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GEOCHEMICAL CHARACTERISTICS OF NEOGENE METHANE-BEARING LIGNITE OF THE BEŁCHATÓW REGION***

1. INTRODUCTION

Generally it is known fact that in the earth's crust creation of gases is very widespread because a large part of the natural chemical processes takes place with the separation of gases. Processes of creation of coal and oil in the earth's crust occurred locally and required for their implementation-specific conditions. This phenomenon also applies to lignite.

Coal beds could contain various amount of methane. This attribute might be dangerous in shafts or quarrying. Among other things, the works in the coal beds, including drilling, potentially there is a risk of exceeding the methane lower explosive limit. But on the other hand it is a source of unconventional hydrocarbon accumulations. In this paper geochemical characteristic of organic matter of tertiary brown coal from central part of Poland were performed. Geochemical surveys helps to know about genesis of methane from study area.

There are 90 documented lignite deposits in Poland. Currently, geological resources of lignite are about 26,132 Mt. On the Polish Lowland, ten lignite (eight major and two accompanying) seams have been distinguished within the Paleogene and Neogene stratigraphic columns [2].

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2. LOCATION

Occurrence of brown coal in Poland was divided into eight regions: Bełchatów, Konin, Legnica, Łódź, North-West, Radom, Western and Wielkopolska [7].

The authors focused their research on the region Bełchatów in the Polish Lowlands. The study area includes the lignite deposits located within the Kleszczów Graben (Fig. 1).

Fig. 1. Research area on the lignite deposits divided by region [7; modified]

In this area the Miocene sediments in the vicinity of the Dębina Salt Dome (Fig. 2) are located directly on the remains of the Oligocene sediments. The Kleszczów Graben forms the easternmost part of the Tertiary graben system, which occurs on the North European Paleozoic platform, in the foreland of the Polish Carpathians Lignite deposits are located within the Kleszczów Graben [1].
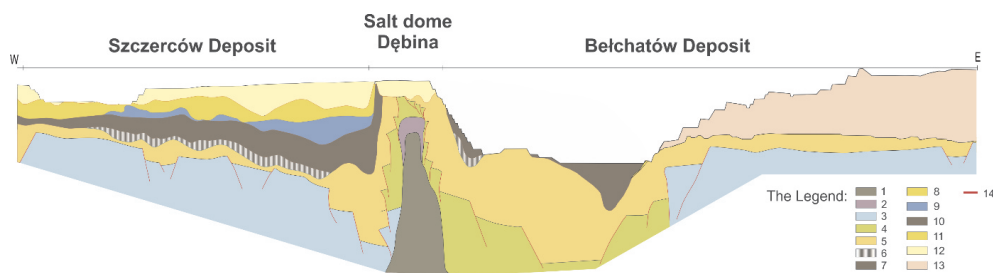
Fig. 2. The Dębina Salt Dome on the cross-section through the Szczerców and Bełchatów lignite deposit [6; modified] 1 – Salt, 2 – Gypsum cap, 3 – Jurassic, 4 – Cretaceous, 5 – Underlying-coal complex, 6 and 7 – Coal complex, 8 – Coal and sandstone complex, 9 and 10 – Clay and coal complex,11 – Clay and sandstone complex 12 – Quaternary, 13 – Dumping ground, 14 – Fault

The deposits are located in the southern part of the Middle Poland Synclinorium. Miocene sediments in the area of the salt dome lie directly on the residually preserved Oligocene sediments, and in the remaining area in the karst limestone and Upper Jurassic limestones and Upper Cretaceous opoka. They provide both a tectonic border of the Kleszczów Graben [1].

Length of the Graben is about 40 km in width from 1.5 to 3.5 km and a depth of 150 to 350 m. By the classification, these lignite deposits belongs to the soft, high--huminite brown coals type [1].

Within these deposits four complexes are separated: Sub-carbon, carbon, carbon--clay and clay-covered sandy sediments of the Pleistocene with a thickness of up to over 100 m. Thickness of the coal exceeding repeatedly 50 m. The complex carbon collapse gradually to the west with increasing its thickness [1].

3.   METHODS

Dry coal samples were crushed to the 0.5–2 cm fraction. Then each sample was milled to the < 0.2 mm fraction for geochemical analyses. Screening pyrolysis analyses of brown coal samples were carried on with a Rock-Eval Model II instrument. Each sample was heated up to 300°C for 3 minutes followed by a programmed growth of temperature at 25°C/min up to 600°C. Process was made under Helium flow. After pyrolysis each sample was buried at 600°C under Oxygen flow. Analytical cycle was began from IFP 160000 standard. Total Organic Carbon (TOC), thermally released hydrocarbons (S_1), pyrolysate hydrocarbons (S_2), carbon dioxide (S_3) and temperature of maximum pyrolysate yield (T_{max}) were measured. (S_2/TOC)*100 – hydrogen index (HI), (S_3/TOC) oxygen index (OI), $S_1 + S_2$ – Potential Yield (Py) and $S_1/(S_1 + S_2)$ – Production Index (PI) were calculated [13].

Subsequently, samples were extracted with dichloromethane:methanol (93:7 v/v) in a SOXTEC™ apparatus. The asphaltene fraction was precipitated with n-hexane. The remaining maltenes were then separated into compositional fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography, using alumina:silica gel (2:1 v/v) columns (0.8 × 25 cm). The fractions were eluted with n-hexane, toluene, and toluene:methanol (1:1 v/v), respectively [12].

The biomarker distributions were determined by analysing the maltene fraction on a computerized GC-mass spectrometer (MS) system using a Hewlett Packard 6890 GC with a DB-1701 60 m × 0.31 mm column (0.25 mm film thickness, bonded phase: 14% cyanopropylphenyl – 86% dimethyl-polysiloxane copolymer) directly interfaced to a JEOL GC-Mate magnetic sector MS [12].

The saturated hydrocarbon fractions of the extracted bitumens were analysed with the GC for n-alkanes and isoprenoids. Analyses were carried out with a Hewlett Packard type 5890 Series II gas chromatograph equipped with fused silica capillary column (25 m × 0.32 mm i.d.) coated with methyl silicone gum phase (HP-1 0.52 mm film thickness) and flame ionisation detector. Nitrogen was used as a carrier gas. The aromatic hydrocarbon fractions were analysed for phenantrene and its derivatives with the same GC, carrier gas and detector using a fused silica capillary column (0.25 mm i.d.) coated with 95% methyl/5% phenylsilicone phase (DB-5, 0.25 mm film thickness) [12].

Gas samples for stable carbon isotope analysis were collected in central part of study area. Stable carbon isotope analyses were ran with the Finnigan Delta Plus mass spectrometer. Stable carbon data were presented in δ-notation relative to the PDB standard. Analytical precision was estimated as ±0.2‰.

4. RESULTS AND DISCUSSIONS

Rock-Eval results allow to define kerogen type, content of hydrocarbons and thermal maturity of organic matter. Hydrogen index equal nearly 140–150 mg HC/g rock indicate that hummic organic matter prevails in all samples except K86D/st and K86D/sp samples where the higher HI values proves that admixture of sappropel organic matter occurs (Tab. 1). On the other hand low values of S_2/S_3 index are suggesting domination of III type kerogene. Results presents in Table 1 shows that all samples contain immature organic matter. T_{max} values range from 354 to 419. According to T_{max} values and RE pirograms more mature organic matter is located in bottom part of analysing beds. Thermal immaturity and domination of III type kerogene, indicate that microbial natural gas should be the only representative of syngenetic hydrocarbons. Present of another hydrocarbons could proves hydrocarbons migration from underburden rocks. On the

other hand PI values suggest that 6 samples contain early mature organic matter. High S_1 values in compare to thermal immaturity could prove slight migration of epigenetic hydrocarbons from underburden rocks [3, 13].

Table 1

Table 1

Rock-Eval analysis results

No.	Sample name	TOC	T_{max}	S_1	S_2	S_1+S_2	S_3	PI	S_2/S_3	HI	OI	PC	RC
1	Zł/st	49.71	361	18.21	73.05	91.26	23.65	0.20	3.09	147	48	7.60	42.11
2	Zł/sp	44.84	413	11.19	62.55	73.74	16.63	0.15	3.76	139	37	6.14	38.70
3	K86D/st	20.74	354	11.45	67.16	78.61	21.86	0.15	3.07	324	105	6.55	14.19
4	K86D/sp	22.18	385	4.5	49.83	54.33	22.83	0.08	2.18	225	103	4.52	17.66
5	75H/st	49.81	384	11.98	74.74	86.72	25.10	0.14	2.98	150	50	7.22	42.59
6	75H/sp	41.75	419	11.28	57.84	69.12	13.93	0.16	4.15	139	33	5.76	35.99
7	sz6p	71.93	360	18.93	111.37	130.3	18.17	0.15	6.13	155	25	10.85	61.08

HI and T_{max} temperature results showing on Figure 3B, confirm that analysed samples contain immature III type kerogene with admixture of II type. This conclusion was proved by S_2 vs. TOC diagram (Fig. 3A). Organic matter deposited in K86D samples could generated oil and gas. All other samples contain gas prone organic matter.
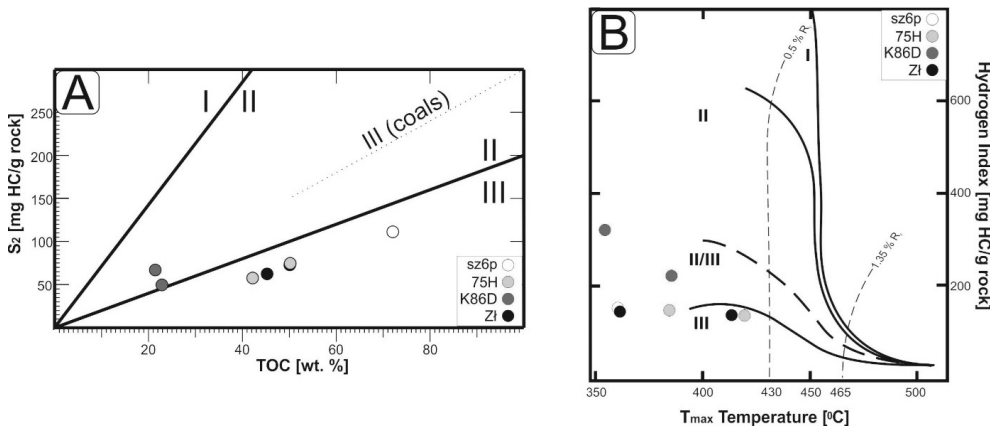

Fig. 3. Rock-Eval pyrolysate hydrocarbons (S_2) versus TOC (A) and hydrogen index versus temperature T_{max} (B) for identification of genetic type and maturity of organic matter [3, 9]

Juxtaposition of S_1 and TOC values (Fig. 4A) suggest that within surveyed samples there are only syngenetic hydrocarbons [4]. High values of TOC, S_1 and S_2 classified analysed samples within excellent source rocks [Fig. 4B].
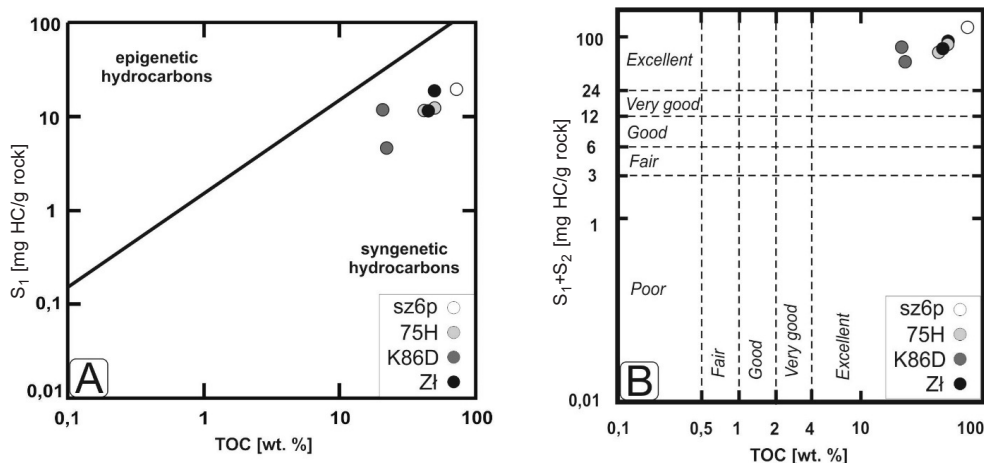

Fig. 4. S_1 versus TOC diagram (A) and Petroleum source quality diagram for organic matter (B) according to Peters and Cassa [10] criteria

Analysis of Pyrograms showed maturity significant increase along with the depth (Figs 6–8). In each case, sample from roof bed is less mature than from floor part. Samples from the eastern part of study area were presented on Figures 6 and 7. Samples from the western part of study area were showed on Figure 8. Pyrogram presented on Figure 5B shows sample from the central part of study area. Additionally, comparison of pyrograms from all study area showed diversity of hydrocarbon distribution (Fig. 5). Pyrogram presented on Figure 5B indicate that sz6p sample has lower content of heavy hydrocarbons than other samples (lower values of S_2 line in higher temperature).

Extraction of bitumens were made in SOXTEC apparatus. Samples contain from 12 998 to 47 960 ppm of bitumens (Tab. 2). The highest amount of bitumens occurred within 2 samples from the western part of study area. Juxtaposition of C15+ hydrocarbon content and TOC values, indicate that surveyed samples are a good oil source (Fig. 9). In case of K86D/st sample presence of epigenetic hydrocarbons was suspected.

In all samples asphaltene fraction are dominating (Tab. 2). Content of this fraction varies from 65% to 80%. Quantities of saturated hydrocarbons and aromatic fraction were low. In almost all cases (except one sample from point H75) values of saturated hydrocarbons were lower than values of aromatic fraction.

N-alkane distribution chromatograms presented only content from range $n\text{-}C_{16}$ to $n\text{-}C_{35}$. Domination of long-chain n-alkanes in all samples, suggest that organic matter from this lignites comes from higher vascular plants. Land genesis was proved by results presented in Table 3, which indicate that nearly 78–88% of all n-alkanes were from range C_{25}–C_{35}. Domination of higher vascular plants origin also proves $\Sigma(n\text{-}C_{12} - n\text{-}C_{22})/\Sigma(n\text{-}C_{23} - n\text{-}C_{35})$ results which were less than 1 [4, 11].
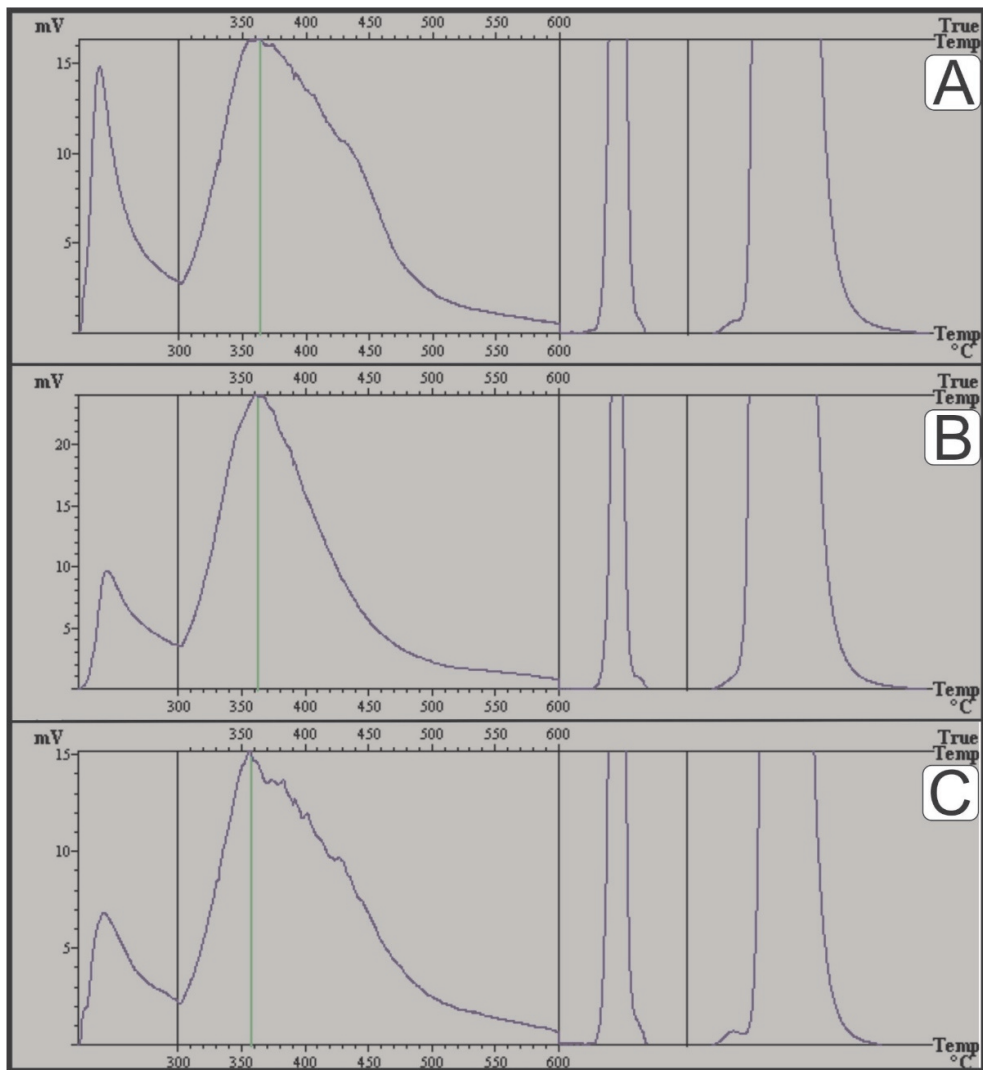

Fig. 5. Pirograms of Zł/st (A), sz6p (B) and K86D/st (C) samples.
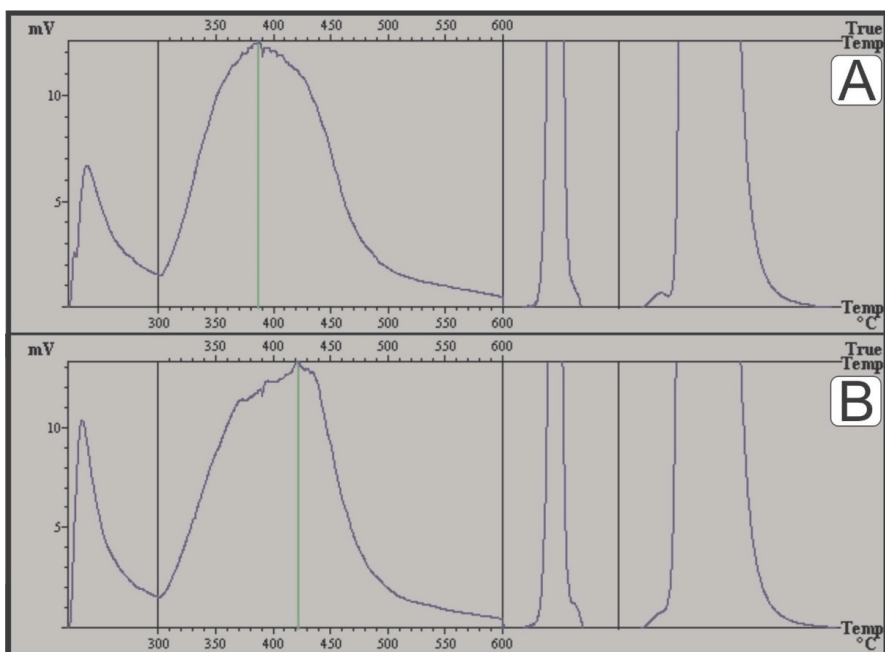Sample A – western part, sample B – central part and sample C – eastern part of study area

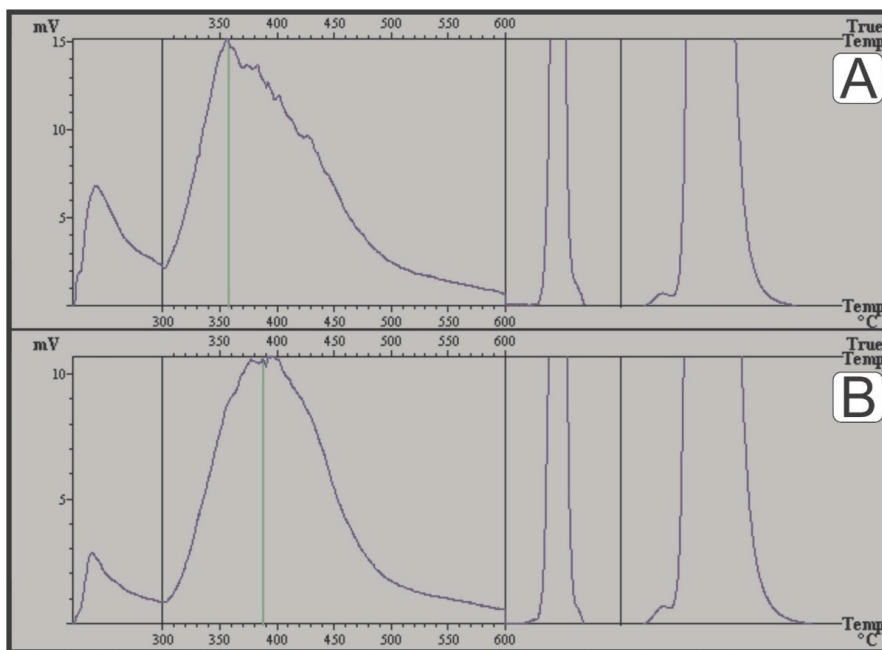**Fig. 6.** Pirograms of H75/st (A) and H75/sp (B) samples
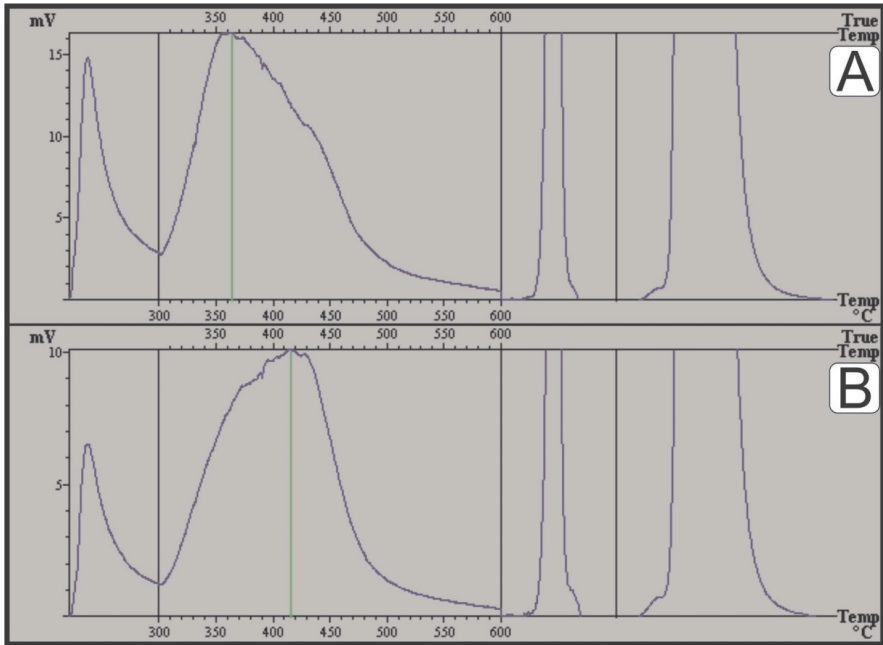

Fig. 7. Pirograms of K86D/st (A) and K86D/sp (B) samples

Fig. 8. Pirograms of Zł/st (A) and Zł/sp (B) samples

Table 2

Contents and quantity of bitumens fractions

Sample name	Content of bitumens [ppm]	Fractions			
		Sat.	Arom.	Res.	Asph.
sz6p	12 998	1	2	24	73
Zł/st	47 960	1	3	28	69
Zł/sp	39 210	2	3	21	74
H75/st	26 871	4	3	25	69
H75/sp	38 480	3	6	27	65
K86D/st	34 299	1	2	17	80

Sat. – saturated hydrocarbons,

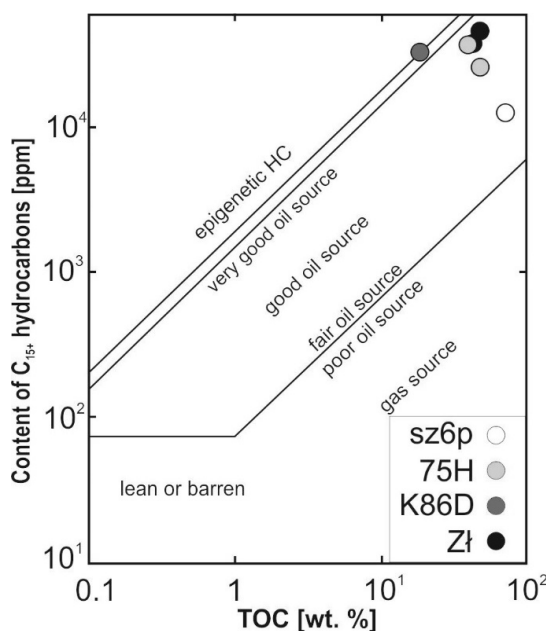Arom. – aromatic hydrocarbons,

Res. – resins,

Asph. – asphaltenes.

Fig. 9. TOC versus contents of bitumens on Hunt's diagram [5; modified]

Table 3

Values of biomarker parameters

Sample name	$\Sigma(C_{12}\text{-}C_{22})/$ $\Sigma(C_{23}\text{-}C_{35})$	$\Sigma C_{13}\text{-}C_{18}$ [%]	$\Sigma C_{19}\text{-}C_{24}$ [%]	$\Sigma C_{25}\text{-}C_{35}$ [%]	C_{23}/C_{31}	Pr/Ph	Pr/C_{17}	Ph/C_{18}	CPI	MPI-1
6psz	0.17	2.71	19.33	77.96	0.29	0.17	0.25	0.75	4.54	0.44
75H/st	0.07	1.28	14.05	84.67	0.34	0.47	0.23	0.23	5.23	0.21
75H/sp	0.08	1.16	14.95	83.90	0.25	0.44	0.23	0.22	3.80	0.43
Zł/sp	0.05	0.96	10.66	88.38	0.16	0.19	0.19	0.40	4.65	0.34

The n-alkanes with odd numbers of carbons to n-alkanes with even numbers of carbons ratio allows to calculate CPI (Carbon Preference Index). There are a few formulas to calculate CPI. In this paper CPI was calculated from the following formula (1) [4]:

$$\frac{0,5\cdot(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})+(C_{23}+C_{25}+C_{27}+C_{29}+C_{31})}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} \tag{1}$$

Low results of CPI indicate that organic matter are more mature. CPI results from 5.23 to 3.80 suggest that all studied samples contain diagenetic organic matter.

Also MPI-1 ratio which does not exceed nearly 0.4 proves that organic matter is not entered into the catagenesis stage. These conclusions were confirmed by results of Pr/n-C_{17} i Ph/n-C_{18} ratio [4].

Palaeoenvirnoment deposition was discovered by Pristane/Phitane ratio. Results less than 1 indicates that studied lignite deposited in anoxic conditions [4]. More anoxic conditions ruled in western and central part of study area.
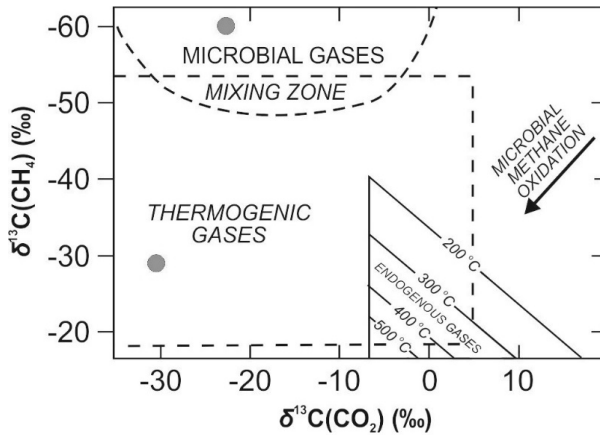

Fig. 10. Stable carbon (δ13C) in methane and carbon dioxide (after [8])

Gases for stable carbon isotope survey was harvested from area of collecting sz6p sample. Results of stable carbon isotope in methane and carbon dioxide (Fig. 10) shows that collected gas has a diverse genesis. In sample M2/4 occurs thermogenic gas came from underburden rocks. In sample M4/4 occurs syngenetic biogenic gas. In two other samples content of methane was too low to measure (Tab. 4). It may suggest that coalbeds from nearly sz6p sample does not contain huge amounts of methane.

Table 4
Results of stable carbon isotope survey

Sample name	Gas	Result 1	Result 2	Average
M 1/4	CO_2	–26.11	–26.23	–26.17
M 2/4	CH_4	–29.26	–29.37	–29.32
	CO_2	–30.36	–30.55	–30.46
M 3/4	CO_2	–15.95	–15.31	–15.63
M 4/4	CH_4	–61.40	–59.69	–60.55
	CO_2	–22.64	–22.70	–22.67

5. CONCLUSIONS

1. Analysed coal samples contains III type kerogene with admixture of II type. Organic matter comes mostly from higher vascular plants.

2. High contents of thermally released and pyrolysate hydrocarbons allow to classify all samples as an excellent source rocks.

3. Organic matter is at the stage of diagenesis what was confirmed by T_{max}, CPI and MPI-1 values. This means that surveyed organic matter is immature in R_o scale.

4. Analysed samples contain only syngenetic hydrocarbons. Presence of epigenetic hydrocarbons is uncertain due to low content of methane in surveyed gases. To prove occurrence of epigenetic hydrocarbons there is need to do more stable carbon analysis in gases collected from all study area.

5. Within entire study area were anoxic conditions during precipitation of analysed lignite. Results of pristane/phitane ratio suggest that more anoxic palaeonvironment conditions was in central and western parts of study area.

6. The lowest content of long-chain n-alkanes indicate that the highest influence of limnic palaeoenvironment was in the central part of study area.

REFERENCES

[1] Bielowicz B., Kasiński J.R.: *The possibility of underground gasification of lignite from Polish deposits.* Reprint. International Journal of Coal Geology, 139, 2015, pp. 191–205.

[2] Bielowicz B.: *Schemat nowej technologicznej klasyfikacji krajowego węgla brunatnego zgodnej z zasadami międzynarodowymi*. Rozprawy Doktorskie. Monografie. Wydawnictwa AGH, Kraków 2012.

[3] Espitalie J., Deroo G., Marquis F.: *La pyrolyse Rock Eval et ses applications*. Rev. l'Inst. Francais Petrole, 1985.

[4] Fabiańska M.: *Geochemia organiczna węgli brunatnych wybranych złóż Polski*. Wydawnictwo Uniwersytetu Śląskiego, Katowice 2007.

[5] Hunt J.M.: *Petroleum Geochemistry and Geology*. 2nd ed. Freeman and Co., New York 1996.

[6] Kasiński J.R., Piwocki M., Sadowska E., Ziembińska-Tworzydło M.: *Lignite of the Polish Lowlands Miocene: characteristics on a base of selected profiles*. Biuletyn Państwowego Instytutu Geologicznego, 439, 2010, pp. 99–154.

[7] Kasiński J., Mazurek S., Piwocki M.: *Waloryzacja i ranking złóż węgla brunatnego w Polsce.* [Valorization and ranking list of lignite deposits in Poland]. Prace Państwowego Instytutu Geologicznego, 187, 2006, 1–79.

[8] Kotarba M.: *Composition and origin of coalbed gases in the Upper Silesian and Lublin basins, Poland*. Org. Geochem., 32, 2001, pp. 163–180.

[9] Langford F.F.: Blanc-Valleron M.M. *Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. total organic carbon*. AAPG Bulletin, 74, 1990, pp. 799–804.

[10] Peters K.E., Cassa M.R.: *Applied source rock geochemistry.* in: Magoon L.B. and Dow W.G. (eds.), The petroleum system. From source to trap. Tulsa, Okla., American Association of Petroleum Geologists Memoir, 60, 1994, pp. 93–117.

[11] Tissot B.P., Welte D.H.: *Petroleum formation and occurrence*. Berlin, 1984.

[12] Więcław D., Kotarba M.J., Kosakowski P., Kowalski A., Grotek I.: *Habitat and hydrocarbon potential of the lower Palaeozoic source rocks in the Polish part of the Baltic region*. Geological Quarterly, 54 (2), 2010, pp. 159–182.

[13] Wilczek T., Merta H.: *Wstępne wyniki badań pirolitycznych metodą Rock-Eval*. Nafta-Gaz, 5–6, 1992, pp. 109–115.