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An evaluation of organic matter dispersed in the Menilite Formation in Silesian Nappe (Polish Outer Carpathians): an optical microscopic approach

Marta Waliczek[1], Grzegorz Machowski[2], Marek Leszek Solecki[3], Michał Stefaniuk[4]

[1] AGH University of Science and Technology, Faculty of Geology Geophysics and Environmental Protection, Department of Energy Resources, Krakow, Poland, e-mail: waliczek@agh.edu.pl, ORCID ID: 0000-0002-5940-7986
[2] AGH University of Science and Technology, Faculty of Geology Geophysics and Environmental Protection, Department of Energy Resources, Krakow, Poland, e-mail: machog@agh.edu.pl, ORCID ID: 0000-0003-4589-0433
[3] AGH University of Science and Technology, Faculty of Drilling, Oil and Gas, Department of Petroleum Engineering, Krakow, Poland, e-mail: mlsoleck@agh.edu.pl, ORCID ID: 0000-0001-8637-8300
[4] AGH University of Science and Technology, Faculty of Geology Geophysics and Environmental Protection, Department of Energy Resources, Krakow, Poland, e-mail: stefaniu@agh.edu.pl, ORCID ID: 0000-0003-4442-9290

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Abstract: In this study, optical microscopic analyses were applied to evaluate the thermal maturity, characteristics of solid bitumen, and other organic matter finely dispersed in Oligocene shales of the Menilite Formation in the Iwonicz-Zdrój–Rudawka Rymanowska Fold (IRF) and Bóbrka–Rogi Fold (BRF) of the Central Carpathian Synclinorium of the Silesian Nappe, Outer Carpathians, Poland. The investigation was carried out at two-unit depths of the shallow and deeper D-1 sections (430 m – IRF and 4,300 m – BRF) and outcrop samples (BRF). The mean random huminite reflectance values indicate immature conditions with respect to hydrocarbon generation in samples from the D-1 shallow section ($VR_o \approx 0.40\%$) and in the outcrop samples ($VR_o = 0.36\%$). The degree of thermal maturity of the organic matter from a depth of about 4,300 m – BRF based on random vitrinite ($VR_o \approx 0.80\%$) and solid bitumen ($BR_o \approx 0.65\%$) reflectance measurements is associated with the "oil window" for petroleum generation. The organic components dispersed in the examined Menilite Formation samples are typical for hydrocarbon-prone organic matter, suggesting the dominant kerogen type II. The potential precursor maceral for solid bitumen occurring in the examined samples from the deeper D-1 sections is largely the alginite maceral.

Keywords: Outer Carpathians, Menilite Formation, organic matter, huminite/vitrinite reflectance, solid bitumen

INTRODUCTION

Organic matter (OM) dispersed in sedimentary rocks provides valuable information about the sedimentary basin. The reflectance of vitrinite maceral is commonly used as a thermal maturity index (e.g. Taylor et al. 1998, Hackley et al. 2019, and references therein). This organic component is applied to evaluate the thermal evolutionary history of the sedimentary basin (e.g. Taylor et al. 1998, Botor et al. 2020, Łuszczak et al. 2020, and references therein) or even in seismic hazard assessment (e.g. Phan et al. 2019). As an alternative, solid bitumen can be used in thermal maturity indices (e.g. Jacob 1989, Suárez-Ruiz et al. 2012, Waliczek et al. 2019, and references therein).

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Sanei (2020) presented a new classification of solid bitumen and discussed five stages of the formation of this organic component. The highlighted components included: diagenetic solid bitumen; initial-oil solid bitumen; primary-oil solid bitumen; late-oil solid bitumen, and pyrobitumen. This model is closely related to the hydrocarbon generation phases and the vitrinite reflectance values. Another organic component – fusinite – can be applied to reconstruct paleoenvironmental conditions, especially by providing evidence for paleo-wildfires temperatures (e.g. Zakrzewski et al. 2020, 2022, and references therein). Moreover, thermal maturity and the type of organic matter evaluated from microscopic analyses are often a subject discussed in the broader context of the petroleum habitat (e.g. Tissot & Welte 1984, Hackley & Cardott 2016, and references therein). In the Outer Carpathians, the Menilite Formation is considered a principal source of hydrocarbons (e.g. Koltun 1992, Pawlewicz 2006, Kosakowski et al. 2018, and references therein). The high total organic carbon and oil-prone organic matter content (kerogens type 1 and II) means that the Menilite Formation is seen as a source rock with excellent prospects.

In this study, Menilite shales collected from the D-1 well section and outcrop samples were examined (Polish Outer Carpathians; Silesian Unit).

The purpose of this study was to: (1) determine the reflectance values of huminite/vitrinite and solid bitumen in terms of hydrocarbon generation potential and the relation of thermal maturity indices, (2) characterize the organic matter components dispersed in the Menilite Formation to evaluate the potential of the source rocks and compare the quality of the source rock from Iwonicz-Zdrój–Rudawka Rymanowska Fold (IRF) and Bóbrka–Rogi Fold (BRF), and (3) characterize the precursor maceral of solid bitumen observed in the analysed rocks to better understand the process of the solid bitumen formation in the Menilite Formation.

This is the first attempt to characterize and indicate the original maceral of solid bitumen formation and deposition in a natural environment using only microscopic investigation. The organic matter from the outcrop samples is considered as the precursor macerals to solid bitumen observed in samples from the D-1 well.

Some of the results of the microscopic and geochemical investigation of the Menilite Formation from the D-1 well section were previously discussed by Kosakowski et al. (2018), Machowski et al. (2017), and Waliczek et al. (2021). The contribution of optical microscopic examinations can be helpful in future petroleum prospection, as well in the reconstruction of the thermal history of the Outer Carpathians.

GEOLOGICAL SETTING

The study area is located in the Central Carpathian Synclinorium of the Silesian Nappe; the eastern part of the Polish Outer Carpathians, close to Dukla (Fig. 1). The Central Carpathian Synclinorium is a geostructural element built of the Silesian Nappe, filled with a thick cover of the youngest flysch sediments, called the Menilite-Krosno Series (Jucha et al. 1958). Older sediments are only exposed in the tectonic axes of the folds: Iwonicz-Zdrój–Rudawka Rymanowska, Bóbrka–Rogi and Potok–Krościenko–Trześniów (Figs. 1, 2). In the Polish part, length of the Outer Carpathians extends for about 140 km along the strike from Gorlice to the eastern border, reaching its greatest width (up to 26 km) in the upper San river (Wdowiarz 1985). The Central Carpathian Synclinorium is one of the most promising areas for petroleum exploration in the Polish part of the Outer Carpathians, both from the point of view of conventional and unconventional hydrocarbon accumulations (Kuśmierek et al. 2016a, Sechman et al. 2020). Hence, numerous studies of organic matter have been carried out for petroleum prospecting purposes (e.g. Kotarba & Koltun 2006, Matyasik & Dziadzio 2006, Matyasik et al. 2006, Kosakowski et al. 2009, Kotarba et al. 2014, Więcław et al. 2020). The Menilite-Krosno Series is dominated by the Krosno Beds lithofacies, which is traditionally subdivided into the following (Jucha 1969):

- the Lower Krosno Beds (thick-bedded sandstones with thin intercalations of shales and mudstones),
- the Middle Krosno Beds (medium- and thin-bedded sandstones with shales and mudstones inter-beds),
- the Upper Krosno Beds (clayey and marly shales with some intercalations of thin-bedded sandstones).

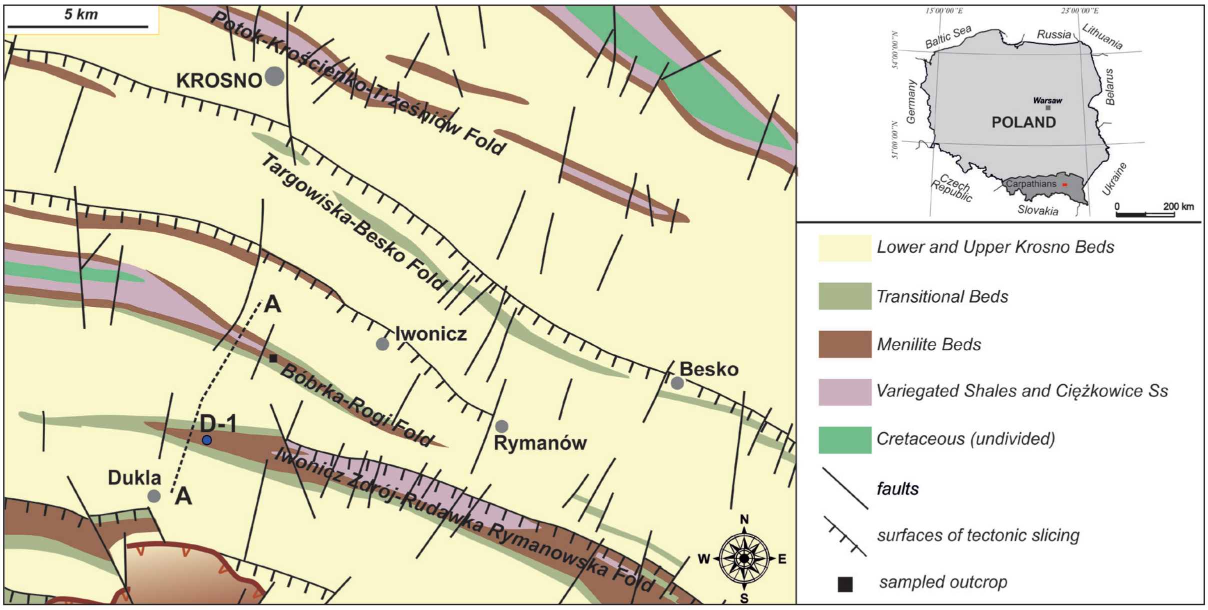

Fig. 1. Geological sketch of the study area (based on Kuśmierek et al. 2016a, modified)

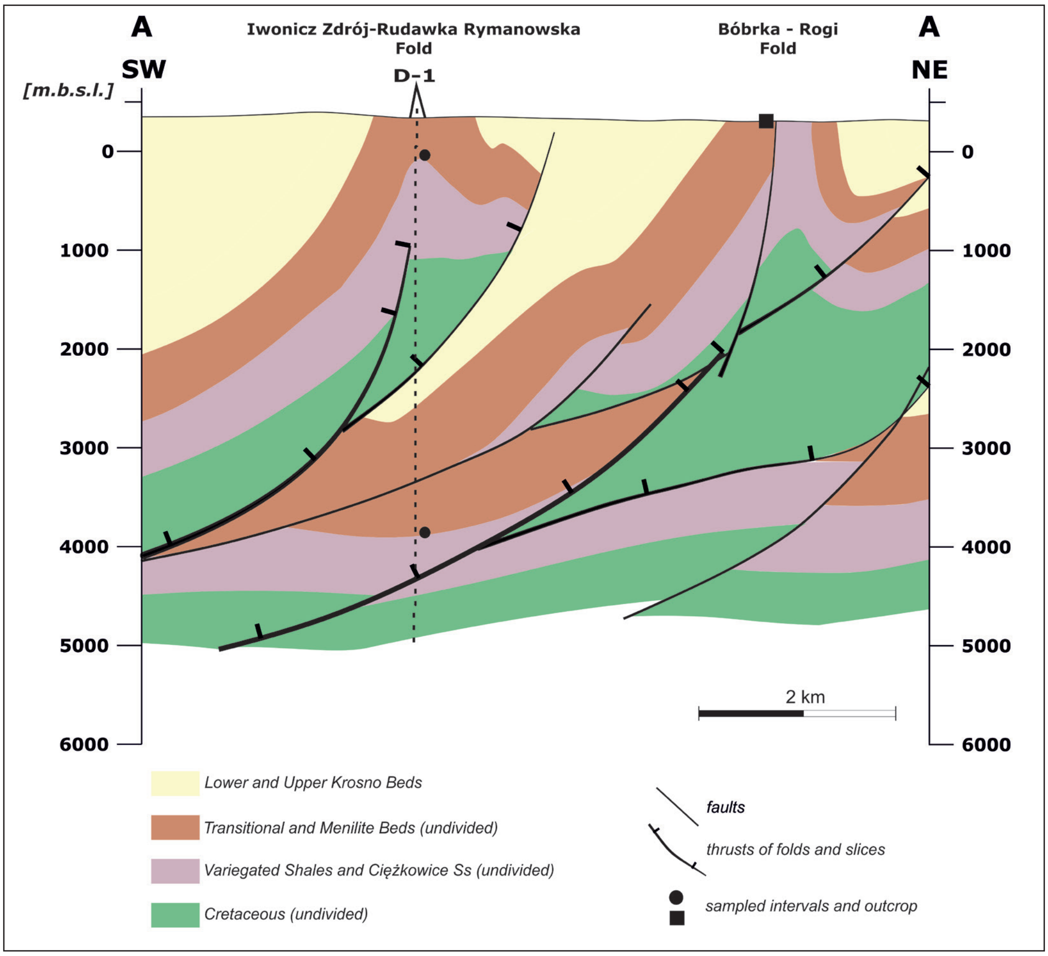

Fig. 2. Geological cross-section of the study area (based on Kuśmierek et al. 2016b, modified)

The Menilite-Krosno Series contain excellent source rocks in the Carpathians: the Menilite shales, in which the liptinite group with humic components is the predominant type of organic matter.

The D-1 borehole was drilled in 2012 to a depth of nearly 5,500 m (Hajto et al. 2013), and the Iwonicz-Zdrój–Rudawka Rymanowska Fold (IRF) and Bóbrka–Rogi Fold (BRF) were recognized. Within the Iwonicz-Zdrój–Rudawka Rymanowska Fold, the Menilite Beds (shallow part – to a depth of 525 m) and Eocene-Cretaceous deposits were drilled. Under the overthrust of the Iwonicz-Zdrój–Rudawka Rymanowska Fold (at a depth of 2,645 m), the Oligocene deposits of the southern limb of the Bóbrka–Rogi Fold were drilled: Krosno Beds, Transitional Beds and Menilite Beds (deeper part, 4,200–4,350 m) covering the Eocene-Cretaceous deposits to a final depth of 5,500 m (Fig. 2).

SAMPLES AND METHODS

For the present study, 11 samples of the Menilite Formation were analyzed. Four core samples were taken from the Iwonicz-Zdrój–Rudawka Rymanowska Fold from the shallow part of the D-1 well section (a depth of ca. 430 m), and seven samples from the Bóbrka–Rogi Fold: five core samples from the deeper part of the D-1 well section (a depth of about 4,300 m), and two from an outcrop (Tab. 1). All of the analyzed rocks are of Oligocene age.

Samples were prepared according to ASTM D2797 (ASTM 2015). The petrological investigations were performed on whole-rock polished sections using a Carl Zeiss Axio Imager optical microscope equipped with a PMT photometer, HBO lamp, and the PMT III software. The identification of organic components was carried out using reflected white (huminite/vitrinite, inertinite group) and blue light excitation (liptinite group). Specific components of organic matter were categorized in accordance with Sýkorová et al. (2005) for the huminite group, ICCP (1998, 2001) for the vitrinite and inertinite group, and Pickel et al. (2017) for the liptinite group. The solid bitumen classification was based on the description by Landis & Castaño (1995). The mean random reflectance measurements of organic matter were performed under monochromatic non-polarized light with a 546 nm peak transmittance filter, in oil immersion (refractive index n = 1.518) and at a temperature of about 23°C, in accordance with the ASTM (2011) guidelines. The photometer was calibrated with the following standards: spinel (R = 0.429%), yttrium aluminum garnet (R = 0.905%) and gadolinium gallium garnet (R = 1.728%). The quantitative analysis of the organic matter components was based upon the point-counting of 500 grains per polished section, as recommended by Taylor et al. (1998). Photomicrographs of organic matter were taken using AxioCam MRc5 Zeiss camera.

Table 1
Location of studied shales from Menilite Formation – Silesian Unit

Latitude N [°]	Longitude E [°]	Sample No.	Depth [m]
49.57518	21.71375	1	430 – shallow part
49.57518	21.71375	2	431 – shallow part
49.57518	21.71375	3	432 – shallow part
49.57518	21.71375	4	433 – shallow part
49.60687	21.73233	5	Outcrop
49.60690	21.73230	6	Outcrop
49.57518	21.71375	7	4,301 – deeper part
49.57518	21.71375	8	4,302 – deeper part
49.57518	21.71375	9	4,303 – deeper part
49.57518	21.71375	10	4,304 – deeper part
49.57518	21.71375	11	4,305 – deeper part

The mean values of the solid bitumen reflectance were recalculated for the vitrinite reflectance using the equation proposed by Waliczek et al. (2019), which was evaluated for solid bitumen dispersed in the Menilite Formation from the Outer Carpathians.

RESULTS

The reflectance measurements of organic matter

The results of the reflectance measurements of organic matter dispersed in Menilite shales are listed in Table 2 and presented as vitrinite or solid bitumen histograms (Figs. 3, 4).

For the four samples from the Iwonicz-Zdrój–Rudawka Rymanowska Fold (D-1 borehole – shallow well section), the mean random reflectance measurements were carried out on huminite particles (VR_o) and range from 0.40 to 0.42% (Tab. 2, Fig. 3).

The thermal maturity of the organic matter in two outcrop samples from the Bóbrka–Rogi Fold was determined using huminite reflectance measurements, which equals to 0.36% VR_o (Tab. 2, Fig. 4A). The reflectance measurements for samples from the D-1 borehole deeper well section (Bóbrka–Rogi Fold) were carried out on the vitrinite and solid bitumen and presented as a VR_o and BR_o (Tab. 3).

The mean reflectance value for the vitrinite particles varies between 0.80 to 0.83% VR_o and for solid bitumen from 0.60 to 0.68% BR_o (Tab. 2, Fig. 4B). The mean equivalent vitrinite reflectance values range from 0.76 to 0.81% VR_E.

The vitrinite reflectance values show bimodality in some samples (Figs. 3, 4).

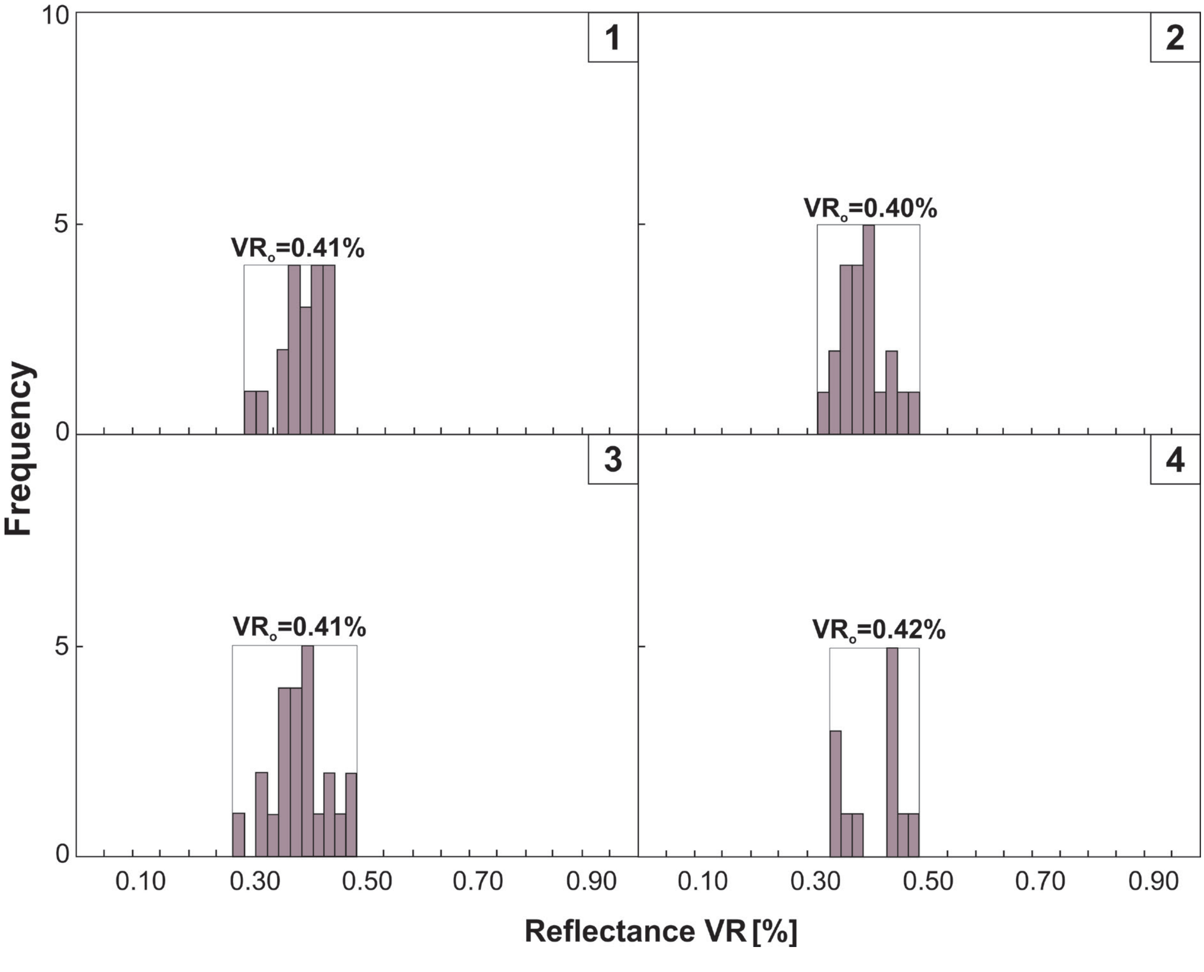

Fig. 3. *Vitrinite histograms of random reflectance measurements for Menilite Formation samples from the Iwonicz-Zdrój–Rudawka Rymanowska Fold – shallow part of D-1 well section*

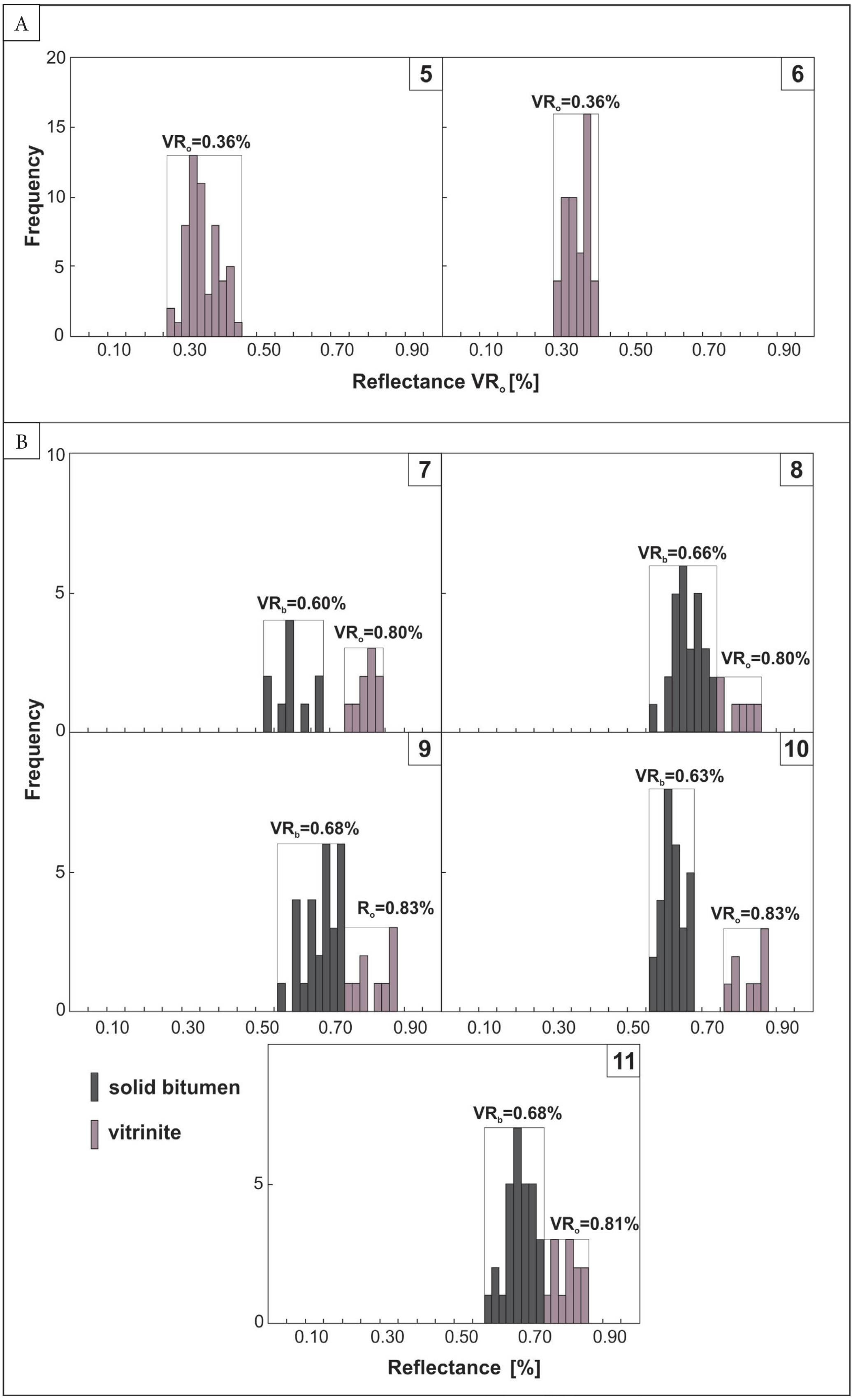

Fig. 4. *Solid bitumen and vitrinite histograms of random reflectance measurements for the Menilite Formation from Bóbrka–Rogi Fold: A) outcrops samples; B) samples from the deeper part of D-1 well section*

Table 2
The results of organic matter reflectance measurements for samples from the Iwonicz-Zdrój–Rudawka Rymanowska and Bóbrka–Rogi Folds

Iwonicz-Zdrój–Rudawka Rymanowska Fold										
D-1 borehole shallow well section										
Sample No.	**Depth [m]**	VR_o **[%]**	***n***	***s***	**Ranges**					
1*	430	0.41	19	0.04	0.32–0.46					
2*	431	0.40	21	0.04	0.33–0.49					
3*	432	0.41	23	0.07	0.29–0.50					
4*	433	0.42	12	0.05	0.34–0.49					
Bóbrka–Rogi Fold										
Outcrop samples – Rogi										
Sample No.		VR_o **[%]**	***n***	***s***	**Ranges**					
5		0.36	56	0.04	0.27–0.44					
6		0.36	50	0.03	0.30–4.10					
D-1 borehole deeper well section										
Sample No.	**Depth [m]**	VR_o **[%]**	***n***	***s***	**Ranges**	BR_o **[%]**	***n***	***s***	**Ranges**	VR_E **[%]**
7	4301	0.80**	9	0.02	0.76–0.84	0.60	10	0.05	0.53–0.67	0.76
8	4302	0.80**	6	0.04	0.75–0.85	0.66	27	0.04	0.56–0.73	0.80
9	4303	0.83**	7	0.04	0.75–0.88	0.68	27	0.05	0.58–0.74	0.81
10	4304	0.83**	8	0.04	0.76–0.87	0.63	28	0.03	0.57–0.67	0.78
11	4305	0.81**	14	0.03	0.75–0.85	0.68	30	0.04	0.59–0.74	0.81

Explanations: VR_o – mean reflectance measurement for huminite/vitrinite [%]; BR_o – mean reflectance measurement for solid bitumen [%]; *n* – number of measured particles; *s* – standard deviation of measured reflectance values [%]; Ranges – minimum and maximum mean reflectance values; $VR_E = (BR_o + 0.75)/1.77$ – equivalent vitrinite reflectance [%] applying the formulas after Waliczek et al. (2019).

* Data from Kosakowski et al. (2018).

** Data from Waliczek et al. (2021).

Characteristic of the organic matter components

The predominant types of organic matter in the samples from the Iwonicz-Zdrój–Rudawka Rymanowska Fold (D-1 borehole shallow well section) are macerals from the liptinite group (12.5% vol., with average ranges from 9.1 to 14.2%) (Tab. 3). They occur mainly as telalginite in Tasmanites form (Fig. 5A, D, E), and less frequently as *Botryococcus braunii* (Fig. 5F). The degradation product of organic matter is bituminite (see Pickel et al. 2017, and references therein) (Fig. 5G) which appears as a structureless groundmass (amorphous organic matter) or dark-brown streaks. The liptinite group is also represented by liptodetrinite, occasionally by sporinite (Fig. 5C), and resinite (Fig. 5A–C). The huminite group (2.2% vol., on average, ranges from 1.4 to 3.1%) (Fig. 5G, Tab. 3) mainly occur as gelohuminite, detrohuminite maceral subgroup, and dark ulminite (ulminite A – see Sýkorová et al. 2005). The inertinite group (0.93% vol. on average, ranges from 0.2 to 1.8%) (Tab. 3) is represented as semifusinite, fusinite, and inertodernite. In two samples, an unidentified zooclast (0.8% vol. on average) was noticed (Fig. 5H, I). Organic matter in the analyzed samples from the D-1 borehole shallow well section accounts from 10.7 to 18.8% (mean 16.0% vol.) (Tab. 3).

The main constituents in two outcrop samples from the Bóbrka–Rogi Fold are macerals from the liptinite group (12.1% vol., on average) (Tab. 3) with major alginite maceral. They are represented mostly by Tasmanites algae (Fig. 6A), lamalginite (Fig. 6B), bituminite, and rarely Botryococcus forms. Liptinite macerals are also represented by sporinite (Fig. 6D) and less frequent liptodetrinite. The huminite group (5.1% vol., on average) (Fig. 6C, D, Tab. 3) occurs mainly as ulminite and detrohuminite. Semifusinite, fusinite and inerdodetrinite represent macerals from the inertinite group (1.5% vol., on average). In two outcrop samples, organic matter accounts for about 18.9% vol.

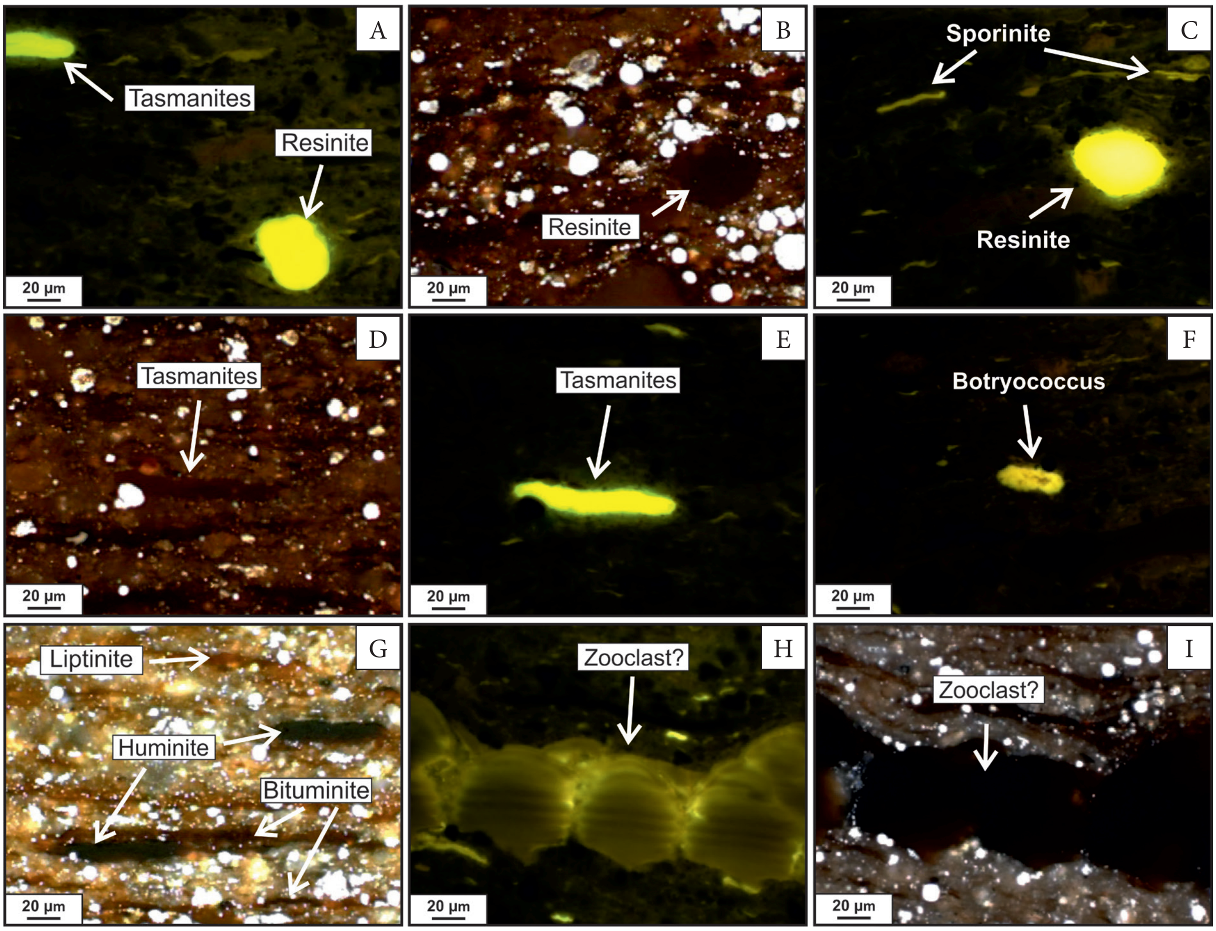

Fig. 5. *Photomicrographs of the organic matter dispersed in the Menilite Shales from the Iwonicz-Zdrój–Rudawka Rymanowska Fold, the D-1 borehole, shallow part. Explanation: reflected white light: sample No. 1, depth 430 m (B, D), sample No. 3, depth 432 m (G), sample No. 4, depth 433 m (I); fluorescent light: sample No. 1, depth 430 m (A, C, E), sample No. 2, depth 431 m (F), sample No. 4, depth 433 m (H). All photomicrographs were taken with oil immersion objective 50×*

Table 3
The results of the organic matter composition [% vol.] for the Menilite shales analysed

Iwonicz-Zdrój–Rudawka Rymanowska Fold

D-1 borehole shallow well section

Sample No.	Hum	Alg		Ld	Sp	Re	Bt	ΣLipt	Sf	Fu	ΣIner	AOM	Zst	Min. mat
		Tas	Oth											
1	1.4	2.9	2.1	1.8	0.1	0.1	2.1	9.1	0.2	–	0.2	–	–	89.3
2	2.0	4.1	3.4	1.8	0.2	–	3.2	12.7	0.5	0.2	0.7	35.0	0.9	48.7
3	3.1	4.8	2.8	2.7	–	0.8	2.8	13.9	0.9	0.1	1.0	–	–	82.0
4	2.1	5.1	2.7	2.4	–	–	4.0	14.2	1.3	0.5	1.8	–	0.7	81.2

Bóbrka–Rogi Fold

Outcrop samples

Sample No.	Hum	Alg			Bt	Sp	Ld	ΣLipt	Sf	Fu	Id	ΣIner	Min. mat
		Tas	Bot	Lam									
5	5.2	2.9	–	2.1	1.8	3.1	1.9	11.8	1.0	0.3	0.6	1.9	81.1
6	4.9	3.9	0.8	3.0	1.0	1.9	1.8	12.4	0.9	–	0.2	1.1	81.6

***Table 3** cont.*

D-1 borehole deeper well section								
Sample No.	**Vit**	**Alg**	**Bt**	**Ld**	**ΣLipt**	**Iner**	**SB**	**Min. mat**
7	2.0	0.8	0.9	1.0	2.7	0.5	1.7	93.1
8	2.1	0.4	0.3	0.9	1.6	0.5	1.0	94.8
9	2.1	0.5	0.5	0.8	1.8	0.8	2.2	93.1
10	2.9	0.5	0.4	0.9	1.8	0.5	2.8	92.0
11	1.6	0.1	1.0	0.8	1.9	0.5	2.9	93.1

Explanations: Hum – huminite; Alg – alginite; Tas – tasmanite; Bot. – *Botryococcus braunii*; Lam – lamalginite; Oth – other alginite components; Ld – liptodetrinite; Sp – sporinite; Re – resinite; Bt – bituminite; ΣLipt – sum of liptinite macerals; Sf – semifusinite; Fu – fusinite; ΣIner – sum of inertinite macerals; AOM – amorfous organic matter mix with mineral matter; zst – zooclast; Min. mat – mineral matter; SB – solid bitumen.

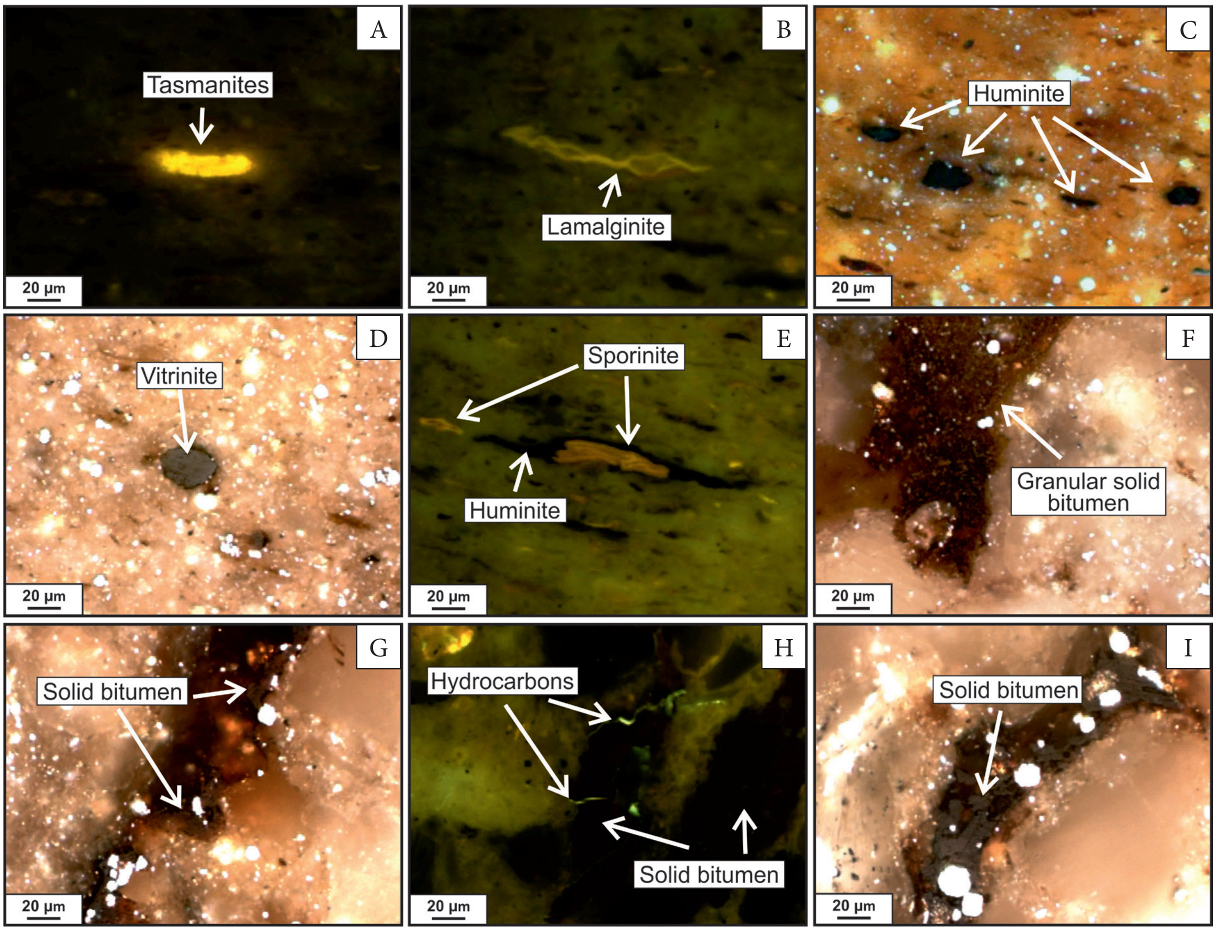

***Fig. 6.** Photomicrographs of organic matter dispersed in Menilite Shales from the Bóbrka–Rogi Fold, outcrop samples, and the D-1 deeper well section. Explanation: reflected white light: sample No. 6, outcrop (C), sample No. 7, depth 4,301 m (E), sample No. 11, depth 4,305 m (F, G, I); fluorescent light: sample No. 5, outcrop (A), sample No. 6, outcrop (B, D), sample No. 11, depth 4,305 m (H). All photomicrographs were taken with oil immersion objective 50×*

In the samples of the Menilite Formation from the deeper part (4,300 m), the organic matter is represented by macerals from the vitrinite, liptinite, and inertinite groups. The vitrinite (2.1% vol., on average, ranges from 1.6 to 2.9%) (Tab. 3) occurred as grain particles (Fig. 6E) or leanses. The primary macerals of the liptinite group (2.0% vol., on average, ranges from 1.6 to 2.7%) (Tab. 3) are alginite and liptodetrinite. The secondary thermal maturity product of liptinite group is solid bitumen (2.1% vol., on average, range from 1.0 to 2.9%) (Fig. 6G–I). The solid bitumen is represented by homogenous (Fig. 6I) and granular (Fig. 6F) forms (Landis & Castaño 1995). The observed inertinite macerals (0.6% vol. on average, ranges from 0.5 to 0.8%) (Tab. 3) are fusinite, semifusinite, and inertodetrinite. In one sample (No. 11, depth 4,305 m), the evidence for liquid hydrocarbons (thin green film impregnated in fissures of solid bitumen) was noticed (Fig. 6H).

Organic matter in the analyzed samples from the deeper well section of the D-1 borehole accounts for 5.7 to 8.5% (mean 7.34% vol.).

All photomicrographs were taken with oil immersion objective 50×.

DISCUSSION

Iwonicz-Zdrój–Rudawka Rymanowska Fold

The mean values of VR_o measurements in the samples from the Iwonicz-Zdrój–Rudawka Rymanowska Fold are about 0.40% R_o, typical for immature organic matter to hydrocarbon generation. However, the organic components dispersed in the discussed sedimentary rocks are typical for oil and gas-prone organic matter. In particular, tasmanites and bituminite forms are characterized by their high hydrocarbon potential when occuring in high amounts (e.g. Hunt & Freeman 1996, Hackley et al. 2017, and references therein). The OM dispersed in the analyzed samples indicates a mixed paleoenvironment. Tasmanites are characteristic for marine planktonic algal (Hackley et al. 2016), *Botryococcus* for freshwater to brakish algal (Tyson 1995), and huminite indicate terrestrial sediments. However, the highly oil-prone marine algae known as Tasmanites are predominant (Tab. 3). The OM in the Menilites from the shallow part of the D-1 well section is closely related to type II kerogen (Fig. 7). The microscopic analysis of the organic matter from IRF presented in this study is coherent with previous geochemical analyses. The T_{max} temperature from Rock-Eval pyrolisis reported by Köster et al. (1998) (avg. 430°C) and Ziemianin (2017) (avg. 425°C) generally confirm the VR_o from this study (avg. VR_o = 0.41 %). High Hydrogen Index (avg. 550 mg HC/g TOC) measured by Köster et al. (1998) and Ziemianin (2017) (avg. 420 mg HC/g TOC) indicates the dominant Type II kerogen. The predominance of alginite macerals has been also confirmed by means of maceral composition from Zieminanin (2017).

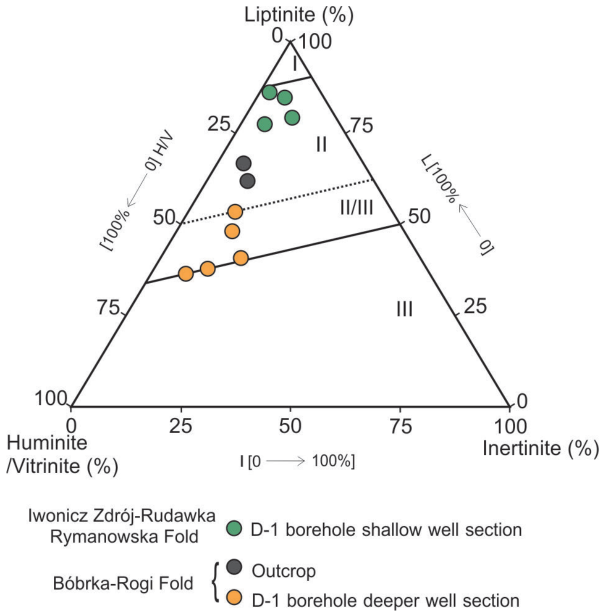

Fig. 7. *Determination of kerogen type with microscopic observations. Ternary plot of maceral composition: H – huminite, V – vitrinite, I – inertinite, L – liptinite; I, II, II/III, III – kerogen types (modified after Cornford 1979)*

Bóbrka–Rogi Fold

Huminite reflectance measurements in the outcrop samples from the Bóbrka–Rogi Fold reach the value of 0.36% VR_o and are immature with respect to hydrocarbon generation of organic matter. The VR_o results (Tab. 2) seem to be close to the VR_o values reported by Ziemianin (2017) taken from the Bóbrka outcrop samples. In addition, T_{max} values from Curtis et al. (2004) and Ziemianin (2017) indicate immature organic matter in BRG samples. Similar to the samples from the shallow part of the D-1 well section, the main components of OM in the analyzed samples are macerals from the liptinite group with the main constituent being alginite. The maceral composition of outcrop samples indicates II type kerogen. This statement is confirmed by the high hydrogen index by Curtis et al. (2004) and Ziemianin (2017) (avg. 470 mg HC/g TOC and 450 mg HC/g TOC, respectively). Some differences have been noticed in maceral composition compared to Ziemianin's (2017) study. In the presented investigation, a diversity of organic matter is reported (Tab. 3), while Ziemianin (2017) distinguished mainly bituminite, alginite, and liptodetrinite. However, as was reported by Köster et al. (1998), the Menilite shales are very inhomogenous in terms of their geochemical composition and display strong facies variation, even if taken from near-distant outcrops.

The thermal maturity of the analyzed samples of the Menilite Formation from the D-1 well section from a depth of about 4,300 m was determined based on vitrinite and solid bitumen reflectance. The solid bitumen dispersed in the discussed sedimentary rocks is probably the intermediate product between kerogen and oil originated during the oil generation process, which was recognized before in the Menilite Formation from the Skrzydlna Thrust Sheet (Waliczek et al. 2019). This is presumably an indigenous, pre-oil solid bitumen type (Curiale 1986) Its occurrence in the source rocks indicates the presence of mature organic matter capable of generating liquid hydrocarbons (Cardott et al. 2015). According to the new solid bitumen classification proposed by Sanei (2020), this secondary organic matter should be termed as primary-oil solid bitumen. Moreover, the hydrocarbon generation process was documented by means of the evidence of fluorescing hydrocarbons in one of the analyzed samples (Fig. 6H). The values of VR_o and BR_o (Tab. 2, Fig. 4) confirm that the organic matter dispersed in the analyzed samples is mature in terms of hydrocarbon generation and is associated with the main stage of the "oil window" (Hackley et al. 2017). The reflectance measurements from the deeper D-1 well section are coherent with a T_{max} from the Rock-Eval analysis presented in previous studies (Matyasik et al. 2015, Waliczek et al. 2021). In a few sample bimodality of vitrinite reflectance value is seen (Fig. 4). The lower values of vitrinite reflectance might have been caused by the impregnation of liptinite maceral. Sample No. 4 from IRF shows a similar effect (Fig. 3).

The ternary plot of maceral composition (Fig. 7) indicates mixed II/III and III/II kerogen type for samples from a deeper section of the D-1 borehole. However, the plot was established to exclude solid bitumen content since it is not a maceral but a secondary product of organic matter (Mastalerz et al. 2018). The Rock-Eval pyrolysis published for the D-1 borehole deeper section (Waliczek et al. 2021) points out a type III kerogen with a very low hydrogen index and high oxygen index. This contradiction between the geochemical and petrological analysis could have been caused by the occurrence of solid bitumen, which might affect the original kerogen characteristics interpreted by means of the Rock-Eval analysis. Another reason could be a presence of carbonates. As concluded in Baudin et al. (2015), poorly crystalized carbonate might increase hydrogen index (OI) value or lower values of hydrogen index determined from Rock-Eval pyrolysis.

To indicate the precursor maceral for solid bitumen, an average maceral composition and secondary product for Bóbrka–Rogi Fold was counted (Fig. 8). As already observed, the average percentage volume of vitrinite (huminite, if <0.5% VR_o, ICCP 1998) and inertinite did not change greatly in samples from the deeper part of D-1 borehole, compared to the average percentage volume of organic matter in the outcrop samples. The significant changes (a more than twofold reduction) are observed for liptinite macerals, with the percentage volume of alginite maceral decreased from 34.1 to 6.8%. The content of solid bitumen (vol. %) in samples from the deeper part of D-1 well is 30.6%. Analyzing the changes in maceral composition, it can be assumed that a potential precursor organic component for solid bitumen in the Menilite shale samples is mainly represented by alginite maceral. The absence of sporinite in the borehole samples may also suggest the conversion of this component into solid bitumen. However, the total conversion of this maceral into a secondary product in the thermal maturity expressed by VR_o = 0.80% seems to be unexemplified, as sporinite is composed of very resistant material (Taylor et al. 1998). More possible is some differentiation in the sedimentation regime during the Oligocene, in the Silesian basin (Köster et al. 1998). The higher amount of huminite and sporinite in the outcrop samples (compared to Menilite from IRF) is possibly related to the greater input of terrestrial organic matter.

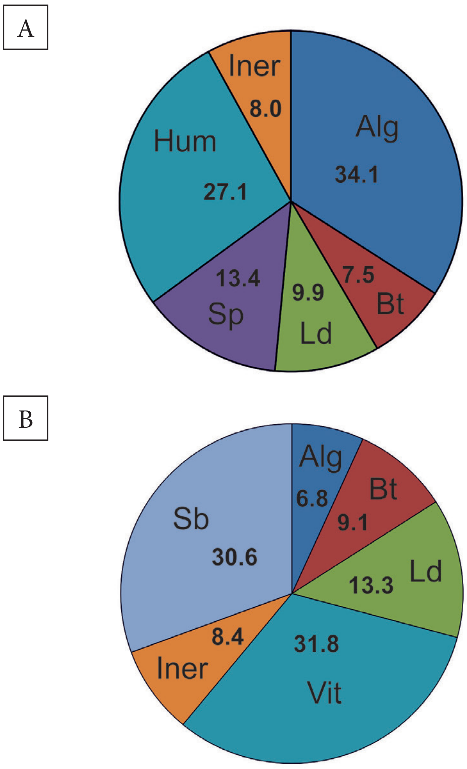

Fig. 8. *An average maceral composition and secondary organic matter for samples from Bóbrka–Rogi Fold: A) an average values of percentage volume organic components for two samples from outcrops; B) an average percentage volume values of organic and secondary organic matter components for five samples from a deeper section of the D-1 borehole. Explanations: Alg – alginite, Bt – bituminite, Ld – liptodetrinite, Hum – huminite, Vit – vitrinite, Sp – sporinite, Iner – inertinite, Sb – solid bitumen*

It can be suggested that the OM dispersed in the outcrop of the Menilite Formation from the Bóbrka–Rogi Fold was the starting material for the thermally matured sediments from the deeper section of the D-1 borehole (Fig. 2). During thermal maturation, its maceral composition changed, with the primary organic matter of mostly alginite (Fig. 8) decreasing and being transformed into a secondary product such as solid bitumen, and finally hydrocarbons.

CONCLUSIONS

- Based on the huminite reflectance values, the OM dispersed in outcrop samples and samples from IRF is thermally immature with respect to hydrocarbon generation. The analyzed successions are dominated by oil-prone macerals from liptinite group characteristic for type II kerogen.
- The organic matter from the Menilite Formation from the BRF, the deeper part D-1 well section (4,300 m), is thermally mature with respect to hydrocarbon generation. The presence of indigenous, solid bitumen and evidence of hydrocarbons confirms that the hydrocarbon generation process has started in the sedimentary rocks analyzed.
- The precursor maceral to solid bitumen occurring in the deeper part of D-1 well section is likely to be an alginite maceral of the liptinite group. In samples from the deeper part of the D-1 borehole, compared to the average percentage volume of organic matter in outcrop samples, alginite maceral decreased from 34.1 to 6.8% and the content of solid bitumen (vol. %) is 30.6%

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