A study of organic matter and habitat of gaseous hydrocarbons in the Miocene strata of the Polish part of the Carpathian Foredeep

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Geochemical studies on the organic matter from the autochthonous Miocene strata of the Carpathian Foredeep demonstrated the presence of gas-prone type III kerogen in both the Upper Badenian and Lower Sarmatian sediments with rare admixtures of algal type II kerogen. The TOC contents vary from 0.02 to 3.22 wt. %. Down to the depth 3,200 meters the organic matter is immature. Its transformation degree corresponds to the vitrinite reflectance R_o from 0.25 to 0.6% and to the Rock Eval T_{max} temperatures from 415 to 438°C. Insignificant variability in spatial and depth distribution of geochemical parameters and indices (TOC, TE/TOC, T_{max}, HI, R_o, CPI, etc.) suggest that deposition conditions of the organic matter were generally homogenous within the full thickness of Miocene sequence down to the recent depth about 3,200 meters. Such conditions resulted in the lack of diversity of the TOC, the genetic type and the transformation degree of the studied kerogen. The Miocene terrestrial OM is immature and generated almost exclusively the microbial methane. The low-temperature thermogenic processes have been active beneath the depth about 3,200 meters i.e., mainly under the Carpathian overthrust.

Key words: *petroleum exploration, geochemical methods, stable isotopes, organic materials, kerogen, natural gas, genesis, Miocene, Carpathian Foredeep, Poland*

Introduction

The studies reported below aimed to measure the geochemical parameters and indices of the potential source rocks (claystones and mudstones) within the autochthonous Miocene sequence of the Carpathian Foredeep in order to evaluate their hydrocarbon generation potential during transformation of the organic matter (OM).

Genetic constrains of depositional environment of the OM can be characterized by hydrocarbon geochemical parameters: Rock Eval hydrogen (HI) and oxygen (OI) indices, n-alkanes and isoprenoids distribution, stable carbon isotope composition in bitumens, their individual fractions (saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes) and kerogen as well as maceral compositions. Transformation degree of the OM was evaluated from the vitrinite reflectance R_o and the Rock Eval T_{max} temperature.

The selection of core material collected from wells for the studies on dispersed OM takes into consideration the spatial lithofacial development of the autochthonous Miocene molasse formation in the Polish part of the Carpathian Foredeep. Thus, the four representative test areas were chosen in the Carpathian Foredeep for comparison of the presumed spatial variability of geochemical parameters and indices of the source rocks which practically reflect the variability of hydrocarbon generation conditions (Fig. 1). The two areas: A (Tarnów) and B (Mielec–Leżajsk) repre-

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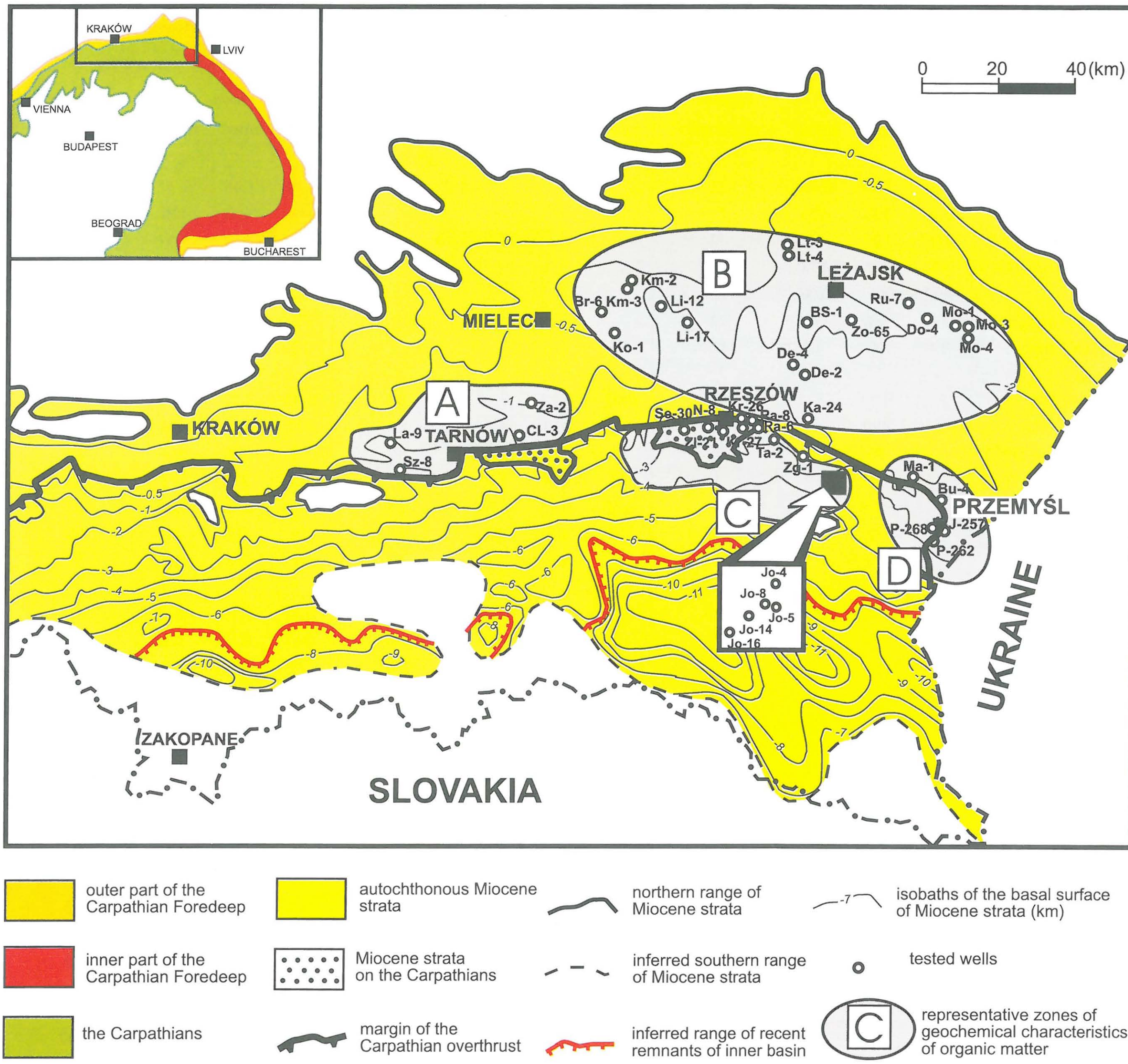

Fig. 1. Sketch map of central and eastern parts of the Polish Carpathian Foredeep and location of studied wells and test areas. For key to the wells see the text

sent the generation conditions of the outer zone of the Carpathian Foredeep, i.e. north of the recent edge of the Carpathian overthrust whereas the areas C (Rzeszów) and D (Przemyśl) ilustrate such conditions along the recent edge of the Flysch Carpathian overthrust (Fig. 1).

For laboratory analyses 237 claystone/mudstone core samples were collected: 55 samples from Upper Badenian strata and 182 samples from Lower Sarmatian strata. Totally, 41 wells were sampled in the four test areas, as specified below:

A test area — 4 wells: Czarny Las 3 (CL-3), Łazy 9 (La-9), Szczepanów 8 (Sz-8) and Zasów 2 (Za-2),

B test area — 18 wells: Brazylia 6 (Br-6), Brzóza Stadnicka 1 (BS-1), Dębina 2 (De-2), Dębina 4 (De-4), Dobra 4 (Do-4), Kańczuga 24 (Ka-24), Komorów 2 (Km-2), Komorów 3 (Km-3), Kosowy 1(Ko-1), Lipnica 12 (Li-12), Lipnica 17 (Li-17), Łętownia 3 (Lt-3), Łętownia 4 (Lt-4), Mołodycz 1 (Mo-1), Mołodycz 3 (Mo-3), Mołodycz 4 (Mo-4), Rudka 7 (Ru-7) and Żołynia 65 (Zo-65),

C test area — 14 wells: Nosówka 8 (N-8), Sędziszów 30 (Se-30), Jodłówka 4 (Jo-4), Jodłówka 5 (Jo-5), Jodłówka 8 (Jo-8), Jodłówka 14 (Jo-14), Jodłówka 16 (Jo-16), Krasne 26 (Kr-26), Krasne 27 (Kr-27), Rączyna 6 (Ra-6), Rączyna 8 (Ra-8), Tarnawka 2 (Ta-2), Zagórze 1 (Zg-1) and Zalesie 21 (Za-2),

D test area — 5 wells: Buszkowiczki 4 (Bu-4), Jaksmanice 257 (J-257), Maćkowice 1 (Ma-1), Przemyśl 262 (P-262) and Przemyśl 268 (P-268).

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Geological setting and gas occurrence

The Carpathian Foredeep is one of the largest sedimentary basins in Central Europe. It forms an Alpine-age tectonic trough filled with the Miocene marine molasse. The

Tab. 1. Ranges and arithmetic mean values of pyrolytic Rock Eval and extraction data for autochthonous Miocene strata

Stratigraphy	UPPER BADENIAN				LOWER SARMATIAN				TOTAL MIOCENE			
	Values			Number	Values			Number	Values			Number
	min.	max.	mean	of samples	min.	max.	mean	of samples	min.	max.	mean	of samples
A Area												
TOC (wt. %)	0.30	1.48	0.74	22					0.30	1.48	0.74	22
T_{max} (°C)	419	430	426	22					419	430	426	22
HI (mg HC/g TOC)	60	120	85	22		NO SAMPLES			60	120	85	22
OI (mg CO_2/g TOC)	83	342	177	22					83	342	177	22
PI	0.02	0.23	0.07	22					0.02	0.23	0.07	22
TE/TOC (mg/g)	32	68	50	22					32	68	50	22
HC/TOC (mg/g)	12	26	19	15					12	26	19	15
B Area												
TOC (wt. %)		0.43		1	0.02	3.22	0.75	89	0.02	3.22	0.75	90
T_{max} (°C)		429		1	422	433	430	87	422	433	430	88
HI (mg HC/g TOC)		76		1	32	160	95	87	32	160	94	88
OI (mg CO_2/g TOC)		153		1	45	274	140	87	45	274	141	88
PI		0.08		1	0.00	0.15	0.04	87	0.00	0.15	0.04	88
TE/TOC (mg/g)		42		1	16	400	41	89	16	400	41	90
HC/TOC (mg/g)		23		1	6	89	20	50	6	89	20	51
C Area												
TOC (wt. %)	0.31	1.08	0.58	31	0.10	1.19	0.62	71	0.10	1.19	0.61	102
T_{max} (°C)	427	438	431	31	415	433	430	70	415	438	430	101
HI (mg HC/g TOC)	89	207	128	31	29	170	111	70	29	207	116	101
OI (mg CO_2/g TOC)	4	231	108	31	41	404	133	70	4	404	125	101
PI	0.01	0.19	0.06	31	0.00	0.08	0.03	70	0.00	0.19	0.04	101
TE/TOC (mg/g)	17	91	46	26	14	78	45	57	14	91	45	83
HC/TOC (mg/g)	15	66	28	15	16	44	24	22	15	66	25	37
D Area												
TOC (wt. %)		0.60		1	0.37	0.78	0.66	22	0.37	0.78	0.66	23
T_{max} (°C)		431		1	426	433	430	22	426	433	430	23
HI (mg HC/g TOC)		106		1	74	132	100	22	74	132	101	23
OI (mg CO_2/g TOC)		60		1	44	237	113	22	44	237	111	23
PI		0.03		1	0.01	0.07	0.03	22	0.01	0.07	0.03	23
TE/TOC (mg/g)		47		1	21	58	37	22	21	58	37	23
HC/TOC (mg/g)		20		1	14	32	23	10	14	32	23	11
TOTAL AREA												
TOC (wt. %)	0.30	1.48	0.64	55	0.02	3.22	0.69	182	0.02	3.22	0.68	237
T_{max} (°C)	419	438	429	55	415	433	430	179	415	438	430	234
HI (mg HC/g TOC)	60	207	109	55	29	170	102	179	29	207	104	234
OI (mg CO_2/g TOC)	4	342	135	55	41	404	134	179	4	404	134	234
PI	0.01	0.23	0.07	55	0.00	0.15	0.04	179	0.00	0.23	0.04	234
TE/TOC (mg/g)	17	91	48	50	14	400	42	168	14	400	43	218
HC/TOC (mg/g)	12	66	23	32	6	89	21	82	6	89	22	114

trough extends along the front of the Carpathian orogenic belt, from Vienna (Austria) in the west towards the Iron Gate (Danube) in Romania in the south-east (Fig. 1) and partly also underlies the Carpathian nappes. The Carpathian Foredeep is divided into the two basins: outer and inner (Ney et al., 1974; Oszczypko, 1996, 1997) (Fig. 1). The folded Miocene strata of the Stebnik and Zgłobice units known from the inner basin in the Polish part of the Carparhian Foredeep (Ney, 1968; Oszczypko, 1996, 1997) are thought to be unimportant for petroleum exploration. The eastern part of the outer basin (east from Kraków) is filled with Badenian and Lower Sarmatian sediments of the following thicknesses: Lower and Middle Badenian — from 0 to 300 m, Upper Badenian — from 0 to 1,700 m, and Lower Sarmatian — from 0 to 2,900 m (Ney et al., 1974). Most of the discovered gas fields is reservoired within the Upper Badenian and Lower Sarmatian strata developed as clay-sandy, mainly deltaic facies (Karnkowski, 1989). Maximum sedimentation rate of Upper Badenian sediments was 1,500 m/Ma, and for the Lower Sarmatian ones it reached 5,000 m/Ma. On the other hand, the Lower and Middle Badenian strata comprise shallow-water, psammitic, argillaceous and chemical sediments. The autochthonous Miocene sediments of the outer basin of the Carpathian Foredeep have not been affected by Alpine orogenic movements and rest almost horizontally upon the Precambrian–Paleozoic–Mesozoic basement (Oszczypko, 1982, 1996).

The gas fields discovered in the autochthonous Miocene of the Polish part of the Carpathian Foredeep contain practically only the methane accompanied by small amounts of higher gaseous hydrocarbons. Cumulative production yielded about $80*10^9$ cubic meters of gas between the years 1945

Tab. 2. Vitrinite reflectance R_o and maceral composition of organic matter from autochthonous Miocene strata

Depth (m)	Strati-graphy	R_o (%)	Maceral groups (%)		
			Vitrinites	Inertinites	Exinites
Łazy 9 well (A area)					
903	U.B.	0.29	74.7	25.3	0.0
Rudka 7 well (B area)					
604	L.S.	0.25	70.9	29.1	0.0
1252	L.S.	0.45	80.1	19.1	0.0
1354	L.S.	0.40	79.5	20.5	0.0
Jodłówka 4 well (C area)					
1769	L.S.	0.35	82.7	17.3	0.0
1997	L.S.	0.43	80.9	19.1	0.0
2191	L.S.	0.45	79.3	20.7	0.0
2349	L.S.	0.45	81.9	18.1	0.0
2519	L.S.	0.50	80.6	19.4	0.0
2668	L.S.	0.55	74.5	25.5	0.0
2792	U.B.	0.55	84.0	16.0	0.0
Krasne 27 well (C area)					
1410	L.S.	0.42	n.a.	n.a.	n.a.
2111	L.S.	0.44	n.a.	n.a.	n.a.
Rączyna 6 well (C area)					
3412	U.B.	0.45	n.a.	n.a.	n.a.
Rączyna 8 well (C area)					
2380	L.S.	0.44	n.a.	n.a.	n.a.
2888	U.B.	0.44	n.a.	n.a.	n.a.

U.B. — Upper Badenian, L.S. — Lower Sarmatian, n.a. — not analysed

Tab. 3. Ranges of geochemical indices of n-alkanes and isoprenoids for autochthonous Miocene strata

Stratigraphy / Ratios	UPPER BADENIAN			LOWER SARMATIAN		
	Values min.	Values max.	Number of samples	Values min.	Values max.	Number of samples
$CPI_{(TOTAL)}$	1.11	1.96	10	0.79	1.84	18
$CPI_{(17-23)}$	0.85	1.33	10	0.92	1.21	18
$CPI_{(25-31)}$	1.16	2.37	10	0.57	3.25	18
Pr/Ph	0.15	1.45	10	0.23	1.17	18
Pr/n-C_{17}	0.81	6.13	10	0.89	4.51	18
Ph/n-C_{18}	1.12	21.00	10	0.79	3.44	18

Tab. 4. Results of stable carbon isotope analyses of bitumins, their fractions and kerogen from autochthonous Miocene strata

Depth (m)	Strati-graphy	Stable carbon isotope composition $\delta^{13}C$ (‰)					
		Bitu-men	Hydrocarbons satura-ted	Hydrocarbons aroma-tic	Resins	Asphal-tenes	Kero-gen
Łazy 9 well (A area)							
903	U.B.	-27.1	-27.3	-26.8	-26.9	-26.8	-26.2
1001	U.B.	-27.0	-28.2	-27.8	-27.2	-26.4	-25.5
Szczepanów 8 well (A area)							
888	U.B.	-27.4	-28.5	-27.6	-27.0	-27.0	-26.7
Brzóza Stadnicka 1 well (B area)							
353	L.S.	-28.1	-28.2	-28.0	-28.3	-27.8	-25.6
886	L.S.	-28.0	-28.6	-27.5	-27.1	-27.8	-26.2
1590	L.S.	-28.2	-28.6	-28.0	-27.3	-27.9	-26.5
Łętownia 3 well (B area)							
756	L.S.	-28.4	-28.4	-27.1	-28.2	-27.2	-25.6
856	L.S.	-27.8	-28.9	-27.9	-27.8	-28.3	-26.0
861	L.S.	-28.2	-28.7	-27.9	-27.7	-28.4	-26.0
Rudka 7 well (B area)							
604	L.S.	-27.7	-28.4	-28.3	-27.2	-27.4	-25.2
1053	L.S.	-28.8	-29.9	-28.8	-28.0	-27.6	-25.3
Jodłówka 4 well (C area)							
2349	L.S.	-28.6	-29.1	-28.2	-27.8	-27.4	-26.4
2670	L.S.	-28.3	-28.6	-27.8	-27.4	-27.9	-26.0
3336	U.B.	-27.3	-28.1	-27.0	-26.9	-26.9	-25.7
Nosówka 8 well (C area)							
3219	U.B.	-26.4	-27.7	-26.3	-26.7	-26.6	-25.5

←

$$CPI_{(TOTAL)} = \frac{(C_{17}+C_{19}+....+C_{27}+C_{29})+(C_{19}+C_{21}+....+C_{29}+C_{31})}{2(C_{18}+C_{20}+....+C_{28}+C_{30})}$$

$$CPI_{(17-23)} = \frac{(C_{17}+C_{19}+C_{21})+(C_{19}+C_{21}+C_{23})}{2(C_{18}+C_{20}+C_{22})}$$

$$CPI_{(25-31)} = \frac{(C_{25}+C_{27}+C_{29})+(C_{27}+C_{29}+C_{31})}{2(C_{26}+C_{28}+C_{30})}$$

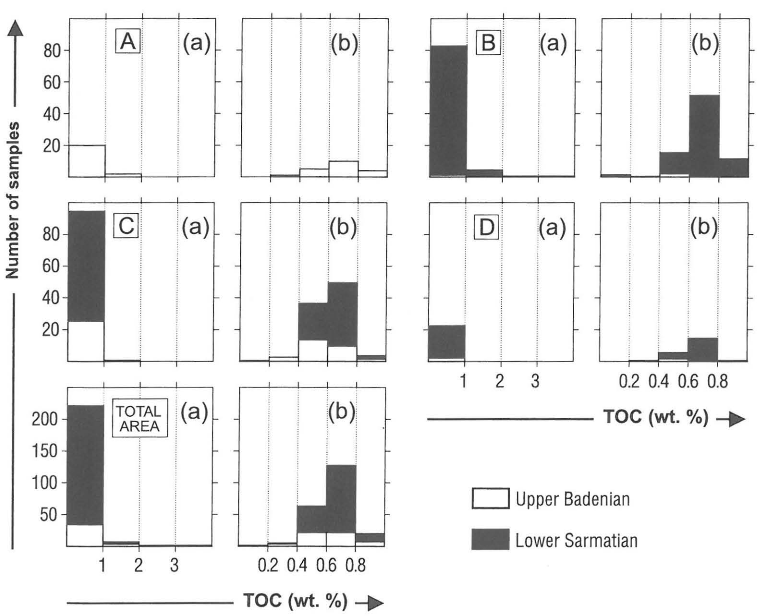

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Fig. 2. Histograms of TOC contents in the autochthonous Miocene strata in test areas: (A) Tarnów, (B) Mielec–Leżajsk, (C) Rzeszów, (D) Przemyśl and Total area, in the ranges **(a)** from 0 to 4 wt. % and **(b)** from 0 to 1 wt. %

and 1998. The remaining proved reserves of about $70*10^9$ cubic meters are still available. Undiscovered resources are estimated to be about $190*10^9$ cubic meters. The production of natural gas from the autochthonous Miocene reservoirs has started in 1924 from the Daszawa field (recently in Ukraine). Since 1945 the 70 gas fields have been discovered in the Polish part of the Carpathian Foredeep, and the Przemyśl–Jaksmanice deposit of initial reserves about $80*10^9$ cubic meters is most important.

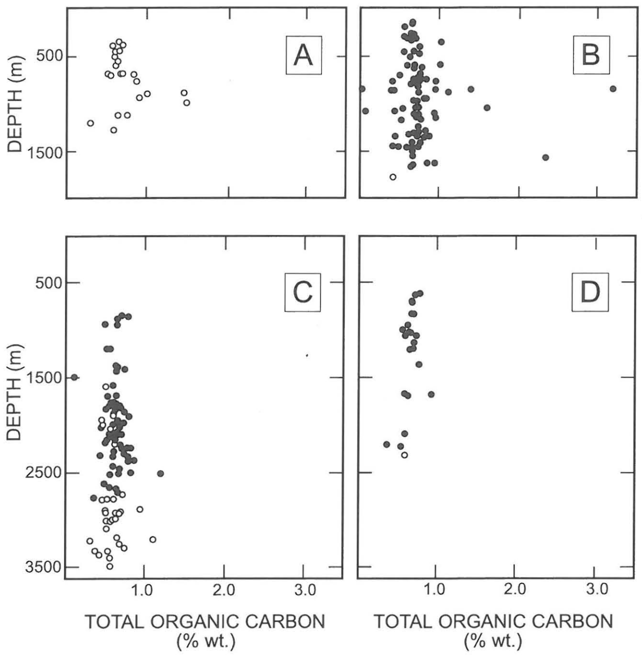

Fig. 3. TOC for organic matter from the autochthonous Miocene strata versus depth in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

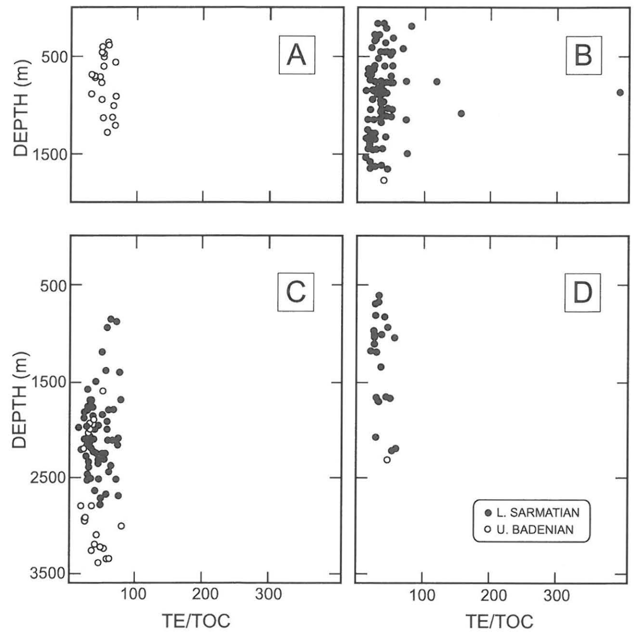

Fig. 4. Bitumen index (Total extract/TOC) for organic matter from the autochthonous Miocene strata versus depth in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

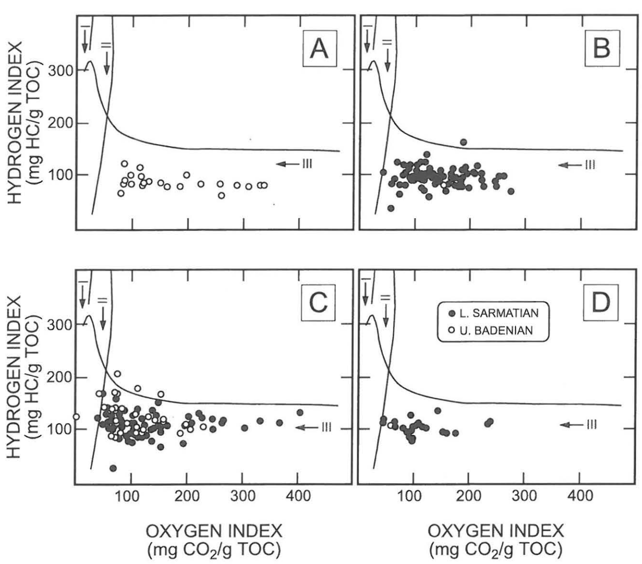

Fig. 5. Hydrogen index versus oxygen index for organic matter from the autochthonous Miocene strata in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

Experimental

Pyrolysis assay of samples was carried on with the Delsi Model II Rock Eval instrument equipped with an organic carbon module, as described in detail by Espitalié et al. (1977), Kotarba & Szafran (1985), Peters (1986) and Wilczek & Merta (1992). Results of Rock Eval pyrolysis of claystones/mudstones are presented in Tab. 1.

The claystone/mudstone samples were pulverized and then extracted with chloroform in the Soxhlet apparatus.

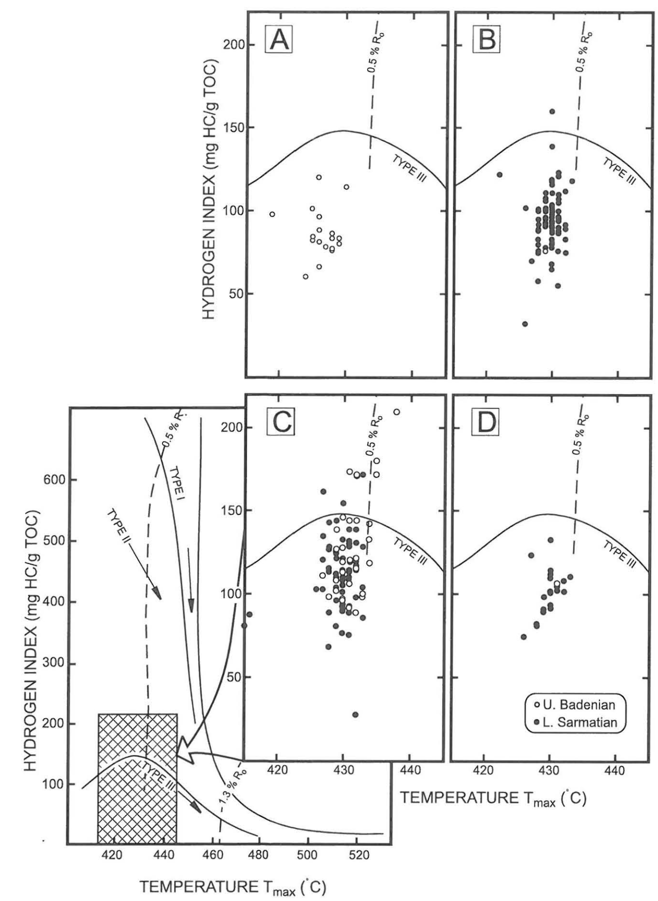

Fig. 6. Hydrogen index versus T_{max} temperature for organic matter from the autochthonous Miocene strata in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

Chloroform extracts were separated into saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes by the column chromatography. Alumina/silica gel (2:1 v/v) columns (0.6x20 cm) were eluted with petroleum benzin, benzene and benzene–methanol (1:1 v/v) in order to obtain first three fractions. Asphaltenes were precipitated with petroleum benzin prior to the column separations. Ranges of bitumen (TE/TOC) and hydrocarbon (HC/TOC) ratios are presented in Tab. 1.

Petrographic studies of the OM included quantitative analyses of vitrinite, exinite and inertinite maceral groups under the Axioplan-Opton microscope. Measurements of mean random vitrinite reflectance (R_o) were carried at 546 mm in oil with the Axioplan-Opton microphotometer and Opton 20 Microscope System Processor. Point-countings were made in accordance with the procedure of the ICCP. Results of petrographic observations and vitrinite reflectance measurements for claystones/mudstones are presented in Tab. 2.

The C_{11+} saturated hydrocarbons (n-alkanes and isoprenoids) were separated on a Hewlett Packard 5890 Series II gas chromatograph with a 25 m x 0.32 mm capillary column coated with methyl silicon gum phase temperature — programmed from 110 to 310°C. Ranges of ratios calculated based on n-alkanes and isoprenoids distribution in bitumens are presented in Tab. 3.

After the removal of carbonates and bitumens, the claystone/mudstone samples selected for stable carbon isotope analyses were combusted in sealed glass tubes, according to the procedure after Sofer (1980). Bitumens and their fractions were prepared for stable carbon isotope analyses in accordance with the same procedure. Stable carbon isotope analyses were run with the Micromass MM 602C and MI-1201 mass spectrometers. The stable carbon isotope data are presented in the standard δ-notation relative to the PDB. Analytical precision is estimated to be ±0.2‰. Results of stable carbon isotope analyses of chloroform extracts (bitumens), their indi-

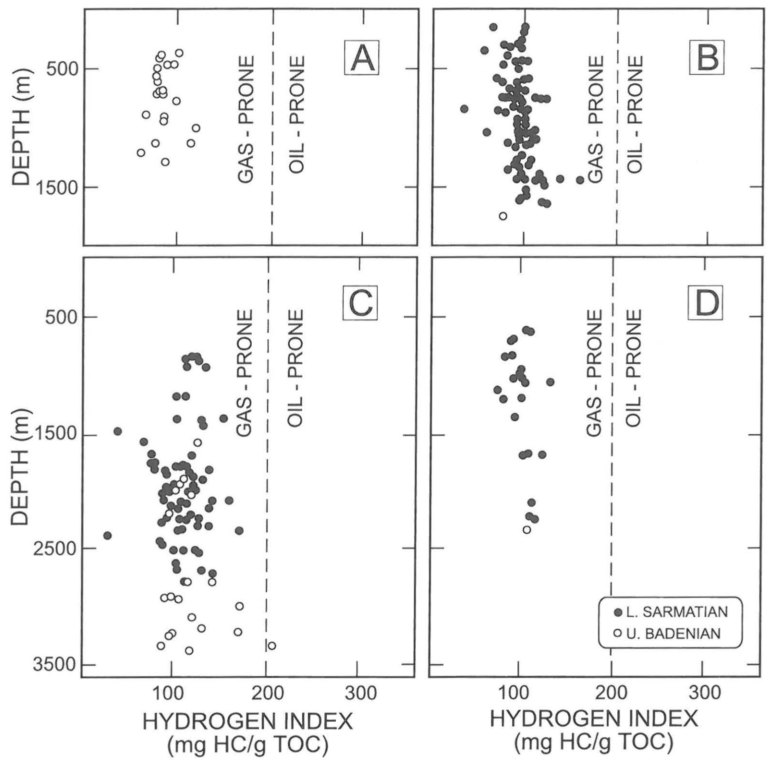

Fig. 7. Hydrogen index for organic matter from the autochthonous Miocene strata versus depth in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

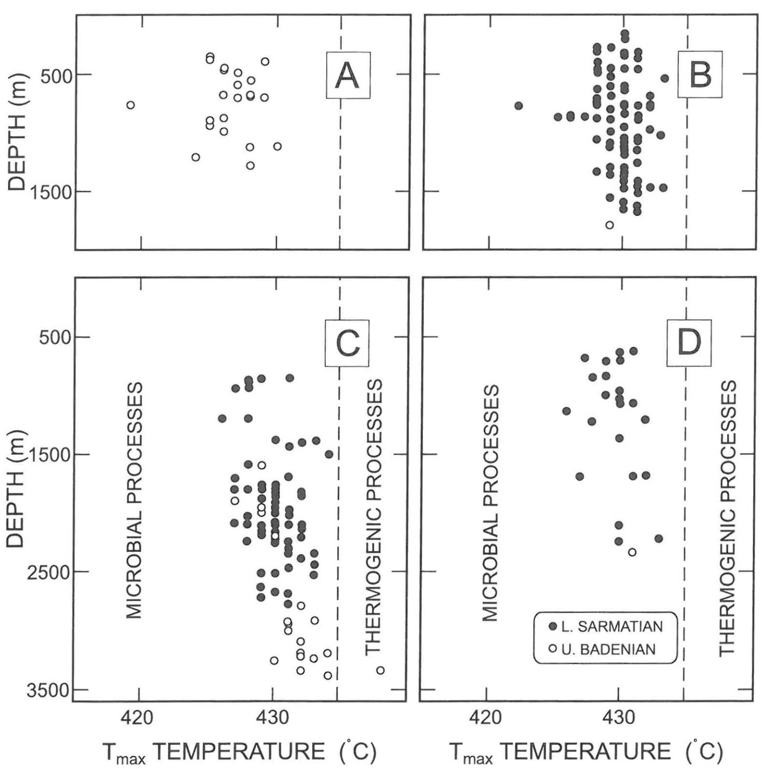

Fig. 8. Rock Eval T_{max} temperature for organic matter from the autochthonous Miocene strata versus depth in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk, **(C)** Rzeszów and **(D)** Przemyśl

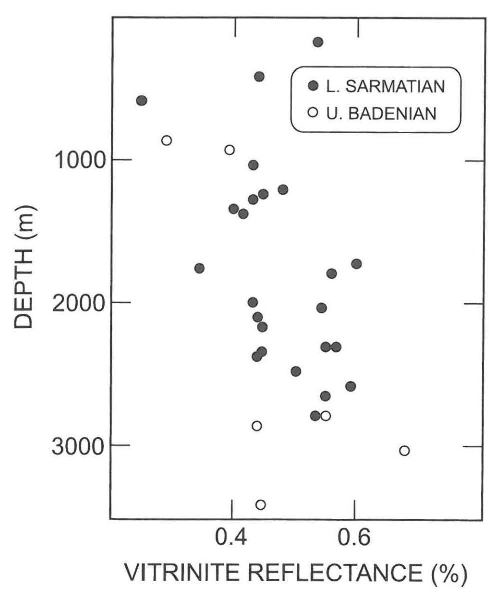

Fig. 9. Vitrinite reflectance for organic matter from the autochthonous Miocene strata versus depth. Data from Table 2 and after Kotarba et al. (1987)

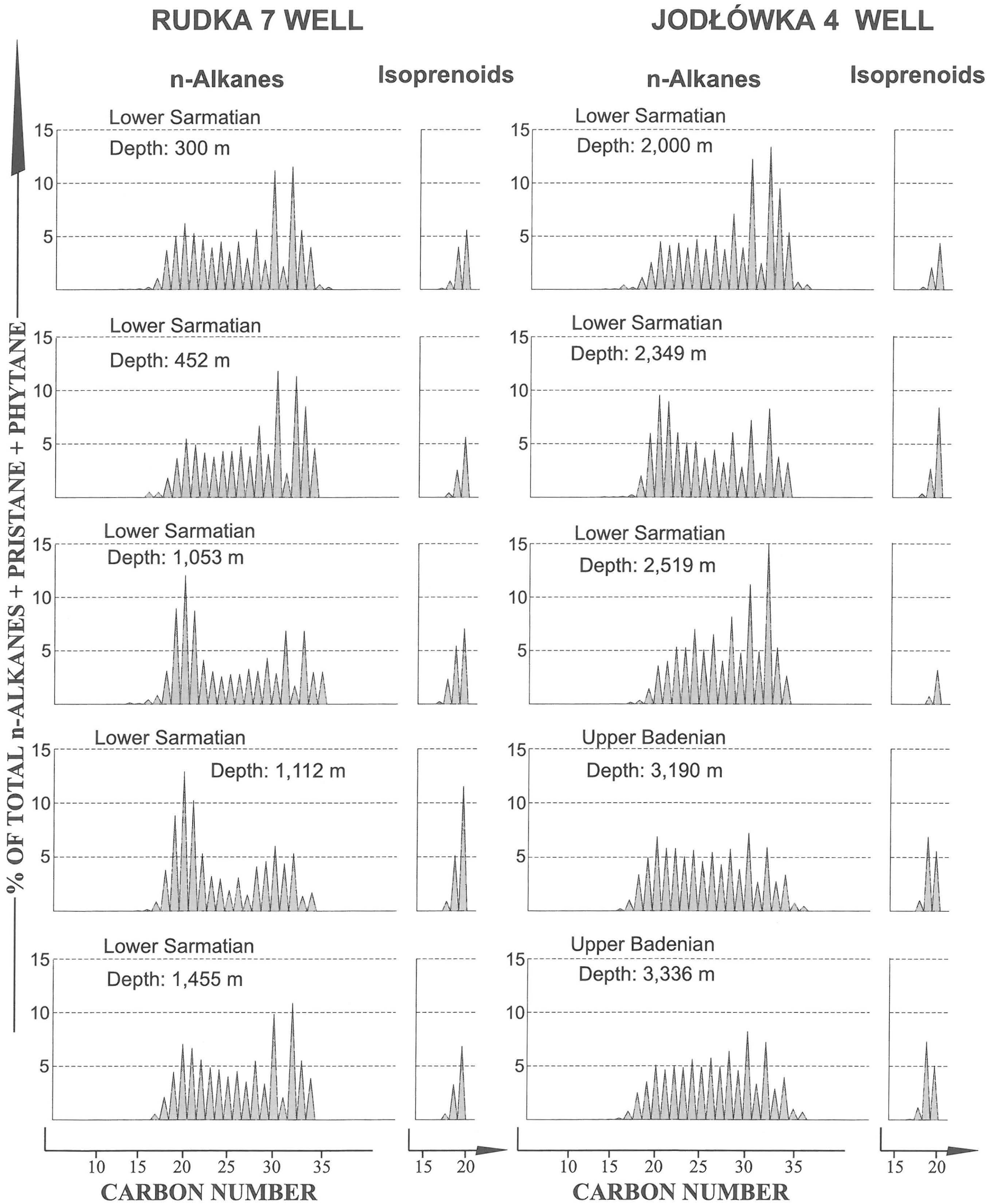

Fig. 10. Examples of distribution of n-alkanes and isoprenoids in bitumens from the autochthonous Miocene sequence from the Rudka 7 and Jodłówka 4 wells

vidual fractions and kerogen from claystones/mudstones are listed in Tab. 4.

Results and discussion

The results of the Rock Eval pyrolytic analyses enable the preliminary assessment of the OM contained in autochthonous Miocene se quence. In the Upper Badenian strata total organic carbon (TOC) contents vary from 0.30 to 1.48 wt. % (average 0.80 wt. %), and in the Lower Sarmatian ones the TOC changes from 0.02 to 3.22 wt. % (average 0.69 wt. %) (Tab. 1). Numerous TOC results obtained in the laboratories of the Polish Oil & Gas Company (unpublished data) are very close to those data and reach up to 5.1 wt. %

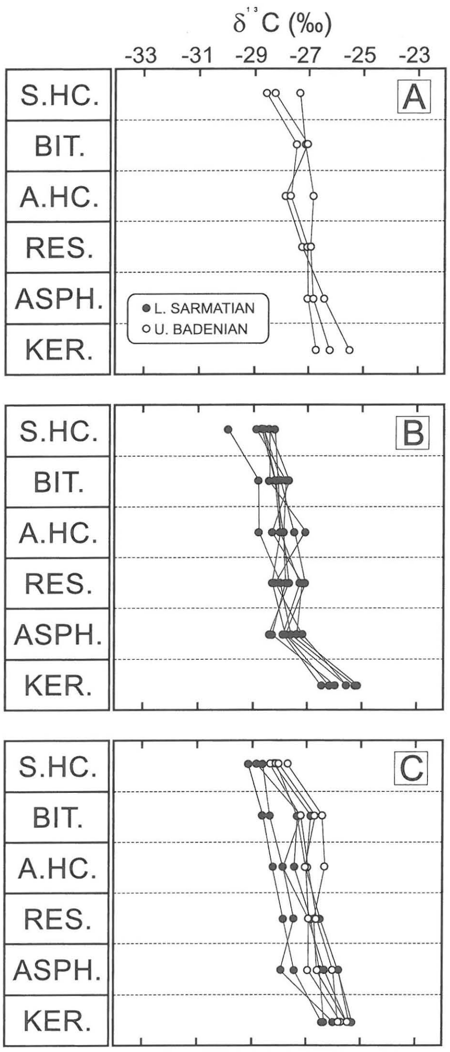

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Fig. 11. Carbon isotopic curves for bitumens of organic matter from the autochthonous Miocene strata in test areas: **(A)** Tarnów, **(B)** Mielec–Leżajsk and **(C)** Rzeszów

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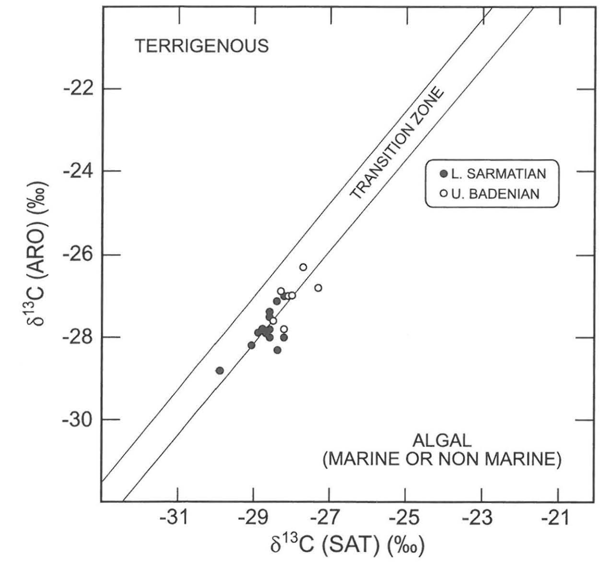
Fig. 12. Carbon isotopic compositions of saturated versus aromatic fractions of bitumens. Compositional fields after Sofer (1984)



(average 0.88 wt. %) and 3.4 wt. % (average 0.82 wt. %) in the Upper Badenian and the Lower Sarmatian strata, respectively. According to Dickey & Hunt (1972), the TOC concentration over 0.5 wt. % is required to qualify a rock as having hydrocarbon potential. The total amounts of extracts normalized to organic carbon vary from 17 to 91 (average 48) mg TE g^{-1} TOC and from 14 to 400 (average 42) mg TE g^{-1} TOC in the Upper Badenian and the Lower Sarmatian strata, respectively (Tab. 1, Fig. 2). Both the TOC and the TE/TOC values in specific lithostratigraphic Miocene members (Upper Badenian and Lower Sarmatian) as well as their spatial and depth distribution show rather poor diversity (Figs 3 and 4). This evidences similar deposition conditions of the OM in the whole Miocene basin of the Polish part of the Carpathian Foredeep.

The values of the Rock Eval HI, OI and T_{max} (Tab. 1 and Figs 5 to 7) evidence the general dominance of the type III terrestrial OM in the whole Miocene sequence. This OM consists mainly of vitrinite-group macerals (from 70.9 to 84.0%) with the complete absence of the members of exinite group (Tab. 2), which also supports the typical terrestrial origin. Moreover, such origin has been also confirmed by the results of elementary analyses of the Miocene fossil remnants (Kotarba et al., 1987). If the terrestrial OM dispersed in claystones/mudstones was capable of generating and expelling oil it should reveal the HI values typically higher than about 200 (Hunt, 1991). However, the HI values close to that limit were found in only few samples (Figs 5 to 7, and Kotarba et al., 1987) which may suggest the presence of small amounts of algal (marine and/or non-marine) OM. The lack of obvious depth trends of the HI values (Fig. 7) advocates the gas-prone character of the whole Miocene sequence.

The immature terrestrial OM shows Rock Eval T_{max} temperature below 435°C (Espitalié & Bordenave 1993). Most of the Miocene samples gave the T_{max} temperatures from 415 to 435°C (Tab. 1). Only in a single sample from Upper Badenian strata (Jo-4 well, depth 3,336 m) the T_{max} = 438°C (Fig. 6) was measured. Such T_{max} values together with no obvious depth trends (Fig. 8) indicate that down to the depths 3,200–3,300 meters the Miocene terrestrial OM is immature and generates almost exclusively the microbial methane. The initial phase of low-temperature thermogenic process proceeds beneath these depths, under the Flysch Carpathian overthrust. Distribution of vitrinite reflectance values of the Miocene OM with the depth (Fig. 9) confirms its low maturation degree. For n-alkanes and isoprenoids distribution there were analyzed 18 samples from Brzóza Stadnicka 1, Jodłówka 4, Łazy 9, Łętownia 3, Nosówka 8, Rudka 7 and Szczepanów 8 wells representing the A, B and C test areas (Fig. 1). The samples originate from wide depth interval (from 300 to 3,219 m) and from various Miocene members (10 from Upper Badenian and 18 from Lower Sarmatian). Ranges of geochemical indices for n-alkanes and are presented in Tab. 3. For most of the measured samples the n-alkanes and isoprenoids distributions are bimodal with distinct maximum for the long-chained hydrocarbons and increased concentrations of odd-number hydrocarbons C_{25}–C_{31}. Such features may be indicative of the terrestrial origin of the OM and of its immaturity. Only few samples taken from greater depths are apparently dominated by long-chained hydrocarbons which may be the result of low-temperature thermogenic processes. The values of Pr/n-C_{17} index are usually much higher than 1 which is typical of terrestrial environments (Didyk et al., 1978) whereas the Pr/Ph index is in most cases less than 0.5 which points to the reducing depositional environment. Examples of analytical results for samples from the Rudka 7 and Jodłówka 4 wells are shown in Fig. 10.

The last two decades have seen a growing interest in the studies on the origin of hydrocarbons and on genetic correlations between oils and source rock based on stable carbon isotope analyses of oils, bitumens, subfractions (saturated and aromatic hydrocarbons, resins and asphaltenes) and kerogens (e.g., Schoell, 1984a, b; Sofer, 1984; Galimov, 1985; Peters et al., 1986; Chung et al., 1992; Curiale, 1994). Stable carbon isotope ratios ($\delta^{13}C$) for autochthonous Miocene samples vary within the following ranges (Tab. 4 and Figs 11 and 12): bitumens — from -28.8 to -26.6‰ (2.2‰ difference), saturated hydrocarbons — from -29.9 to -27.3‰ (2.6‰ difference), aromatic hydrocarbons — from -28.8 to -26.3‰ (2.5‰ difference), resins — from -28.3 to -26.7‰ (1.6‰ difference), asphaltenes — from -28.4 to -26.4‰ (2.0‰ difference), and kerogen — from -26.7 to -25.2‰ (1.5‰ difference). Shapes of isotopic curves (Fig. 11) indicate that organic matter of all analyzed samples have terrestrial character (gas-prone type III kerogen) and that the bitumens are always co-genetic with kerogen. The Sofer's correlation (Sofer, 1984) between $\delta^{13}C$ (saturated hydrocarbons) and $\delta^{13}C$ (aromatic hydrocarbons) suggests that the OM accumulated within the autochthonous Miocene strata contains also the algal component (Fig. 12). However it must be emphasized that the Sofers correlation was initially designed for studies on oils and, thus, some doubts arise to what an extent such approach is applicable to the extracted bitumens. During expulsion of hydrocarbons from the source rocks the isotopic fractionation may appear between the expelled oils, bitumens and kerogens. However, the studied terrestrial OM from the autochthonous Miocene is immature and, undoubtedly, the expulsion of liquid hydrocarbons has not taken place. Hence, it can be concluded that the stable carbon isotope composition of saturated and aromatic hydrocarbons of Miocene bitumens represents the indigenous liquids which may not match the criteria of Sofer's oil genetic classification. This problem apparently needs detailed studies and explanation.

Conclusions

The geochemical studies of the OM from the Autochthonous Miocene of the Carpathian Foredeep proved its terrestrial origin (gas-prone III type kerogen) both in the Upper Badenian and the Lower Sarmatian strata. The admixtures of algal organic matter (kerogen II) are rare. The TOC contents vary from 0.02 to 3.22 wt. % with the mean value 0.68 wt. % for 237 samples. Down to the depth 3,200 meters the OM is immature. Its transformation degree is very low and corresponds to the vitrinite reflectance R_o from 0.25 to 0.6%, (dominating value 0.4%) and the Rock Eval T_{max} temperatures from 415 to 438°C. Insignificant changes in spatial and depth distribution of geochemical parameters and indices (TOC, TE/TOC, T_{max}, HI, R_o, CPI, etc.) suggest the homogenous depositional environment of the OM in the Miocene sequence down to the recent depth 3,200 meters. Such conditions resulted in the lack of remarkable differences in the TOC, the genetic types and the transformation degree of the studied OM. Considering the hydrocarbon generation model for type III kerogen, the maturity of the OM does not exceed the T_{max} = 435°C threshold for microbial methane generation. The low-temperature thermogenic processes could commence only at greater depths (below about 3,200 meters) under the Carpathian overthrust.

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