Konrad Ziemianin, Paweł Brzuszek, Tomasz Słoczyński

Oil and Gas Institute – National Research Institute

Leszek Jankowski

Polish Geological Institute – National Research Institute, Carpathian Branch in Cracow

Dispersed organic matter in shales from Menilite Beds within Polish Outer Carpathians – preliminary diagnosis

Samples of shales from Menilite Beds from different units were analyzed (Skole, Silesian, Dukla, Magura and Boryslav–Pokuttya Units). The aim of this paper was to present the diversity in organic matter type, maturity and composition between different units and within each unit. Obtained results revealed that collected shales share similar petrographic composition of organic matter, dominated by bituminite, alginite and vitrinite (present in different proportions). The maturity (determined on the basis of both T_{max} and R_o parameters) varies from immature to late "oil window" phase or even to early "gas window". The content of organic matter changes in a wide range – obtained TOC values are in the range of below 1.5% up to 13%. Such a diversity in results revealed the need for more detailed field work, focusing on collecting samples in relation to both local and regional geology.

Key words: Menilite Beds, shale, organic matter, alginite, vitrinite.

Rozproszona materia organiczna w łupkach z warstw menilitowych Karpat Zewnętrznych – wstępna charakterystyka

Przebadano próbki łupków z warstw menilitowych z różnych jednostek w obrębie Karpat Zewnętrznych (jednostka skolska, śląska, węglowiecka, dukielska, magurska oraz borysławsko-pokucka). Celem niniejszej pracy było przedstawienie zróżnicowania materii organicznej (pod kątem jej zawartości w skale, rodzaju i dojrzałości) pomiędzy próbkami z różnych jednostek, a także w obrębie każdej z nich. Uzyskane wyniki ujawniły, iż badane próbki łupków menilitowych charakteryzują się zbliżonym składem petrograficznym materii organicznej, zdominowanym przez alginit, bituminit oraz witrynit (obecnymi w różnych proporcjach). Jej dojrzałość (oszacowana na podstawie wyników pirolizy Rock-Eval oraz pomiarów refleksyjności witrynitu) zmienia się od niedojrzałej do późnej fazy „okna ropnego"/wczesnej fazy „okna gazowego". Udział materii organicznej w badanych łupkach jest zmienny w szerokim zakresie – wartości TOC mieszczą się w przedziale od 1,5% do 13%. Różnorodność uzyskanych wyników ujawniła potrzebę bardziej zaawansowanych prac terenowych, skupionych na poborze próbek z jednoczesnym uwzględnieniem sytuacji geologicznej zarówno lokalnej (w skali odsłonięcia), jak również regionalnej.

Słowa kluczowe: warstwy menilitowe, łupek, materia organiczna, alginit, witrynit.

Introduction

This paper deals with dispersed organic matter in shales from Menilite Beds localized in the Polish part of the Outer Carpathians. Characteristics of both its composition and maturity in the aspect of spatial variability is extremely important, because menilite shales are considered to be very important (if not the most important) source rocks for hydrocarbons in the Outer Carpathians. The paper is an introduction to the topic, which will be extended in further, more detailed publications.

The results presented in this study will be used to develop the best strategy for collecting samples, as they give a general view of the nature of changes in organic matter (both in terms of composition and maturity) and therefore provide information of what can be expected in different parts of the studied area.

The paper presents the results of analyses of geochemical (Rock-Eval pyrolysis) and micro- and macroscopic investigations of 17 samples collected from outcrops within Units: Skole, Silesian (with Węglówka Unit), Magura, Dukla and Boryslav–Pokuttya. Naturally, such a large study area cannot be characterized fully with such a small amount of samples, however, the results allow to make general conclusions that can be treated as a good base for more detailed work in the future.

Menilite Beds as a source formation for hydrocarbons in the Outer Carpathians

Menilite Beds is one of the most interesting formation in the Carpathians, both in terms of their diverse lithology and occurrence, and also because of the high content of dispersed organic matter, its composition and maturity. Mentioned features have a huge impact on considering these sediments as potential source rocks. That is a reason why menilite shales are the topic of many geological and geochemical papers [2, 6–10, 12, 13, 16–19, 22, 23].

Menilite Beds were first described by Glocker in Moravia and referred to as "rocks with menilite" [3, 20]. These sediments are developed mainly as clay rich and marly shales, with characteristic cleavage and dispersed organic matter content that may excess 20% [1, 9, 15]. In the area of the Polish Outer Carpathians Menilite Beds begin the final stage of flysch sedimentation. The sediments belonging to this formation are commonly found in the Skole, Silesian, Weglowka and Dukla Units and rarely in the most southern part of the Magura Unit. They are also present in the Grybow Unit, occurring in tectonic windows within the Magura Unit [20]. The thickness of menilites is variable and ranges from 100 m in the Silesian Unit to 500 m in the Skole Unit [2]. Paleontological research showed that the bottom of menilites is isochronous, while the top part of the formation is variable in time – sedimentation was ended first in the southern part of the basin, while in northern parts it lasted longer [11, 20]. Paleobathymetry is considered to be extremely variable – from shallow to deep water environments [6, 14].

Menilite shales are also heterogeneous in terms of geochemical parameters – with a wide range of TOC values (from less than 1% to over 20%) and a different level of maturity (from immature, through the stage of "oil window" to the early stage of "gas window"). Most often type II kerogen is described, with minor contents of types III and I [8].

Samples

Samples from 17 outcrops were collected (fig. 1), one sample from each outcrop was obtained. The localities of outcrops were chosen in a way, that they could represent many tectonic units, especially the Skole, Silesian and Dukla Units. After field work, collected samples represented 5 tectonic units: Skole (5 samples), Silesian (with Węglówka) (5 samples), Dukla (3 samples), Magura (2 samples) and Boryslav–Pokuttya (2 samples). These were mostly dark grey and gray, often silicified, calcareous or noncalcareous, clay rich shales. The map of outcrops localizations is given in fig. 1.

Methods

The results were obtained with the use of optical microscopy and the Rock-Eval pyrolysis. For optical investigations microscopes: Nikon Opthiphot, Zeiss Axioplan and Nicon Eclipse were used.

Samples were analysed using both reflected (polished samples) and transmitted light (isolated kerogen) and also under fluorescence mode. Magnifications from 200 to 500x were used. Vitrinite reflectance (R_o) was measured using Zeiss Axioplan microscope. Proportions between different macerals were obtained only on the basis of microscopic observations – no quantitative analysis was performed for these samples.

The Rock-Eval pyrolysis was performed with the Rock-Eval-6 standard model.

From all the samples kerogen was isolated, using standard procedure – sample undergoes HCl and HF treatment to remove carbonates and silicates, and then organic matter is separated from heavy minerals using high density liquid (CdJ_2, density 2.2 g/cm^3). The final stage is removing the finest fraction of kerogen by sieving (15 µm).

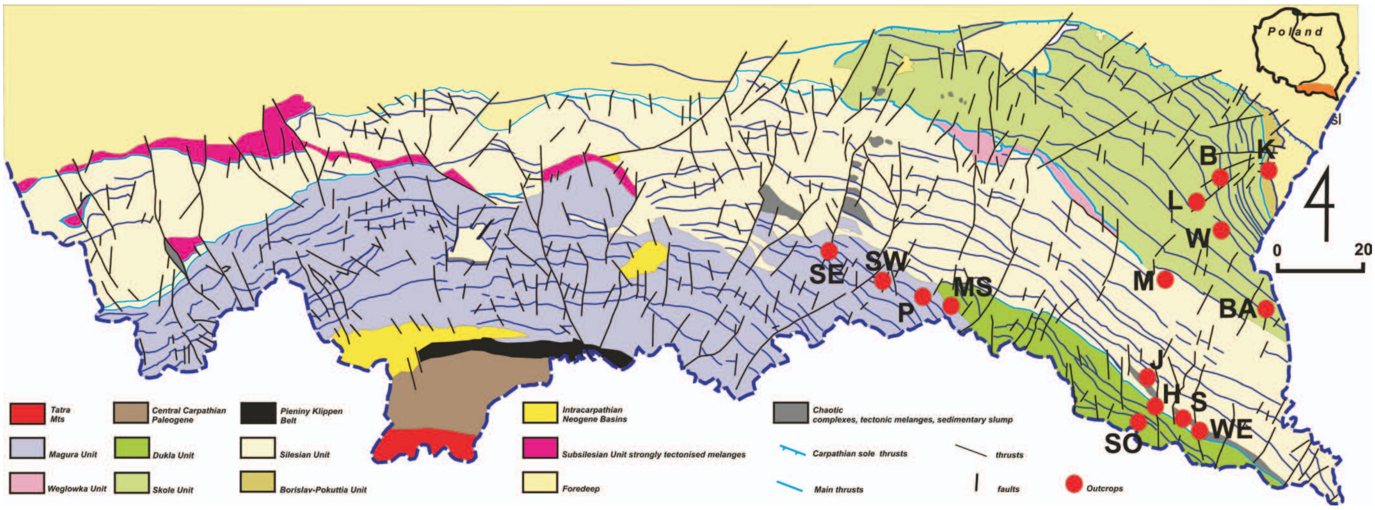

Fig. 1. Geological map of study area with the localization of outcrops [4, 5]

Localization of outcrops: K – Kniażyce-1 and 2, B – Bircza, L – Leszczawa Górna-1 and 2, W – Wojtkowa, M – Monasterzec, BA – Bandrów, J – Jabłonki, H – Habkowce, S – Strzebowiska, WE – Wetlina, SO – Solinka, MS – Mszana, P – Polany, SW – Świątkowa, SE – Sękówka

Results

Analyzed samples represent a wide range of lithological diversity of Menilite Beds. These rocks are mostly dark grey and dark brown, often silicified and calcareous (rarely noncalcareous), clay rich shales, splitting into parts around 1 cm thick, sometimes with visible yellow or rusty signs of weathering. In mineralogical composition clay minerals dominate. Carbonates, quartz and feldspars are also present, but in smaller amounts. Dispersed organic matter is always present, but TOC values are variable and reach from 1% to 13% (average 4.75%).

Petrographic composition of dispersed organic matter is dominated by bituminite, alginite and vitrinite, which occur in different proportions. Other macerals like liptodetrinite or inertinite are less frequently or rarely observed. These observations are confirmed by investigations of isolated kerogen, which is developed as amorphous matter, exhibiting fluorescence (algal-derived material) or showing its lack (terrestrial-derived organic matter). Maturity level ranges from immature, through all stages of "oil window" to early stage of "gas window". Measured reflectance of vitrintie is in the range from 0.24 to 1.33% (average 0.75%), while T_{max} parameter, obtained from the Rock-Eval pyrolysis, reaches from 400°C to 478°C (average 430°C). Detailed results of the Rock-Eval pyrolysis are shown in table 1, 2 and in figures 2 and 3.

All analyzed samples are characterized by a similar composition of kerogen (oil-prone type I/II, represented by bituminite and alginite, and gas-prone type III represented by vitrinite). However, significant changes can be noticed both in the degree of maturity of the organic matter and its content in rock (tab. 1, 2). This means that Menilite Beds are certainly not homogeneous in terms of hydrocarbons generation potential. Hydrocarbons generation and thermal history must have proceeded to different stage in different parts of the basin. As a result of this situation, overall interpretation is rather complex and more detailed field work is needed to solve it.

Skole Unit

Within Menilite Beds belonging to the Skole Unit, 5 samples were collected during the filled work from outcrops: Leszczawa Górna (2 outcrops), Wojtkowa, Bandrów and Bircza (fig. 1). These are very similar lithologically rocks – dark brown or dark grey, silicified, noncalcareous (except the sample from Bircza outcrop, which is calcareous and contains 30% vol. of carbonates), clay rich shales, splitting into very small (few mm thickness) plates. They all exhibit yellow color related to the weathering process.

In organic matter composition, bituminite and alginite dominates, although vitrinite is also present and often been noticed (samples from Leszczawa Górna and Bircza outcrops). In case of samples from Wojtkowa and Bandrów, vitrinite is less frequent. The isolated kerogen is dominated by fluorescent amorphous organic matter which is algal derived and exhibits medium to strong fluorescence.

On the basis of the Rock-Eval analysis (tab. 1, 2), two groups of samples can be distinguished. The first one is composed of samples from the Leszczawa Górna and Bandrów outcrops and has HI value in range from 360 to 456, which indicates type II kerogen. The values of TOC for this group of samples ranges from 6.37% to 12.95%, which is relatively high, compared to all other samples. The T_{max} parameter is in the range from 410°C to 423°C and corresponds to lower maturity of organic matter, while the vitrinite reflectance (R_o = 0.63÷0.70%) is suggesting the early oil window [21]. The second group of samples (from the Bircza and Wojtkowa outcrops) differs from the first one and has much lower HI values, which range from 156 to 209, which is typical for organic matter belonging to type III kerogen. These samples, as compared to the first group, also have high TOC values (4.29÷7.74%). Values of the T_{max} parameter are similar, in range of 410÷419°C, which imply on low maturity of these samples. Some changes are observed in vitrinite reflectance, which is 0.70% for sample from the Bandrów outcrop (early oil window) and 1.09% for sample from the Bircza outcrop (late oil window).

To sum up, samples from Skole Unit have both type II and type III kerogen (fig. 2, 3), represented by bituminite, alginite (fig. 4) and vitrinite, present in different proportions, mostly dominated by bituminite exhibiting fluorescence. The content of organic matter is high, which is evidenced by TOC values ranging from 4.29% to 12.95% (average is around 8%). It is, for most samples investigated, immature and only the sample from the Bircza outcrop exhibits a higher level of maturity. No visible geographical trends in the diversity of HI and TOC parameters can be noticed.

Silesian and Węglówka Units

Within the Silesian and Węglówka Units, samples from 5 outcrops were analysed: Jabłonki, Wetlina, Monasterzec, Strzebowiska and Mszana (fig. 1). Samples from these outcrops are mostly grey or dark grey, dark brown or black, calcareous (samples from outcrops: Jabłonki, Wetlina, Mszana) or noncalcareous (samples from outcrops: Monasterzec and Strzebowiska) clay rich shales, splitting into plates of up to 1 cm thick, sometimes with yellow colors indicating weathering.

In organic matter composition 3 petrographic components are most common: bituminite, alginite and vitrinite. Bituminite generally dominates. Proportions between alginite and vitrinite are changing. In samples from the Mszana and Monasterzec outcrops alginite content is higher than vitrinite, while opposite is in samples from Jabłonki, where vitrinite seems to be present in larger amount than alginite. In the Wetlina and Strzebowiska outcrops, organic matter content is generally very low, and both alginite and vitrinite are very rare. In isolated kerogen, amorphous organic matter dominates. It exhibits fluorescence (strong – Mszana, medium – Monasterzec), which indicates aquatic origin, or is lacking fluorescence, which may suggest terrestrial origin (Jabłonki, Wetlina, Strzebowiska).

From the geochemical point of view 2 groups of samples can be distinguished (tab.1, fig. 2, 3). The first group is composed of samples from the western part of the study area, from the outcrops of Mszana and Monasterzec. These samples have HI values ranging between 400 and 625, which is related to type II kerogen. The TOC values within this group range from 3.50% to 3.65%, which seems to be typical for samples from the Silesian/Węglówka Units, but it is also much lower than TOC values for samples from the Skole Unit. The T_{max} parameter indicates an immature stage of maturity, reaching values 414÷427°C. This is confirmed by vitrinite reflectance measurements (R_o = 0.59÷0.62%), which suggest an immature/early oil window stage. The second group of samples contains samples from Jabłonki, Wetlina and Strzebowiska. These samples can be characterized by lower HI values, ranging from 41 to 109, which corresponds to type III kerogen. They also have TOC values changing in quite a wide range (1.99% for sample from Wetlina, 3.09% for sample from Strzebowiska and 6.91% for sample from Jabłonki). The T_{max} parameter is higher than in the first group and reaches 441÷465°C, indicating the main and late phase of oil generation (oil window). This is, at least partly, confirmed by R_o values, which are 1.33% (Jabłonki) and 1.16% (Wetlina) – suggesting the late oil window or even early gas window. Only the sample from Strzebowiska shows a lower value of R_o (0.54%). and does not correlate with T_{max}, indicating the immature/early oil window phase. This can be explained by the imperfect vitrinite grains, which are often small, heterogeneous and may affect the results of the reflectance measurements.

To sum up, in the case of samples from the Silesian and Weglowka Units some changes in composition of the organic matter (alginite and vitrinite proportions – from common alginite and rare vitrinite to common vitrinite and rare alginite), its content (TOC values from 1.99% to 6.91%) and maturity (from immature, through the early and main oil window to late oil window or early gas window) can be evidenced. Considering the small amount of samples any clear geographical trends in theses changes are not possible to be indicated, but some very general directions can be suggested. It seems that samples from the western part of the Silesian and Węglówka Units (Mszana, Monasterzec) have a higher content of alginite and at the same time this organic matter is less mature than samples from the eastern part of the study area (Jabłonki, Strzebowiska, Wetlina) for which a higher content of vitrinite and also higher maturity level is observed.

Dukla Unit

Within the Dukla Unit 3 samples were collected during field work, from outcrops: Habkowce, Świątkowa and Solinka (fig. 1). These shales are grey and dark grey, calcareous (Świątkowa) or noncalcareous (Habkowce, Solinka), rich in clay minerals.

In organic matter composition, bituminite, alginite and vitrinite are present. Vitrinite seems to occur in higher content than alginite, which is very rare. These observations were confirmed by investigations of isolated kerogen, which is dominated by nonfluroescent (terrestrial derived), amorphous organic matter.

Microscopic observations can be convincingly correlated with geochemical results (fig. 2, 3, tab. 1, 2). And so, the increased content of vitrinite results in low HI values, which are characteristic for type III kerogen (gas-prone) and range from 52 (Solinka) to 135 (Habkowce). The values of the T_{max} parameter are from 442°C to 478°C, which indicates both the early (Świątkowa, Habkowce) and late phase of the oil window or the early phase of the gas window (Solinka). Vitrinite reflectance also suggest higher maturity of organic matter for samples from Habkowce and Solinka (R_o = 1.02÷1.05%, which corresponds to the late oil window). For sample from Świątkowa outcrop this parameter suggest an immature/early oil window phase (R_o = 0.55%). The content of the organic matter is generally lower than in other units, with TOC as low as 0.88÷214%.

Generally, samples from the Dukla Unit are relatively homogeneous in terms of both organic matter composition (with higher content of vitrinite and only traces of alginite) and its content, which is low. On the basis of 3 samples it is difficult to draw any geographical trends, but it seems that the sample form the western part of the study area (Świątkowa) is less mature, while samples from the eastern part (Solinka, Habkowce) show higher maturity levels. This situation is quite unusual, because the Świątkowa outcorp is located in a tectonic window within the Magura Unit, which in composed of sediments that are generally immature.

Boryslav–Pokuttya Unit

Within the Boryslav–Pokuttya Unit samples from 2 outcrops (fig. 1) were collected (Kniażyce-1 and 2). These shales are dark gray and dark brown, noncalcareous, silicified, rich in clay minerals, splitting into thin fragments of a few mm thick or showing a high level of disintegrity. In the case of the sample from the Kniażyce-2 outcrop, weathering signs are visible (yellow color).

In organic matter composition bituminite and alginite dominate over vitrinite. This is confirmed by the analysis of isolated kerogen, which is dominated by amorphous organic matter, showing strong (Kniażyce-2) or medium fluorescence (Kniażyce-1).

The results of geochemical analysis (tab. 1, fig. 2, 3) show that these samples have both similar and different features. For example HI parameter values are different with 54 for the Kniażyce-1 and 373 for the Kniażyce-2, which corresponds to type III (Kniażyce-1) and type II (Kniażyce-2) kerogen. On the other hand, values of the T_{max} parameter are similar, indicating that these samples are immature (400°C for Kniażyce-1 and 414°C for Kniażyce-2). Values of measured vitrinite reflectance are also similar (0.73% for Kniażyce-1 and 0.86% for Kniażyce-2), suggesting the main oil window phase. The content of organic matter is also similar – TOC values range from 2.26% (Kniażyce-2) to 3,43% (Kniażyce-1).

For obvious reasons, any geographical trends are not possible to be drown. However, it is important to state that these samples are similar from a geochemical point of view (content and level of maturity) and at the same time they consist of organic matter belonging to different types of kerogen. It may suggest that these samples might have had the same thermal history, but paleobathymetry in the basin and conditions during sedimentation might have been diversified.

Magura Unit

Within the Magura Unit 2 samples were collected for analysis, from the outcrops Sękówka and Polany (fig. 1). These shales are grey, calcareous (Polany) or noncalcareous (Sękówka), rich in clay minerals, splitting up into fragments of up to 1 cm thick.

In organic matter composition bituminite dominates, but alginite and vitrinite are also present. In sample from Polany outcrop alginite is more common than vitrinite, in Sękówka the situation is opposite (fig. 5). In isolated kerogen amorphous organic matter dominates and shows only weak fluorescence (algal derived, Polany) or is nonfluorescent (terrestrial derived, Sękówka).

From the geochemical point of view, only sample from Sękówka outcrop can be interpreted (tab. 1). The T_{max} and HI results for sample from Polany outcrop does not seem to be reliable. Firstly, T_{max} is very high, with value of 519°C, which would suggest main gas phase. If that would be true, higher values of vitrinite reflectance (around 1÷3%) should be expected, while obtained value of this parameter is much lower and equals 0÷24%, which suggests very immature phase. The result of vitrinite reflectance seems to be more reliable, as similar result was obtained for sample from Sękówka (0.28%). Also obtained HI value is around 0 cannot be correct, due to presence of algal material in the sample. The wrong result may be a consequence of a very low content of organic matter in the sample. For second sample (Polany) the obtained results are more reliable – it is very rich in organic matter (TOC = 8.99%), which is, however, immature (T_{max} = 422°C, R_o = 0.28%). The HI is 283 and corresponds to type II/III kerogen.

On the basis of the obtained data, it is possible to state, that samples from the Magura Unit are similar in terms of maturity (immature), but differ in both types of organic matter (alginite to vitrinite relations) and its content (TOC from below 1.5% to around 9%). Naturally, due to the small amount of samples, all these statements are very preliminary.

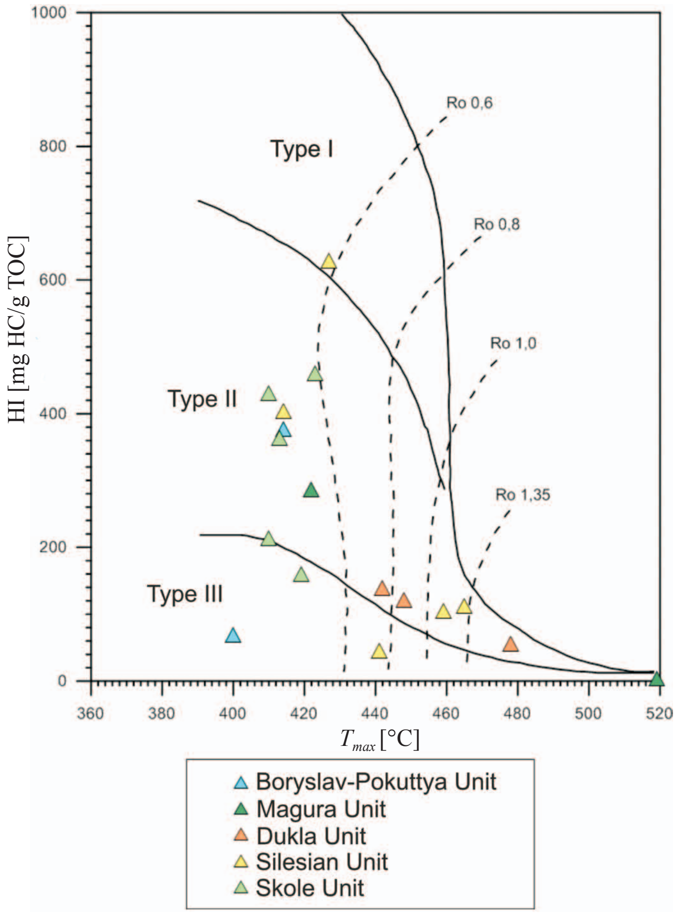

Fig. 2. HI vs. T_{max} diagram for analyzed samples

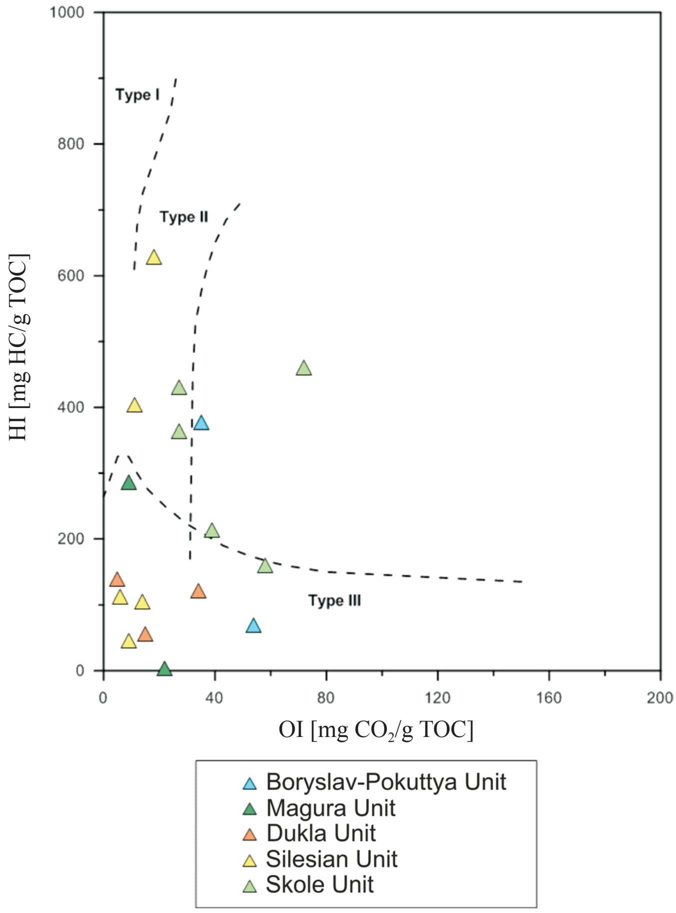

Fig. 3. HI vs. OI diagram for analyzed samples

Table 2. Comparison of geochemical parameters and vitrinite reflectance between samples from different units

Unit	TOC [% wag.]	HI [mg HC/g TOC]	T_{max} [°C]	R_o [%]
Skole	4.29÷12.95 (8.16*)	156÷456 (321)	410÷423 (415)	0.63÷1.09 (0.76)
Silesian	1.99÷6.91 (3.82)	41÷625 (255)	414÷465 (441)	0.54÷1.33 (0.85)
Dukla	0.88÷2.14 (1.69)	52÷135 (102)	442÷478 (456)	0.55÷1.05 (0.87)
Magura	1.18÷8.99 (5.09)	283	422	0.24÷0.28 (0.26)
Boryslav–Pokuttya	2.26÷3.43 (2.85)	65÷373 (219)	400÷414 (407)	0.73÷0.86 (0.80)

* Average value is given in brackets.

Table 1. Results of the Rock-Eval pyrolysis and vitrinite reflectance measurements

Unit	Localization	T_{max} [°C]	S1 [mg HC/g rock]	S2 [mg HC/g rock]	S3 [mg CO2/g rock]	PI [S1/(S1 + S2)]	PC [%]	RC [%]	TOC [%]	HI [mg HC/g TOC]	OI [mg CO2/g TOC]	Total MINC [%]	R_o [%]
Skole	Leszczawa Górna-1	410	0.97	55.30	3.47	0.02	4.96	7.99	12.95	427	27	0.36	0.63
	Wojtkowa	410	0.27	16.21	3.01	0.02	1.55	6.19	7.74	209	39	0.28	0.73
	Leszczawa Górna-2	423	0.80	43.02	6.82	0.02	3.96	5.47	9.43	456	72	0.43	0.67
	Bandrów	413	0.20	22.96	1.73	0.01	2.08	4.29	6.37	360	27	4.84	0.70
	Bircza	419	0.08	6.69	2.49	0.01	0.70	3.59	4.29	156	58	0.33	1.09
Silesian and Węglówka	Jabłonki	465	0.96	7.53	0.43	0.11	0.73	6.18	6.91	109	6	3.75	1.33
	Wetlina	459	0.59	2.01	0.27	0.23	0.26	1.73	1.99	101	14	0.78	1.16
	Monasterzec	414	0.23	14.52	0.39	0.02	1.25	2.38	3.63	400	11	0.11	0.62
	Strzebowiska	441	0.11	1.27	0.27	0.08	0.13	2.96	3.09	41	9	0.09	0.54
	Mszana	427	1.19	21.86	0.63	0.05	2.00	1.50	3.50	625	18	5.95	0.59
Dukla	Habkowce	442	0.05	2.89	0.10	0.02	0.25	1.89	2.14	135	5	0.09	1.02
	Świątkowa	448	0.33	2.42	0.70	0.12	0.28	1.77	2.05	118	34	3.22	0.55
	Solinka	478	0.04	0.46	0.13	0.07	0.06	0.82	0.88	52	15	0.30	1.05
Magura	Sękówka	422	0.42	25.48	0.78	0.02	2.23	6.76	8.99	283	9	0.62	0.28
	Polany	519	0.00	0.00	0.26	0.00	0.01	1.17	1.18	0	22	2.02	0.24
Boryslav–Pokuttya	Kniażyce-1	400	0.10	2.23	1.85	0.04	0.32	3.11	3.43	65	54	0.47	0.73
	Kniażyce-2	414	0.18	8.43	0.80	0.02	0.78	1.48	2.26	373	35	0.13	0.86

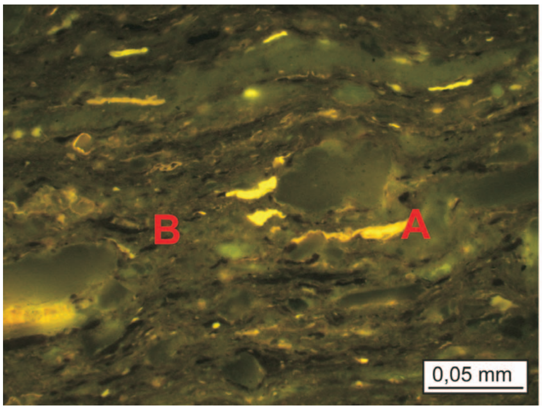

Fig. 4. Alginite (A) and bituminite (B) in sample from Leszczawa Górna-1 outcrop, Skole Unit. Fluorescence mode

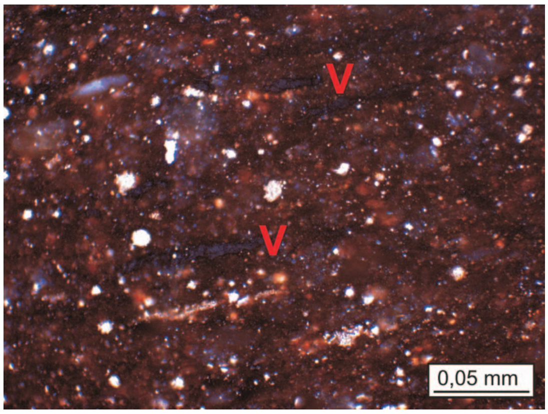

Fig. 5. Vitrinite (V) in sample from Sękówka outcrop, Magura Unit. Reflected light

Conclusions

The obtained results showed that Menilite Beds are very heterogeneous. This diversity is related to the composition of organic matter, its content in a rock and maturity. The analyzed material was sufficient for some general statements to be made, but definitely was too poor to characterize trends in changes of different parameters within each of the analyzed units.

Menilite Beds within the Skole Unit are characteristic, due to the highest content of organic matter (average TOC is around 8%), which is dominated by bituminite and alginite (type I/II kerogen).Vitrinite (type III kerogen) is also present, but in lower amounts. This is confirmed by the highest average HI values, which is 321 mgHC/gTOC. Maturity level suggest the immature phase (on the basis of T_{max}) or all stages of the oil window (on the basis of vitrinite reflectance).

In comparison to the Skole Unit, Menilite Beds from the Silesian and Węglówka Units reach medium values of organic matter content (TOC values are in range of 1.99÷6.91%). Average value of HI is also not as high as in the Skole Unit and reaches 255, which is a result of higher vitrinite content. Maturity level ranges from the immature/early oil phase to the late oil window.

Menilite Beds within the Dukla Unit in comparison to those within the Skole and Silesian/Węglówka Units seem to be poorer in organic matter (average TOC value is 1.69%), but the maturity level is higher (average T_{max} is highest and suggest oil window, average R_o is also the highest – only one sample suggest the immature phase, the rest can be interpretated as the late oil window phase).

The Boryslav–Pokuttya Unit can be characterized by a little higher average content of organic matter than samples from the Dukla Unit (TOC is between 2.26% and 3.43%) and at the same time much lower than samples from the Skole Unit. In the composition of organic matter, there is a dominance of bituminite and alginite over vitrinite, which results in HI values being from 65 (for the sample with the highest content of vitrinite) to 373 (for the sample with the lowest content of vitrinite). These samples are immature or in the main phase of the oil window.

From the Magura Unit only very general conclusions can be made. So far, it seems that Menilite Beds from this unit are heterogeneous with both organic matter content (TOC from 1.18% to 8.99%) and its type (there are samples with the dominance of type I/II kerogen, but also samples with a high content of type III kerogen are present), but quite homogeneous when it comes to its maturity level – interpretation of both the T_{max} and R_o suggest the immature phase.

The results described above are only preliminary to the topic. More detailed work is needed, in order to obtain the information of not only the difference in organic matter composition and its maturity between different units, but also to find out, if there are any trends in changes of these parameters in different parts of the same unit. The detailed field work will not only be needed to be focused on the amount of samples collected from outcrops within the study area, but also the results of analyses needed to be attached to the geological situation on both the local and regional scale.

Please cite as: Nafta-Gaz 2015, no. 9, pp. 615–623

Article contributed to the Editor 26.01.2015. Approved for publication 22.04.2015.

The article was written on the basis of the following statutory work: *Characteristics of dispersed organic matter in menilite shales from selected localizations* – the Oil and Gas Institute – National Research Institute work, funded by the Ministry of Science and Higher Education, order no. 44/SG/14, archival no. SG-4101-44/14.

References

[1] Bessereau G., Roure F., Kotarba M., Kusmierek J., Strzetelski W.: *Structure and hydrocarbon habitat of the Polish Carpathians*. In: Ziegler, P.A., Horvath, F. (Eds.): *Structure and Prospects Alpine Basins and Forelands. Peri-Tethys Memoir 2*, Memories du Museum National dHistoire Naturelle 170, Pari 1996, pp. 343–373.

[2] Curtis J. B., Kotarba M. J., Lewan M. D., Wieclaw D: *Oil/source rock correlations in the Polysch Flysch Carpathians and Mesozoic basement and organic facies of the Oligocene Menilite Shales: insights from hydrous pyrolisis experiments*, Organic Geochemistry 2004, 35, pp. 1573–1596.

[3] Glocker E. F.: *Menilitschifer in Mähren*. Amtl. Bericht der deutschen Naturf. Vers. In Gratz. Gratz 1843.

[4] Jankowski L., Kopciowski R., Rylko W. (red.): *Geological map of the Outer Carpathians: boreland of Ukraine and Romania. 1:200 000.* Państwowy Instytut Geologiczny, Warszawa 2007.

[5] Jankowski L., Kopciowski R., Rylko W., Danych V., Tsarnenko P., Janočko J., Jacko S. (red.): *Geological map of the Outer Carpathians: borderlands of Poland, Ukraine and Slovakia. 1:200 000*, Państwowy Instytut Geologiczny, Warszawa 2004.

[6] Jarmolowicz-Szulc K., Jankowski L.: *Analiza geochemiczna i korelacje genetyczne bituminow i skal typu czarnych lupkow w jednostkach tektonicznych Karpat zewnetrznych w poludniowo-wschodniej Polsce i na obszarze przyleglym*. Biuletyn Państwowego Instytutu Geologicznego 2011, 444, pp. 73–98.

[7] Koltun Y. V.: *Organic matter in Oligocene Menilite Formation rocks of the Ukrainian Carpathians: palaeoenvironment and geochemical evolution*. Organic Geochemistry 1992, 18, pp. 423–430.

[8] Kosakowski P., Wieclaw D., Kotarba M. J.: *Charakterystyka macierzystosci wybranych utworow fliszowych w przygranicznej strefie polskich Karpat Zewnętrznych*. Geologia 2009, 35, pp. 155–190.

[9] Köster J., Kotarba M., Lafargue E., Kosakowski P.: S*ource rock habitat and hydrocarbon potential of Oligocene Menilite Formation (Flysch Carpathians, Southeast Poland): an organic geochemical and isotope approach*. Organic Geochemistry 1998, 29, pp. 543–558.

[10] Köster J., Rospondek M., Schouten S., Kotarba M., Zubrzycki A., Sinninghe Damste, J.S.: *Biomarker geochemistry of a foreland basin: Oligocene Menilite Formation in the Flysch Carpathians of Southeast Poland*. Organic Geochemistry, 1998, 29, pp. 649–669.

[11] Koszarski L., Zytko K.: *Lupki jasielskie i ich znaczenie dla stratygrafii i sedymentologii serii meilitowo-krosnienskiej (Karpaty fliszowe)*. Biuletyn Instytutu Geologicznego 1961, 116, pp. 87–214.

[12] Kotarba M. J., Wieclaw D., Koltun Y. V., Kusmierek J., Marynowski L., Dudok I. V.. *Organic geochemical study and genetic correlation of natural gas, oil and Menilite source rocks in the San and Stryi rivers region (Polish and Ukrainian Carpathians)*. Organic Geochemistry 2007, 38, pp. 1431–1456.

[13] Kotarba M. J., Wieclaw D., Koltun Y. V., Lewan M. D., Marynowski L., Dudok I. V.: *Organic geochemical study and genetic correlations between the Oligocene Menilite source rocks and oil and natural gas from surface seepages and from deep accumulations in the Starunia area (Ukrainian Carpathians)*. In: Kotarba M.J. (Ed.), *Polish and Ukrainian geological survey in 2004–2005 years in Starunia at the area of finds of woolly rhinoceroses and other extinct vertebrates*, Polish Geological Institute and "Geosphere", Warszawa–Kraków 2005, pp. 125–146.

[14] Kotlarczyk J.: *Models of sedimentary basins of Skole Unit and „Rzeszów Bay"*. In: Kotlarczyk J. (Ed.): *Paleontology and Bathymetry*, XIVth Conference of Palaeontologes in the Rzeszów Carpathians, Wydawnictwo Instytutu Geologii i Surowców Mineralnych Akademii Górniczo-Hutniczej, Kraków 1991, pp. 11–21.

[15] Kruge M. A., Mastalerz M., Solecki A., Stankiewicz B. A.: *Organic geochemistry and petrology of oil source rocks, Carpathian Overthrust region, southeastern Poland –implications for petroleum generation*. Organic Geochemistry 1996, 24, pp. 897–912.

[16] Lewan M. D., Kotarba M. J., Curtis J. B., Wieclaw D., Kosakowski P.: *Oil-generation kinetics for organic facies with Type-II and -IIS kerogen in the Menilite Shales of the Polish Carpathians*. Geochimica et Cosmochimica Acta 2006, 70, pp. 3351–3368.

[17] Matyasik I., Bielen W., Janiga M., Jankowski L.: *Geochemiczna charakterystyka powierzchniowych wycieków węglowodorowych na podstawie badań GC-MS*. Nafta-Gaz 2012, 11, pp. 788–796.

[18] Matyasik I., Kupisz L.: *Geological and geochemical conditions of the hydrocarbon generation in the Menilite Beds from the south part of the Strzyżów Depression*. The 2nd Conference on the Geochemical and Petrophysical Investigations in Oil and Gas Exploration, Janowice 10–12.04.1996, pp. 179–197.

[19] Matyasik I.: *Badania geochemiczne warstw menilitowych, inoceramowych i spaskich jednostki skolskiej fliszu karpackiego*. Nafta-Gaz 1994, 40, pp. 234–243.

[20] Olszewska B.: *Uwagi o biostratygrafii serii menilitowo-krosnienskiej w polskich Karpatach zewnetrznych*. Kwartalnik Geologiczny 1982, 26, pp. 137–145.

[21] Peters E. K., Cassa M. R.: *Applied Source Rock Geochemistry*. In: Magoon L.B., Dow W.G.: *The petroleum system – from source to trap*. AAPG Memoir 1994, 60.

[22] Rospondek M. J., Köster J., Sinninghe Damsté J. S.: *Novel C26 highly branched isoprenoid thiophenes and alkane from the Menilite Formation, Outer Carpathians, SE Poland*. Organic Geochemistry 1997, 26, pp. 295–304.

[23] Wieclaw D., Kotarba M. J., Koltun Y.: *Identification of kerogen type in the menilite shales of the Skole and Silesian units of the Polish and Ukrainian Carpathians*. 23rd International Meeting on Organic Geochemistry, Torquay (England) 9–1.09.2007, P22-M.

Konrad ZIEMIANIN
M.Sc., Assistant at Geology and Geochemistry Department
Oil and Gas Institute – National Research Institute
ul. Lubicz 25A
31-503 Kraków
E-mail: *ziemianin@inig.pl*

PAWEŁ BRZUSZEK
M.Sc., Eng., Assistant at Geology and Geochemistry Department
Oil and Gas Institute – National Research Institute
ul. Lubicz 25A
31-503 Kraków
E-mail: *brzuszek@inig.pl*

Tomasz SŁOCZYŃSKI
M.Sc., Eng., Senior Research Support Specialist, Department of Geology and Geochemistry
Oil and Gas Institute – National Research Institute
ul. Lubicz 25A
31-503 Kraków
E-mail: *sloczynski@inig.pl*

Leszek JANKOWSKI Ph.D.
Polish Geological Institute – National Research Institute
Carpathian Branch in Cracow
ul. Skrzatów 1
31-560 Kraków
E-mail: *leszek.jankowski@pgi.gov.pl*