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Characteristics of dispersed organic matter in selected lithostratigraphic divisions within the Skole Unit (Carpathian Mts., SE Poland)

Charakterystyka rozproszonej materii organicznej w wybranych wydzieleniach litostratygraficznych na obszarze jednostki skolskiej

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ABSTRACT: This article is devoted to the characteristics of dispersed organic matter in selected lithostratigraphic divisions of the Skole Unit in the area of the Polish fragment of the Carpathian Mountains. The aim of this research was to broaden the state of knowledge about the Skole Unit by aspects of organic matter petrography. Due to the size of the investigated area and the numerous lithostratigraphic divisions, the presented results should be treated as an introduction to the issue. The main emphasis is placed on microscopic analyses in reflected and UV light. Microscopic observations are enriched with the results of Rock-Eval pyrolytic analysis. The research material consisted of 37 rock samples collected from 3 selected regions. The samples represented various lithostratigraphic divisions – from Spas Shales, through Inoceramian Beds, Hieroglyphic Beds, Variegated Shales, up to Menilite and Krosno Beds. The analysed rocks are characterised by a variable content of organic matter - from trace (Variegated Shales), through low (TOC up to 0.5% – Inoceramian, Hieroglyphic and Krosno Beds), to relatively high (Spas Shales and Menilite Beds). In the maceral composition, macerals from all 3 groups – vitrinite (collotelinite, vitrodetrinite), liptinite (alginite, bituminite, sporinite, liptodetrinite) and inertinite (fusinite, semifusinite, inertodetrinite) – are observed. The group of liptinite macerals dominates in samples within the Spas Shales and Menilite Beds, as well as in some of the shales from the Krosno Beds. In the case of Inoceramian and Hieroglyphic Beds, macerals of the vitrinite and inertinite groups predominate. In the Spas Shales and Krosno Beds, the dominant maceral within the liptinite group is alginite, while in Menilite Beds, bituminite dominates. Alginite is present in nearly all (except Variegated Shales) investigated lithostratigraphic divisions. The content of macerals of the inertinite group is higher than the content of macerals from vitrinite group in the Spas Shales, Inoceramian Beds and in some rocks from Hieroglyphic Beds. The situation is opposite in the case of Menilite and Krosno Beds. The organic matter within all the investigated rocks is in the phase of thermal changes referred to as immature, as evidenced by the T_{max} parameter reaching values lower than 435ºC. The examined rocks clearly differ in terms of the assessment of their hydrocarbon generation potential, which is the poorest for Variegated Shales and slightly better (but still poor) in the case of Inoceramian, Hieroglyphic and Krosno Beds. The best generation potential is observed in rocks collected from Spas Shales and Menilite Beds, with the latter having a generation potential defined as very good and even excellent.

Key words: organic matter, Skole Unit, macerals, Rock-Eval-pyrolysis, generation potential.

STRESZCZENIE: Niniejszy artykuł poświęcony jest charakterystyce rozproszonej materii organicznej w wybranych wydzieleniach litostratygraficznych jednostki skolskiej na obszarze polskiego fragmentu Karpat zewnętrznych. Celem badań było poszerzenie stanu wiedzy o jednostce skolskiej o aspekty petrografii materii organicznej. Ze względu na wielkość obszaru badań oraz mnogość wydzieleń litostratygraficznych przedstawione wyniki traktować należy jako wstęp do zagadnienia. W trakcie realizacji pracy główny nacisk położono na analizy mikroskopowe w świetle odbitym i UV. Obserwacje mikroskopowe wzbogacono o wyniki analizy pirolitycznej Rock-Eval. Materiał badawczy stanowiło 37 próbek skalnych, pobranych z 3 wytypowanych rejonów. Próbki reprezentowały różne wydzielenia litostratygraficzne – od łupków spaskich, przez warstwy inoceramowe, hieroglifowe, łupki pstre, aż do warstw menilitowych i krośnieńskich. Przebadane próbki charakteryzują się zmiennym udziałem materii organicznej – od śladowego (łupki pstre), przez niski (TOC do 0,5% – warstwy inoceramowe, hieroglifowe i krośnieńskie), do relatywnie wysokiego (łupki spaskie i warstwy menilitowe). W składzie macerałowym obserwuje się macerały z wszystkich grup – witrynitu (kolotelinit, witrodetrynit), liptynitu (alginit, bituminit, sporynit, liptodetrynit) i inertynitu (fuzynit, semifuzynit, inertodetrynit). Grupa macerałów liptynitu dominuje w próbkach łupków spaskich i warstw menilitowych, jak również w części próbek z warstw krośnieńskich. W przypadku warstw inoceramowych i hieroglifowych dominują macerały witrynitu i inertynitu. W łupkach spaskich i warstwach krośnieńskich dominującym macerałem w obrębie grupy liptynitu jest alginit, podczas gdy w warstwach menilitowych – bituminit. Alginit występuje we wszystkich (poza łupkami pstrymi) przebadanych wydzieleniach litostratygraficznych. Grupa macerałów inertynitu jest liczniejsza od grupy macerałów

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witrynitu w łupkach spaskich, warstwach inoceramowych i w części próbek z warstw hieroglifowych. Sytuacja jest odwrotna w przypadku warstw menilitowych i krośnieńskich. Wszystkie przebadane skały charakteryzowały się obecnością materii organicznej będącej w fazie przemian termicznych określanych jako stadium niedojrzałe, o czym świadczy parametr T_{max} osiągający wartości niższe niż 435°C. Przebadane skały wyraźnie różnicują się pod kątem oceny ich potencjału generacyjnego. Najsłabszy jest on w przypadku łupków pstrych. Nieco lepszym (ale wciąż słabym) potencjałem generacyjnym charakteryzują się skały reprezentujące warstwy inoceramowe, hieroglifowe i krośnieńskie. Najlepszy potencjał generacyjny wykazują skały pobrane z łupków spaskich i warstw menilitowych, przy czym te ostatnie cechują się potencjałem generacyjnym określanym jako bardzo dobry, a nawet doskonały.

Słowa kluczowe: materia organiczna, jednostka skolska, macerały, piroliza Rock-Eval, potencjał generacyjny.

Introduction and work objectives

This article is devoted to the characteristics of dispersed organic matter in selected lithostratigraphic divisions of the Skole Unit in the area of the Polish part of the Outer Carpathians. Organic matter petrography is a source of very important information, such as the composition of organic matter and its maturity level, and is commonly used by petroleum geologists to draw conclusions about the possibility of hydrocarbon generation within the area of interest. Unfortunately, the data obtained from microscopic observations, despite its important role, is often marginalised or limited only to vitrinite reflectance measurements. This can be explained by the relatively long time of analysis compared to, e.g., Rock-Eval pyrolytic analysis, which necessitates a more careful sample selection, and thus a smaller number of samples chosen for detailed petrographic investigations.

Scientific studies from the Carpathian region regarding the characteristics of dispersed organic matter or papers where the results of this type of research are mentioned are rather rare (e.g. Koltun, 1992; Kruge et al., 1996; Kotulová, 2004; Kosakowski et al., 2009, 2018; Semyrka, 2009; Zielińska, 2012; Kotarba et al., 2013; Waliczek et al., 2017; Wendorff et al., 2017; Wójcik-Tabol et al., 2019). Moreover, most of them focus only on the Menilite shales, as they play a key role in the hydrocarbon system in the Carpathian area (e.g. Ziemianin, 2017, 2018, 2019a, 2019b). This article is intended to provide data on the maceral composition of some other lithostratigraphic divisions of the Skole Unit and is considered to be an introduction to the issue, with the possibility of more detailed investigations in the future.

Methods

Fieldwork and research material

Fieldwork was performed in three selected regions within the Skolska Unit (Fig. 1). The first area included outcrops in the north-western part of the Unit. From the outcrops located near Niedźwiada, Mała and Gębiczyna, a total of 12 samples were taken. The second area included outcrops located south-east of the first area. A total of 6 samples were taken near Blizianka and Gwoźnica Dolna. The last, south-easternmost

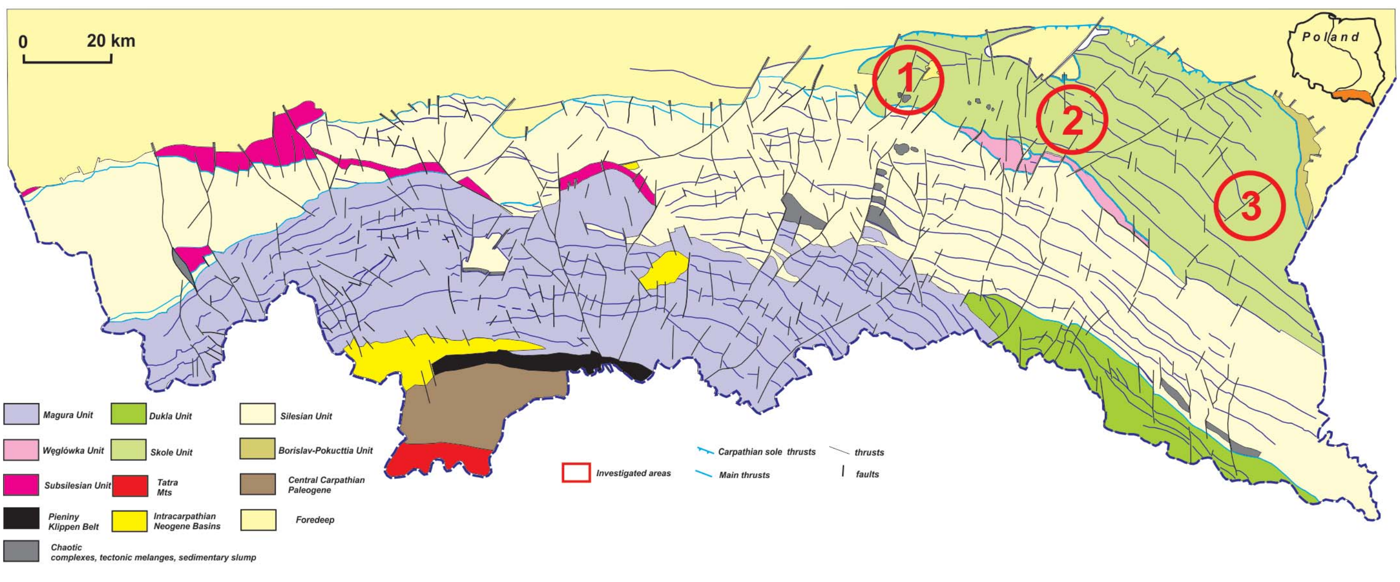

Fig. 1. Investigated areas and outcrops within the Polish part of the Carpathians (Jankowski, 2008; Jankowski, Probulski, 2011, modified); area 1 – Niedźwiada, Mała, Gębiczyna; area 2 – Blizianka, Gwoźnica Dolna, Area 3 – Korzeniec

Fig. 1. Obszar badań i lokalizacja odsłonięć na tle polskiej części Karpat (Jankowski, 2008; Jankowski, Probulski, 2011, zmieniony); odsłonięcia: rejon 1 – Niedźwiada, Mała, Gębiczyna; rejon 2 – Blizianka, Gwoźnica Dolna, Rejon 3 – Korzeniec

region included outcrops located near Korzeniec, from which 17 samples were taken for further analyses. After completing the fieldwork, 37 samples representing various lithostratigraphic divisions were collected.

Microscopic investigations

Microscopic observations were performed in reflected light and UV on polished samples. They were carried out on a Carl Zeiss Axioplan microscope, at 500x magnification, in immersion (immersol oil 518 N, $n = 1.518$). In order to obtain maceral composition, a planimetric analysis (500–600 points counted) was performed.

Measurements of vitrinite reflectance, which usually accompany microscopic observations, were not possible in most cases, as the samples were usually highly weathered and very difficult for proper polishing. Vitrinite fragments were also usually rare and poorly preserved. All these factors lowered the chance for obtaining statistically representative results of the vitrinite reflectance measurements. Due to the mentioned difficulties, the organic matter maturity analysis was based on the results of Rock-Eval pyrolysis (T_{max} parameter).

Rock-Eval pyrolytic analysis

Microscopic observations were supplemented with Rock-Eval pyrolytic analysis performed using Rock-Eval-6 apparatus. Selected samples (17) were analyzed and a number of parameters were obtained, of which (from the point of view of this study) the most significant was the T_{max} parameter, on the basis of which the maturity of organic matter was determined, as well as HI (hydrogen index) and OI (oxygen index) parameters (for kerogen type determination).

Results

In the investigated samples (representing Spas Shales, Inoceramian Beds, Hieroglyphic Beds, Variegated Shales, Menilite Beds and Krosno Beds), macerals from all three maceral groups (vitrinite, liptinite and inertinite) are usually observed. However, their content is most times very small – rarely any of these groups exceeds 1% of the planimetric surface of the sample. This is confirmed by the results of Rock-Eval pyrolytic analysis, where the TOC parameter is usually lower than 1%.

Within the vitrinite group, larger fragments (>10 µm) of collotelinite and smaller vitrodetrinite (<10 µm) were distinguished. Vitrinite fragments are usually either larger and rare (usually in the siltstone type of samples) or finer

Table 1. Results of the Rock-Eval pyrolysis
Tabela. 1. Wyniki analizy pirolitycznej Rock-Eval

Stratigraphy	Localisation	Sample ID	T_{max}	S_1	S_2	S_3	PI	PC	RC	TOC	HI	OI	MINC
			[°C]		[mg/g]			[%]	[%]	[%]			[%]
Spas Shales	Niedźwiada	1	428	0.03	1.08	0.38	0.03	0.12	0.63	0.75	144	51	0.03
	Niedźwiada	4	427	0.14	5.11	0.35	0.03	0.47	1.89	2.36	217	15	0.07
	Niedźwiada	5	427	0.10	4.1	0.24	0.02	0.38	2.57	2.95	139	8	0.59
Inoceramian Beds	Mała	3	425	0.01	0.32	0.32	0.04	0.05	0.41	0.46	70	70	1.83
	Blizianka	5	430	0.01	0.17	0.30	0.03	0.03	0.58	0.61	28	49	1.15
	Korzeniec	7	415	0.01	0.03	0.16	0.16	0.01	0.12	0.13	23	123	0.06
Hieroglyphic Beds	Gębiczyna	2	431	0.01	0.29	0.49	0.04	0.05	0.42	0.47	62	104	0.07
	Gwoźnica Dolna	3	426	0.05	8.24	1.84	0.01	0.84	3.50	4.34	190	42	4.38
	Gwoźnica Dolna	5	427	0.01	0.93	0.71	0.01	0.11	0.45	0.56	166	127	2.12
	Korzeniec	10	421	0.01	0.70	0.77	0.02	0.10	0.59	0.69	101	112	0.13
Variegated Shales	Korzeniec	1	432	0.00	0.03	0.26	0.10	0.01	0.00	0.01	300	2600	0.08
	Korzeniec	2	415	0.01	0.05	0.25	0.13	0.01	0.03	0.04	125	625	0.18
Menilite Beds	Korzeniec	2	411	0.26	25.27	3.60	0.01	2.46	9.01	11.47	220	31	0.96
	Korzeniec	4	402	0.28	14.02	1.27	0.02	1.32	3.92	5.24	268	24	0.33
Krosno Beds	Mała	2	418	0.01	0.49	0.81	0.02	0.08	0.42	0.50	98	162	2.63
	Korzeniec	4	423	0.00	0.46	0.52	0.01	0.06	0.37	0.43	107	121	2.93
	Korzeniec	5	426	0.01	0.83	0.35	0.01	0.09	0.42	0.51	163	69	3.15

Table 2. Maceral content and composition within the investigated samples (with mineral matter)

Tabela 2. Udział i skład macerałowy materii organicznej w przebadanych próbkach (z uwzględnieniem materii mineralnej)

Stratigraphy	Sample ID	Localisation	Vitrinite		Inertinite			Liptinite					Mineral matter
			collotelinite	vitrodetrinite	fusinite	semifusinite	inertodetrinite	alginite	bituminite	sporinite	cutinite	liptodetrinite	
Spas Shales	1	Niedźwiada	trace	trace	trace	0.37	trace	0.55	n.o.	trace	n.o.	0.92	98.15
	2	Niedźwiada	trace	trace	trace	0.19	trace	0.38	n.o.	trace	n.o.	0.38	99.05
	3	Niedźwiada	trace	trace	trace	0.19	trace	1.3	0.93	trace	n.o.	0.37	97.22
	4	Niedźwiada	trace	trace	trace	0.18	trace	0.54	n.o.	trace	n.o.	0.71	98.57
	5	Niedźwiada	trace	trace	trace	0.37	0.19	1.31	n.o.	trace	n.o.	0.19	97.94
Inoceramian Beds	1	Mała	0.56	trace	trace	0.19	trace	trace	n.o.	trace	trace	trace	99.26
	2	Mała	trace	0.19	trace	trace	trace	trace	n.o.	trace	n.o.	trace	99.81
	3	Mała	trace	0.19	trace	trace	trace	0.38	n.o.	trace	trace	trace	99.42
	4	Blizianka	0.18	trace	trace	0.18	trace	trace	n.o.	trace	n.o.	trace	99.64
	5	Blizianka	0.38	0.19	trace	0.19	trace	trace	n.o.	trace	n.o.	n.o.	99.24
	6	Blizianka	0.2	0.39	trace	0.20	trace	trace	n.o.	trace	trace	trace	99.21
	7	Korzeniec	trace	trace	trace	trace	trace	trace	n.o.	n.o.	n.o.	trace	100.00
	8	Korzeniec	trace	trace	trace	0.19	trace	trace	n.o.	n.o.	n.o.	trace	99.81
Hieroglyphic Beds	1	Gębiczyna	trace	trace	trace	trace	trace	trace	n.o.	trace	n.o.	trace	100.00
	2	Gębiczyna	trace	trace	trace	0.92	trace	trace	n.o.	trace	n.o.	trace	99.08
	3	Gwoźnica Dolna	0.2	trace	0.2	trace	trace	trace	6.14	trace	n.o.	0.2	93.27
	4	Gwoźnica Dolna	0.19	trace	trace	trace	trace	trace	n.o.	trace	n.o.	trace	99.81
	5	Gwoźnica Dolna	trace	trace	trace	trace	trace	0.19	n.o.	trace	trace	trace	99.81
	6	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	trace	n.o.	n.o.	n.o.	0.19	99.81
	7	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	0.75	n.o.	n.o.	n.o.	0.19	99.06
	8	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	0.37	n.o.	n.o.	n.o.	0.37	99.26
	9	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	0.18	n.o.	trace	n.o.	0.18	99.64
	10	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	0.79	n.o.	n.o.	n.o.	0.39	98.82
Variegated Shales	1	Korzeniec	n.o.	trace	n.o.	n.o.	trace	n.o.	n.o.	n.o.	n.o.	n.o.	100.00
	2	Korzeniec	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	100.00
	3	Korzeniec	n.o.	trace	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	100.00
Menilite Beds	1	Korzeniec	1.11	0.19	trace	trace	trace	0.19	4.26	trace	n.o.	0.37	93.89
	2	Korzeniec	0.95	0.76	trace	trace	trace	1.14	2.46	trace	n.o.	0.57	94.13
	3	Korzeniec	0.4	0.2	trace	trace	trace	1.19	6.15	n.o.	n.o.	0.2	91.87
	4	Korzeniec	0.22	trace	trace	trace	trace	0.86	7.31	trace	n.o.	0.43	91.18
	5	Korzeniec	2,0	trace	trace	trace	trace	0.2	3.41	n.o.	n.o.	trace	94.39
Krosno Beds	1	Mała	trace	trace	trace	n.o.	n.o.	0.19	trace	n.o.	n.o.	trace	99.81
	2	Mała	trace	trace	n.o.	trace	n.o.	trace	n.o.	n.o.	n.o.	trace	100.00
	3	Korzeniec	n.o.	n.o.	trace	trace	n.o.	0.19	n.o.	n.o.	n.o.	trace	99.81
	4	Korzeniec	n.o.	n.o.	n.o.	n.o.	n.o.	trace	n.o.	n.o.	n.o.	trace	100.00
	5	Korzeniec	trace	trace	trace	trace	trace	0.19	n.o.	n.o.	n.o.	trace	99.81
	6	Korzeniec	trace	trace	n.o.	n.o.	n.o.	trace	n.o.	n.o.	n.o.	trace	100.00

n.o. – not observed

Table 3. Maceral content and composition within the investigated samples

Tabela 3. Udział i skład macerałowy materii organicznej w przebadanych próbkach

Stratigraphy	Sample ID	Localisation	Vitrinite		Inertinite			Liptinite				
			collotelinite	vitrodetrinite	fusinite	semifusinite	inertodetrinite	alginite	bituminite	sporinite	cutinite	liptodetrinite
Spas Shales	1	Niedźwiada	trace	trace	trace	20.11	trace	29.89	n.o.	trace	n.o.	50.00
	2	Niedźwiada	trace	trace	trace	20.00	trace	40.00	n.o.	trace	n.o.	40.00
	3	Niedźwiada	trace	trace	trace	6.81	trace	46.59	33.33	trace	n.o.	13.26
	4	Niedźwiada	trace	trace	trace	12.59	trace	37.76	n.o.	trace	n.o.	49.65
	5	Niedźwiada	trace	trace	trace	17.96	9.22	63.59	n.o.	trace	n.o.	9.22
Inoceramian Beds	1	Mała	74.67	trace	trace	25.33	trace	trace	n.o.	trace	trace	trace
	2	Mała	trace	100.00	trace	trace	trace	trace	n.o.	trace	n.o.	trace
	3	Mała	trace	33.33	trace	trace	trace	66.67	n.o.	trace	trace	trace
	4	Blizianka	50.00	trace	trace	50.00	trace	trace	n.o.	trace	n.o.	trace
	5	Blizianka	50.00	25.00	trace	25.00	trace	trace	n.o.	trace	n.o.	n.o.
	6	Blizianka	25.32	49.37	trace	25.32	trace	trace	n.o.	trace	trace	trace
	7	Korzeniec	trace	trace	trace	trace	trace	trace	n.o.	n.o.	n.o.	trace
	8	Korzeniec	trace	trace	trace	100.00	trace	trace	n.o.	n.o.	n.o.	trace
Hieroglyphic Beds	1	Gębiczyna	trace	trace	trace	trace	trace	trace	n.o.	trace	n.o.	trace
	2	Gębiczyna	trace	trace	trace	100.00	trace	trace	n.o.	trace	n.o.	trace
	3	Gwoźnica Dolna	2.97	trace	2.97	trace	trace	trace	91.10	trace	n.o.	2.97
	4	Gwoźnica Dolna	100.00	trace	trace	trace	trace	trace	n.o.	trace	n.o.	trace
	5	Gwoźnica Dolna	trace	trace	trace	trace	trace	100.00	n.o.	trace	trace	trace
	6	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	trace	n.o.	n.o.	n.o.	100.00
	7	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	79.79	n.o.	n.o.	n.o.	20.21
	8	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	50.00	n.o.	n.o.	n.o.	50.00
	9	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	50.00	n.o.	trace	n.o.	50.00
	10	Korzeniec	n.o.	n.o.	n.o.	trace	n.o.	66.95	n.o.	n.o.	n.o.	33.05
Variegated Shales	1	Korzeniec	n.o.	trace	n.o.	n.o.	trace	n.o.	n.o.	n.o.	n.o.	n.o.
	2	Korzeniec	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
	3	Korzeniec	n.o.	trace	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
Menilite Beds	1	Korzeniec	18.14	3.10	trace	trace	trace	3.10	69.61	trace	n.o.	6.05
	2	Korzeniec	16.16	12.93	trace	trace	trace	19.39	41.84	trace	n.o.	9.69
	3	Korzeniec	4.91	2.46	trace	trace	trace	14.62	75.55	n.o.	n.o.	2.46
	4	Korzeniec	2.49	trace	trace	trace	trace	9.75	82.88	trace	n.o.	4.88
	5	Korzeniec	35.65	trace	trace	trace	trace	3.57	60.78	n.o.	n.o.	trace
Krosno Beds	1	Mała	trace	trace	trace	n.o.	n.o.	100.00	trace	n.o.	n.o.	trace
	2	Mała	trace	trace	n.o.	trace	n.o.	trace	n.o.	n.o.	n.o.	trace
	3	Korzeniec	n.o.	n.o.	trace	trace	n.o.	100.00	n.o.	n.o.	n.o.	trace
	4	Korzeniec	n.o.	n.o.	n.o.	n.o.	n.o.	trace	n.o.	n.o.	n.o.	trace
	5	Korzeniec	trace	trace	trace	trace	trace	100.00	n.o.	n.o.	n.o.	trace
	6	Korzeniec	trace	trace	n.o.	n.o.	n.o.	trace	n.o.	n.o.	n.o.	trace

but more common (mainly in shales). The preservation of the observed fragments is usually very poor, which is a result of the weathering process affecting samples collected from outcrops.

Macerals of the liptinite group are dominated by the association of alginite and small fragments of liptodetrinite (probably of algae origin). In some samples, alginite and liptodetrinite is accompanied by bituminite, the content of which in several samples is high and can reach even 6–7% vol. Apart from the macerals mentioned, very few macerals of terrigenous genesis – sporinite and cutinite – are observed. Macerals of the liptinite group are characterised by a strong yellow fluorescence (except bituminite, which shows a weaker brown fluorescence).

Macerals of the inertinite group are represented most often by fragments of semifusinite and fusinite. Both semifusinite and fusinite are usually observed in the form of crushed, sharp-edged fragments (relicts of cellular structure). These macerals have high reflectance, with fusinite showing the highest value of this parameter. Although the observed fragments of inertinite (semifusinite, fusinite) are most often relatively larger than fragments of vitrinite, in some cases smaller, rare fragments of inertodetrinite can also be observed.

Geochemical studies show that organic matter in the investigated rocks is in the phase of thermal changes referred to as "immature" – the T_{max} parameter values are in the range of 402–432ºC. The hydrogen index (HI) values range from 23 to 268, which suggest type III and mixed type II/III of kerogen.

Spas Shales

Five samples of the Spas Shales from outcrops in the Niedźwiada area (fig 1) were analysed. These are dark shales with a TOC parameter in a range from 0.75 to nearly 3% (Table 1). These samples are characterised by the predominance of macerals of the liptinite and inertinite groups in the composition of organic matter (Tables 2 and 3, Plate 1). The group of liptinite macerals is dominated by alginite, the content of which is about 0.5–1.5% vol. This is usually lamalginite, although telalginite is also present. Alginite occurs in association with the finer fragments of liptodetrinite (0.2–0.9% vol.). Bituminite (approx. 1% vol.) was found in one sample. Few occurrences of sporinite were also observed in all the samples. The inertinite group is mainly represented by semifusinite (0.2–0.4% vol.). In addition, relatively frequent occurrences of fusinite and fine inertodetrinite are observed. Within the vitrinite group, fine fragments of collotelinite and even smaller fragments of vitrodetrinite are distinguished. Their content is very low (traces). Small fragments of solid bitumen can also be observed in these samples.

The organic matter of the analysed samples is immature, as indicated by a T_{max} of approx. 427–428ºC (Table 1). The hydrogen index (HI) values are in the range of 139 to 217, which suggest type III and II/III of kerogen (Fig. 2). The oxygen index (OI) values of the investigated samples are in the range of 8–51.

Inoceramian Beds

Samples representing Inoceramian Beds were collected from outcrops in the area of Mała (3 samples), Blizianka (3 samples) and Korzeniec (2 samples). The collected samples are characterised by a lower organic matter content compared to the Spas Shales – the TOC parameter does not exceed 0.5% (Table 1).

In the maceral composition, macerals of the vitrinite and inertinite groups are dominant, while macerals of the liptinite group are less often observed (Tables 2 and 3, Plate 2). The vitrinite fragments do not exceed 0.5%. Vitrinite is represented by collotelinite and vitrodetrinite. The group of inertinite macerals is represented mainly by semifusinite, although fusinite and inertodetrinite can also be noticed. The content of macerals from the inertinite group is similar to the content of macerals from the vitrinite group. Within the investigated samples, sample 1, collected in the region of Mała, definitely stands out. In the mentioned sample, the content of macerals of the vitrinite and inertinite groups is not only the highest, but also the size of the fragments is clearly larger than in the other samples. Macerals of the liptinite group are not very common, and their content does not exceed traces. Alginite

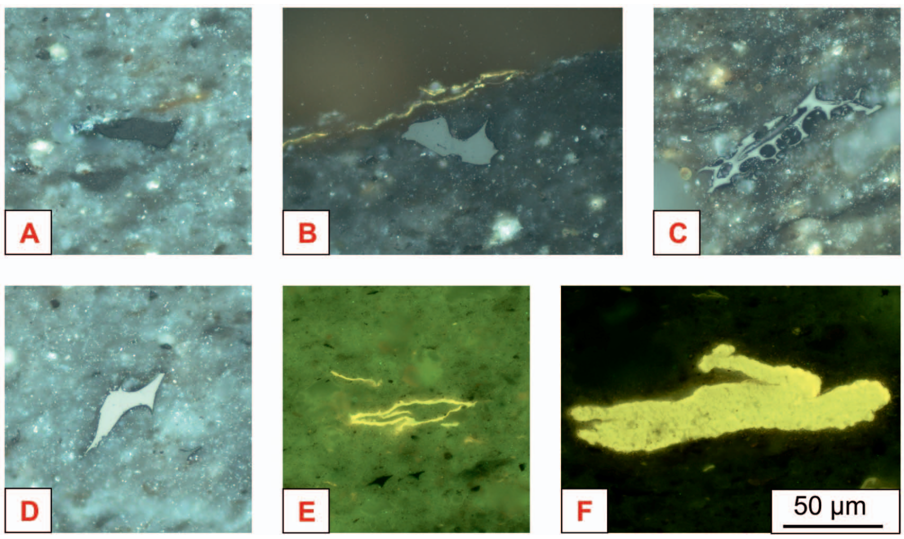

Plate 1. Macerals observed in Spas Shales; A – Collotelinite, B – Semifusinite, C, D – Fusinite, E – Alginite, F – Megasporinite; A–D – reflected light, E–F – UV mode

Tablica 1. Macerały obserwowane w łupkach spaskich; A – kolotelinit, B – semifuzynit, C, D – fuzynit E – alginit, F – megasporynit; A–D – światło odbite, E–F – światło UV

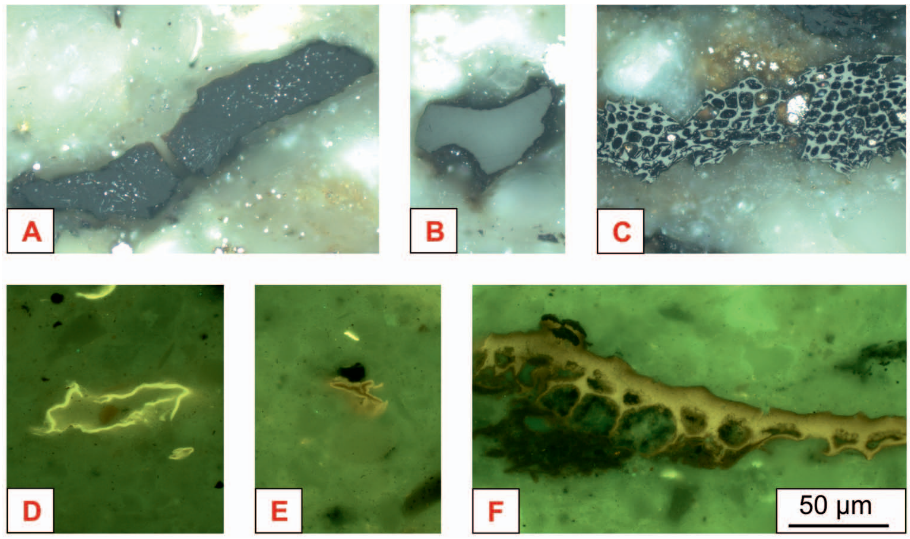

Plate 2. Macerals observed in Inoceramian Beds; A – Collotelinite, B – Semifusinite, C – Fusinite, D – Alginite, E – Sporinite, F – Cutinite; A–C – reflected light, D–F – UV mode

Tablica 2. Macerały obserwowane w warstwach inoceramowych; A – kolotelinit, B – semifuzynit, C – fuzynit, D – lamalginit, E – sporynit, F – kutynit; A–C – światło odbite, D–F – światło UV

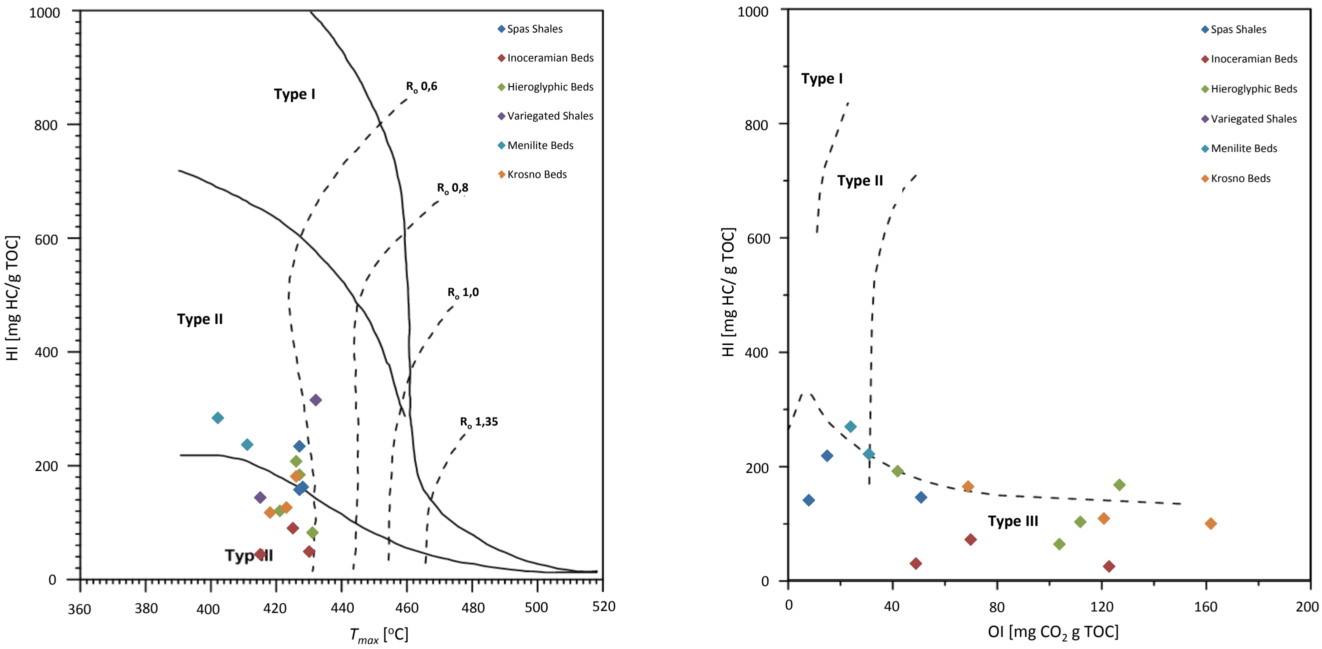

Fig. 2. Kerogen types on the basis of T_{max} – HI (left) and OI – HI parameters (right)

Fig. 2. Typy kerogenu na podstawie parametrów T_{max} i HI (po lewej) oraz HI i OI (po prawej)

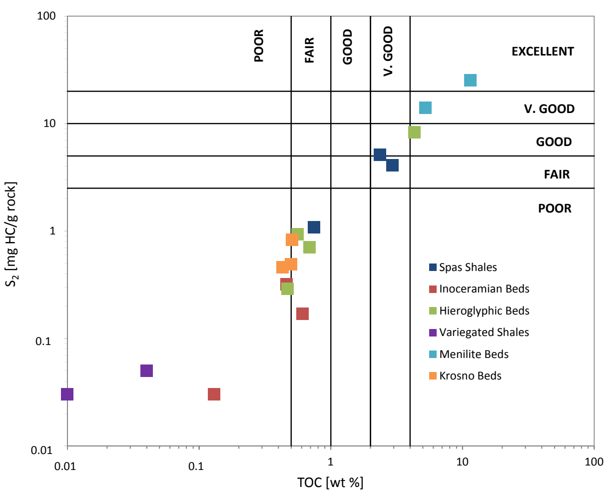

Fig. 3. Hydrocarbon generation potential of the investigated rocks

Fig. 3. Potencjał generacyjny przebadanych próbek

and liptodetrinite are mainly observed. In addition, sporinite and cutinite can also be distinguished. Liptinite macerals are most numerous in the samples from the Mała region and are slightly less observed in samples from Blizianka, while their content in the Korzeniec region is the lowest.

The organic matter of the investigated samples is immature, as indicated by T_{max} values in the range from 415 to 430°C (Table 1). The hydrogen index (HI) shows very low values from 23 to 70, which indicate the presence of kerogen type III and IV (Fig. 2). The oxygen index (OI) values are in the range of 49–123.

Hieroglyphic Beds

Samples representing Hieroglyphic Beds were collected from outcrops in the areas of Gębiczyna (2 samples), Gwoźnica

Dolna (3 samples) and Korzeniec (5 samples). All samples (except for sample 3 from Gwoźnica Dolna) have a low organic matter content of about 0.5% TOC (Table 1). The aforementioned sample 3 is distinguished by a significantly higher TOC value of approx. 4.5%.

Some differences in maceral composition are observed between the samples (Tables 2 and 3, Plate. 3). In the samples from Gębiczyna, macerals of the inertinite group dominate (up to 1% of the planimetric surface; mainly semifusinite, while fusinite and inertodetrinite are slightly rarer) over macerals of the vitrinite group (collotelinite, vitrodetrinite). These macerals are accompanied by rather rarely observed macerals of the liptinite group (alginite, liptodetrinite, sporinite). Samples from Gwoźnica Dolna are characterised by a slightly higher content of fine fragments of vitrinite macerals (approx. 0.2% of the planimetric surface; fine collotelinite, vitrodetrinite) and lower inertinite (fusinite and semifusinite). Just as in the case of samples from Gębiczyna, rare alginite, liptodetrinite and sporinite are also observed. Sample 3 should be distinguished here, because (apart from the macerals mentioned) bitumenite, which is absent in other samples, is observed (6% vol.). Samples from the Korzeniec area are characterised by a lack of macerals from the vitrinite group and only single occurrences of semifusinite. Alginite and liptodetrinite dominate here, and their content is the highest (in total, approx. 1% vol.) among all the investigated outcrops of the Hieroglyphic Beds.

The organic matter in these samples, regardless of the location of collection, is immature. The T_{max} parameter values are in the range from 421 to 431°C (Table 1). Hydrogen index (HI) values range from 62 to 190, which indicates type III of kerogen (Fig. 2). Oxygen index values (OI) are in the range of 42 to 127.

Variegated Shales

Samples representing Variegated Shales were collected in the Korzeniec area. These samples are characterised by an extremely low organic matter content (<0.05% TOC, Table 1). Only a few fine, highly degraded fragments of vitrinite and inertodetrinite can be observed (Tables 2 and 3).

Menilite Beds

Menilite shale samples were taken from the Korzeniec area. These rocks are clearly distinguished by a high content of organic matter – the TOC parameter (Table 1) for the two investigated samples is 5.2% (sample 2) and 11.5% (sample 4).

In the maceral composition (Tables 2 and 3, Plate 4), a dominance of macerals of the liptinite group is observed, while the content of macerals of the vitrinite and inertinite groups is lower. Within the macerals of the liptinite group, bituminite is most common (2.5–7.5% vol.). This usually occurs as a background or in a form of fine laminae. Apart from bituminite, alginite (up to 1% vol., lam– and telalginite) and liptodetrinite (up to 0.5% vol.) are also present. Individual occurrences of sporinite have also been observed in several samples. Macerals of the vitrinite group are slightly less common (up to 2% vol.) and are represented by larger, often elongated fragments of collotelinite and finer fragments of vitrodetrinite. Macerals of the inertinite group are represented by fusinite, semifusinite and inertodetrinite. These macerals are rarely observed.

The values of the T_{max} parameter (Table 1) in the case of these samples are rather low and reach only 402–411. Therefore, the organic matter of these samples can be considered as immature. HI parameter values of 220 and 268 indicate type II/III of kerogen (Fig. 2). The OI parameter values are rather low (24 and 31).

Krosno Beds

Samples belonging to the Krosno Beds are the youngest rocks examined. They were collected from outcrops in the region of Mała and Korzeniec (Fig. 1). As in the case of most of the previously described samples, these samples are also poor in organic matter content – the TOC parameter values are about 0.5% (Table 1).

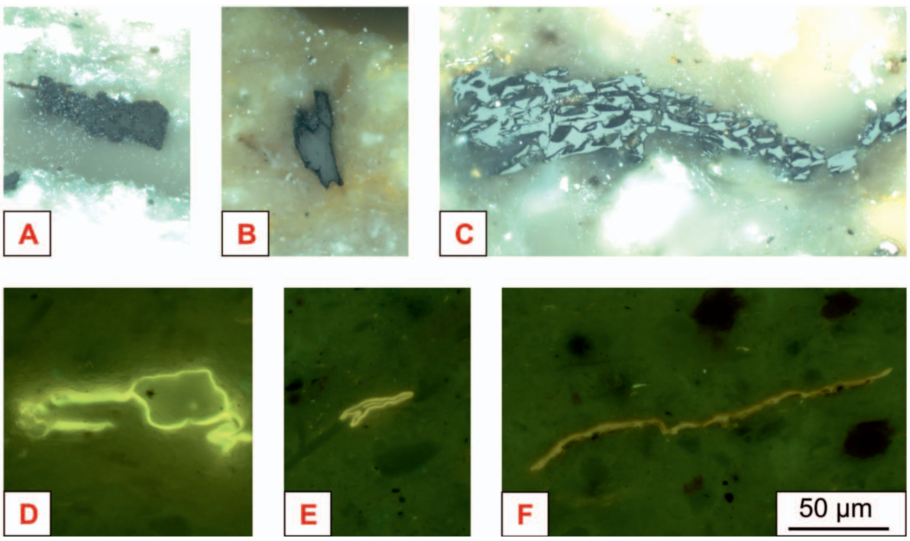

Plate 3. Macerals observed in Hieroglyphic Beds; A – Collotelinite, B – Semifusinite, C – Fusinite, D – Alginite, E – Sporinite, F – Cutinite; A–C – reflected light, D–F – UV mode

Tablica 3. Macerały obserwowane w warstwach hieroglifowych; A – kolotelinit, B – semifuzynit, C – fuzynit, D – alginit, E – sporynit, F – kutynit; A–C – światło odbite, D–F – światło UV

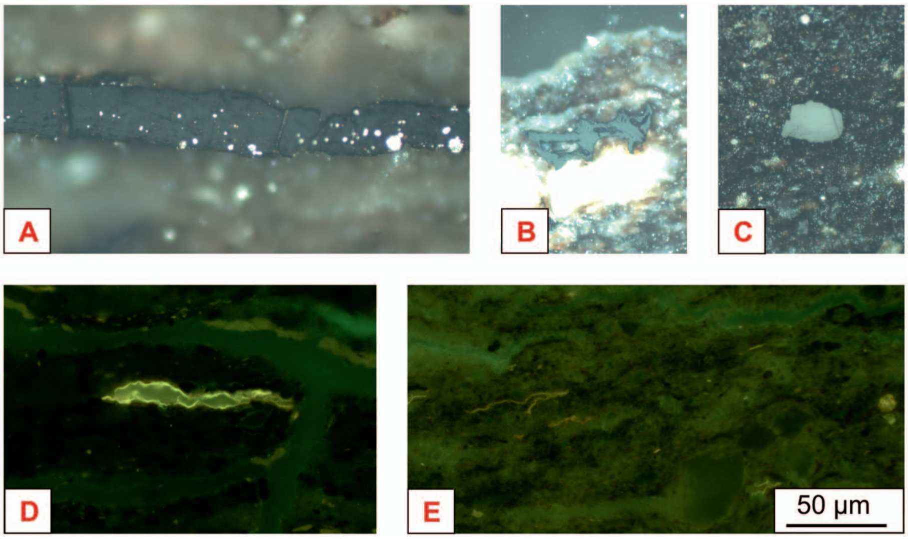

Plate 4. Macerals observed in Menilite Beds; A – Collotelinite, B – Semifusinite, C – Fusinite, D – Alginite, E – Bituminite with alginite and v. fine liptodetrinite; A–C – reflected light, D–E – UV mode

Tablica 4. Macerały obserwowane w warstwach menilitowych; A – kolotelinit, B – semifuzynit, C – fuzynit, D – alginit, E – bituminit z alginitem i bardzo drobnym liptodetrynitem; A–C – światło odbite, D–E – światło

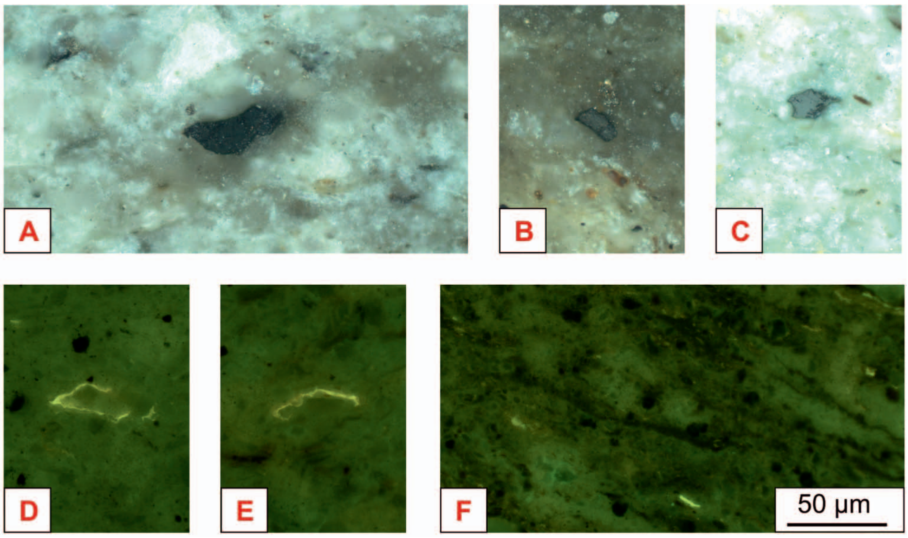

Plate 5. Macerals observed in Krosno Beds; A – Collotelinite, B–C – Semifusinite, D–E – Alginite, F – Bituminite, A–C – reflected light, D–F – UV mode

Tablica 5. Macerały obserwowane w warstwach krośnieńskich; A – kolotelinit, B–C – semifuzynit, D–E – alginit, F – bituminit; A–C – światło odbite, F–J – światło UV

In the composition of organic matter (Tables 2 and 3), vitrinite macerals (collovitrinite and detrovitrinite) are usually observed. Most often they are rare and small. In the case of two samples from Korzeniec, they were not observed at all. Macerals of the inertinite group (fusinite, semifusinite, inertodetrinite) are present, but their content is lower than macerals of the vitrinite group. Macerals of the liptinite group are mainly represented by alginite, the content of which (<0.2% vol.) is similar (or in some cases even higher) to the content of the macerals from the vitrinite group. In sample 1, in addition to alginite, bituminite is also observed. In addition, numerous but fine fragments of solid bitumen are also present.

The analysed organic matter is immature, as indicated by values of the T_{max} parameter in the range of 418–426°C (Table 1). The hydrogen index (HI) values range from 98 to 163, which suggest type III kerogen (Fig. 2).

Summary

Although the number of analysed samples does not allow one to examine regional trends of variability in the composition and maturity of organic matter, nevertheless, due to similar results from different outcrops, some general statements can be made.

The investigated lithostratigraphic divisions can be divided into four groups in terms of organic matter content. Group 1, with a generally negligible content of organic matter, which includes Variegated Shales. Group 2, with a TOC of approx. 0.5%, which includes samples collected from Inoceramician, Hieroglyphic and Krosno Beds. Group 3 contains Spas Shales, where TOC values of up to 3% are observed. Finally, Group 4, covering the samples with the highest TOC, which includes samples collected from Menilite Beds.

Regardless of the actual content of organic matter, some similarities in the maceral composition, as well as some characteristic features for most of the rocks studied, can be observed. Thus:

- the group of liptinite macerals dominates in samples within the Spas Shales and Menilite Beds, as well as in some of the shales from the Krosno Beds. In the case of Inoceramian and Hieroglyphic Beds, macerals of vitrinite and inertinite groups predominate;
- in the Spas Shales and Krosno Beds, the dominant maceral within the liptinite group is alginite, while in Menilite Beds, bituminite dominates;
- alginite is present in all (except Variegated Shales) investigated lithostratigraphic divisions;

- the content of macerals of the inertinite group is higher than the content of macerals of the vitrinite group in the Spas Shales, Inoceramian Beds and in some rocks from Hieroglyphic Beds. The situation is opposite in the case of Menilite and Krosno Beds.

Organic matter within all the investigated rocks is in the phase of thermal changes referred to as immature, as evidenced by the T_{max} parameter reaching values lower than 435ºC. However, these are samples were collected from the outcrops, while samples collected from the same lithostratigraphic divisions, but derived from the core material, may have higher maturity.

The examined rocks clearly differ in terms of the assessment of their hydrocarbon generation potential (Fig. 3), which is the poorest for Variegated Shales and slightly better (but still poor) in the case of Inoceramian, Hieroglyphic and Krosno Beds. The best generation potential is observed in rocks collected from Spas Shales and Menilite Beds, with the latter having a generation potential defined as very good and even excellent.

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