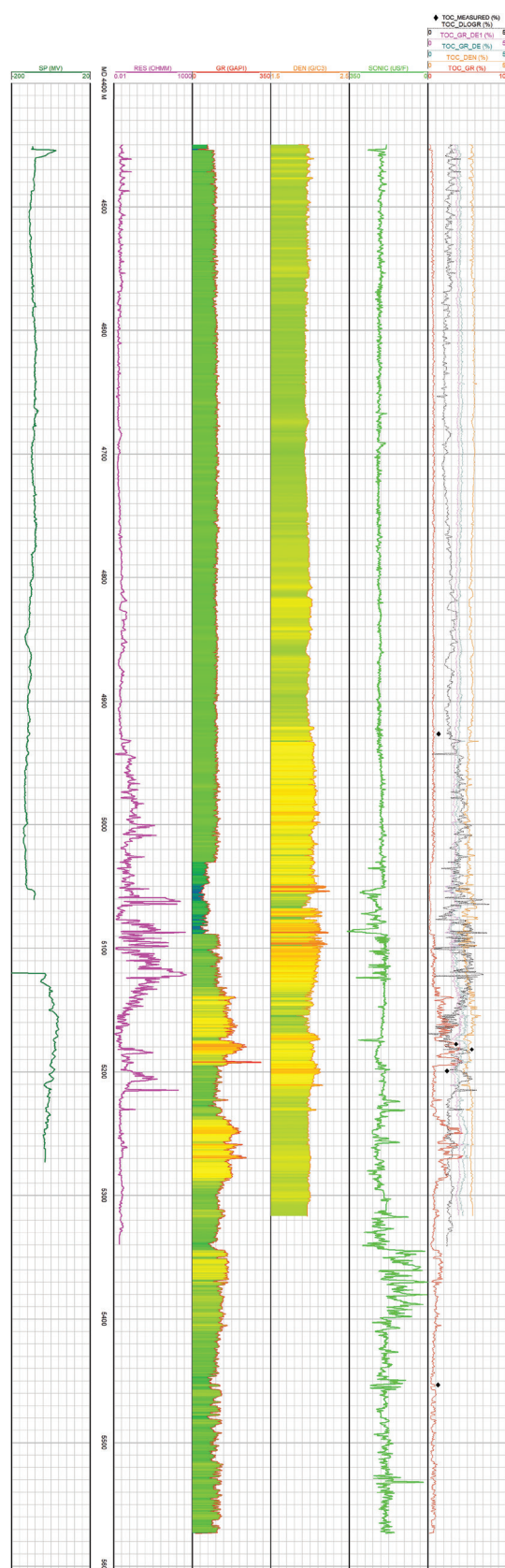


Fig. 9. Correlation between well-log curves and TOC estimation by logs (TOC calculated) calibrated by laboratory data (TOC measured).

The best approach using the Shmocker method was identified to be the TOC estimated from density (RHOB) and gamma-ray (GR) logs in equation (7).

Secondly, TOC was also estimated using the $\Delta\log R$ method of Passey *et al.* (1990), which is a slightly more complicated approach that requires deep resistivity and sonic logs as well as maturity information of R_o or T_{max} data in equation (2). Moreover, Passey *et al.* (1990) pointed out that the $\Delta\log R$ method is more applicable when the LOM values are in the range of the catagenesis zone. Beyond the range, this method should be used prudently, because in other cases erroneous results may be gained. According to the calculated R_o values further in this paper (with R_o from 2.00% to 2.85%, 2.4% on average), there are some limitations in estimating TOC by the $\Delta\log R$ method, and the estimated TOC may be lower than the actual TOC.

In the present study, the close statistical correlation between gamma-ray and TOC content (Šliaupa *et al.*, 2016) was applied. The highest TOC values are modelled in the Silurian mudstones and shales and exceed 10%. The overlying Lower–Middle Devonian section shows minor variations; the average TOC content is about 0.83%.

The data yielded when measuring TOC from geochemical studies is correlated with the calculated TOC from the gamma-ray logs and the results show a good correlation with a correlation coefficient R_2 reaching 0.84 (Fig. 10).

Reflectance measurement interpretation

Based on polished section microscopy on a few representative samples, it can be seen that the matrix is composed of quartz and clay minerals, with abundant pyrite and organic material (Fig. 11). It can be examined in the representative polished section image that dark-coloured amorphous organic matter clusters are situated within the quartz and clay or shale matrix. In the same image, organic matter appears as grey aggregates, which probably prompted a high reflectance level.

The random reflectance measurements were taken on different organic materials, such as graptolites, vitrinite-like particles, chitinozoa and solid bitumen with the total amount of readings in individual samples ranging between 51 and 81. The observed random reflectance values of graptolites and vitrinite-like particles vary in the range of 1.5% to 3.9%, but as it is shown on the representative histogram the average measured value is 3.1% (Fig. 12).

It is generally accepted that graptolites are more reflective than vitrinite at equivalent thermal matur-

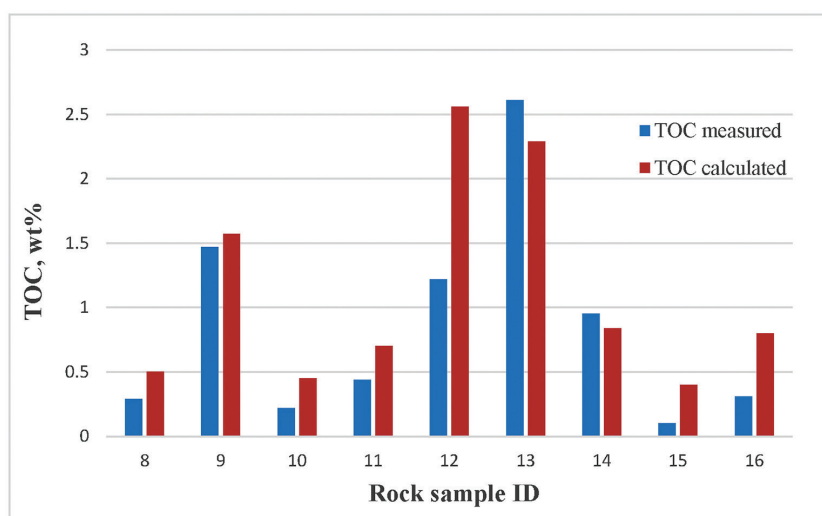


Fig. 10. Histogram diagram between TOC measured and TOC calculated for one of the wells.

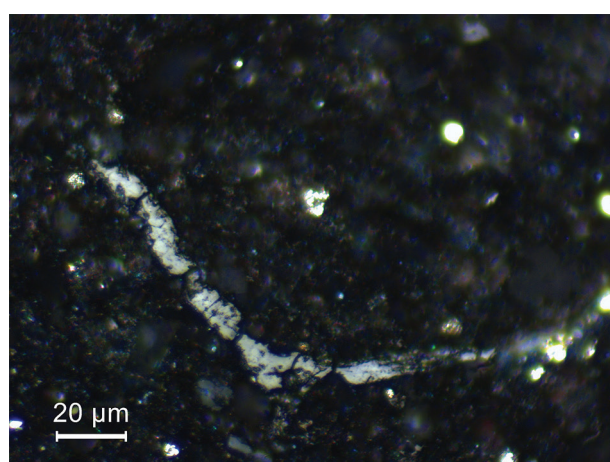


Fig. 11. Organic matter in section image of selected and representative shale samples.

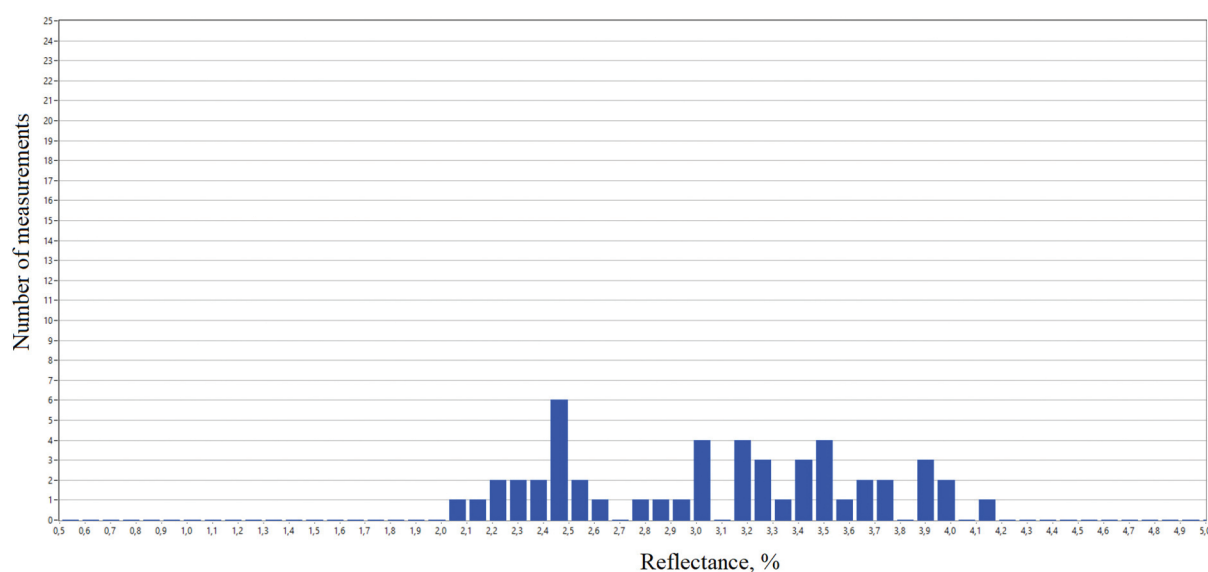


Fig. 12. Representative histogram of the total reflectance distribution for different organic particles (graptolites, vitrinite-like particles, solid bitumen) measured in the Silurian shales.

Table 2

Vitrinite-equivalent reflectance (EqVR_e) converted from measured graptolite reflectance (GR)

Measured graptolite reflectance	Vitrinite-equivalent reflectance			
	Cole (1994)	Bertrand and Malo (2012)	Petersen <i>et al.</i> (2013)	Luo <i>et al.</i> (2020)
GR	EqVRo (1) = 0.8*GR (%)	EqVRo (2) = 0.9376*GR+0.0278 (%)	EqVRo (3) = 0.73*GR+0.16 (%)	EqVRo (4) = 0.99*GR+0.08 (%)
2.95	2.41	2.79	2.31	2.02
3.10	2.54	2.93	2.42	2.10

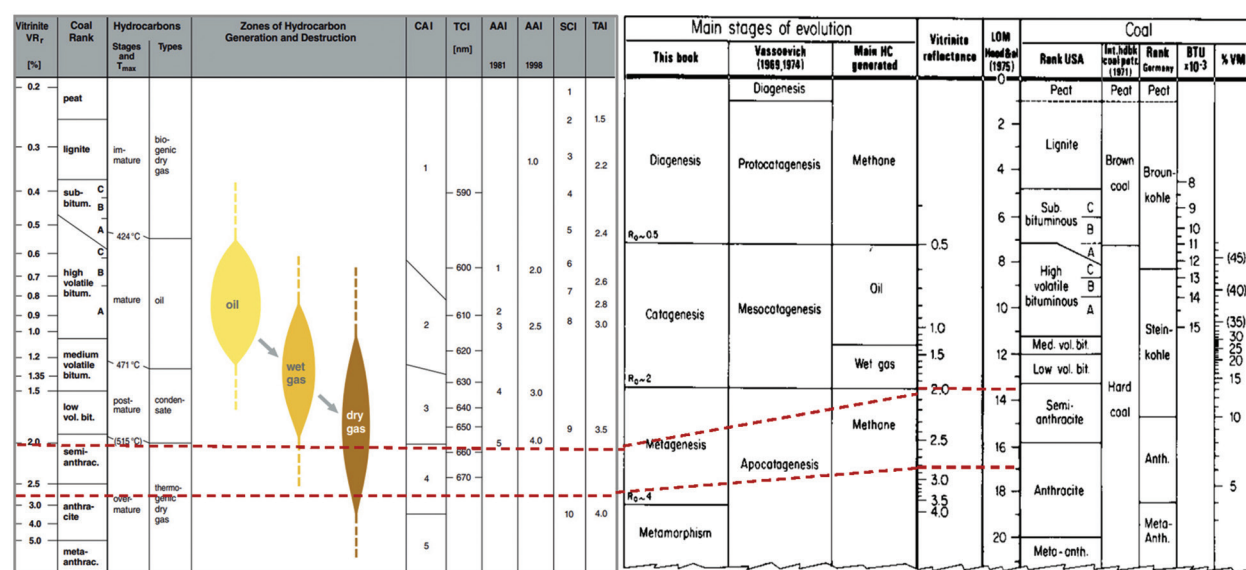


Fig. 13. Correlation between thermal maturity parameters, phases of hydrocarbon generation, and main stages of evolution of organic matter. The zone within dashed red lines indicates obtained and calculated in the current study optical reflectance data for the analysed samples of mudstones and shales with Silurian age. The figure is adapted from Hood *et al.* (1975), Tissot and Welte (1984) and Hartkopf-Fröder *et al.* (2015).

ities (Cole, 1994; Petersen *et al.*, 2013). Most equations derived for converting graptolite reflectance to its vitrinite equivalent also include allowance for vitrinite-like particles, which are often assumed to be graptolite fragments but cannot be definitively identified as graptolites by morphology (Petersen *et al.*, 2013). It is assumed that the vitrinite-like particles are graptolite fragments, based on a linear relationship and strong positive correlation between the reflectance of the positively identified graptolite fragments and the vitrinite-like particles. Hence, the applied equation derived by Petersen *et al.* (2013) is used for both organic particles. The maturity levels differ depending on the empirical formula used. Therefore, the vitrinite reflectance equivalent for the analysed samples was calculated using four different empirical formulas (Table 2). Based on the

calculation of the average reflectance values from measured reflectance of organic materials (graptolite, chitinozoa, vitrinite-like particles and solid bitumen) it is shown that the thermal maturity of the analysed rocks with Silurian age is equivalent to a vitrinite reflectance range of approximately 2.02–2.93%. According to the correlation of Hartkopf-Fröder *et al.* (2015), this corresponds to thermal maturity in the peak of the dry gas generation window to the end of the dry gas window (Fig. 13).

By correlation, the obtained maturity information from both geochemical (T_{max} values) and optical reflectance measurement (calculated R_o from graptolite reflectance), the LOM is derived on the scale comparison table (Fig. 13; Tissot and Welte, 1984). LOM values correlated to reflectance measurement vary in the range 12–17, but those values

correlated to $T_{\max}$ are plotted within a broad maturity range from immature to overmature stage and LOM is difficult to be determined.

CONCLUSIONS

The combination of applied geochemical, geophysical, and organic petrography methods for the characterisation of pelitic sediments with Late Ordovician–Early Devonian ages and assessment of their hydrocarbon potential allow us to draw the following conclusions:

- The comparison between the TOC values measured in the geochemical laboratory and those calculated from the well-logs demonstrate a good matching;
- The geochemical evaluation of the analysed samples indicates that the TOC content is moderate, with the highest values in the Silurian mudstones and shales. Based on these results, it can be assumed that the Lower Palaeozoic succession could be characterised by “fair to good” organic richness, with “poor to fair” hydrocarbon potential;
- The OM of the analysed successions are characterised predominantly by kerogen type III and mixed type II/III in some intervals;
- According to the results obtained by Rock-Eval pyrolysis, organic matter is immature to mature in the studied sediment section at depths with the capability to expel both oil and some gas hydrocarbons in case of maturation. Thus, the results obtained have been compared to another method for thermal maturity evaluation;
- In the case of vitrinite absence in pre-Devonian sediments, other organic components present in the rock, such as graptolite and vitrinite-like particles and bitumen were considered. Widely used equations developed to convert these organic components into values equivalent to vitrinite were applied. Calculated vitrinite-equivalent values from the obtained reflectance measurements indicate that the investigated samples are in a highly mature to overmature stage of maturity and that could assume dry gas productive phase. Combined geochemical and petrographic

results prove that several datasets need to be used to provide an estimate of maturity.

The results obtained in this research are based on geological, geochemical, and geophysical data from a few wells and consideration must be given to the fact that many other factors may affect the correlation. At the same time, if the calculated and measured TOC is well correlated in some intervals, then source rock evaluation of such intervals is useful for further analysis and research.

To better understand the timing, type, and quantity of generated hydrocarbons from the Lower Palaeozoic shale interval, it is crucial to use additional types of research. It is recommended that several complementary analyses for determining geochemical properties should be used. Further analyses of the maturity of this source interval from wells in other structural elements of the study area will assist with future basin-wide burial history studies.

The integration of the geochemical data with the geophysical survey in the wells, as well as the combination with an optical petrographic method, which was applied in the current research, would significantly be beneficial to improve the approach of assessing the potential of shale intervals with Early Palaeozoic age in NE Bulgaria. The implemented geological, geophysical, and geochemical study can be considered as indispensable for the assessment of the hydrocarbon potential of shale successions as a source of fossil fuels.

Acknowledgements

This research is financially supported by the Bulgarian Ministry of Education and Science under the National Program “Young Scientists and Postdoctoral Students – 2”. We express our sincere gratitude to the Laboratory of Organic Petrology and Geochemistry at Sofia University for polish block preparation and microscopic reflectance measurement. The authors are grateful to the anonymous reviewers for their constructive remarks that significantly improved the quality of this manuscript.

REFERENCES

- Bertrand, R., Malo, M. 2012. *Dispersed organic matter reflectance and thermal maturation in four hydrocarbon exploration wells in the Hudson Bay Basin: regional implications*. Geological Survey of Canada Open File 7066, 52 pp., <https://doi.org/10.4095/289709>.
- Cole, G.A., 1994. Graptolite-chitinozoan reflectance and its relationship to other geochemical maturity indicators in the Silurian Qusaiba Shale, Saudi Arabia. *Energy Fuels* 8 (6), 1443–1459, <https://doi.org/10.1021/ef00048a035>.
- Dabovski, H., Zagorchev, I. 2009. Alpine tectonic subdivision of Bulgaria. In: Zagorchev, I., Dabovski, H., Nikolov, T. (Eds), *Geology of Bulgaria. Volume II, Mesozoic Geology*. “Prof. Marin Drinov” Academic Publishing House, Sofia, 30–37 (in Bulgarian, with English abstract).

- Espitalié, J., Deroo, G., Marquis, F. 1985a. La pyrolyse Rock Eval et ses applications. *Revue de l'Institut Français du Pétrole* 40 (5), 563–579, <https://doi.org/10.2516/ogst:1985035>.
- Espitalié, J., Deroo, G., Marquis, F. 1985b. La pyrolyse Rock Eval et ses applications. Deuxième partie. *Revue de l'Institut Français du Pétrole* 40 (6) 755–784, <https://doi.org/10.2516/ogst:1985045>.
- Hartkopf-Fröder, C., Königshof, P., Littke, R., Schwarzbauer, J. 2015. Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: A review. *International Journal of Coal Geology* 150–151, 74–119, <https://doi.org/10.1016/j.coal.2015.06.005>.
- Hester, T.C., Schmoker, J.W., Sahl, H.L. 1990. Log-derived regional source-rock characteristics of the Woodford Shale, Anadarko Basin, Oklahoma. *US Geological Survey Bulletin* 1886-D, 42 pp.
- Jacob, H. 1989. Classification, structure, genesis and practical importance of natural solid oil bitumen (migrabitumen). *International Journal of Coal Geology* 11 (1), 65–79, [https://doi.org/10.1016/0166-5162\(89\)90113-4](https://doi.org/10.1016/0166-5162(89)90113-4).
- Lakova, I., Hristov, N. 2018. Ordovician to Devonian palynostratigraphy of well Rogozina of the Moesian Platform in Bulgaria: implications to the palaeogeography and earliest land plant evolution. *Review of the Bulgarian Geological Society* 79 (3), 95–96.
- Landis, C.R., Castaño, J.R. 1995. Maturation and bulk chemical properties of a suite of solid hydrocarbons. *Organic Geochemistry* 22 (1), 137–149, [https://doi.org/10.1016/0146-6380\(95\)90013-6](https://doi.org/10.1016/0146-6380(95)90013-6).
- Luo, Q., Fariborz, G., Zhong, N., Wang, Y., Qiu, N., Skovsted, C.B., Suchý, V., Schovsbo, N.H., Morga, R., Xu, Y., Hao, J., Liu, A., Wu, J., Cao, W., Min, X., Wu, J. 2020. Graptolites as fossil geo-thermometers and source material of hydrocarbons: an overview of four decades of progress. *Earth Science Review* 200, 1–28, 103000, <https://doi.org/10.1016/j.earscirev.2019.103000>.
- Ma, Y.Z. 2016. Chapter 1 – Unconventional Resources from Exploration to Production. In: Ma, Y.Z., Holditch, S.A. (Eds), *Unconventional Oil and Gas Resources Handbook*. Gulf Professional Publishing, Houston, Texas, 3–52, <https://doi.org/10.1016/B978-0-12-802238-2.00001-8>.
- Nachev, I.K., Nachev, C.I. 2003. *Alpine Plate Tectonics of Bulgaria*. Artic-2001, Sofia, 200 pp.
- Passey, Q.R., Moretti, F.J., Kulla, J.B., Creaney, S., Stroud, J.D. 1990. A practical model for organic richness from porosity and resistivity logs. *AAPG Bulletin* 74 (12), 1777–1794.
- Peters, K. 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG Bulletin* 70, 318–329, <https://doi.org/10.1306/94885688-1704-11D7-8645000102C1865D>.
- Peters, K.E., Cassa, M.R. 1994. Applied source-rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds), *The Petroleum System*. American Association of Petroleum Geologists Memoirs 60, 93–120, <https://doi.org/10.1306/M60585>.
- Petersen, H.L., Schovsbo, N.H., Nielsen, A.T. 2013. Reflectance measurements of zooclasts and solid bitumen in lower Palaeozoic shales, southern Scandinavia: correlation to vitrinite reflectance. *International Journal of Coal Geology* 114, 1–18, <https://doi.org/10.1016/j.coal.2013.03.013>.
- Poprawa, P. 2020. Lower Paleozoic oil and gas shale in the Baltic Podlasie-Lublin Basin (central and eastern Europe) – a review. *Geological Quarterly* 64 (3), 515–566, <https://doi.org/10.7306/gq.1542>.
- Schmoker, J. 1993. Use of formation-density logs to determine organic-carbon content in Devonian shales of the Western Appalachian Basin and an additional example based on the Bakken Formation of the Williston Basin: Reston, Virginia. *US Geological Survey Bulletin* 1909, J1–J14.
- Selley, R.C. 1998. *Elements of petroleum geology*, Second Edition. San Diego, London, Boston, New York, Sydney, Tokyo, Toronto: Academic Press, 470 pp.
- Šliaupa, S., Šliaupienė, R., Žaludienė, G., Vaskaboinikava, T., Bibikava, A., Evstratenko, L., Kovkhuto, A. 2016. Prospects of Lithuanian Silurian shale gas, Baltic sedimentary basin. *Oil Shale* 33 (4), 357–372, <https://doi.org/10.3176/oil.2016.4.04>.
- Steemans, P., Lakova, I. 2004. The Moesian Terrane during the Lochkovian—a new palaeogeographic and phytogeographic hypothesis based on miospore assemblages. *Palaeogeography, Palaeoclimatology, Palaeoecology* 208 (3–4), 225–233, <https://doi.org/10.1016/j.palaeo.2004.03.006>.
- Tan, J., Horsfield, B., Mahlstedt, N., Zhang, J., di Primio, R., Vu, T.A.T., Boreham, C.J., van Graas, G., Tocher, B.A. 2013. Physical properties of petroleum formed during maturation of Lower Cambrian shale in the upper Yangtze Platform, South China, as inferred from Phase Kinetics modelling. *Marine and Petroleum Geology* 48, 47–56, <https://doi.org/10.1016/j.marpetgeo.2013.07.013>.
- Tari, G., Poprawa, P., Krzywiec, P. 2012. Silurian Lithofacies and Paleogeography in Central and Eastern Europe: Implications for Shale Gas Exploration. *SPE 151606, SPE/EAGE European Unconventional Resources Conference and Exhibition*, Vienna, 20–22, <https://doi.org/10.2118/151606-MS>.
- Tari, G., Poprawa, P., Krzywiec, P., Popadyuk, I., Krezsek, C. 2014. Interpretation of the Silurian Basin of Central and Eastern Europe as a Pro-Foreland Flexural Basin: Implications for Shale Gas Exploration. *SPE 167744 SPE/EAGE European Unconventional Resources Conference and Exhibition*, Vienna, 25–27, <https://doi.org/10.2118/167744-MS>.
- Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P. 1998. *Organic Petrology*. Gerbrüder Born Traeger, Berlin, 704 pp.
- Tissot, B.P., Welte, D.H. 1984. *Petroleum Formation and Occurrence*. Springer-Verlag, Berlin, 699 pp., <https://doi.org/10.1007/978-3-642-87813-8>.
- Yanev, S., Göncüoğlu, M.C., Gedik, I., Lakova, I., Boncheva, I., Sachanski, V., Okuyucu, C., Özgül, N., Timur, E., Malikov, Y., Saydam, G., 2006. Stratigraphy, correlations and palaeogeography of Palaeozoic terranes in Bulgaria and NW Turkey: a review of recent data. In: Robertson, A.H.F., Mountrakis, D. (Eds), *Tectonic Development of the Eastern Mediterranean Region*. Geological Society London Special Publication 260, 51–67, <https://doi.org/10.1144/GSL.SP.2006.260.01.04>.
- Yanev, S., Boncheva, I. 1995. Contribution to the Paleozoic evolution of the recent Moesian platform. *Geologica Balcanica* 25 (5–6), 3–21, <https://doi.org/10.52321/GeolBalc.25.5-6.3>.
- Yanev, S., Lakova, I., Boncheva, I., Sachanski, V. 2005b. The Moesian and Balkan terrains in Bulgaria: Palaeozoic marine basin development, palaeogeography and tectonic evolution. *Geologica Belgica* 8 (4), 185–192.
- Zhao, P., Mao, Z., Huang, Z., Zhang, C. 2016. A new method for estimating total organic carbon content from well logs. *AAPG Bulletin* 100 (8), 1311–1327, <https://doi.org/10.1306/02221615104>.
- Zou, C. 2017. *Unconventional Petroleum Geology*. Elsevier, Amsterdam, 500 pp., <https://doi.org/10.1016/B978-0-12-812234-1.00002-9>.