

## ASSESSMENT OF HYDROCARBON POTENTIAL OF THE LOWER PALAEOZOIC STRATA IN THE TARNOGRÓD–STRYI AREA (SE POLAND AND WESTERN UKRAINE)

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**Abstract:** Quantity, genetic type and maturity of organic matter dispersed in the Lower Palaeozoic sequence from the Lower Cambrian to Silurian strata of the Polish and Ukrainian parts of the Carpathian Foredeep basement in the Tarnogród–Stryi area were evaluated based on the results of geochemical analyses of 475 rock samples collected from 45 wells. The best source rocks were found in the Silurian strata where the present total organic carbon (TOC) content is up to 2.6 wt%. They occur in the vicinity of Wola Obszańska, where the median of the present and the initial total organic carbon (TOC) contents in the individual wells amount to 0.98 and 1.6 wt%, respectively. The Cambrian and Ordovician strata have a poorer hydrocarbon potential and their present TOC content never exceeds 1 wt%. In all of the investigated Lower Palaeozoic strata, organic matter is represented by the oil-prone Type-II kerogen deposited in anoxic or sub-oxic conditions. The maturity of source rocks ranges from early mature (the initial phase of the low-temperature thermogenic processes) in selected zones of the Silurian strata in the vicinity of Wola Obszańska, through the middle and the final phase of “oil window” in the Ordovician and Cambrian strata in the Polish part of the study area, to the overmature stage in the Ordovician strata in the south-eastern part of the study area (Ukraine).

**Key words:** source rock, hydrocarbon potential, Cambrian, Ordovician, Silurian, Carpathian Foredeep basement, SE Poland, western Ukraine.

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### INTRODUCTION

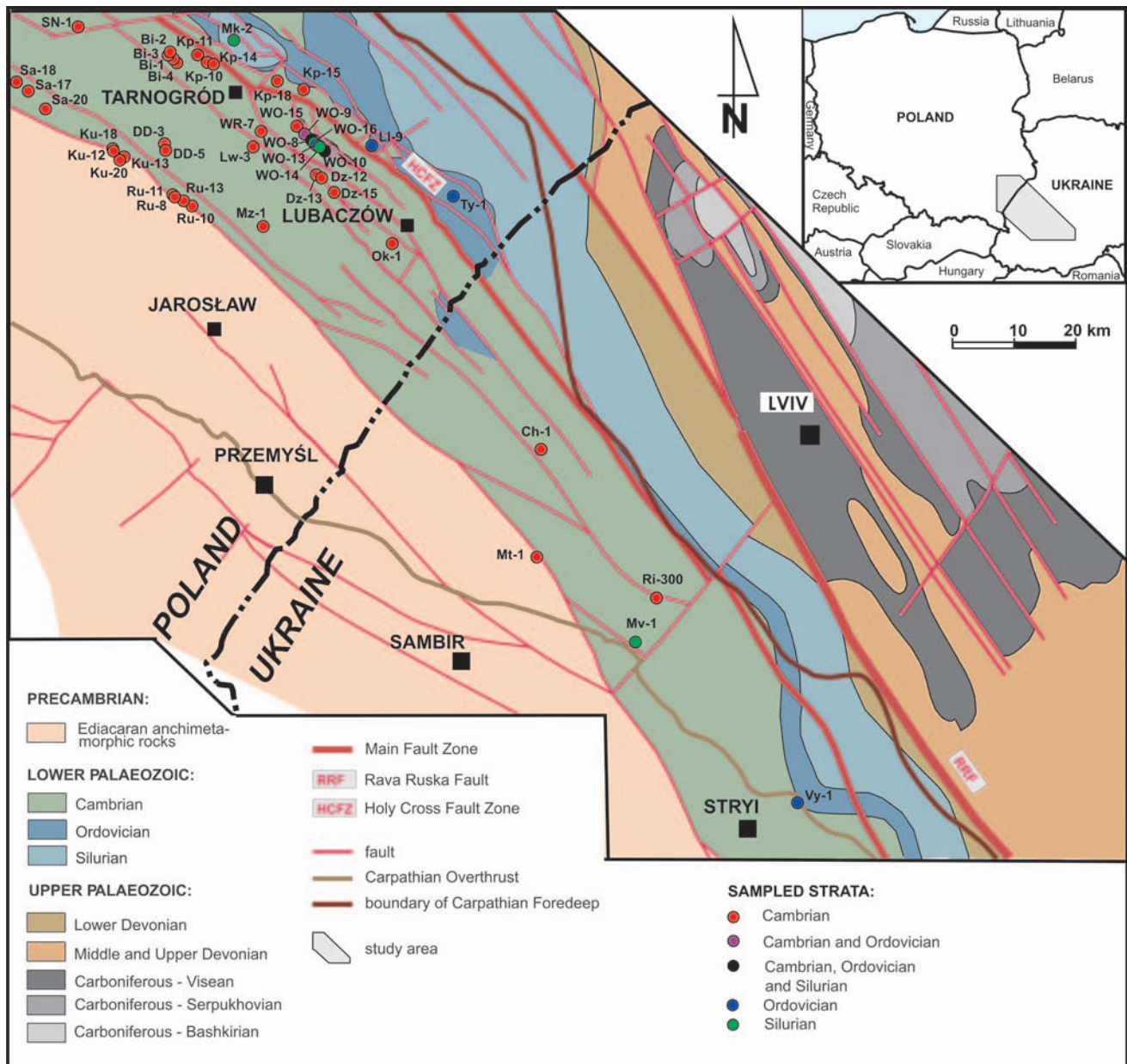
The Silurian and Ordovician strata in the Polish part of the Palaeozoic basement of the Carpathian Foredeep between Kraków and Rzeszów characterized by good hydrocarbon potential (Więclaw *et al.*, 2011) are ranked among the most probable source rocks of the oils accumulated in the Palaeozoic–Mesozoic sequence of this area (Więclaw, 2011). The objective of our study is to define the hydrocarbon potential of source rocks within the Lower Palaeozoic sequence in the marginal zone of the basement of the Carpathian Foredeep in the Tarnogród–Lubaczów region of the Małopolska Block (Poland) and in the Mosty–Stryi region (Ukraine) (Fig. 1). We examined the TOC content, the organic matter type, the thermal maturity and petroleum generation potential and assessed the source rock quality of Cambrian, Ordovician and Silurian strata based on the geochemical criteria proposed by Peters and Cassa (1994) and Hunt (1996). In the Polish part of the study area (Fig. 1), the

source rock horizons were identified, and their thickness and the initial total organic carbon (TOC<sub>0</sub>) content in the individual areas were estimated. In contrast, for the Ukrainian part, the sampling was sparse and not representative enough to identify and characterise the source rock horizons and in this area only selected data are available. The analyses conducted in this study provided basic data for the 1-D and 2-D modelling (Kosakowski *et al.*, in press) of generation, expulsion and migration processes.

The preliminary geochemical studies of organic matter deposited within the Lower Palaeozoic strata of the study area were presented by Kotarba *et al.* (2008).

### GEOLOGICAL SETTING

The Precambrian–Palaeozoic–Mesozoic basement of the Carpathian Foredeep includes four main structural stages associated with strong and diversified diastrophic ep-



**Fig. 1.** Geological map of SE Poland and western Ukraine without Tertiary and Mesozoic strata and location of sampled wells. Geology of the Polish part after Buła and Habryn (2011) and Ukrainian part after Shulga and Zdanowski (2007)

isodes: (i) the Upper Proterozoic stage (the Assynthian orogenic phase), (ii) the Cambrian–Silurian stage (the Caledonian orogeny), (iii) the Devonian–Carboniferous stage (the Variscan orogeny), and (iv) the Zechstein–Mesozoic stage (the Laramide orogenic phase) (Medvedev, 1979; Buła & Habryn, 2008).

The Lower Palaeozoic suite in the study area (Fig. 1) is composed of (i) the Cambrian strata, represented by strongly deformed clastic rocks usually up to 1,000 m thick (Buła & Habryn, 2011; Drygant 2000); (ii) the Ordovician carbonate and clastic complex, usually less than a hundred metres thick (Drygant *et al.*, 2006; Buła & Habryn, 2011); and (iii) the Silurian dark-coloured fine-grained claystone and mudstone sequence, up to 200 m thick (Kowalska *et al.*, 2000; Medvedev, 1979).

At the bottom of the Palaeozoic section the Lower Cambrian strata occur, contacting directly the Precambrian Lower San Horst Structure. Above them, the Middle and Upper Cambrian strata were recognised. The Cambrian strata are developed as a mixture of changeable proportions of claystones, sandy mudstones and quartz sandstones, often heterolithic (Buła & Habryn, 2011).

The Ordovician carbonate and clastic complex unconformably overlies the Cambrian strata of different age (Buła & Habryn, 2008). The oldest Ordovician strata (late Tremadocian–early Arenigian) are represented by thin glauconite and quartz sandstones with conglomerates (Trela, 2006). The sandstones are covered by thin (0.5–4 m) dolomites and limestones (Kowalska *et al.*, 2000). The uppermost Arenigian and Llanvirnian are represented by limestones and

**Table 1**

Quantity and stratigraphy of the rock samples collected from individual wells

Well	Well code	Stratigraphy					
		Cambrian				Ordo- vician	Silu- rian
		Lower	Middle	Upper	(undi- vided)		
Poland							
Biszczka-1	Bi-1	-	7	-	-	-	-
Biszczka-2	Bi-2	-	1	-	-	-	-
Biszczka-3	Bi-3	-	2	-	-	-	-
Biszczka-4	Bi-4	-	1	-	-	-	-
Dąbrowica Duża-3	DD-3	5	-	-	-	-	-
Dąbrowica Duża-5	DD-5	3	-	-	-	-	-
Dzików-12	Dz-12	-	3	-	-	-	-
Dzików-13	Dz-13	-	5	-	-	-	-
Dzików-15	Dz-15	-	4	-	-	-	-
Księżpol-10	Kp-10	-	35	-	-	-	-
Księżpol-11	Kp-11	-	6	-	-	-	-
Księżpol-14	Kp-14	-	5	-	-	-	-
Księżpol-15	Kp-15	-	-	7	-	-	-
Księżpol-18	Kp-18	-	7	-	-	-	-
Kuryłówka-12	Ku-12	6	-	-	-	-	-
Kuryłówka-13	Ku-13	12	-	-	-	-	-
Kuryłówka-18	Ku-18	1	-	-	-	-	-
Kuryłówka-20	Ku-20	1	-	-	-	-	-
Lubliniec-9	LI-9	-	-	-	-	2	-
Luchów-3	Lw-3	3	-	-	-	-	-
Markowice-2	Mk-2	-	-	-	-	-	24
Mołodycz-1	Mz-1	-	-	2	-	-	-
Opaka-1	Ok-1	-	-	5	-	-	-
Rudka-8	Ru-8	5	-	-	-	-	-
Rudka-10	Ru-10	8	-	-	-	-	-
Rudka-11	Ru-11	9	-	-	-	-	-
Rudka-13	Ru-13	22	-	-	-	-	-
Sarzyna-17	Sa-17	9	-	-	-	-	-
Sarzyna-18	Sa-18	8	-	-	-	-	-
Sarzyna-20	Sa-20	5	-	-	-	-	-
Sieraków Nowy-1	SN-1	-	5	-	-	-	-
Tymce-1	Ty-1	-	-	-	-	6	-
Wola Obszańska-8	WO-8	-	-	10	-	12	7
Wola Obszańska-9	WO-9	-	-	1	-	2	-
Wola Obszańska-10	WO-10	-	-	2	-	12	109
Wola Obszańska-13	WO-13	-	-	-	-	9	-
Wola Obszańska-14	WO-14	-	-	-	-	-	9
Wola Obszańska-15	WO-15	-	-	9	-	-	-
Wola Obszańska-16	WO-16	-	-	-	-	-	9
Wola Różaniecka-7	WR-7	-	19	-	-	-	-

**Table 1 continued**

Well	Well code	Stratigraphy					
		Cambrian				Ordo- vician	Silu- rian
		Lower	Middle	Upper	(undi- vided)		
Ukraine							
Chornokuntsi-1	Ch-1				21		
Makuniv-1	Mv-1						2
Mosty-1	Mt-1	14					
Rudky-300	Ri-300	3					
Verchany-1	Vy-1					1	
TOTAL		114	100	36	21	44	160

dovician strata are preserved within fold, fold-and-block and block structures (Drygant *et al.*, 2006; Buła & Habryn, 2008). The Silurian strata represent a relatively deep-water depositional environment (Malec, 2006). North-eastwardly they are replaced by the thinner, predominantly carbonate shelf sediments. In the study area the Silurian strata represent the full stratigraphic section, from Llandovery to Pridoli (Kowalska *et al.*, 2000). The Devonian and Carboniferous deposition did occur in the study area, but currently the strata are not present because they were eroded during the Hercynian orogeny in the late Carboniferous time (Narkiewicz *et al.*, 1998). These successive Palaeozoic events resulted in a significant burial and thermal maturation of the Lower Palaeozoic strata during the late Palaeozoic, with subsequent erosion and uplift. The tectonic position and lithostratigraphic characteristics of the study area were described in detail by Buła and Habryn (2011). Generalized lithostratigraphic column of the Palaeozoic–Mesozoic basement, showing also the distribution of petroleum accumulations and organic-rich facies, was presented by Kotarba and Koltun (2006, Fig. 15) and Kotarba *et al.* (2011, Fig. 2).

## SAMPLES

The rock samples were collected from cores representing all stratigraphically recognised strata from the Polish and Ukrainian parts of the Carpathian Foredeep basement. In total, 475 core samples from 45 wells (about 400 g each), dominantly claystones and siltstones as well as marls and carbonates (Fig. 1), were collected and analysed. Table 1 includes the number of samples collected from the individual wells and stratigraphic levels. From the Cambrian strata 271 samples were collected, from the Ordovician strata – 44, and from the Silurian ones – 160 samples (Table 1). From the Ukrainian part, 41 samples from 5 wells were collected (Table 1, Fig. 1).

## METHODS

The core samples were cleaned from mud contaminations and crushed to 0.5–2 cm fraction. Then, 200 g of each sample were milled to fraction <0.2 mm for geochemical

marls. The Caradocian–Ashgillian claystones, locally marly, mudstones with graptolites and marly sandstones are finishing the section of the Ordovician (Kowalska *et al.*, 2000). In the study area, they do not form a continuous cover. The Or-

analyses. Screening pyrolysis analyses were carried out with the use of the Rock-Eval Model II instrument equipped with an organic carbon module. Aliquots of the pulverised samples were extracted with dichloromethane:methanol (93:7 v/v) in the 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 x 25 cm). The fractions were eluted with *n*-hexane, toluene, and toluene:methanol (1:1 v/v), respectively.

The stable carbon isotope analyses of kerogen, bitumen and bitumen fractions were performed using the Finnigan Delta Plus mass spectrometer. Selected samples of kerogen were pre-treated with hydrochloric acid. The stable carbon isotope data are presented in the  $\delta$ -notation relative to the V-PDB standard (Coplen, 1995), at the estimated analytical accuracy of  $\pm 0.2$  ‰.

Isolation of kerogen for elemental analysis was achieved by the SOXTEC™ extraction of pulverised samples, decalcification of the solid residue with hydrochloric acid at room temperature, removal of silicates with concentrated hydrofluoric acid, removal of newly formed fluoride phases with hot concentrated HCl, heavy liquid separation (aqueous ZnBr<sub>2</sub> solution, density 2.1 g/ml) and repeated extraction with dichloromethane:methanol (93:7 v/v). Elemental analysis of isolated kerogen (C, H, N and S) was made with the Carlo Erba EA 1108 elemental analyser. The quantity of pyrite contaminating the kerogen was analysed as iron, using the Perkin-Elmer Plasma 40 ICP-AES instrument after digesting the ash from burned kerogen (815°C, 30 min.) with hydrochloric acid. The organic sulphur content in kerogen was calculated as the difference of the total and pyritic sulphur. The oxygen content was calculated as the difference to 100 %, taking into account C, H, N, S, moisture and ash contents.

The isolated saturated hydrocarbon fractions from the bitumen were diluted in isooctane and analysed by the GC-MS for biomarker determination. The analysis was carried out with the Agilent 7890A gas chromatograph equipped with the Agilent 7683B automatic sampler, an *on-column* injection chamber and a fused silica capillary column (60 m x 0.25 mm i.d.) coated with 95 % methyl/5 % phenylsilicone phase (DB-5MS, 0.25  $\mu$ m film thickness). Helium was used as the carrier gas. The GC oven was programmed: 80°C held for 1 min, then increased to 120°C at the rate of 20°C/min, then increased further to 300°C at the rate of 3°C/min and finally held for 35 min. The gas chromatograph was coupled with the 5975C mass selective detector (MSD). The MS was operated with an ion source temperature of 230°C, ionisation energy of 70 eV, and a cycle time of 1 sec in the mass range from 45 to 500 Daltons.

The aromatic hydrocarbon fractions of the bitumen were analysed by the GC-MS for phenanthrene, dibenzothiophene and their derivatives determination. The analysis was carried out using the same equipment as for the saturate hydrocarbon fraction. The GC oven was programmed from 40 to 300°C at the rate of 3°C min<sup>-1</sup>. The MS was operated with a cycle time of 1 sec in the mass range from 40 to 600 Daltons.

Measurements of the mean random reflectance of vitrinite-like macerals ( $R_o$ ) were carried out with the Zeiss-Opton microphotometer at 546 nm wavelength, in oil. Sample preparation and point counts were carried out in accordance with the ICCP procedure (Taylor *et al.*, 1998).

The initial TOC contents for the strata from which geochemical data were available were determined based on their present TOC content and values of the H/C atomic ratio, by the method proposed by Baskin (1997) and assuming the presence of the Type-II kerogen in all strata. The initial TOC<sub>0</sub> content was calculated from the equation:

$$\text{TOC}_0 = \text{TOC}/(1 - x) \quad (1)$$

where:  $x$  – relative mass loss of the TOC in relation to maturity level described by the (H/C)<sub>at</sub> value (after Baskin, 1997).

In the case when directly measured elemental data were not available, the H/C values were calculated based on the measured  $R_o$  values using the equation calculated as the best-fit for the H/C –  $R_o$  relationship worked out by Behar *et al.* (1995) from pyrolysis experiments with the Toarcian shale in France:

$$(\text{H/C})_{\text{at}} = 1.519e^{-0.52R_o} \quad R^2 = 0.943 \quad (2)$$

If direct measurements of the  $R_o$  or (H/C)<sub>at</sub> values were unavailable, the thermal maturity of organic matter was assumed to be similar to that in the neighbouring wells or it was estimated based on the  $R_o$  – depth relationship in the individual wells.

The present TOC content was determined as a median value of above-threshold values. Due to the high transformation ratio in some places, the assumed threshold TOC quantity was 0.3 wt%. Taking into account the maturity level corresponding to H/C<sub>at</sub> = 0.9, this value refers to an initial TOC of 0.5 wt%, which is the minimum TOC content for potential hydrocarbon source rocks (Peters & Cassa, 1994).

## RESULTS AND DISCUSSION

### Hydrocarbon potential of individual stratigraphic units

#### *Cambrian strata*

From the Cambrian strata, 271 samples from 37 wells were collected (Table 1). In the Polish part, the Lower, Middle and Upper Cambrian strata were identified based on microfossils (Jachowicz–Zdanowska, 2011) whereas in the Ukrainian part, due to poor preservation of fossils, it was impossible to identify the age.

The Cambrian strata are lean in organic matter. The total organic carbon (TOC) content ranges from *ca.* 0.0 to 0.40 wt%, with the median of 0.05 wt% in the Lower Cambrian, from 0.0 to 0.41 wt% with the median of 0.21 wt% in the Middle Cambrian, from 0.04 to 0.44 wt% with the median of 0.26 wt% in the Upper Cambrian, and from 0.09 to 0.34 wt% with the median of 0.14 wt% in the undivided Cambrian strata (Table 2). The residual hydrocarbon potential is also very low and only in 6 samples (1 from the Lower

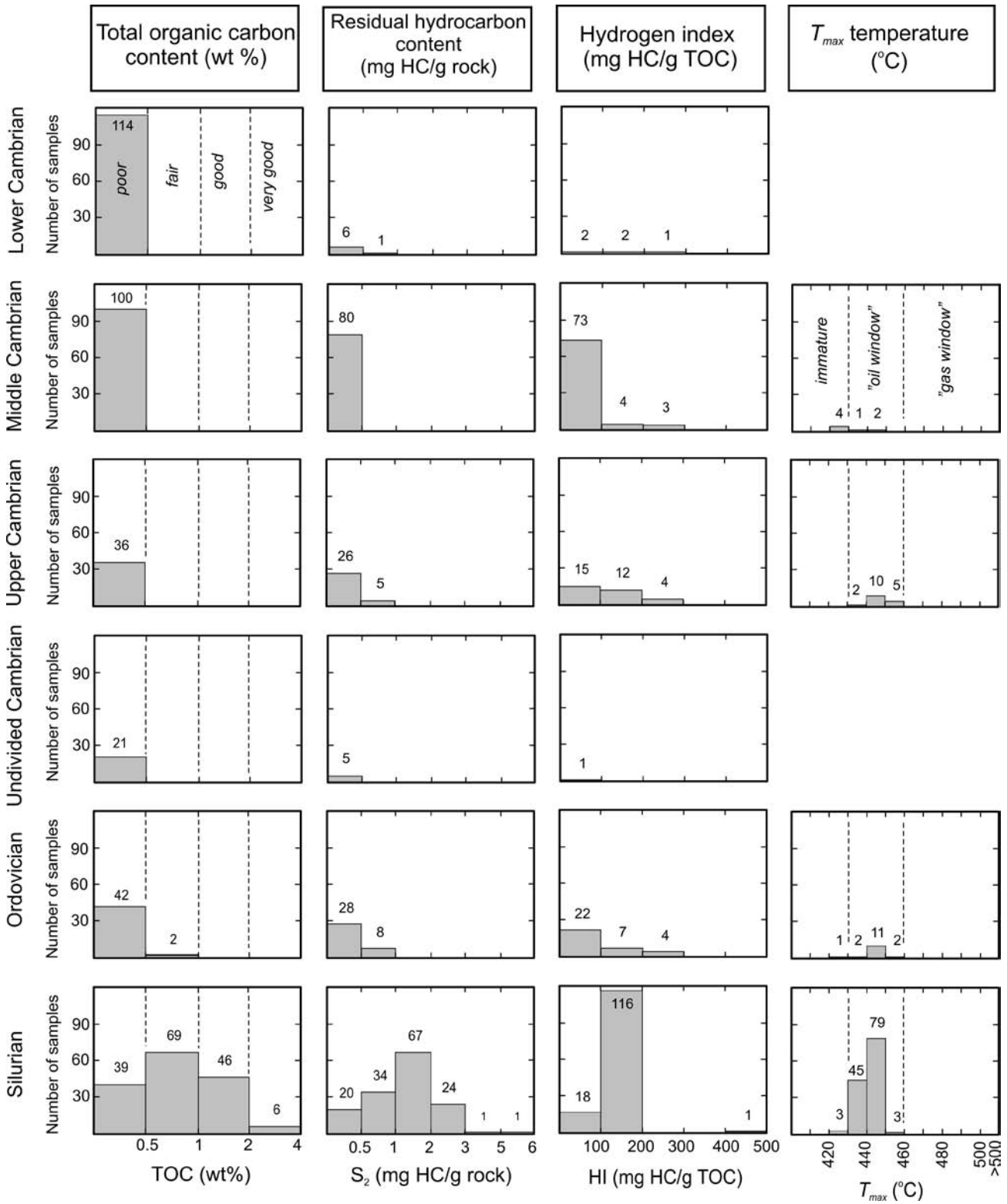
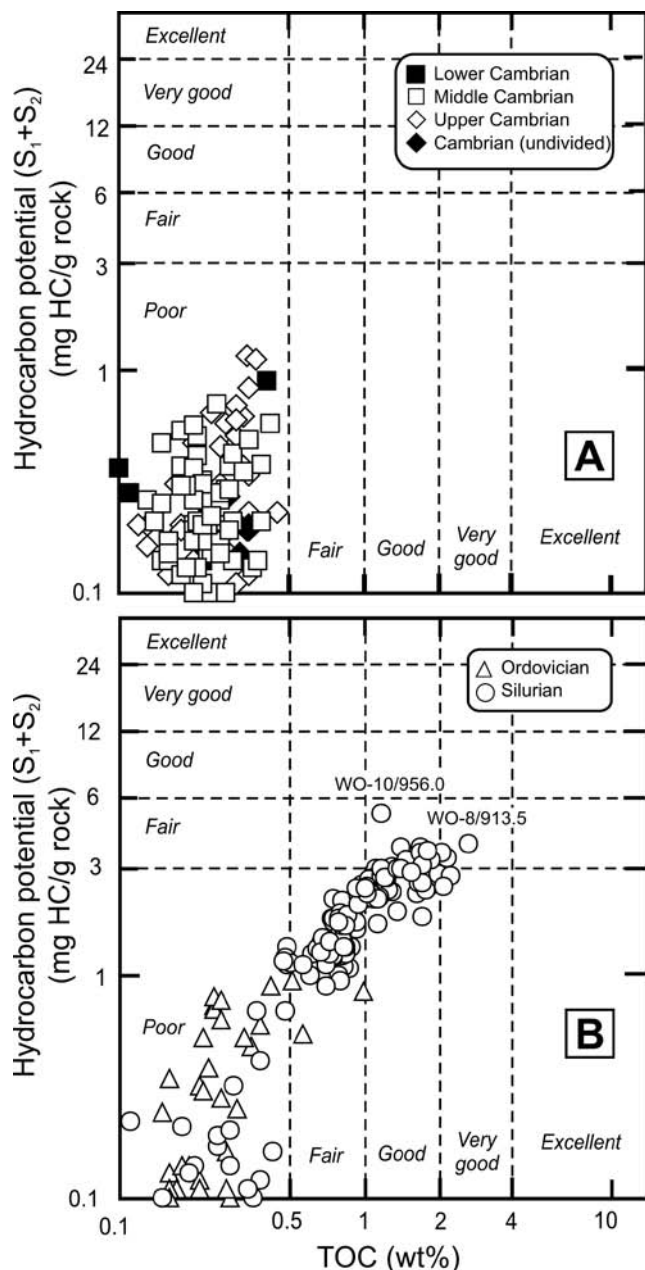


Fig. 2. Histograms of total organic carbon, residual hydrocarbon contents, hydrogen index and  $T_{max}$  temperature for the identified Lower Palaeozoic strata

and 5 from the Upper Cambrian) exceeds 0.5 mg HC/g rock (Fig. 2). The highest TOC and hydrocarbon potential values were recorded in the Upper Cambrian strata in the Wola Obszańska-8 well section where two samples are characterized by  $S_1+S_2$  values over 1 mg/g rock (Fig. 3A). Also in the Luchów-1 well, a level with an increased hydrocarbon

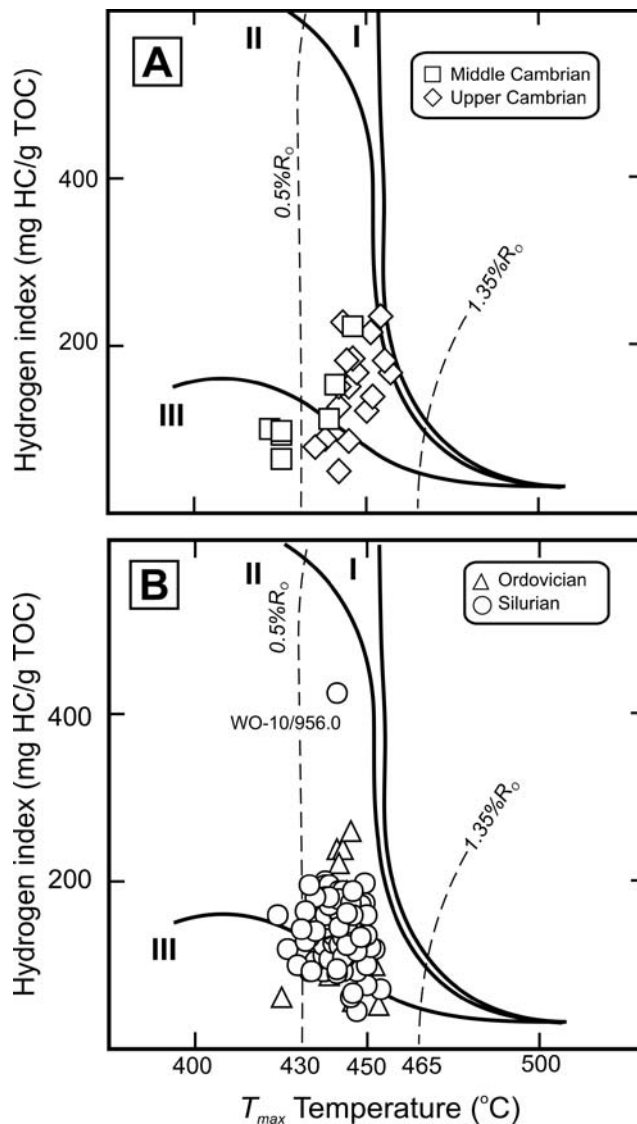
potential was observed (Fig. 3A). The relationship between the hydrogen index HI and the  $T_{max}$  temperature indicates the presence of the oil-prone Type II kerogen (Fig. 4A). The low values of the HI observed in some samples, suggesting the presence of the terrigenous Type III kerogen, are probably the result of the partial oxidation of the organic matter at



**Fig. 3.** Petroleum source quality diagram for organic matter of (A) Cambrian, (B) Ordovician and Silurian strata. Classification after Peters and Cassa (1994)

the sedimentation stage. Elevated values of the oxygen index (OI) support this thesis. This situation is especially well expressed in the Middle Cambrian strata, where the OI values reach up to 435 mg CO<sub>2</sub>/g TOC (Table 2). A similar situation was earlier observed by Więclaw *et al.* (2010) in the sandy Middle Cambrian strata of the Baltic Basin.

The distribution of *n*-alkanes and isoprenoids (Table 3, Figs 5, 6A), the stable carbon isotope composition (Table 4, Figs 7A, 8) and the biomarker data (Table 5, Fig. 9) support the algal origin of the organic matter dispersed in the investigated strata. The organic matter was deposited usually in the reducing conditions (Pr/Ph < 1, Table 3). Only in the sample WO-10/1193, the value of this ratio is close to two



**Fig. 4.** Rock-Eval hydrogen index versus  $T_{max}$  temperature for (A) Cambrian and (B) Ordovician and Silurian strata. Maturity paths of individual kerogen types after Espitalié *et al.* (1985)

indicating sub-oxic conditions of the organic matter deposition (Didyk *et al.*, 1978; ten Haven, 1996), although the elevated values of this ratio can also be a result of increased maturity (e.g., Al-Aroui *et al.*, 1998). The stable carbon isotope composition indicates the presence of the same type and facies of the organic matter in all epochs (Figs 7A, 8). The composition of the regular steranes (Fig. 9) supports this statement and shows that only in the Bi-1/1045.5 sample the organic matter slightly differs from other samples.

The thermal maturity of the investigated strata was determined based on the pyrolytic data (Table 2), the measurements of the vitrinite-like macerals reflectance (Table 2), as well as the biomarker (Table 5) and the aromatic hydrocarbons distribution (Table 6). Due to a low residual hydrocarbon content, the  $T_{max}$  values were determined only for 24 samples from the Middle and Upper Cambrian strata (Table 2). The  $T_{max}$  values indicate maturity from the initial, through the middle up to the final phase of the “oil window”

Table 2

Geochemical characteristics and hydrocarbon potential of the Lower Palaeozoic strata

Stratigraphy Index	Lower Cambrian	Middle Cambrian	Upper Cambrian	Undivided Cambrian	Ordovician	Silurian
<b>TOC (wt%)</b>	$\frac{0.00 \text{ to } 0.40}{0.05}$ (114) (16)	$\frac{0.00 \text{ to } 0.41}{0.21}$ (100) (13)	$\frac{0.04 \text{ to } 0.44}{0.26}$ (36) (7)	$\frac{0.09 \text{ to } 0.34}{0.14}$ (21) (1)	$\frac{0.04 \text{ to } 0.97}{0.21}$ (44) (7)	$\frac{0.02 \text{ to } 2.6}{0.82}$ (160) (6)
<b>T<sub>max</sub> (°C)</b>	no data	$\frac{422 \text{ to } 446}{425}$ (7) (2)	$\frac{435 \text{ to } 457}{445}$ (17) (6)	no data	$\frac{425 \text{ to } 453}{443}$ (16) (4)	$\frac{424 \text{ to } 454}{442}$ (130) (5)
<b>S<sub>2</sub> (mg HC/g rock)</b>	$\frac{0.01 \text{ to } 0.74}{0.13}$ (7) (3)	$\frac{0.00 \text{ to } 0.41}{0.08}$ (80) (9)	$\frac{0.03 \text{ to } 0.85}{0.23}$ (31) (6)	$\frac{0.04 \text{ to } 0.15}{0.08}$ (5) (1)	$\frac{0.01 \text{ to } 0.91}{0.18}$ (36) (6)	$\frac{0.00 \text{ to } 4.9}{1.27}$ (147) (6)
<b>S<sub>1</sub>+S<sub>2</sub> (mg HC/g rock)</b>	$\frac{0.05 \text{ to } 0.90}{0.25}$ (7) (3)	$\frac{0.03 \text{ to } 0.58}{0.16}$ (80) (9)	$\frac{0.11 \text{ to } 1.16}{0.31}$ (31) (6)	$\frac{0.15 \text{ to } 0.27}{0.19}$ (5) (1)	$\frac{0.06 \text{ to } 1.31}{0.29}$ (36) (6)	$\frac{0.05 \text{ to } 5.3}{1.83}$ (147) (6)
<b>PI</b>	$\frac{0.18 \text{ to } 0.57}{0.32}$ (5) (2)	$\frac{0.19 \text{ to } 1.00}{0.47}$ (66) (9)	$\frac{0.00 \text{ to } 0.73}{0.26}$ (31) (6)	0.44 (1)	$\frac{0.00 \text{ to } 0.83}{0.33}$ (33) (5)	$\frac{0.07 \text{ to } 0.62}{0.28}$ (135) (6)
<b>HI (mg HC/g TOC)</b>	$\frac{27 \text{ to } 290}{173}$ (5) (2)	$\frac{0 \text{ to } 253}{34}$ (80) (9)	$\frac{10 \text{ to } 258}{107}$ (31) (6)	54 (1)	$\frac{6 \text{ to } 258}{77}$ (33) (5)	$\frac{26 \text{ to } 425}{145}$ (135) (6)
<b>OI (mg CO<sub>2</sub>/g TOC)</b>	$\frac{0 \text{ to } 195}{30}$ (5) (2)	$\frac{0 \text{ to } 435}{47}$ (80) (9)	$\frac{0 \text{ to } 35}{0}$ (31) (6)	50 (1)	$\frac{0 \text{ to } 153}{0}$ (33) (5)	$\frac{1 \text{ to } 126}{20}$ (134) (5)
<b>BR (mg bit./g TOC)</b>	110 (1)	$\frac{60 \text{ to } 156}{100}$ (5) (4)	$\frac{89 \text{ to } 153}{121}$ (9) (3)	$\frac{114 \text{ and } 137}{126}$ (2) (1)	$\frac{89 \text{ to } 188}{124}$ (7) (4)	$\frac{57 \text{ to } 148}{104}$ (15) (6)
<b>R<sub>o</sub> (%)</b>	$\frac{1.87 \text{ to } 2.44}{1.94}$ (3) (2)	$\frac{1.06 \text{ to } 2.02}{1.27}$ (8) (3)	$\frac{0.9 \text{ to } 1.43}{1.21}$ (4) (3)	$\frac{1.52 \text{ to } 1.70}{1.58}$ (3) (1)	$\frac{0.93 \text{ to } 2.70}{0.96}$ (4) (4)	$\frac{0.88 \text{ and } 1.07}{0.98}$ (2) (2)
<b>Kerogen type</b>	<i>n.d.</i>	<i>II</i>	<i>II</i>	<i>n.d.</i>	<i>II</i>	<i>II</i>
<b>Maturity</b>	<i>overmature</i>	<i>mature/overmature</i>	<i>mature</i>	<i>overmature</i>	<i>mature/overmature</i>	<i>mature</i>
<b>Hydrocarbon potential</b>	<i>poor</i>	<i>poor</i>	<i>poor</i>	<i>poor</i>	<i>poor</i>	<i>good</i>

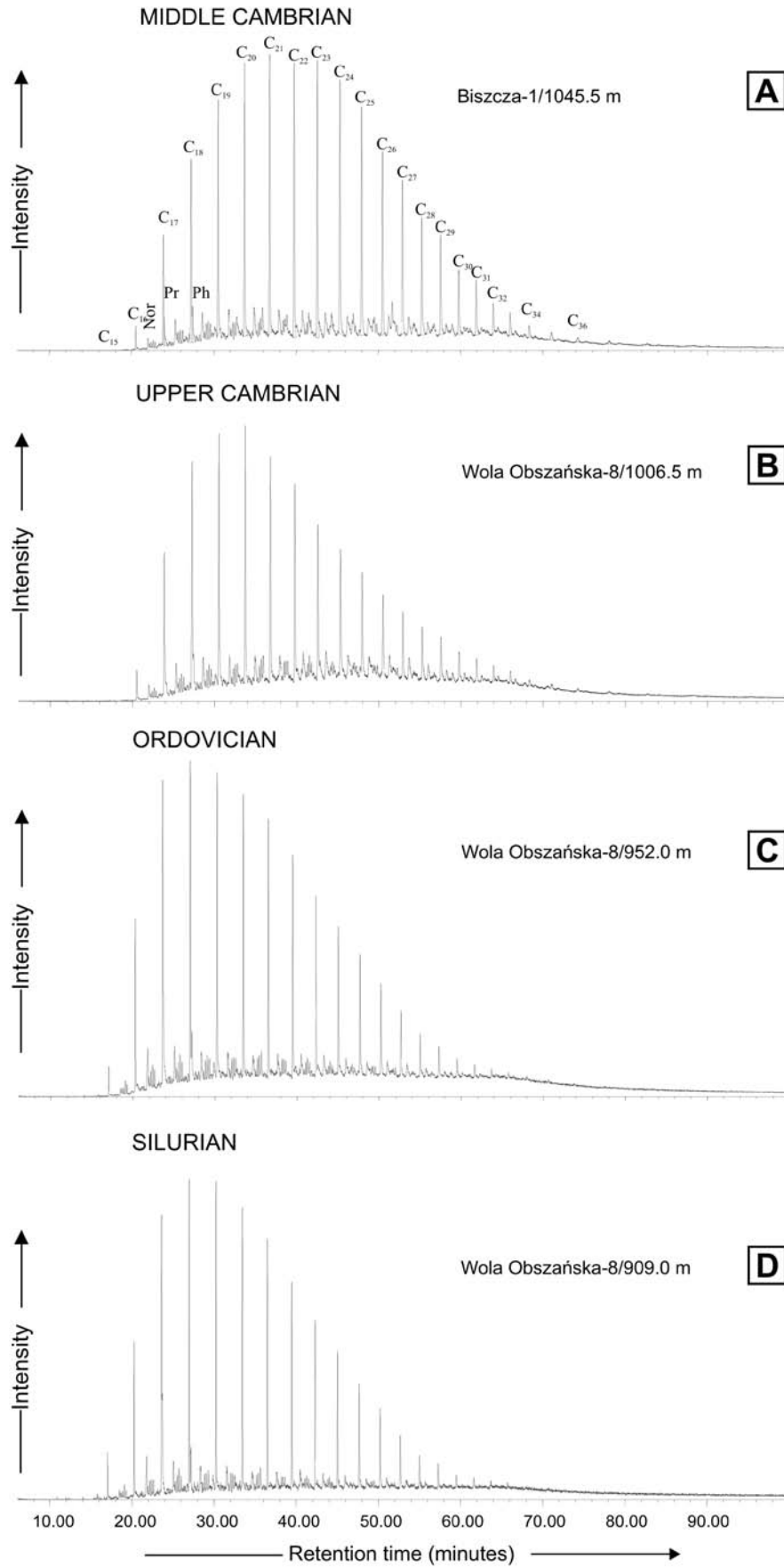
TOC – total organic carbon; T<sub>max</sub> – temperature of maximum of S<sub>2</sub> peak; S<sub>2</sub> – residual hydrocarbon content; S<sub>1</sub> – oil and gas yield (mg HC/g rock); PI – production index; HI – hydrogen index; OI – oxygen index; BR – bitumen ratio. R<sub>o</sub> – vitrinite-like macerals reflectance. Range of geochemical parameters is given as numerator; median values in denominator, in parentheses: number of samples from wells (numerator) and number of sampled wells (denominator); n.d. – not determined

(from 422 to 457°C; Table 2, Figs 2, 4A). The maturities calculated based on the biomarkers, methylphenanthrenes and methyl dibenzothiophenes distribution (Tables 5, 6) correspond to those assessed based on the T<sub>max</sub> values. Some discrepancies between the MPI and MDR values may be connected with an analytical error caused by generally low concentrations of methyl dibenzothiophenes. In the majority of the wells, however, it was impossible to determine these values due to the absence of hydrocarbons. The reflectance of vitrinite-like macerals in the samples from the Chornokuntsi-1, Mosty-1 and Rudky-300 wells (Ukraine) and the Książpol-10, -11 and -15 wells (Poland) reveals the maturity of the organic matter from 1.4 to over 2 % R<sub>o</sub> (Table 2) indicating full thermal transformation. Thus, the TOC in these wells represents non-generative residual carbon. The measured vitrinite-like macerals reflectance of the organic

matter from the Opaka-1 and Wola Obszańska-8 wells is lower than in the previously discussed wells (Table 2) and corresponds well to the Rock-Eval data (Table 2 and Fig. 4A).

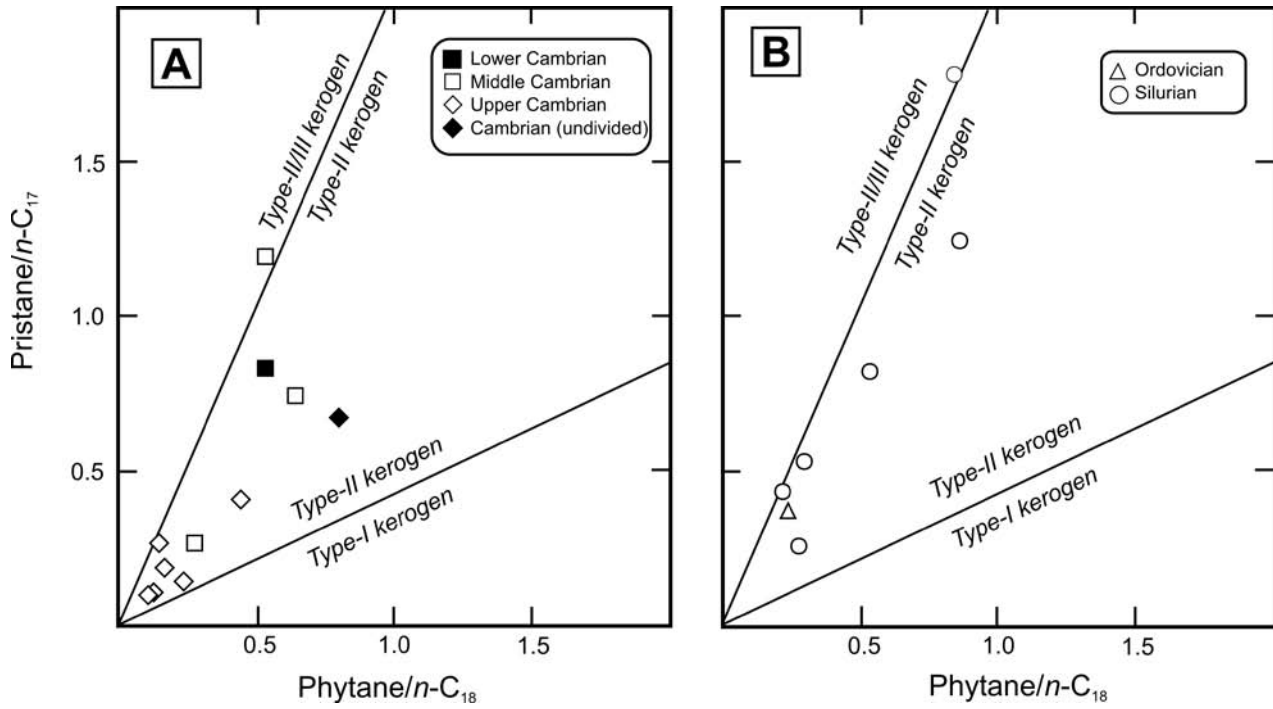
#### Ordovician strata

From the Ordovician strata 44 samples were collected (Table 1). Most of them came from a small area in the vicinity of Wola Obszańska, Lubliniec and Tymce (Poland) and only one sample was taken from the Ukrainian Verchany-1 well section (Table 1, Fig. 1). The total organic carbon (TOC) content varies in the strata of this period from 0.04 to 0.97 wt%, with the median of 0.21 wt% (Table 2). Only for two samples the TOC does exceed the value of 0.5 wt% (Fig. 2) classifying the analysed strata as generally lean for the generation of hydrocarbons. The residual hydrocarbon



**Fig. 5.** Examples of *n*-alkanes and isoprenoids distributions in (A) Middle Cambrian, (B) Upper Cambrian, (C) Ordovician and (D) Silurian strata. Nor – *nor*-pristane; Pr – pristane; Ph – phytane





**Fig. 6.** Genetic characterization of bitumen from (A) Cambrian and (B) Ordovician and Silurian strata in terms of pristane/*n*-C<sub>17</sub>H<sub>36</sub> and phytane/*n*-C<sub>18</sub>H<sub>38</sub> according to the categories of Obermajer *et al.* (1999)

**Table 3**

Indices calculated from distribution of the *n*-alkanes and isoprenoids in bitumen

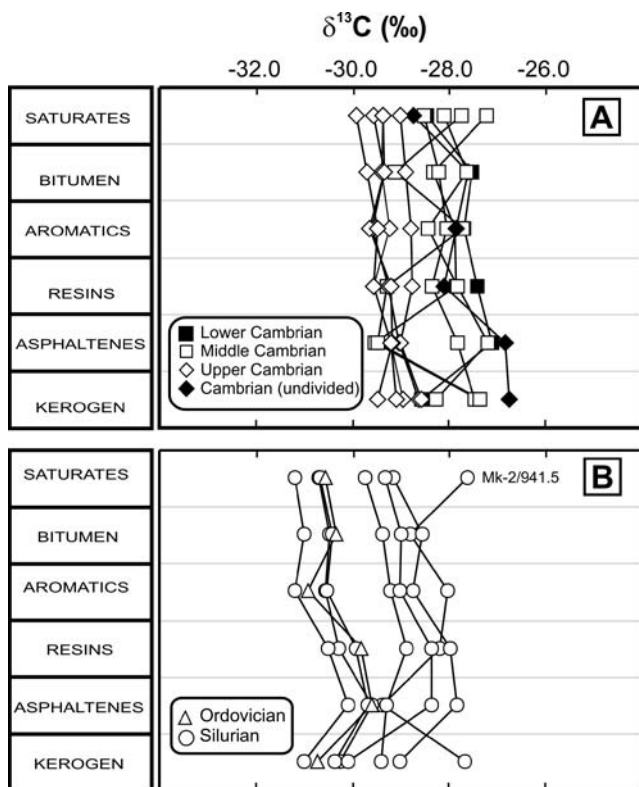
Well	Depth (m)	Stratigraphy	CPI <sub>(17-31)</sub>	CPI <sub>(17-23)</sub>	CPI <sub>(25-31)</sub>	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>
Luchów-3	1,280.5	Lower Cambrian	n.c.	n.c.	n.c.	n.c.	0.83	0.54
Biszczka-1	1,045.5	Middle Cambrian	n.c.	n.c.	1.05	n.c.	0.27	0.28
Książpol-10	978.8		n.c.	n.c.	n.c.	n.c.	n.c.	0.53
	1,096.4		n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Książpol-11	940.5		0.87	0.79	1.12	0.14	0.74	0.64
Opaka-1	1,278.3	Upper Cambrian	1.16	0.98	1.39	0.34	0.41	0.44
	1,006.5		0.96	0.94	1.03	0.41	0.14	0.24
	1,064.4		0.92	0.89	1.06	0.56	0.19	0.17
	1,068.5		0.94	0.89	1.01	0.55	0.11	0.13
	1,096.3		0.99	0.96	1.10	0.70	0.09	0.11
Wola Obszańska-10	1,193.0		1.01	1.02	0.98	1.86	0.26	0.15
Chornokuntsi-1	2,183-2,190	Cambrian (undivided)	1.01	0.86	1.36	0.30	0.67	0.80
Wola Obszańska-8	952.3	Ordovician	1.01	0.99	1.08	1.53	0.38	0.23
Markowice-2	941.5	Silurian	n.c.	n.c.	n.c.	n.c.	n.c.	0.37
Wola Obszańska-8	909.9		1.01	0.99	1.13	1.70	0.44	0.22
Wola Obszańska-14	928.7		0.93	0.94	0.91	1.20	1.79	0.85
Wola Obszańska-8	913.5		0.97	0.94	1.01	1.25	0.83	0.54
Wola Obszańska-10	956.0		1.15	1.18	1.04	2.03	0.53	0.30
Wola Obszańska-14	927.9		0.99	0.98	0.98	1.38	1.25	0.86
Wola Obszańska-16	910.5		0.99	0.98	1.03	0.88	0.25	0.27

$$CPI_{(17-31)} = [(C_{17}+C_{19}+\dots+C_{27}+C_{29})+(C_{19}+C_{21}+\dots+C_{29}+C_{31})]/[2*(C_{18}+C_{20}+\dots+C_{28}+C_{30})]$$

$$CPI_{(17-23)} = [(C_{17}+C_{19}+C_{21})+(C_{19}+C_{21}+C_{23})]/[2*(C_{18}+C_{20}+C_{22})]$$

$$CPI_{(25-31)} = [(C_{25}+C_{27}+C_{29})+(C_{27}+C_{29}+C_{31})]/[2*(C_{26}+C_{28}+C_{30})]$$

Pr – pristane; Ph – phytane; n.c. – not calculated

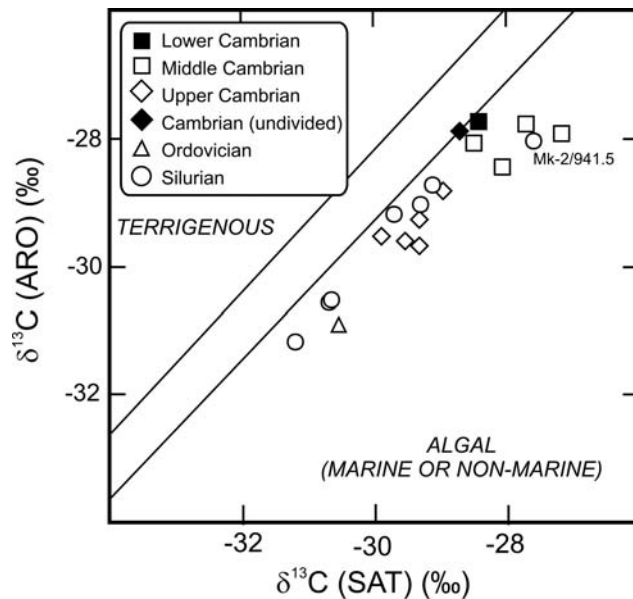


**Fig. 7.** Stable carbon isotope composition of bitumen, its fractions and kerogen from (A) Cambrian and (B) Ordovician and Silurian strata

content ( $S_2$ ) as well as the hydrocarbon potential ( $S_1+S_2$ ), comparable to the TOC values, are low and range from 0.01 to 0.91 and from 0.06 to 1.31 mg HC/g rock, respectively, with the median values of 0.18 and 0.29 mg HC/g rock, respectively (Table 2, Fig. 3B). In two samples collected from the Wola Obszańska-8 section, the  $S_1+S_2$  values are ca. 1 mg HC/g rock and 0.5 wt% TOC (Fig. 3B) indicating a fair hydrocarbon potential.

In the Ordovician strata, like in the Cambrian strata, the oil-prone Type II kerogen is present. This thesis is supported by the relationship between the hydrogen index HI and the  $T_{max}$  temperature (Fig. 4B), the  $n$ -alkanes and isoprenoids distribution (Table 3, Figs 5, 6B), the stable carbon isotope composition (Table 4, Figs. 7B, 8), the biomarker distribution (Table 5, Fig. 9) and the kerogen elemental composition (Table 7, Fig. 11). The organic matter was deposited in normal marine conditions ( $1 < Pr/Ph < 3$ , Table 3) (Didyk *et al.*, 1978). The stable carbon isotope composition reveals the presence of a very light organic matter, much lighter than in the Cambrian strata (Figs. 7B, 8). This phenomenon can be explained by the fact that the change in the depositional environment caused the change in organic assemblages assimilating  $CO_2$  enriched in  $^{12}C$ . The composition of the regular steranes (Fig. 9) indicates the same type of organic matter in the Ordovician strata as in the Cambrian ones.

The thermal maturity of the Ordovician strata, comparable to the Cambrian ones, was determined based on the pyrolytic data (Table 2), the measurements of the vitrinite-



**Fig. 8.** Genetic characterization of bitumen from (A) Cambrian and (B) Ordovician and Silurian strata based on stable carbon isotope composition of saturated and aromatic hydrocarbons. Genetic fields after Sofer (1984)

like macerals reflectance (Table 2), the biomarker (Table 5) and the aromatic hydrocarbons distribution (Table 6). Indirectly, the results of the kerogen elemental composition analyses were also used for this purpose (Table 7). Similarly to the Cambrian strata, due to the low residual hydrocarbon content, the  $T_{max}$  values were also determined for 16 samples only (Table 2, Fig. 2). These values indicate the maturity from the initial, through the middle, up to the final phase of the “oil window” (from 425 to 453°C; Table 2, Figs. 2, 4B). The maturity indices calculated based on the biomarkers, methylphenanthrenes and methyl dibenzothiophenes distribution of a single sample (Tables 5, 6, Fig. 10) correspond with the  $T_{max}$  value (441°C) of the sample indicating the middle phase of the oil window. Similarly to the Cambrian strata, in the majority of the wells it was impossible to determine other maturity indices than the reflectance of vitrinite-like macerals due to the absence of hydrocarbons. An extremely high maturity was observed in the sample from the Verchany-1 well (Ukraine) – 2.7%  $R_o$  (Table 2) indicating full thermal transformation of the organic matter. Thus, the TOC in this well represents the non-generative residual carbon. The vitrinite-like material reflectance of the organic matter from the Lubliniec-9, Tymce-1 and Wola Obszańska-8 wells is lower than in the above-mentioned well (Table 2) and corresponds with the Rock-Eval, biomarkers, aromatic hydrocarbons and kerogen elemental composition data.

#### Silurian strata

160 samples were collected from the Silurian strata (Table 1) and, except for two samples taken from the Makuńiv-1 section, they all come from the vicinity of Wola Obszańska and Markowice (Poland) (Table 1, Fig. 1). The total organic carbon (TOC) content varies in these strata

Table 4

Fractions and stable carbon isotope composition of bitumen, its individual fractions and kerogen

Well	Depth (m)	Stratigraphy	Fractions (wt%)				$\delta^{13}\text{C}$ (‰)					
			Sat	Aro	Res	Asph	Sat	Bit	Aro	Res	Asph	Ker
Luchów-3	1,280.5	Lower Cambrian	20	9	34	37	-28.5	-27.5	-27.7	-27.4	-27.1	-28.6
Biszczka-1	1,045.5	Middle Cambrian	25	8	29	38	-27.2	-28.3	-27.9	-27.9	-29.5	-27.4
Książpol-10	978.8		25	9	38	28	-28.5	-28.2	-28.1	-28.4	-27.8	-27.5
	1,096.4		13	1	60	26	-27.7	-29.1	-27.7	-29.3	-29.5	-27.4
Książpol-11	940.5		10	7	42	41	-28.1	-27.6	-28.4	-27.8	-27.2	-28.3
Wola Obszańska-8	1,006.5	Upper Cambrian	35	12	29	24	-29.6	-29.4	-29.6	-29.3	-29.0	-28.6
	1,064.4		31	11	37	21	-29.4	-29.4	-29.2	-29.6	-29.2	-29.0
	1,068.5		36	17	35	12	-29.4	-29.3	-29.7	-29.2	-29.2	-29.5
	1,096.3		44	16	32	8	-29.0	-28.9	-28.8	-28.8	-29.0	-28.6
Wola Obszańska-10	1,193.0		51	18	20	11	-29.9	-29.7	-29.5	-29.6	-29.2	-29.1
Chornokuntsi-1	2,183-2,190	Cambrian (undivided)	13	12	31	44	-28.8	-27.6	-27.9	-28.1	-26.8	-26.8
Wola Obszańska-8	952.3	Ordovician	50	16	25	9	-30.6	-30.3	-30.9	-29.8	-29.6	-30.7
Markowice-2	941.5	Silurian	5	6	36	53	-27.6	-28.8	-28.0	-28.2	-29.4	-27.7
	909.9		45	20	22	13	-29.7	-29.4	-29.2	-28.9	-29.3	-29.4
913.5			32	28	26	14	-29.2	-28.5	-28.7	-28.0	-27.8	-29.0
Wola Obszańska-10	956.0		44	22	21	13	-31.2	-31.0	-31.2	-30.5	-30.1	-31.0
Wola Obszańska-14	927.9		49	23	21	7	-30.7	-30.4	-30.5	-29.9	-29.7	-30.4
	928.7		40	21	31	8	-30.7	-30.5	-30.6	-30.3	-29.6	-30.3
Wola Obszańska-16	910.5		34	29	25	12	-29.3	-29.0	-29.0	-28.4	-28.3	-30.1

Sat – saturated hydrocarbons; Aro – aromatic hydrocarbons; Res – resins; Asph – asphaltenes; Bit – bitumen; Ker – kerogen

from 0.02 to 2.6 wt%, with the median of 0.82 wt% (Table 2). Samples with the TOC content from 0.5 to 1 wt% dominate, but also good source rocks with the TOC content from 1 to 2 wt% have a significant share (Figs. 2, 3B). In six samples, the TOC values over 2 wt% were determined (Fig. 2). The residual hydrocarbon content ( $S_2$ ) as well as the hydrocarbon potential ( $S_1+S_2$ ), are directly proportional to the TOC values, and vary from 0.0 to 4.9 and 0.05 to 5.3 mg HC/g rock, respectively, with the median values of 1.27 and 1.83 mg HC/g rock, respectively (Table 2, Fig. 3B). The Silurian strata in the Wola Obszańska-8 and 10 wells have the best hydrocarbon potential (Fig. 3B).

In the Silurian strata, like in the previously discussed older strata, the oil-prone Type II kerogen is present. This thesis is supported by the results of pyrolytic data (Fig. 4B), the  $n$ -alkanes and isoprenoids distribution (Table 3, Figs 5, 6B), the stable carbon isotope composition (Table 4, Figs 7B, 8), the biomarker distribution (Table 5, Fig. 9) and the kerogen elemental composition (Table 7, Fig. 11). The hydrogen index values are usually from 100 to 200 mg HC/g TOC (Figs 2, 3B), with a local decrease below 100 mg HC/g TOC and one exceptionally high value determined for the WO-10/956 sample (Table 2, Figs 2, 3B). The lowest HI values suggesting the presence of the Type III kerogen were obtained for the samples poorest in the organic matter. The organic matter in the Silurian strata was deposited, similarly to the Ordovician strata, in normal marine conditions ( $1 < \text{Pr}/\text{Ph} < 3$ ; Table 3) (Didyk *et al.*, 1978). The stable carbon isotope composition reveals the presence of a very light organic matter (Figs 7B, 8), usually of algal origin (Lewan,

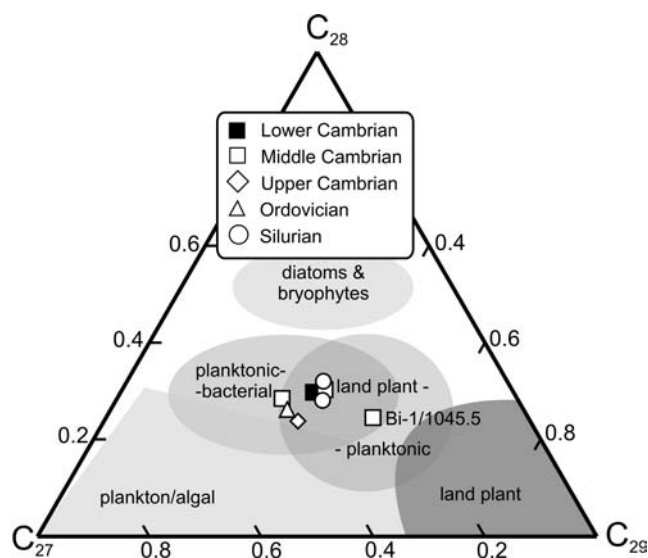


Fig. 9. Ternary diagram of distribution of the regular steranes with  $\alpha\alpha\alpha$  configuration in bitumen. Classification after Peters *et al.* (2005) modified by authors

1986). Two distinct organic facies characterized by a different stable carbon isotope composition can be observed: the first one in the Markowice-2, Wola Obszańska-8 and -16 wells, and the second one – enriched in  $^{12}\text{C}$  isotope – in the Wola Obszańska-10 and -14 wells (Figs 7B, 8). The enrichment in  $^{13}\text{C}$  isotope in the stable carbon isotope composition of saturated hydrocarbons of the sample collected from

Table 5

Selected biomarker characteristics of bitumen from the Lower Palaeozoic strata

Well	Depth (m)	Stratigraphy	S/(S+T)	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	Dia/Reg	Mor/Hop	C <sub>27</sub> dia/reg	C <sub>29</sub> S/R	C <sub>29</sub> ββ/αα	H <sub>31</sub> S/(S+R)	Ts/Tm	GI	C <sub>29</sub> /C <sub>27</sub> sterane	C <sub>29</sub> Ts/C <sub>29</sub> H	C <sub>35</sub> /C <sub>34</sub>
Luchów-3	1,280.50	Lower Cambrian	0.25	36	30	35	0.65	0.17	0.65	0.79	1.22	0.56	0.56	0.53	0.94	0.09	0.84
Biszczka-1	1,045.50	Middle Cambrian	0.78	28	24	48	0.47	0.07	0.47	0.57	0.72	0.51	1.60	0.45	1.24	0.12	1.05
Książpol-10	978.80		0.26	33	30	36	0.69	0.05	0.69	0.62	1.30	0.62	0.60	0.44	0.91	0.15	0.77
	1,096.40		0.30	42	28	30	0.36	0.08	0.36	0.98	1.44	0.57	0.78	0.51	0.79	0.09	0.83
Wola Obszańska-8	1,006.50	Upper Cambrian	0.35	41	24	35	0.45	0.07	0.45	1.03	1.33	0.49	0.54	0.28	0.72	0.04	1.18
	1,064.40	n.c.	n.c.	n.c.	n.c.	n.c.	0.13	n.c.	n.c.	n.c.	n.c.	0.64	0.85	0.85	n.c.	0.22	n.c.
	952.30	Ordovician	0.32	42	26	32	0.36	0.13	0.36	0.94	1.12	0.61	0.57	0.64	0.75	0.13	0.97
Markowice-2	941.50	Silurian	0.33	35	28	37	0.45	0.11	0.45	0.60	0.88	0.54	0.86	0.31	0.88	0.10	0.88
Wola Obszańska-8	909.90		n.c.	33	32	35	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
	928.70		n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.

S/(S+T) = all steranes/(all steranes + all terpanes); C<sub>27</sub> = C<sub>27</sub>ααα20R sterane/(C<sub>27</sub>+C<sub>28</sub>+C<sub>29</sub>)ααα20R steranes\*100; C<sub>28</sub> = C<sub>28</sub>ααα20R sterane/(C<sub>27</sub>+C<sub>28</sub>+C<sub>29</sub>)ααα20R steranes\*100; C<sub>29</sub> = C<sub>29</sub>ααα20R sterane/(C<sub>27</sub>+C<sub>28</sub>+C<sub>29</sub>)ααα20R steranes\*100; Dia/Reg = C<sub>27</sub> βα 20S diasterane/ C<sub>29</sub>ααα20R sterane; Mor/Hop = Moretane/17α hopane; C<sub>27</sub> dia/reg = C<sub>27</sub> βα 20(S+R) diasterane/ΣC<sub>27</sub> regular steranes; C<sub>29</sub>S/R = epimerisation of regular steranes C<sub>29</sub> ratio; C<sub>29</sub>ββ/αα = ratio of ββ-epimeres to αα-epimeres of regular steranes C<sub>29</sub>; H<sub>31</sub>S/(S+R) = homohopane 22S/(22S+22R); Ts/Tm = C<sub>27</sub> 18α trisnorhopane/C<sub>27</sub> 17α trisnorhopane; GI = Gammacerane/17α hopane; C<sub>29</sub>/C<sub>27</sub>sterane = ΣC<sub>29</sub> regular steranes/ΣC<sub>27</sub> regular steranes; C<sub>29</sub>Ts/C<sub>29</sub>H = C<sub>29</sub> 18α norneohopane/C<sub>29</sub> norhopane; C<sub>35</sub>/C<sub>34</sub> = C<sub>35</sub> (22S+22R) homohopanes/C<sub>34</sub> (22S+22R) homohopanes; n.c. – not calculated due to lack of biomarkers

Table 6

Maturity indices calculated based on distribution of phenanthrene and dibenzothiophene and their methyl derivatives in bitumen

Well	Depth (m)	Stratigraphy	MPI1	MPR	MPR1	R <sub>cal</sub> (%)	R <sub>cal</sub> (MPR) (%)	MDR	R <sub>cal</sub> (DBT) (%)	T <sub>max</sub> (DBT) (°C)
Luchów-3	1,280.5	Lower Cambrian	1.38	1.48	0.54	1.2	1.0	1.3	0.6	429
Biszczka-1	1,045.5	Middle Cambrian	0.45	0.97	0.44	0.6	0.8	2.4	0.7	435
Książpol-10	978.8		1.13	1.16	0.47	1.0	0.9	1.2	0.6	429
	1,096.4		0.72	0.91	0.42	0.8	0.8	traces		
Wola Obszańska-8	1,006.5	Upper Cambrian	0.84	0.80	0.40	0.9	0.7	5.3	0.9	450
	1,064.4	Upper Cambrian	1.17	1.12	0.46	1.1	0.9	3.5	0.8	441
	1,068.5		1.20	1.28	0.50	1.1	1.0	n.a.		
	1,096.3		1.22	1.41	0.51	1.1	1.0	n.a.		
Chornokuntsi-1	2,183-2,190	Cambrian (undivided)	0.91	1.38	0.53	0.9	1.0	n.a.		
Wola Obszańska-8	952.3	Ordovician	0.90	0.89	0.42	0.9	0.8	5.7	0.9	452
	952.3		0.92	1.01	0.43	0.9	0.8	n.a.		
Markowice-2	941.5	Silurian	1.70	1.80	0.55	1.4	1.1	1.3	0.6	430
Wola Obszańska-8	909.9		0.64	0.82	0.38	0.8	0.7	traces		
	913.5		0.79	1.25	0.38	0.8	0.7	n.a.		
Wola Obszańska-14	927.9		0.87	1.29	0.42	0.9	0.8	n.a.		
	928.7		0.80	0.95	0.38	0.9	0.7	8.6	1.1	467
	910.5		1.05	1.21	0.44	1.0	0.8	n.a.		

MPI1 = 1.5(2-MP+3-MP)/(P+1-MP+9-MP), P - phenanthrene; MP - methylphenanthrene, MPR = 2-MP/1-MP, MPR1 = (2-MP+3-MP)/(1-MP+9-MP+2-MP+3-MP); R<sub>cal</sub> = 0.60MPI1+0.37 for MPR<2.65 (Radke, 1988); R<sub>cal</sub>(MPR) = -0.166+2.242(MPR1) (Kvalheim *et al.*, 1987); MDR = 4-MDBT/1-MDBT; MDBT – methyl dibenzothiophene; R<sub>cal</sub>(DBT) = 0.51+0.073MDR; T<sub>max</sub>(DBT) = 423+5.1MDR

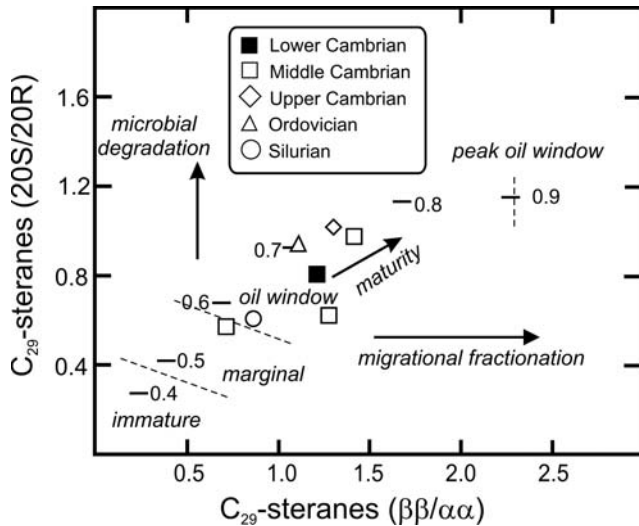


Fig. 10. Sterane  $C_{29}$  20S/20R ratio versus  $C_{29}$   $\beta\beta/\alpha\alpha$  ratio. Maturity fields after Peters and Moldowan (1993)

the Markowice-2 section is probably caused by oxidation and/or biodegradation of organic matter (e.g., Stahl, 1980). The composition of regular steranes (Fig. 9) indicates the same type of the organic matter as in the Ordovician and Cambrian strata.

The thermal maturity of the Silurian strata, like in the previously discussed Ordovician strata, was determined based on pyrolytic data (Table 2), measurements of the vitrinite-like macerals reflectance (Table 2), the biomarker (Table 5), the aromatic hydrocarbon distribution (Table 6) and the results of the kerogen elemental composition analyses (Table 7). The  $T_{max}$  values indicate maturity from the initial to the final phase of the "oil window" (from 424 to 454°C; Table 2, Figs 2, 4B). The maturity indices calculated based on the biomarkers, methylphenanthrenes and methyl-dibenzothiophenes distribution (Tables 5, 6, Fig. 10) correspond with the  $T_{max}$  values. The vitrinite-like material reflectance of the organic matter corresponds with the Rock-Eval, biomarker, aromatic hydrocarbon and kerogen elemental composition analysis data.

#### Identification and geochemical characteristics of the source rocks

The identification of source rock horizons is an essential element of petroleum system analyses for the calculation of the volumetric hydrocarbon potential. Usually, for the 1-D modelling of the generation and expulsion of hydrocarbons, the source rocks thickness and the initial organic carbon content are estimated for an individual stratigraphic complex within each well section. In the areas where the sampled wells were close to one another, the average source rocks thickness and the initial organic carbon content of an individual stratigraphic division were calculated. These source rock data were used in the hydrocarbon generation modelling procedure by Kosakowski *et al.* (in press).

The results of geochemical analyses indicate that source rocks may be present in all the analysed time divi-

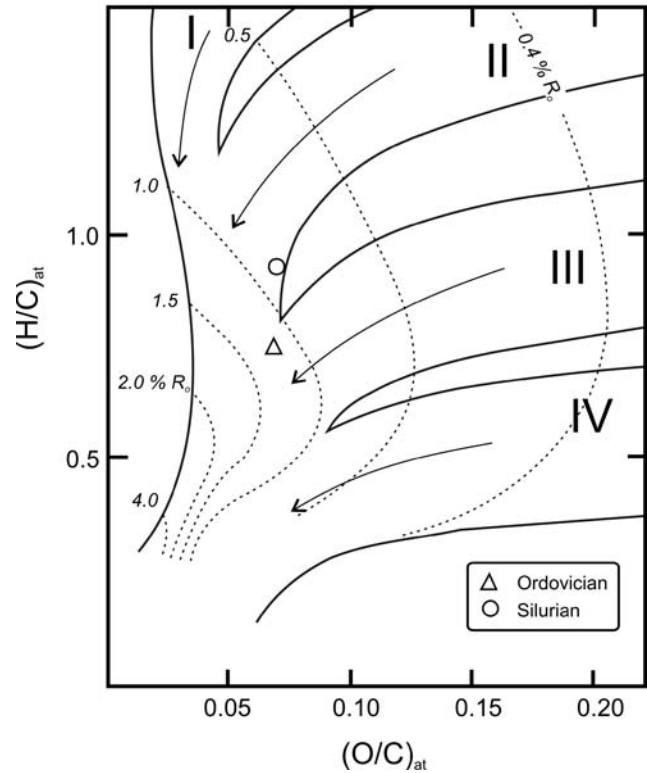


Fig. 11. Elemental composition of organic matter from Ordovician and Silurian strata. Fields represent natural maturity paths for individual kerogens after Hunt (1996)

sions from the Cambrian to the Silurian. The Silurian strata have the best hydrocarbon potential in the study area and can be classified as good source rocks (Tables 2, 8). The Cambrian and Ordovician horizons with elevated organic carbon contents could be considered as an additional local source of hydrocarbons. Due to the very high maturity of the Cambrian siliclastic strata, resulting in a mass loss of the Type-II kerogen of ca. 40 wt% (Baskin, 1997), the organic carbon threshold of the source rocks, routinely accepted at 0.5 wt% (e.g., Peters & Cassa, 1994), was lowered down to 0.3 wt% TOC. Due to the domination of carbonates in the Ordovician strata (Buła & Habryn, 2011), the threshold of the source rock TOC was lowered for these strata to the same level as for the Cambrian strata.

An attempt to estimate the source rock potential was made for 24 wells in the Polish part of the analysed area, where the TOC content was determined and the lithology was available (Table 8). A precise determination of the source rock thickness could not be achieved during this study. This was due to the non-representative sampling in the individual wells, where the drilling did not cover the entire section of the investigated strata (Table 8). Therefore, the source rock thickness could only be estimated. Especially for the Cambrian strata, whose thickness was estimated up to ca. 1,000 m (Buła & Habryn, 2011), the sampling interval covered, at most, a few dozen metres (Table 8). In the case of these strata, the 50 m thickness of source rock was arbitrarily assumed for the test purposes (Table 8).

The primary element of the source rock thickness determination of the Silurian strata was estimation of the thick-

Table 7

## Elemental composition of kerogen from the Ordovician and Silurian strata

Well	Depth (m)	Stratigraphy	Elemental composition (daf, wt%)					Atomic ratio				Mole fraction			
			C	H	O	N	S	H/C	O/C	N/C	S/C	H/(H+C)	O/(O+C)	N/(N+C)	S/(S+C)
Wola Obszańska-8	952.3	Ordovician	84.2	5.3	7.6	2.2	0.7	0.75	0.07	0.023	0.003	0.43	0.06	0.022	0.003
Wola Obszańska-14	928.7	Silurian	82.9	6.4	7.7	2.5	0.6	0.92	0.07	0.026	0.003	0.48	0.06	0.025	0.003

daf – dry, ash-free basis

Table 8

## Estimated thickness and initial organic carbon content of the identified source rocks in the Tarnogród-Lubaczów area

Well	Stratigraphy	Total thickness* (m)	Source-rock thickness* (m)	n	TOC (wt%)	R <sub>o</sub> (%)	H/C	x	TOC <sub>0</sub> (wt%)
Biszczka-1, Księżpol-10, Księżpol-11, Księżpol-14	Middle Cambrian	70 (n.p.)	50 (test)	57	0.37 (7)	1.9	<i>0.57</i>	0.45	0.7
Markowice-2	Silurian	133 (n.p.)	60	24	0.36 (4)	1.1	<i>0.86</i>	0.39	0.6
Luchów-3, Rudka-8, -10, -11, -13	Lower Cambrian	40 (n.p.)	50 (test)	47	0.4 (1)	1.1	<i>0.86</i>	0.39	0.7
Księżpol-15, Wola Obszańska-15	Upper Cambrian	48 (n.p.)	50 (test)	16	0.34 (5)	1.4	<i>0.73</i>	0.43	0.6
Księżpol-18, Wola Różaniecka-7	Middle Cambrian	64 (n.p.)	50 (test)	26	0.34 (5)	1.1	<i>0.86</i>	0.39	0.6
Mołodycz-1, Wola Obszańska-8, -9, -10	Upper Cambrian	104 (n.p.)	50 (test)	15	0.32 (9)	1.1	<i>0.86</i>	0.39	0.5
Dzików-12, -13, -15	Middle Cambrian	11 (n.p.)	50 (test)	12	<0.3				0.6#
Lubliniec-9, Wola Obszańska-8, -9, -10, -13	Ordovician	48 (n.p.)	20	37	0.45 (8)	0.95	0.75	0.42	0.8
Wola Obszańska-8, -10, -13, -14, -16	Silurian	46 (n.p.)	100	134	0.98 (127)	0.88	0.92	0.38	1.6

\* – average thickness when at least two wells were taken into consideration; n – total quantity of rock samples; TOC – mean present organic carbon content in the source-rock levels (in brackets – quantity of up-threshold TOC measurements); R<sub>o</sub> – vitrinite-like macerals reflectance; H/C – hydrogen/carbon atomic ratio in kerogen; x – relative loss of TOC mass responding the maturity described by H/C value after Baskin (1997); TOC<sub>0</sub> – initial organic carbon content; n.p. – not penetrated to bottom; values of H/C typed in italic were calculated from R<sub>o</sub> values by equation worked out by Behar *et al.* (1995) or, in the case of lack of R<sub>o</sub> measurements were taken the same values as in neighbouring wells; test – synthetic thickness taken due to poor drilling of the strata; # – value estimated based on data from neighbouring wells

ness of clayey rocks. This was done based on available well data (core descriptions, well-logs) as well as, occasionally, by analogy with the neighbouring wells. Although these sediments were usually not intersected by drilling, the thickness values can be estimated based on geological data (Buła & Habryn, 2008; 2011). The results of geochemical analyses were the second element determining the source rock thickness (TOC content). The estimated thickness of source rocks was calculated by multiplying the total clayey complexes thickness by the fraction of quantity of samples having up-threshold TOC content (above 0.5 wt%) and all the analysed samples.

Based on similar assumptions for the Ordovician strata, it was assessed that the thickness of the source rocks in the vicinity of Lubliniec and Wola Obszańska was *ca.* 20 m (Table 8). For the Silurian strata, the 60 m and 100 m thick source rocks were estimated in the Markowice-2 well and in the vicinity of Wola Obszańska, respectively (Table 8).

The highest values of the initial organic carbon content (TOC<sub>0</sub>) were estimated in the Silurian strata in the vicinity of Wola Obszańska – 1.6 wt% (Table 8). In the remaining identified source rock horizons, the source rocks potential is much inferior. The TOC<sub>0</sub> values in the Ordovician strata in the vicinity of Lubliniec and Wola Obszańska equalled to

*ca.* 0.8 wt%, whereas the TOC<sub>0</sub> values in the other areas and sediments probably ranged from 0.5 to 0.7 wt%, identifying these horizons as fair source rocks (Table 8).

## CONCLUSIONS

Among the Cambrian to Silurian succession of the Tarnogród–Stryi area, the Silurian mudstones and claystones display the best source-rock characteristics with the TOC values up to 2.6 wt% and the median of 0.8 wt%. The best source rocks are present in the Wola Obszańska-8 and -16 wells, where the present median of the TOC equals *ca.* 1.5 and 1.7 wt%, respectively. The Cambrian and Ordovician rocks are lean in the organic matter with the present TOC content rarely exceeding 0.50 wt%. The present hydrocarbon potential of the investigated strata is low and usually does not exceed 200 mg HC/g TOC. The highest medians of the HI were calculated for the Lower Cambrian and Silurian strata (173 and 145 mg HC/g TOC, respectively). The oil-prone Type II kerogen is the dominant organic matter type throughout the section studied. Due to the high maturity it is impossible to determine the kinetic type of kerogen. The organic matter was deposited in reducing and sub-oxic

conditions. Its thermal maturity ranges from the initial phase of the “oil window” in the Silurian, through the middle phase in the Ordovician and selected areas of the Cambrian strata, up to the overmature phase in the Ordovician section of Verchany-1 and the Cambrian sections of the Chornokunsi-1, Mosty-1 and Książpol-11 wells.

The estimated initial total organic carbon content in the source rock of the Cambrian strata was from 0.6 to 0.7 wt% indicating their poor source rock potential. The Ordovician source rocks are characterized also by a poor source-rock potential with the calculated median TOC<sub>0</sub> value of 0.8 wt%. The estimated initial organic carbon content in the Silurian strata equals ca. 1.6 wt% indicating a good or very good source-rock potential of the investigated strata. The presented data indicate a poorer hydrocarbon potential of the analysed Lower Palaeozoic strata than that of the corresponding sequence in the Kraków–Rzeszów area (Więclaw *et al.*, 2011).

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