

## HABITAT AND HYDROCARBON POTENTIAL OF THE PALAEOZOIC SOURCE ROCKS IN THE KRAKÓW–RZESZÓW AREA (SE POLAND)

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Więclaw, D., Kotarba, M. J., Kowalski, A. & Kosakowski, P., 2011. Habitat and hydrocarbon potential of the Palaeozoic source rocks in the Kraków–Rzeszów area (SE Poland). *Annales Societatis Geologorum Poloniae*, 81: 375–394.

**Abstract:** The quantity, genetic type and maturity of organic matter dispersed in Ordovician, Silurian, Devonian and Lower Carboniferous strata in the basement of the Carpathian Foredeep between Kraków and Rzeszów were determined based on the results of organic geochemical analyses of 600 rock samples collected from 44 wells. The best source rocks were found in the Silurian strata where the total organic carbon (TOC) content is up to 6.6 wt% and the median value equals ca. 1.5 wt%. The median values of the initial organic carbon contents in individual wells vary from 1.2 to 3.5 wt%. The Ordovician, Lower Devonian and clastic facies of the Lower Carboniferous strata can be considered as an additional source of hydrocarbons with the median TOC values of 0.27, 0.56 and 0.53 wt%, respectively. The Middle and Upper Devonian strata as well as the carbonate facies of the Lower Carboniferous strata have much lower quantities of organic carbon, although in these strata levels with elevated TOC contents were observed. In the Lower Palaeozoic and Lower Devonian strata, the oil-prone, low-sulphur Type II kerogen is present, whereas in the younger divisions presence of the gas-prone Type III kerogen is visible. In the Lower Carboniferous clastics gas-prone kerogen dominates. The Silurian and clastic facies of the Lower Carboniferous strata have been deposited in the normal marine conditions, whereas the Ordovician, Devonian and carbonate facies of the Lower Carboniferous strata usually experienced reducing conditions. The source rocks are mostly at the initial and middle phase of the low-temperature thermogenic processes. Locally, immature (in the Lower Carboniferous carbonates in the vicinity of Łakta gas-condensate field) or late-mature (in the Middle and Upper Devonian strata in the area of Grobla–Pławowice oil field) source rocks were observed.

**Key words:** source rock, hydrocarbon potential, Rock-Eval pyrolysis, biomarkers, stable carbon isotopes, Palaeozoic basement, Małopolska Block, Polish Carpathian Foredeep.

*Manuscript received 29 May 2011, accepted 13 October 2011*

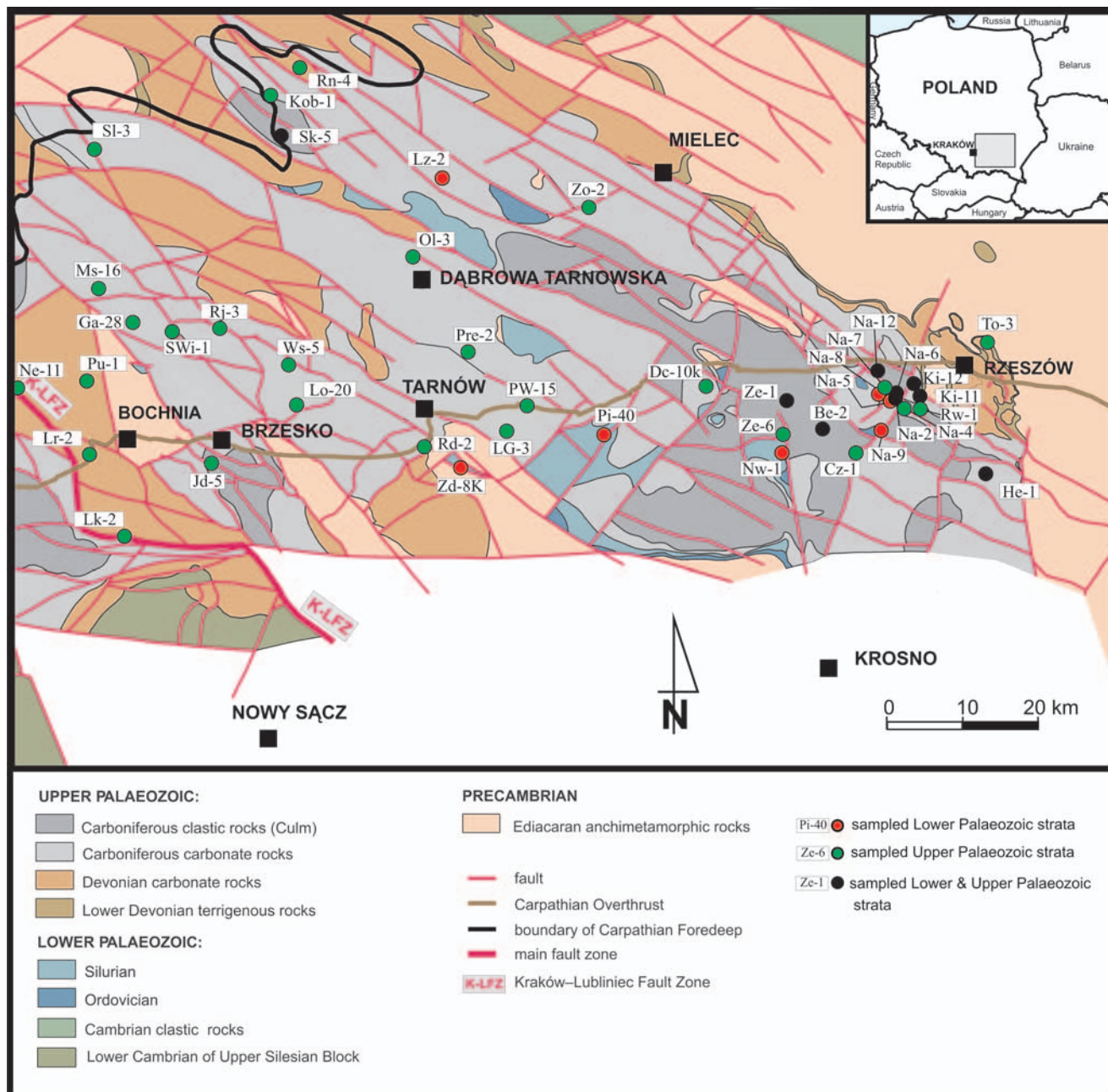
### INTRODUCTION

Palaeozoic strata in the Carpathian Foredeep basement and beneath the Carpathian Overthrust in the Kraków–Rzeszów area (SE Poland) occupy an area of ca. 6,000 km<sup>2</sup> (Fig. 1) and are part of the tectonic unit called the Małopolska Block (Buła *et al.*, 2004; Buła & Habryn, 2011). Numerous oil and gas fields or inflows were recorded in this area in reservoirs that range in age from the Devonian to the Miocene (*e.g.*, Karnkowski, 1999). Apart from the autochthonous Miocene strata where microbial gases dominate (Kotarba *et al.*, 2011), gas and oil are mostly accumulated in the Upper Jurassic carbonates and Upper Cretaceous sandstones sealed by Miocene molasse (Karnkowski, 1999). Więclaw (2011) defined the origin of the various oils as mostly generated from the Palaeozoic source rocks.

Only a few papers do describe hydrocarbon potential of the Palaeozoic source rocks in the analysed area. Based on

the results of Rock-Eval and petrographic analyses of Carboniferous, Silurian and Ordovician samples, Matyasik *et al.* (2001) notes the good source rock potential of the oil-prone kerogen dispersed in the Silurian sequence. Dudek *et al.* (2003) analysed Carboniferous and Devonian strata recording generally high gas and oil potential of the Carboniferous section. Matyasik *et al.* (2004) based on analyses of samples taken from the Lower and Middle Devonian strata from Trzebowisko-3 well indicate good oil-prone source rocks in the clayey intercalations within the Lower Devonian sequence. Kotarba *et al.* (2004) show the presence of good oil and gas source rocks in the Carboniferous from their analyses of 204 samples from 20 boreholes.

This paper describes a quantitative and qualitative evaluation of source rocks from the Palaeozoic section of the Małopolska Block in the basement of the Carpathian Fore-



**Fig. 1.** Geological map of the south-eastern Poland after Buła & Habryn (2011) and location of sampled wells. For the explanation of well codes see Table 1

deep in the Kraków–Rzeszów area (Fig. 1). We examined TOC content, petroleum potential, organic matter type and the thermal maturity of the entire Palaeozoic sequence. The source rock assessment was performed according to geochemical criteria proposed by Peters and Cassa (1994), and Hunt (1996). Interpretation of the results benefited from data published by Matyasik *et al.* (2001, 2004), Dudek *et al.* (2003) and Kotarba *et al.* (2004).

The thickness and the initial total organic carbon (TOC<sub>0</sub>) content of the source rocks in individual areas were estimated. The results of the conducted investigations are the basic data for the 1-D modelling of generation, expulsion and migration processes (Kosakowski & Wróbel, 2011).

## GEOLOGICAL SETTING

The Lower Palaeozoic suite of the Małopolska Block is composed of the Ordovician carbonate and clastic complex of a changeable thickness, up to a few hundred metres, and the Silurian dark-coloured, fine-grained claystone and mudstone sequence, up to 200 m thick (Moryc, 2006; Kowalska *et al.*, 2000). The Silurian strata, representing a relatively deep-water depositional environment (Malec, 2006), are usually black or dark brown claystones and shales with graptolites, which are replaced by the thinner, predominantly carbonate shelf sediments at the top of the sequence. In the study area, the Silurian strata represent the lower part of the stratigraphic section, from the Llandovery to the

Wenlock (Moryc, 2006). Intensive Late Silurian or Early Devonian erosion and hiatus in the late Silurian resulted in deposits of thin sheets (Buła & Habryn, eds, 2008). The Lower Devonian strata developed as terrigenous deposits, up to 200 m thick. The carbonaceous deposits of the Middle and Upper Devonian range from 300 to 400 m in thickness in the vicinity of Rzeszów (Maksym *et al.*, 2003) and more than 1,000 m in the western part of the study region (Zajac, 1984). The Carboniferous deposits in the study area are of the late Tournaisian–early Namurian age, and represent carbonate and clastic facies (Jawor & Baran, 2004). Their thicknesses range from 80 to 600 m and from a few metres to 500 m, respectively. Erosion during the Variscan orogeny removed the Upper Carboniferous and Lower Permian strata. The Upper Permian strata developed mainly as conglomerates and sandstones with variegated claystones and mudstones in the uppermost part of the interval. These were deposited in local depressions only, and their thicknesses rarely exceed a few tens of metres (Jawor & Baran, 2004). The tectonic position and lithostratigraphic characteristics of the study area were presented and described in detail by Buła and Habryn (2008, 2011).

## SAMPLES

Samples were taken from cores representing all recognised strata from the Carpathian Foredeep basement. A total of 600 core samples from 44 wells (Fig. 1), weighing about 400 g each, mainly claystones and siltstones as well as marls and carbonates, were collected for analysis. Table 1 includes the number of samples collected, well names, stratigraphic names and depth.

## ANALYTICAL METHODS

The core samples were cleaned from mud contaminations and crushed to the 0.5 – 2 cm fraction. Then, 200 g of each sample were milled to the fraction of <0.2 mm for geochemical analyses. Screening pyrolysis analyses of rock samples were carried out with the Rock-Eval Model II instrument equipped with an organic carbon module. Aliquots of the selected 77 pulverised samples were extracted with dichloromethane : methanol (93:7 v/v) in the Soxhlet 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.

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 treated with hydrochloric acid prior to the analysis. The stable carbon isotope data are presented in the  $\delta$ -notation relative to the V-PDB standard (Coplen, 1995). The analytical precision is estimated to be  $\pm 0.2\%$ .

**Table 1**

The number and stratigraphy of rock samples collected from individual wells

Well	Well code	Ordovician	Silurian	Lower Devonian	Middle & Upper Devonian	Lower Carboniferous	
						carbonates	clastic
Będzienia-2	Be-2	-	4	-	-	15	5
Czudec-1	Cz-1	-	-	-	-	-	15
Dębica-10k	Dc-10k	-	-	-	-	5	-
Grobla-28	Ga-28	-	-	-	6	-	-
Hermanowa-1	He-1	21	20	-	-	-	22
Jadowniki-5	Jd-5	-	-	-	-	15	-
Kielanówka-11	Ki-11	5	-	3	3	9	-
Kielanówka-12	Ki-12	8	-	-	-	20	-
Kobylniki-1	Kob-1	-	-	-	8	3	-
Łakta-2	Lk-2	-	-	-	-	6	-
Łapczyca-2	Lr-2	-	-	-	13	-	-
Łęki Górne-3	LG-3	-	-	-	-	-	5
Lubasz-2	Lz-2	3	1	-	-	-	-
Łętowice-20	Lo-20	-	-	-	1	-	1
Mniszów-16	Ms-16	-	-	-	10	-	-
Nawsie-1	Nw-1	-	8	-	-	-	-
Niepołomice-11	Ne-11	-	-	3	20	-	-
Nosówka-2	Na-2	25	-	-	-	10	-
Nosówka-4	Na-4	-	-	-	-	4	2
Nosówka-5	Na-5	12	-	-	-	2	-
Nosówka-6	Na-6	9	-	-	-	6	14
Nosówka-7	Na-7	-	-	-	-	3	-
Nosówka-8	Na-8	8	-	-	-	-	-
Nosówka-9	Na-9	1	-	-	-	-	-
Nosówka-12	Na-12	4	-	-	-	12	2
Oleśnica-3	Ol-3	-	-	-	3	-	-
Pilzno-40	Pi-40	6	5	-	-	-	-
Pogórska Wola-15	PW-15	-	-	-	-	-	1
Prendolówka-2	Pre-2	-	-	-	-	2	-
Puszcza-1	Pu-1	-	-	-	25	-	-
Raławówka-1	Rw-1	-	-	-	-	-	3
Radlna-2	Rd-2	-	-	-	-	2	-
Radzanów-4	Rn-4	-	-	-	5	-	-
Rajsko-3	Rj-3	-	-	2	17	-	-
Skalbmierz-3	Sl-3	-	-	-	25	-	-
Stróżyska-5	Sk-5	5	12	1	5	-	-
Strzelce Wielkie-1	SWi-1	-	-	-	-	11	18
Tarnów-19	Ta-19	-	-	-	-	4	-
Trzebownisko-3	To-3	-	-	8	7	-	-
Waryś-5	Ws-5	-	-	-	2	-	-
Zagorzyce-1	Ze-1	4	-	-	-	6	8
Zagorzyce-6	Ze-6	-	-	-	-	-	20
Zawada-8K	Zd-8K	-	20	-	-	-	-
Zgórsko-2	Zo-2	-	-	-	-	1	-
TOTAL		111	70	17	150	136	116



The isolation of kerogen for the 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). The elemental analysis of the 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 on the Perkin-Elmer Plasma 40 ICP-AES instrument after digesting the ash from the 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 the C, H, N, S, moisture and ash contents.

The isolated saturated hydrocarbon fractions from the selected bitumen were diluted in isooctane and analysed by the GC-MS for biomarker determination. The analyses were 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 × 0.25 mm i.d.) coated with 95% methyl/5% phenylsilicone phase (DB-5MS, 0.25 µm 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 hydrocarbons 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.

The measurements of the mean random reflectance of vitrinite-like macerals (R<sub>o</sub>) were carried out with the use of the Zeiss-Opton microphotometer at 546 nm wavelength, in oil. The standards used were 0.496%, 0.921%, 1.141% and 1.662% reflectance (R<sub>o</sub>). Sample preparation and point counts were carried out in accordance with the ICCP procedure (Taylor *et al.*, 1998).

The initial TOC content for the strata where geochemical data were available was 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 the Lower Palaeozoic, Devonian and Lower Carboniferous carbonates (Table 2). The initial TOC content was calculated from the equation:

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

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

In the case of leaching directly measured kerogen elemental composition data, the H/C values were calculated based on the measured R<sub>o</sub> values using the equation calculated as the best-fit of the H/C – R<sub>o</sub> relationship worked out by Behar *et al.* (1995):

– for the Type II organic matter (present in all identified strata without the Lower Carboniferous clastic facies) based on pyrolysis experiments of the Toarcian shale:

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

– for the Type III/II organic matter (present in the Lower Carboniferous clastic facies) based on pyrolysis experiments of the Mahakam coal:

$$(\text{H/C})_{\text{at}} = 1.045e^{-0.34R_o} \quad R^2 = 0.987 \quad (3)$$

If direct measurements of the R<sub>o</sub> or (H/C)<sub>at</sub> values were unavailable, thermal maturity of organic matter was assumed as in the neighbouring wells or based on the R<sub>o</sub> – depth relationship in individual wells.

The present TOC content was determined as a median value of above-threshold values. For the carbonate facies (the Middle and Upper Devonian and Lower Carboniferous carbonates), the assumed threshold TOC quantity was 0.3 wt% (Bordenave, 1993). In the other cases, the minimum TOC content for potential hydrocarbon source rocks equal to 0.5 wt% was taken (Peters & Cassa, 1994).

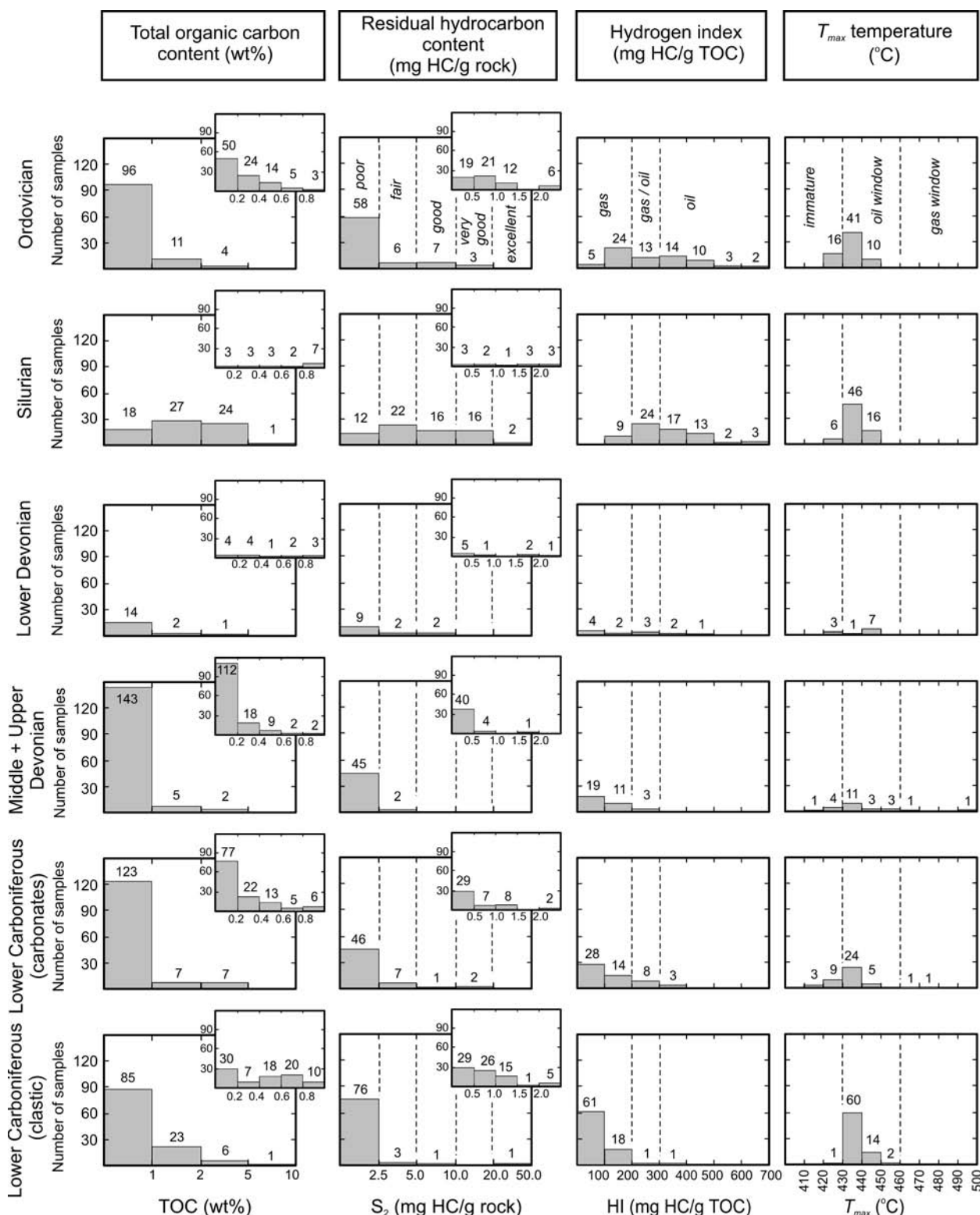
## RESULTS AND DISCUSSION

### Hydrocarbon potential of individual stratigraphic units

#### Ordovician strata

From the Ordovician strata, 111 samples from of 13 wells were collected (Table 1, Fig. 1). The total organic carbon (TOC) content varies in the strata of this period from 0 to 2.9 wt%, with the median of 0.27 wt% (Table 2). Samples with the low TOC values dominate, but in four samples collected from wells in the vicinity of Rzeszów (Kielanówka-11, Nosówka-6 and Zagorzyce-1) high organic carbon content, over 2 wt%, was recorded (Figs 1, 2). The residual hydrocarbon content (S<sub>2</sub>) as well as total hydrocarbon content (S<sub>1</sub>+S<sub>2</sub>), similarly to the TOC values, are usually low and range from 0.08 to 15.8 and 0.16 to 16.9 mg HC/g rock, respectively, with the median values of 0.89 and 1.01 mg HC/g rock, respectively (Table 2, Fig. 3A), indicating that the analysed strata are generally poor for generation of hydrocarbons. In ten samples the S<sub>2</sub> values exceed 5 mg HC/g rock (Fig. 2) indicating good and very good hydrocarbon potential. The best source rock properties are noted in the vicinity of Rzeszów (Kielanówka-11 and Hermanowa-1 wells, Fig. 1).

The correlation between the hydrogen index HI and the T<sub>max</sub> temperature (Fig. 4A), the n-alkanes and isoprenoids distribution (Table 3, Figs 5, 6A), the stable carbon isotope composition (Table 4, Figs 7A, 8A), the biomarker distribution (Table 5, Fig. 9) and the kerogen elemental composition (Table 6, Fig. 10) provides evidence that in the Ordovician strata the oil-prone Type II kerogen is present. Organic matter was deposited usually in the normal marine condi-



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

tions ( $1 < Pr/Ph < 3$ , Table 3) (Didyk *et al.*, 1978) and locally (in the Hermanowa-1 section) in anoxic conditions ( $Pr/Ph < 1$ ). Low values of gammacerane index (GI) indicate absence of hypersaline sedimentation environment (Sinighe Damste *et al.*, 1995). The stable carbon isotope composition reveals the presence of organic matter enriched in

lighter isotope (Figs 7A, 8A), typical for the Lower Palaeozoic sediments where organic matter came primarily from algae (Riding, 2001). The composition of the regular steranes (Fig. 9) as well as values of the ratios calculated based on steranes, diasteranes and hopanes distribution (Table 5) indicate the same type of organic matter in all the Ordovi-

Table 2

Geochemical characteristics and hydrocarbon potential of the Palaeozoic strata in the Kraków-Rzeszów area

Stratigraphy Index	Ordovician	Silurian	Lower Devonian	Middle + Upper Devonian	Lower Carboniferous (carbonates)	Lower Carboniferous (clastic)
<b>TOC (wt%)</b>	0.00 to 2.9 (111) 0.27 (13)	0.10 to 6.6 (70) 1.57 (7)	0.02 to 2.4 (17) 0.56 (5)	0.00 to 2.6 (150) 0.05 (15)	0.00 to 5.0 (137) 0.12 (19)	0.00 to 6.3 (115) 0.64 (13)
<b>T<sub>max</sub> (°C)</b>	422 to 445 (67) 436 (11)	424 to 444 (68) 437 (7)	427 to 448 (11) 442 (4)	420 to 499 (24) 437 (10)	416 to 478 (43) 436 (14)	428 to 458 (77) 439 (12)
<b>S<sub>2</sub> (mg HC/g rock)</b>	0.08 to 15.8 (74) 0.89 (12)	0.26 to 40.3 (68) 5.0 (7)	0.12 to 9.3 (13) 1.64 (4)	0.00 to 4.5 (47) 0.16 (11)	0.00 to 13.7 (56) 0.44 (14)	0.09 to 22.8 (81) 0.64 (12)
<b>S<sub>1</sub>+S<sub>2</sub> (mg HC/g rock)</b>	0.16 to 16.9 (74) 1.01 (12)	0.35 to 43.8 (68) 5.6 (7)	0.15 to 9.4 (13) 1.67 (4)	0.06 to 4.7 (47) 0.26 (11)	0.02 to 14.3 (56) 0.47 (14)	0.10 to 23.0 (81) 0.70 (12)
<b>PI</b>	0.00 to 0.41 (67) 0.13 (10)	0.03 to 0.32 (68) 0.13 (7)	0.00 to 0.40 (12) 0.02 (4)	0.02 to 0.82 (30) 0.34 (8)	0.00 to 0.62 (52) 0.08 (14)	0.00 to 0.35 (81) 0.06 (12)
<b>HI (mg HC/g TOC)</b>	62 to 631 (71) 241 (11)	119 to 618 (68) 306 (7)	45 to 442 (12) 228 (4)	4 to 271 (33) 70 (10)	0 to 341 (53) 96 (14)	15 to 362 (82) 85 (12)
<b>OI (mg CO<sub>2</sub>/g TOC)</b>	0 to 408 (69) 16 (10)	0 to 268 (68) 18 (7)	17 to 200 (12) 59 (4)	12 to 448 (30) 81 (8)	0 to 331 (52) 30 (14)	0 to 84 (76) 13 (11)
<b>BR (mg bit./g TOC)</b>	60 to 650 (27) 120 (7)	22 to 199 (36) 127 (6)	17 to 64 (5) 41 (2)	9 to 78 (5) 59 (4)	12 to 300 (19) 68 (10)	11 to 153 (31) 57 (8)
<b>R<sub>o</sub> (%)</b>	0.66 to 1.03 (5) 0.71 (4)	0.56 to 0.75 (11) 0.66 (5)	0.57 to 0.98 (5) 0.61 (3)	0.72 to 1.10 (3) 0.80 (3)	0.61 to 1.60 (9) 0.88 (7)	0.64 to 1.16 (21) 0.74 (5)
<b>Vitrinite macerals (%)</b>	2 to 33 (5) 8 (4)	5 to 68 (11) 23 (5)	2 to 54 (5) 4 (3)	78 (1 analysis)	0 to 100 (6) 35 (4)	6 to 69 (15) 42 (3)
<b>Liptinite macerals (%)</b>	67 to 98 (5) 83 (4)	30 to 95 (11) 77 (5)	46 to 97 (5) 93 (3)	22 (1 analysis)	0 to 100 (6) 50 (4)	13 to 91 (15) 40 (3)
<b>Inertinite macerals (%)</b>	0 to 8 (5) 0 (4)	0 to 5 (11) 2 (5)	0 to 8 (5) 1 (3)	0 (1 analysis)	0 to 44 (6) 7 (4)	3 to 24 (15) 18 (3)
<b>Kerogen type</b>	II	II	II	II (II/III)	II (II/III)	III (III/II)
<b>Maturity</b>	<i>mature</i>	<i>mature</i>	<i>mature</i>	<i>mature/overmature</i>	<i>immature/mature</i>	<i>mature</i>
<b>Hydrocarbon potential</b>	<i>poor/fair</i>	<i>good</i>	<i>fair</i>	<i>poor</i>	<i>poor</i>	<i>fair</i>

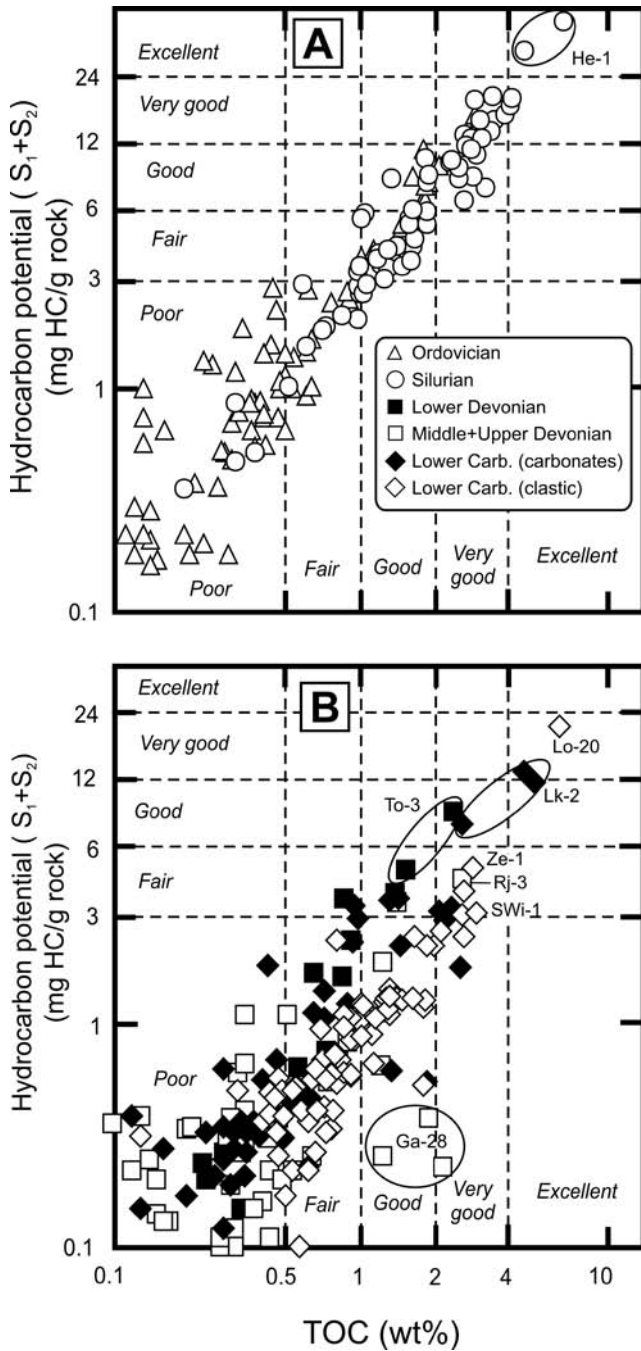
TOC – total organic carbon; T<sub>max</sub> – temperature of maximum of S<sub>2</sub> peak; S<sub>2</sub> – residual petroleum potential; S<sub>1</sub> – oil and gas yield (mg HC/g rock); PI – production index; HI – hydrogen index; OI – oxygen index; BR – bitumen ratio. Range of geochemical parameters is given as numerator; median values in denominator, in parentheses: number of samples from wells (numerator) and number of sampled wells (denominator); kerogen type in brackets – secondary occurrence

Ordovician samples deposited mostly in marine shales. Only in single samples is enrichment in carbonates visible, *i.e.* in sample He-1/4918.5, where homohopane index (C<sub>35</sub>/C<sub>34</sub>) is above 1 (*e.g.*, Mello *et al.*, 1988). Also for sample Na-6/4019.6, characterizing lowered Ts/(Ts+Tm) and C<sub>27</sub> dia/(dia+reg) ratios (Fig. 11A) in comparison to samples collected only few meters above and below it, the effect of pH increase in the anoxic carbonate environment is visible (Moldowan *et al.*, 1994; *vide* Peters *et al.*, 2005, p. 614). Domination of the liptinite macerals in the analysed samples (Table 2) supports the results of geochemical analyses and

indicates the presence of the oil-prone Type II kerogen. The low values of the S/C atomic ratio in kerogen, below 0.04 (Table 6) reveal the presence of the low-sulphur (slow-generative) kerogen (Orr, 1986).

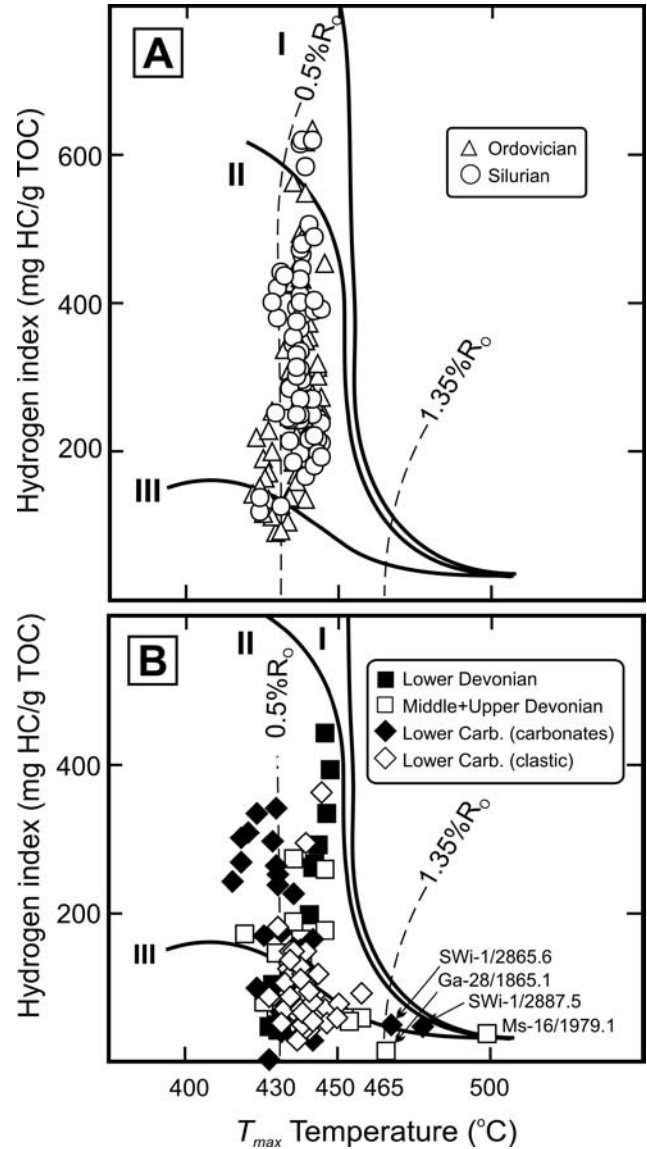
The thermal maturity of the Ordovician strata was determined based on the Rock-Eval data (Table 2), the measurements of the vitrinite-like macerals reflectance (Table 2), and the biomarker (Table 5) and aromatic hydrocarbons distribution (Table 7). Also indirectly for this purpose, the results of the kerogen elemental composition analysis (H/C and O/C values) were used (Table 6). Due to the low resid-





**Fig. 3.** Petroleum source quality diagram for organic matter of (A) Ordovician and Silurian and (B) Devonian and Lower Carboniferous strata. Classification after Peters and Cassa (1994). For the explanation of well codes see Table 1. Carb. – Carboniferous

ual hydrocarbon content, the  $T_{max}$  values were determined for 67 samples only (Table 2, Fig. 2). Values of this parameter indicate the maturity of the investigated strata from the final stage of microbial process to the middle phase of the “oil window” (from 422 to 445°C, Table 2, Figs 2, 4A). The maturity indices calculated based on the biomarkers, methylphenanthrenes and methylidibenzothiophenes distributions (Tables 5, 6, Figs 11, 12) as well as the vitrinite-like macerals reflectance of the discussed organic matter (Table 2) generally correspond with  $T_{max}$  values indicating the ini-



**Fig. 4.** Rock-Eval hydrogen index versus  $T_{max}$  temperature for (A) Ordovician and Silurian and (B) Devonian and Lower Carboniferous strata. Maturity paths of individual kerogen types after Espitalié *et al.* (1985). For the explanation of well codes see Table 1. Carb. – Carboniferous

tial and the middle phase of the oil window. The most mature levels were recorded in Hermanowa-1 well section (Figs 11, 12).

**Silurian strata**

From the Silurian strata, 70 samples from 7 wells were collected (Table 1). The total organic carbon (TOC) content varies from 0.1 to 6.6 wt%, with the median of 1.57 wt% (Table 2). Most of the samples are characterized by the TOC content from 1 to 5 wt% indicating good and very good source rock potential (Table 2, Fig. 2). The highest TOC contents, *i.e.* over 4 wt%, were recorded in the Hermanowa-1 well (Figs 1, 3A). The residual hydrocarbon contents ( $S_2$ ) as well as total hydrocarbon content ( $S_1+S_2$ ), are directly proportional to the TOC values, and vary from 0.26 to 40.3 and from 0.35 to 43.8 mg HC/g rock, respectively,

Table 3

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

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>	
Hermanowa-1	4,912.5	Ordovician	0.99	0.99	0.96	0.98	0.55	0.35	
	4,918.5		0.94	0.94	0.91	1.38	0.58	0.33	
Kielanówka-11	3,725.0		traces						
	3,726.5		0.87	0.84	0.98	1.37	0.95	0.33	
Kielanówka-12	3,653.5		0.90	0.85	1.42	1.76	0.99	0.35	
Nosówka-2	3,432.0		n.c.	n.c.	1.17	n.c.	n.c.	0.55	
Nosówka-6	4,015.3		n.c.	n.c.	1.19	n.c.	n.c.	0.34	
	4,019.6		n.c.	n.c.	1.13	n.c.	n.c.	0.38	
	4,020.5		1.01	0.98	1.13	1.73	1.34	0.46	
Będzienia-2	4,594.5		n.c.	n.c.	0.91	n.c.	n.c.	0.69	
Hermanowa-1	4,659.5		n.c.	n.c.	0.85	n.c.	n.c.	0.52	
	4,699.5		n.c.	n.c.	0.78	1.44	n.c.	0.39	
	4,699-4,701		0.97	1.02	0.85	2.18	1.92	0.88	
			0.94	0.97	0.88	1.10	1.28	0.80	
Nawsie-1	4,818.5	Silurian	0.95	0.94	0.93	1.27	2.00	1.06	
	4,821.5		1.01	1.01	1.00	1.89	3.17	1.28	
Pilzno-40	2,875.7		0.83	0.74	0.93	0.80	0.61	0.28	
	2,977.2		0.74	0.64	0.86	0.40	1.47	0.99	
Zawada-8K	3,326.5		n.c.	n.c.	1.00	0.05	n.c.	n.c.	
	3,332.5		n.c.	n.c.	1.19	0.90	n.c.	n.c.	
	3,335.0		1.13	1.16	1.12	1.02	0.65	1.04	
Kielanówka-11*	3,671.1		L. Devonian	1.13	0.99	1.32	0.14	0.25	0.76
Stróżyska-5	2,333.8		M. + U. Devonian	n.c.	n.c.	0.94	0.18	n.c.	0.05
Będzienia-2*	4,521.0		L. Carboniferous (carbonates)	0.99	0.96	1.02	0.75	0.34	0.36
Jadowniki- 5*	2,880.0			1.21	0.99	1.46	0.91	1.68	0.48
Kielanówka-12*	3,294.2			1.03	1.04	1.00	1.47	0.99	0.48
Strzelce Wielkie-1*	2,865.6			0.98	0.93	1.09	0.50	0.21	0.25
Będzienia-2*	4,364.0		L. Carboniferous (clastic)	1.22	1.11	1.37	0.17	1.33	0.66
	4,367.0	1.20		1.07	1.42	1.30	2.16	0.65	
Czudec-1*	4,285.5	1.02		0.97	1.09	1.54	1.04	0.58	
Nosówka-6*	3,698.2	1.37		1.19	1.62	0.76	3.46	0.79	
	3,734.2	1.15		1.04	1.24	2.07	1.96	0.67	
Strzelce Wielkie-1*	1,922.3	1.06		1.03	1.08	1.78	1.21	0.49	
Zagorzyce-6*	4,320.0	1.31		1.10	1.62	1.46	2.72	0.63	
	4,500.5	1.15		1.04	1.43	0.43	0.81	0.53	

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

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

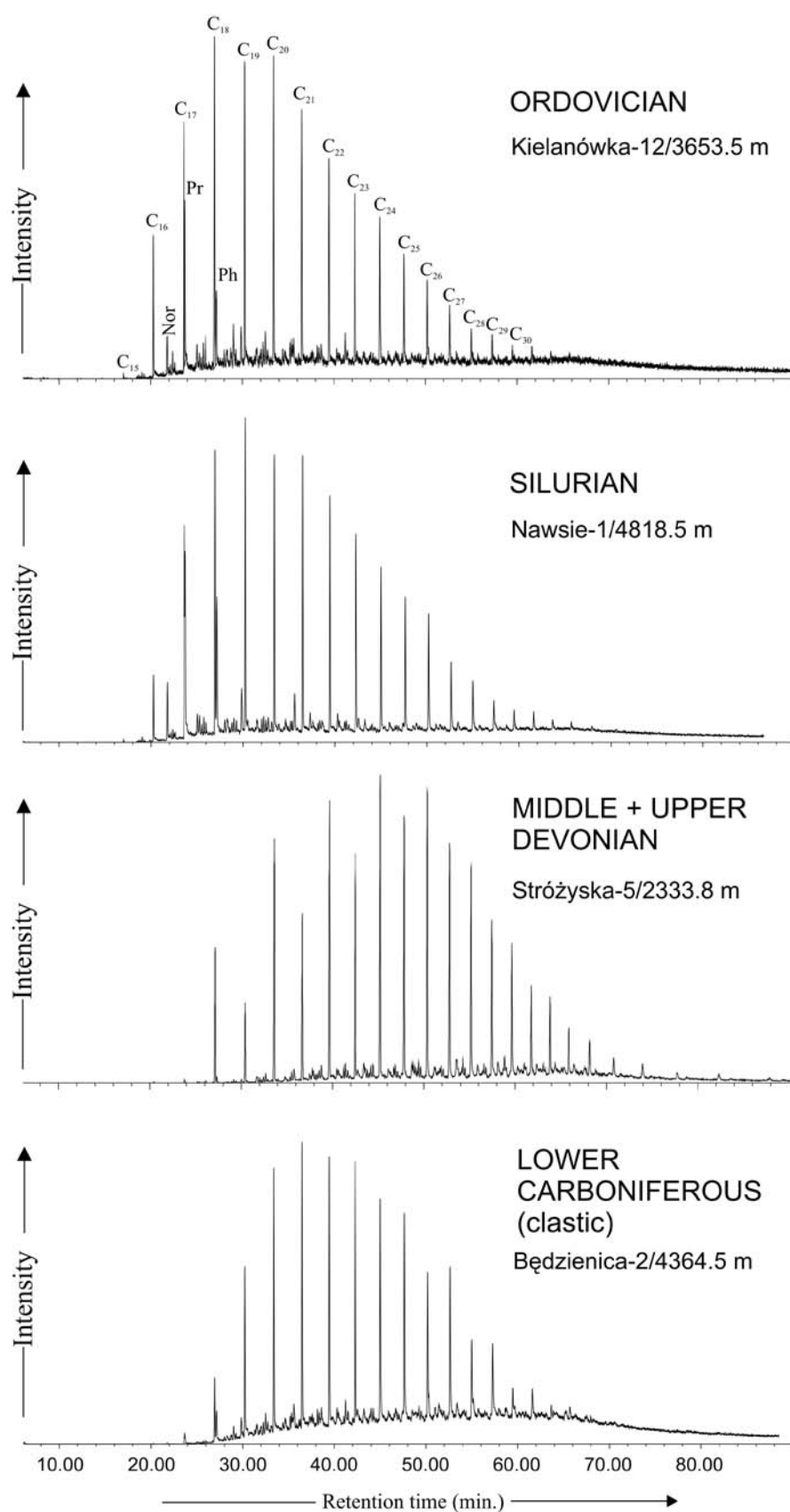
Pr – pristane; Ph – phytane; \* – data after Kotarba *et al.* (2004); n.c. – not calculated; L. – Lower; M. – Middle; U. – Upper

with the median values of 5.0 and 5.6 mg HC/g rock, respectively (Table 2, Fig. 3A). The best hydrocarbon potential was recorded in the Hermanowa-1 well (Fig. 3A).

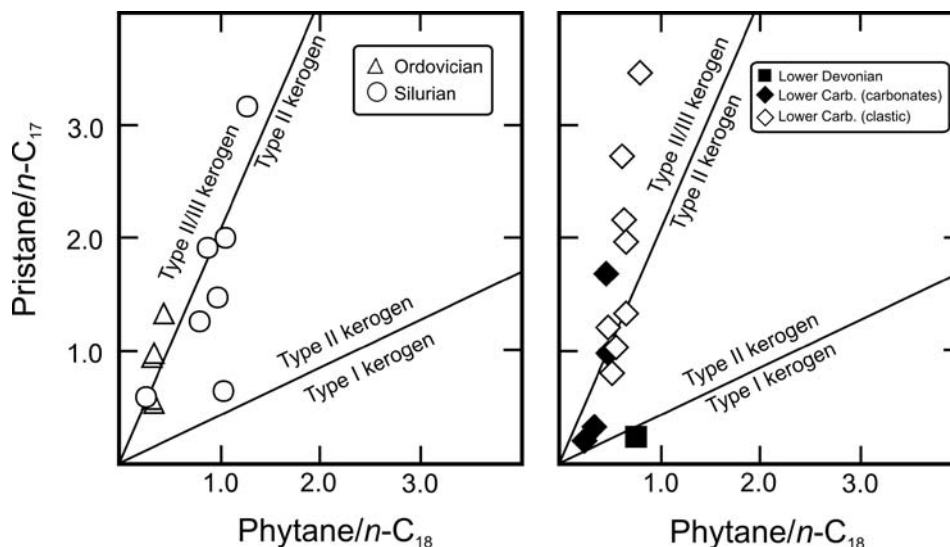
In the Silurian strata, like in the Ordovician ones, the oil-prone Type II kerogen is present. This statement is supported by the results of the pyrolytic data (Fig. 4A), the *n*-alkanes and isoprenoids distribution (Table 3, Figs 5, 6A), the stable carbon isotope composition (Table 4, Figs 7A, 8A), the biomarker distribution (Table 5, Fig. 9), and the kerogen elemental composition (Table 7, Fig. 10). The hydrogen index values are usually from 200 to 400 mg HC/g TOC (Figs

2, 4A). The lowest HI values, suggesting the presence of the Type III kerogen, were evidenced for the samples characterizing very low organic carbon contents, what is probably caused by partial oxidation of organic matter during sedimentation (Marynowski *et al.*, 2011). Organic matter in the Silurian strata was deposited, like in the Ordovician strata, in the normal marine ( $1 < Pr/Ph < 3$ ) and anoxic conditions (Table 3) (Didyk *et al.*, 1978). Values of biomarker indices evidence its deposition in marine shales (Peters *et al.*, 2005) and some differences in values between individual samples are results of thermal maturity (Fig. 11A). The stable carbon





**Fig. 5.** Examples of ion chromatograms ( $m/z = 71$ ) showing the distributions of  $n$ -alkanes and isoprenoids in saturated fraction of bitumens from the Ordovician, Silurian, Middle and Upper Devonian, and clastic Lower Carboniferous strata. Nor – *nor*-pristane; Pr – pristane; Ph – phytane



**Fig. 6.** Genetic characteristic of bitumen from (A) Ordovician and Silurian and (B) Devonian and Lower Carboniferous strata in terms of pristane/ $n$ -C<sub>17</sub> and phytane/ $n$ -C<sub>18</sub>, according to the categories of Obermajer *et al.* (1999). Carb. – Carboniferous

isotope composition reveals the presence of very light organic matter (Figs 7A, 8A), probably of algal origin (Lewan, 1986). The wide range of  $\delta^{13}\text{C}$  values is probably caused by facies changes. The composition of the regular steranes (Fig. 9) indicates the same type of organic matter as in the Ordovician strata. Domination of the liptinite macerals in the analysed samples (Table 2) suggests the presence of the same as in the previously discussed strata, oil-prone Type II kerogen. Also in these strata, like in the Ordovician ones, the low-sulphur kerogen is present (Table 6).

The thermal maturity of the Silurian samples, similarly to the previously discussed Ordovician ones, was determined based on the pyrolytic data (Table 2), measurements of the vitrinite-like macerals reflectance (Table 2), biomarker (Table 5) and aromatic hydrocarbons distribution (Table 7), and the results of the kerogen elemental composition (Table 6). The  $T_{max}$  values indicate the maturity from the final phase of the microbial process to the middle phase of the “oil window” (from 424 to 444°C; Table 2, Figs 2, 4A). The maturity indices calculated based on the biomarkers, methylphenanthrenes and methyl dibenzothiophenes distributions (Tables 5, 6, Figs 11, 12) correspond with  $T_{max}$  values. The less mature Silurian strata are in the Zawada-8K section (immature organic matter) and the most mature organic matter occurs in Stróżyńska-5 and Hermanowa-1 wells (Figs 11, 12). The vitrinite-like macerals reflectance of organic matter corresponds with the Rock-Eval, biomarker, aromatic hydrocarbon and kerogen elemental composition data (Table 2).

#### Lower Devonian strata

From the terrigenous Lower Devonian strata, 17 samples from 5 wells were analysed (Table 1). They mainly came from the Trzebowniko-3 well section described by Matyasik *et al.* (2004). The total organic carbon (TOC) content varies in these strata from 0.02 to 2.4 wt%, with the median of 0.56 wt% (Table 2). Samples with the low TOC values dominate, but in three samples the organic carbon con-

tent higher than 1 wt% was recorded (Fig. 2). The residual hydrocarbon as well as total hydrocarbon contents, comparable to the TOC values, are usually low and range from 0.12 to 9.3 and from 0.15 to 9.4 mg HC/g rock, respectively, with the median values of 1.64 and 1.67 mg HC/g rock, respectively (Table 2, Fig. 3B) indicating that the analysed strata are generally fair for generation of hydrocarbons. In four samples the  $S_2$  values exceed 2.5 mg HC/g rock (Fig. 2) indicating fair and good hydrocarbon potential. The best source rock properties are noted in the vicinity of Rzeszów (Trzebowniko-3 well, Figs 1, 3B).

In the Lower Devonian strata, like in the above-mentioned Lower Palaeozoic divisions, the oil-prone Type II kerogen is present. This hypothesis is supported by the correlation between the hydrogen index HI and the  $T_{max}$  temperature (Fig. 4B) and the  $n$ -alkanes and isoprenoids distribution (Table 3, Fig. 6B). Values of the pristane/phytane ratio below one suggest deposition in anoxic conditions, although increased values of the oxygen index up to 200 with the median value of 59 mg CO<sub>2</sub>/g TOC (Table 2) indicate synsedimentary oxidation or weathering (*e.g.*, Marynowski *et al.*, 2011) of organic matter. Domination of the liptinite macerals in the analysed samples (Table 2) supports the results of geochemical analyses and records the presence of the oil-prone Type II kerogen.

The thermal maturity of the Lower Devonian strata was determined based on the pyrolytic data (Table 2), measurements of the vitrinite-like macerals reflectance (Table 2), and aromatic hydrocarbons distribution (Table 7). Due to the low residual hydrocarbons content in 6 samples, the  $T_{max}$  values were determined for 11 samples only (Table 2, Fig. 2). Values of this parameter indicate the maturity of the investigated strata from the initial to the main phase of the “oil window” (from 427 to 448°C; Table 2, Figs 2, 4B). The maturity indices calculated for the single sample based on the methylphenanthrenes distribution (Table 7) correspond with its  $T_{max}$  value indicating the initial phase of the oil window. The vitrinite material reflectance of the discussed or-

Table 4

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

Well code	Depth (m)	Stratigraphy	Fractions (wt%)				$\delta^{13}\text{C}$ (‰)					
			Sat	Aro	Res	Asph	Sat	Bit	Aro	Res	Asph	Ker
He-1	4912.5	Ordovician	42	22	23	13	-31.3	-31.2	-31.2	-30.8	-30.9	-30.8
	4918.5		40	22	28	10	-31.3	-31.1	-31.0	-31.0	-31.0	-30.9
Ki-11	3726.5		27	25	33	15	-30.7	-30.8	-30.8	-30.1	-29.9	-30.7
	3725.0		14	13	31	42	-29.9	-30.2	-30.6	-28.9	-31.1	-30.6
Ki-12	3653.5		19	8	33	40	-29.2	-29.8	-29.6	-29.5	-30.4	-29.5
Na-2	3432.0		18	12	30	40	-31.2	-30.6	-31.3	-29.5	-31.0	-30.9
Na-6	4015.3		18	15	27	40	-30.6	-30.7	-31.2	-30.6	-30.6	-30.9
	4019.6		17	16	43	24	-30.2	-30.8	-31.3	-30.7	-30.9	-30.9
	4020.5		20	12	37	31	-31.0	-30.9	-31.1	-30.7	-30.8	-30.8
Be-2	4594.5		30	14	36	20	-30.7	-30.6	-30.5	-30.3	-29.9	-30.3
He-1	4659.5	26	21	31	22	-30.8	-30.8	-30.7	-30.1	-30.4	-30.5	
	4699.5	21	24	30	25	-30.3	-29.9	-29.9	-29.6	-29.4	-29.8	
	4699-4701	32	26	21	21	-30.2	-30.2	-30.5	-29.2	-29.6	-29.9	
Nw-1	4818.5	24	18	29	29	-29.0	-28.8	-28.8	-28.7	-28.9	-28.5	
	4821.5	24	16	33	27	-28.7	-28.7	-28.7	-28.8	-28.4	-28.1	
Pi-40	3551.0	26	20	29	25	-28.9	-28.3	-28.8	-27.8	-28.0	-27.8	
Sk-5	2875.7	37	23	28	12	-32.0	-31.6	-31.6	-31.1	-31.3	-31.2	
	2977.2	25	21	33	21	-28.5	-27.7	-27.2	-27.5	-27.5	-27.7	
Zd-8K	3326.5	14	20	27	39	-29.5	-29.2	-29.5	-28.6	-29.0	-28.1	
	3332.5	10	15	27	48	-30.7	-30.3	-31.0	-29.6	-30.4	-29.6	
	3335.0	15	16	27	42	-30.5	-29.8	-30.8	-29.5	-29.3	-29.1	
Sk-5	2333.8	M. + U. D.	12	24	36	28	-28.4	-27.5	-27.3	-27.3	-27.5	-27.8
Be-2*	4521.0	L. C. (carbonates)	29	33	24	14	-23.9	-24.2	-24.3	-24.3	-24.5	-24.4
Jd-5*	2880.0		8	13	19	60	-29.2	-25.3	-26.1	-25.8	-24.5	-26.1
Ki-12*	3294.2		11	24	23	42	-28.0	-26.6	-26.4	-27.0	-26.5	-25.5
Be-2*	4367.0	L. C. (clastic)	5	20	18	57	-29.2	-24.5	-25.4	-24.7	-24.2	-24.8
Cz-1*	4285.5		17	12	47	24	-29.4	-26.7	-26.8	-26.9	-24.6	-24.1
Na-6*	3734.2		21	17	14	48	-29.8	-25.4	-26.8	-25.2	-23.8	-23.7
SWi-1*	1922.3		13	26	19	42	-29.0	-28.6	-29.3	-28.3	-28.2	-26.9
Ze-1*	3642.0		20	9	18	53	-26.4	-25.4	-25.8	-25.8	-24.8	n.a.
Ze-6*	4320.0		4	14	19	63	-29.1	-24.5	-25.2	-24.6	-24.3	-24.3
	4500.5		9	23	19	49	-30.0	-26.4	-26.9	-26.4	-25.4	-25.6

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

\* – data after Kotarba *et al.* (2004); M. – Middle; U. – Upper; L. – Lower; n.a. – not analysed; D. – Devonian; C. – Carboniferous

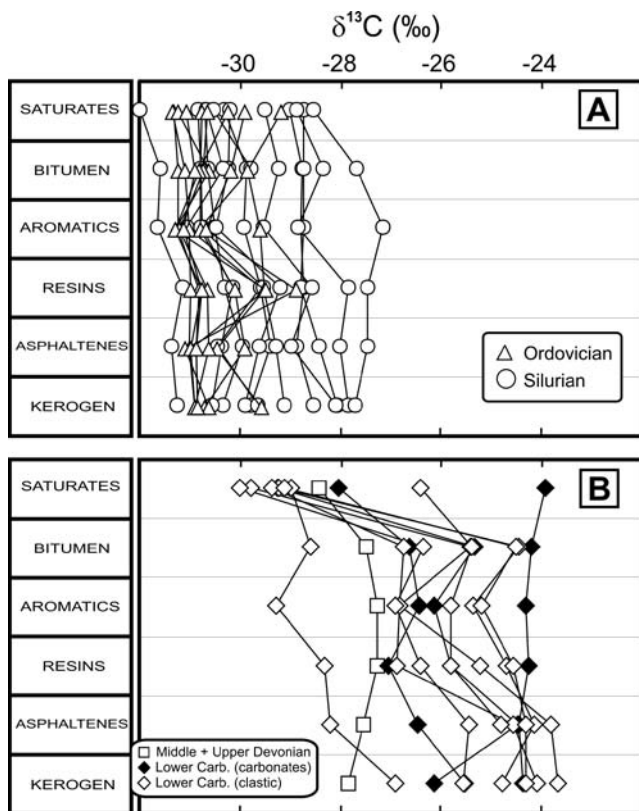
ganic matter corresponds with the Rock-Eval and aromatic hydrocarbon distribution data (Table 2).

#### Middle and Upper Devonian strata

From the carbonaceous Middle and Upper Devonian strata, 150 samples from 15 wells were analysed (Table 1). They mainly came from the well sections located in the western part of the analysed area (Fig. 1) where thicknesses of these strata are the highest (Zajac, 1984). The total organic carbon (TOC) content varies from 0 to 2.6 wt%, with the median of 0.05 wt% (Table 2). Samples lean in organic carbon dominate, but in seven samples the organic carbon

content higher than 1 wt% was recorded (Fig. 2). The  $S_2$  as well as  $S_1+S_2$  values, similarly to the TOC values, are usually very low and range from 0 to 4.5 and from 0.06 to 4.7 mg HC/g rock, respectively, with the median values of 0.16 and 0.26 mg HC/g rock, respectively (Table 2, Fig. 3B) indicating that the analysed strata are generally poor source rocks. In two samples the  $S_2$  values exceed 2.5 mg HC/g rock (Fig. 2) indicating fair hydrocarbon potential. The best source rock properties are noted in the Grobla area (Grobla-28 and Rajsco-3 wells; Figs 1, 3B). The only traces of hydrocarbons in the Grobla-28 well and at the same time high TOC contents (Fig. 3B) are the result of elevated or-

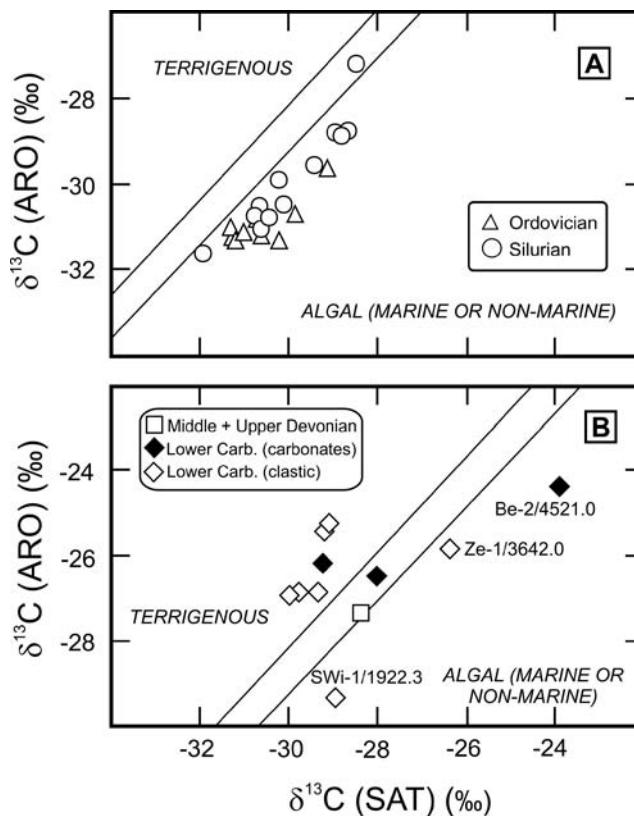




**Fig. 7.** Stable carbon isotope composition of bitumen, their fractions and kerogen from (A) Ordovician and Silurian and (B) Devonian and Lower Carboniferous strata. Carb. – Carboniferous

ganic matter maturity in this area. High TOC contents at high maturity level suggest that the initial hydrocarbon potential of some parts of this section could be very good and even excellent.

In the Middle and Upper Devonian carbonates, similarly to the above-mentioned divisions, the oil-prone Type II kerogen dominates with local admixtures of the gas-prone Type III kerogen. This hypothesis is supported by the correlation between the hydrogen index HI and the  $T_{max}$  temperature (Fig. 4B) and the *n*-alkanes and isoprenoids distribution (Table 3, Fig. 5), the stable carbon isotope composition (Table 4, Figs 7B, 8B), and the biomarker distribution (Table 5, Fig. 9). *n*-Alkane and isoprenoid distributions suggest that organic matter was deposited in reducing conditions ( $Pr/Ph < 1$ ) (Didyk *et al.*, 1978) without hypersalinity (traces of gammacerane, Table 5). Low values of sterane/ (sterane+terpane) ratio (Table 5) point to carbonate environment of deposition (Peters *et al.*, 2005). Also low values of  $Ts/(Ts+Tm)$  ratio (Table 5, Fig. 11) may be connected with anoxic carbonate environment (Rullkötter *et al.*, 1985). Increased value of  $C_{27} dia/(dia+reg)$  ratio, suggesting suboxic conditions of deposition (Moldowan *et al.*, 1994; *vide* Peters *et al.*, 2005, p. 617), are probably a result of thermal maturation processes (Seifert & Moldowan, 1978). Elevated values of the oxygen index up to 448 with the median value of 81 mg  $CO_2/g$  TOC (Table 2) may indicate syndimentary oxidation of organic matter, but these values can be a result of decomposition of carbonates present in rock mineral ma-



**Fig. 8.** Genetic characterization of bitumen from (A) Ordovician and Silurian and (B) Devonian and Lower Carboniferous strata, based on stable carbon isotope composition of saturated and aromatic hydrocarbons. Genetic fields after Sofer (1984). For the explanation of well codes see Table 1. Carb. – Carboniferous

trix during pyrolysis (Espitalié *et al.*, 1985). Domination of the vitrinite macerals in the single sample (Table 2), suggesting the presence of mixed (Type II/III) organic matter, is probably a result of partial decomposition of liptinite macerals during maturation of organic matter; the results of geochemical analyses indicate domination of the oil-prone Type II kerogen, as described earlier by Dudek *et al.* (2003).

The thermal maturity of the Middle and Upper Devonian strata was determined based on the pyrolytic data (Table 2), measurements of the vitrinite-like macerals reflectance (Table 2), sterane and hopane indices (Table 5, Figs 11, 12), and the aromatic hydrocarbons distribution (Table 7). Due to the low residual hydrocarbons content in most of the samples, the  $T_{max}$  values were determined for 24 samples only (Table 2, Fig. 2). Values of this parameter, from 420 to 499°C (Table 2, Figs 2, 4B), indicate the maturity of the investigated strata from the final stage of immature (microbial processes) to the overmature zones (high-temperature thermogenic processes). The maturity indices calculated for the single sample based on the methylphenanthrenes and methyl dibenzothiophenes distribution (Table 7) correspond with its  $T_{max}$  value indicating the initial phase of the oil window. The vitrinite macerals reflectance of the discussed organic matter corresponds with the Rock-Eval and aromatic hydrocarbon distribution data (Table 2). The most mature organic matter was recorded in the vicinity of Grobla (western part of the study area).

Table 5

Selected biomarker characteristics of bitumen from the Palaeozoic strata

Well code	Depth (m)	Strat.	S/(S+T)	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	Dia/Reg	Mor/Hop	C <sub>27</sub> dia/(dia+reg)	C <sub>29</sub> SR	C <sub>29</sub> ββ $\alpha\alpha$	H <sub>31</sub> S/(S+R)	Ts/(Ts+Tm)	GI	C <sub>29</sub> /C <sub>27</sub> ster	C <sub>29</sub> Ts/C <sub>29</sub> H	C <sub>35</sub> /C <sub>34</sub>	
He-1	4,912.5	Ordovician	0.39	38	16	46	1.33	0.29	0.38	0.47	0.59	0.65	0.62	0.14	1.19	0.83	0.52	
He-1	4,918.5		0.46	38	22	39	1.34	0.16	0.30	0.53	0.65	0.64	0.74	0.14	1.02	1.22	1.20	
Ki-11	3,726.5		0.40	35	18	47	0.52	0.21	0.29	0.44	0.39	0.62	0.33	0.11	1.36	0.30	0.84	
Ki-11	3,725.0		traces of biomarkers															
Ki-12	3,653.5		0.27	35	18	47	1.23	0.15	0.39	0.57	0.45	0.61	0.59	0.15	1.35	0.14	0.55	
Na-2	3,432.0		0.51	27	20	54	0.17	0.26	0.23	0.30	0.25	0.63	0.31	0.14	2.01	0.35	0.37	
Na-6	4,015.3		0.41	30	24	46	0.52	0.23	0.35	0.41	0.33	0.61	0.46	0.13	1.55	0.24	0.46	
Na-6	4,019.6		0.37	36	19	46	0.43	0.15	0.24	0.45	0.33	0.60	0.30	0.14	1.27	0.27	0.50	
Na-6	4,020.5		0.37	33	15	51	0.56	0.26	0.32	0.46	0.34	0.61	0.44	0.13	1.55	0.13	0.31	
Be-2	4,594.5		Silurian	0.39	28	19	53	0.80	0.18	0.27	0.52	0.51	0.59	0.58	0.15	2.13	1.19	0.49
He-1	4,659.5	0.51		34	23	43	0.83	0.19	0.28	0.54	0.49	0.65	0.74	0.17	1.24	0.44	0.74	
He-1	4,699.5	0.53		31	22	48	0.57	0.15	0.25	0.53	0.49	0.66	0.67	0.19	1.55	0.43	0.94	
Nw-1	4,818.5	0.67		40	16	44	1.04	0.12	0.30	0.41	0.59	0.56	0.70	0.07	1.08	0.46	tr.	
Nw-1	4,821.5	traces of biomarkers																
Pi-40	3,551.0	0.74		37	15	48	0.23	0.21	0.20	0.30	0.26	0.64	0.54	0.08	1.27	0.53	0.58	
Sk-5	2,875.7	0.33		30	21	48	0.94	0.16	0.49	0.47	0.56	0.64	0.69	tr.	1.58	0.81	0.83	
Sk-5	2,977.2	0.29		28	20	52	0.51	0.17	0.34	0.67	0.58	0.57	0.82	tr.	1.86	0.98	0.72	
Zd-8K	3,326.5	0.78		26	19	55	0.11	0.38	0.20	0.15	0.27	0.56	0.33	0.12	2.11	0.08	0.58	
Zd-8K	3,332.5	0.71		29	16	55	0.11	0.44	0.20	0.15	0.24	0.52	0.28	0.20	1.88	0.02	0.31	
Zd-8K	3,335.0	0.73	29	15	56	0.10	0.41	0.18	0.16	0.26	0.51	0.21	0.16	1.91	0.11	tr.		
Sk-5	2,333.8	M. + U. D.	0.08	36	20	44	0.53	0.23	0.35	0.40	0.37	0.59	0.12	tr.	1.22	1.13	0.52	

M. – Middle; U. – Upper; D. – Devonian; 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>β $\alpha$  20S diasterane/C<sub>29</sub>ααα20R sterane; Mor/Hop = Moretane/17 $\alpha$  hopane; C<sub>27</sub> dia/(dia+reg) = C<sub>27</sub>β $\alpha$  20(S+R) diasterane/(C<sub>27</sub>β $\alpha$  20(S+R) diasterane +  $\Sigma$ C<sub>27</sub> regular steranes); C<sub>29</sub>SR = epimerisation of regular steranes C<sub>29</sub> ratio; C<sub>29</sub>ββ $\alpha\alpha$  = ratio of ββ-epimeres of regular steranes C<sub>29</sub> to their total quantity; H<sub>31</sub>S/(S+R) = homohopane 22S/(22S+22R); Ts/(Ts+Tm) = C<sub>27</sub> 18 $\alpha$  trisnorhopane/(C<sub>27</sub> 18 $\alpha$  trisnorhopane + C<sub>27</sub> 17 $\alpha$  trisnorhopane); GI = Gammacerane/17 $\alpha$  hopane; C<sub>29</sub>/C<sub>27</sub>ster =  $\Sigma$ C<sub>29</sub> regular steranes/ $\Sigma$ C<sub>27</sub> regular steranes; C<sub>29</sub>Ts/C<sub>29</sub>H = C<sub>29</sub> 18 $\alpha$  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; tr. – traces; explanation of well codes – see Table 1

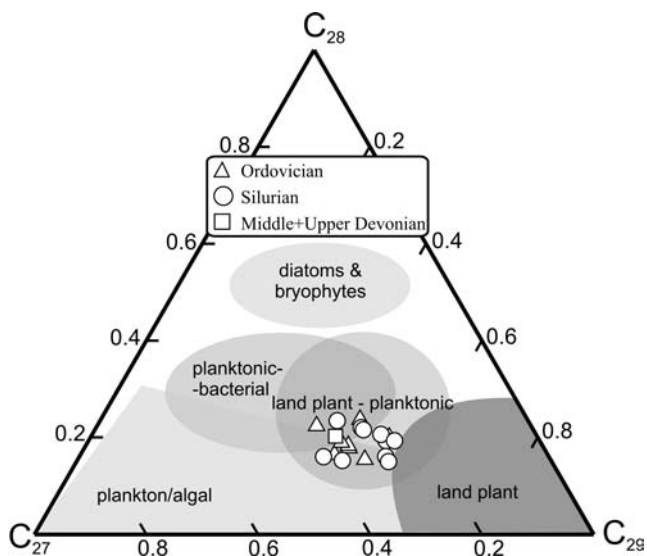
### Lower Carboniferous carbonate facies

From the carbonaceous facies of the Lower Carboniferous strata, 137 samples from 19 wells were analysed (Table 1). The total organic carbon (TOC) content varies in these strata from 0 to 5.0 wt%, with the median of 0.12 wt% (Table 2). Samples lean in organic carbon dominate, but in 14 samples the organic carbon content over 1 wt% was recorded (Fig. 2). The highest TOC contents, up to 5 wt%, were recorded by Kotarba *et al.* (2004) in the Łakta-2 well (Figs 1, 3B). The S<sub>2</sub> as well as S<sub>1</sub>+S<sub>2</sub> values, like the TOC values, are usually very low and range from 0.00 to 13.7 and from 0.02 to 14.3 mg HC/g rock, respectively, with the median values of 0.44 and 0.47 mg HC/g rock, respectively (Table 2, Fig. 3B), indicating that the analysed strata are generally poor for generation of hydrocarbons. In three samples the S<sub>2</sub> value exceeds 5 mg HC/g rock (Fig. 2) indicating good hydrocarbon potential. The best source rock properties are noted in the vicinity of Łakta (Łakta-2 well; Figs 1, 3B).

In the Lower Carboniferous carbonates, like in the above-mentioned divisions, the oil-prone Type II kerogen dominates with local admixtures of the gas-prone Type III

kerogen. This hypothesis is supported by the correlation between the hydrogen index HI and the T<sub>max</sub> temperature (Fig. 4B), the n-alkanes and isoprenoids distribution (Table 3, Fig. 6B) and the stable carbon isotope composition (Table 4, Figs 7B, 8B). The highest share of the Type III kerogen is observed in the western part of the analysed area (Fig. 8B). According to the n-alkane and isoprenoid distribution, organic matter was deposited in changeable (reducing to sub-oxic) conditions (the Pr/Ph ratio above and below 1) (Didyk *et al.*, 1978). Domination of the liptynite macerals in the analysed samples with a sometimes high percent of the vitrinite macerals (Table 2) suggests the presence of mixed (Type II/III) organic matter with the domination of the oil-prone Type II kerogen.

The thermal maturity of the Lower Carboniferous carbonate facies was determined based on the pyrolytic data (Table 2), vitrinite reflectance (Table 2) and the aromatic hydrocarbons distribution (Table 7). Due to the low residual hydrocarbon content in most of the samples, the T<sub>max</sub> values were determined for 42 samples only (Table 2, Fig. 2). Values of this parameter indicate the maturity of the investi-



**Fig. 9.** Ternary diagram of distribution of the regular steranes with  $\alpha\alpha\alpha$  configuration in bitumen from the Ordovician, Silurian and Middle and Upper Devonian strata. Classification modified after Peters *et al.* (2005)

gated strata from the immature zone to the gas window phase (from 416 to 478°C; Table 2, Figs 2, 4B). The maturity indices calculated based on the methylphenanthrenes and methyl dibenzothiophenes distribution (Table 7) and the vitrinite macerals reflectance (Table 2) correspond with  $T_{max}$  values. The less mature levels were observed in the section of the Łakta-2 well and the most mature strata were recorded by Dudek *et al.* (2003) at the bottom of the investigated strata in the Strzelce Wielkie-1 well section (Table 2, Fig. 1).

#### Lower Carboniferous clastic facies

From the clastic facies of the Lower Carboniferous strata, 115 samples from 13 wells were analysed (Table 1). The total organic carbon (TOC) content varies from 0 to 6.3 wt%, with the median of 0.64 wt% (Table 2). Samples characterized by the poor and fair organic carbon content (below 1 wt%) dominate, but in 7 samples the organic carbon con-

tent was higher than 2 wt% (Fig. 2). The highest TOC content, 6.3 wt%, was recorded by Dudek *et al.* (2003) in the Łętowice-20 well (Figs 1, 3B). The residual hydrocarbon contents ( $S_2$ ) as well as total hydrocarbon contents ( $S_1+S_2$ ), similarly to the TOC values, are usually low and range from 0.09 to 22.8 and from 0.10 to 23.0 mg HC/g rock, respectively, with the median values of 0.64 and 0.70 mg HC/g rock, respectively (Table 2, Fig. 3B), indicating that the analysed strata are generally poor source rocks. The best source rock properties are noted in the area north of Brzesko (Łętowice-20 and Strzelce Wielkie-1 wells) and in the vicinity of Rzeszów (Zagorzycze-1, Czudec-1 and Nosówka-6 wells) (Figs 1, 3B).

In the Lower Carboniferous clastic deposits, contrary to the previously discussed divisions, the gas-prone Type III kerogen dominates. Local admixtures of the oil-prone Type II kerogen are observed. This hypothesis is supported by the correlation between the hydrogen index HI and the  $T_{max}$  temperature (Fig. 4B), the  $n$ -alkanes and isoprenoids distribution (Table 3, Figs 5, 6B) and the stable carbon isotope composition (Table 4, Figs 7B, 8B). The highest share of the Type III kerogen is observed in the eastern part of the study area (Fig. 8B). According to the  $n$ -alkane and isoprenoid distribution, organic matter was deposited in changeable (reducing and sub-oxic) conditions (the Pr/Ph ratio above and below one) (Didyk *et al.*, 1978). The comparable amounts of the vitrinite and liptinite macerals in the analysed samples (Table 2) suggest the presence of mixed (Type III/II) organic matter.

The thermal maturity of the Lower Carboniferous clastic facies was determined based on the results of the Rock-Eval pyrolysis (Table 2), vitrinite reflectance (Table 2) and the aromatic hydrocarbons distribution (Table 7). Due to the low residual hydrocarbon content in the numerous samples, the  $T_{max}$  values were determined for 78 samples (Table 2, Fig. 2). Values of this parameter indicate the maturity of the investigated strata from the initial to the final phase of the oil window (from 428 to 458°C; Table 2, Figs 2, 4B). The maturity indices calculated based on the methylphenanthrenes and methyl dibenzothiophenes distribution (Table 7) and vitrinite reflectance (Table 2) correspond with  $T_{max}$  values indicating the maturity of the analysed samples from the ini-

**Table 6**

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

Well code	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)
He-1	4,912.5	Ordovician	79.4	8.4	6.0	2.3	3.9	1.27	0.06	0.025	0.018	0.56	0.05	0.024	0.018
Ki-11	3,726.5		81.5	8.4	7.0	2.5	0.6	1.24	0.06	0.026	0.003	0.55	0.06	0.026	0.003
Be-2	4,594.5	Silurian	80.9	7.2	8.6	2.6	0.8	1.07	0.08	0.027	0.004	0.51	0.07	0.026	0.004
He-1	4,699.5		80.7	7.6	8.3	2.8	0.5	1.14	0.08	0.030	0.002	0.53	0.07	0.029	0.002
He-1	4,699-4,701		80.4	7.8	8.0	3.4	0.4	1.17	0.07	0.036	0.002	0.54	0.07	0.035	0.002
Nw-1	4,818.5		79.8	7.5	9.4	2.4	0.9	1.13	0.09	0.026	0.004	0.53	0.08	0.025	0.004
Pi-40	3,551.0		76.3	7.6	11.6	2.8	1.7	1.20	0.11	0.031	0.008	0.54	0.10	0.030	0.008
Zd-8K	3,326.5		79.0	7.9	9.5	3.2	0.3	1.21	0.09	0.035	0.001	0.55	0.08	0.033	0.001

daf – dry, ash-free basis; explanation of well codes – see Table 1



tial to the middle phase of the oil window. The less mature levels were observed in the vicinity of Rzeszów (Będzianica-2 and Nosówka-6 wells) and the most mature strata were recorded by Dudek *et al.* (2003) at the bottom of the investigated strata in the Strzelce Wielkie-1 well section (Table 2, Fig. 1).

### Identification and geochemical characteristics of the source rocks

The identification of source rock horizons is an essential element of petroleum system analyses of the petroleum basin in the aspect of calculation of volumetric hydrocarbon potential of its structural area unit. Due to sampling in some areas many closely-spaced wells, a summary characteristic of organic matter occurring in those wells in individual areas was conducted. The source rock characteristics of these sets of wells were directly used in the hydrocarbon generation modelling procedure by Kosakowski and Wróbel (2011).

The results of geochemical analyses indicate that in all analysed divisions possible source rocks are present. The poorest hydrocarbon potential was recorded for the Middle and Upper Devonian strata and the Lower Carboniferous carbonates (Table 2), but also in these strata levels with the high TOC and hydrocarbon contents are observed (Fig. 2). The Silurian strata have the best hydrocarbon potential in the Palaeozoic sequence in the analysed area and these strata can be recognised as good source rocks (Tables 2, 8). Other units, in which sometimes up-threshold organic carbon contents were observed, may be considered in local areas as an additional source of hydrocarbons. The threshold of the TOC content in the potential source rocks was set at 0.5 wt% (Peters & Cassa, 1994). For the divisions where carbonaceous rocks prevail (the Middle and Upper Devonian strata and Lower Carboniferous carbonates), due to a

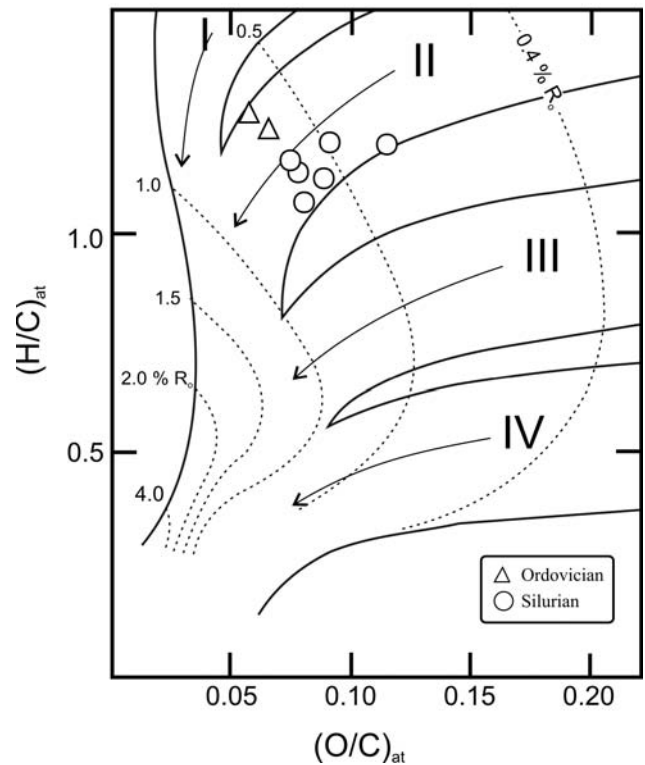


Fig. 10. Elemental composition of organic matter from the Ordovician and Silurian strata. Fields represent natural maturity paths for individual kerogens after Hunt (1996)

different kinetics of organic matter decomposition in these strata than in the clastic rocks, the source rock threshold was lowered up to 0.3 wt% TOC (Bordenave, 1993).

An attempt to estimate the source rock potential was made for 26 wells from the entire analysed area, in which the TOC content was determined and the lithology was

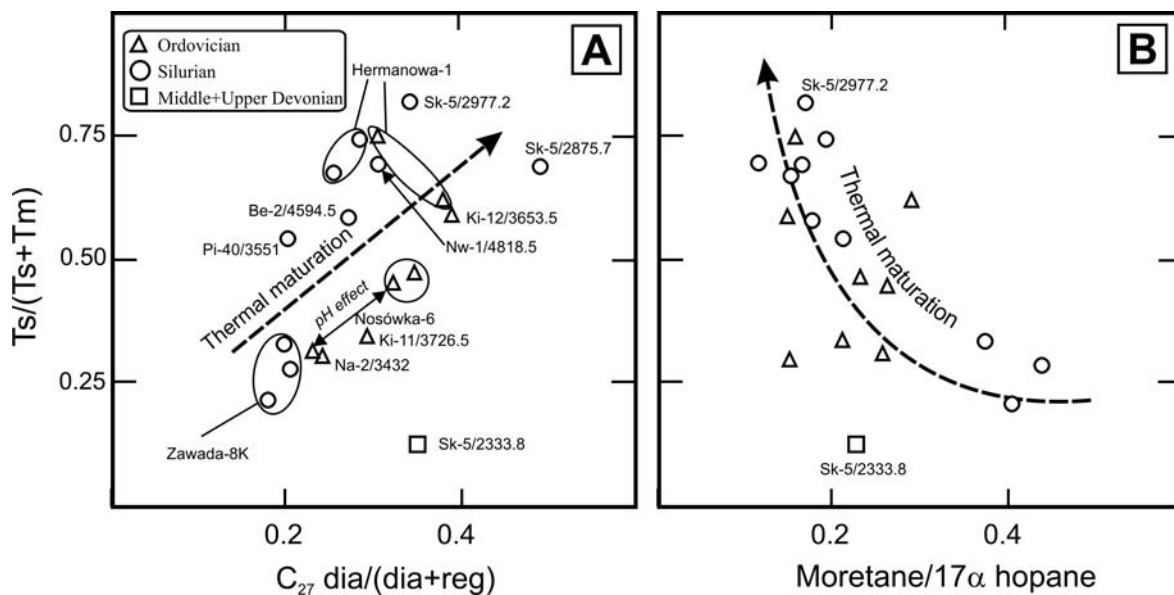


Fig. 11.  $Ts/(Ts+Tm)$  ratio versus (A)  $C_{27} \beta\alpha 20(S+R)$  diasterane/ $(C_{27} \beta\alpha 20(S+R)$  diasterane +  $\Sigma C_{27}$  regular steranes) ratio, and (B) moretane/ $17\alpha$  hopane ratio for bitumen from the Ordovician, Silurian and Middle and Upper Devonian strata. For the explanation of well codes see Table 1

Table 7

Maturity indices calculated based on distribution of phenanthrene and dibenzothiophene and their methyl derivatives in bitumens of the Palaeozoic strata

Well code	Depth (m)	Stratigraphy	MPI1	MPR	MPR1	R <sub>cal</sub> (%)	R <sub>cal(MPR)</sub> (%)	MDR	R <sub>cal(DBT)</sub> (%)	T <sub>max(DBT)</sub> (°C)	
He-1	4,912.5	Ordovician	0.65	0.72	0.37	0.76	0.66	4.9	0.9	448	
He-1	4,918.5		0.63	0.71	0.37	0.75	0.67	5.5	0.9	451	
Ki-11	3,726.5		0.58	1.03	0.47	0.72	0.88	1.8	0.6	432	
Ki-11	3,725.0		0.97	0.95	0.44	0.95	0.82	1.0	0.6	428	
Ki-12	3,653.5		0.65	0.67	0.36	0.76	0.64	1.8	0.6	432	
Na-2	3,432.0		0.74	0.61	0.34	0.81	0.59	0.7	0.6	427	
Na-6	4,015.3		0.73	0.68	0.38	0.81	0.68	0.9	0.6	428	
Na-6	4,019.6		0.75	0.61	0.35	0.82	0.61	0.8	0.6	427	
Na-6	4,020.5		0.72	0.72	0.38	0.80	0.68	1.6	0.6	431	
Be-2	4,594.5		Silurian	0.99	0.76	0.41	0.97	0.75	1.9	0.6	432
He-1	4,659.5	0.80		0.73	0.36	0.85	0.64	1.3	0.6	430	
He-1	4,699.5	0.69		0.88	0.39	0.79	0.72	2.2	0.7	434	
Nw-1	4,818.5	0.68		0.72	0.37	0.78	0.67	3.3	0.8	440	
Nw-1	4,821.5	0.68		0.70	0.37	0.78	0.67	3.0	0.7	438	
Pi-40	3,551.0	0.76		0.95	0.47	0.83	0.88	1.0	0.6	428	
Sk-5	2,875.7	0.73		0.78	0.38	0.81	0.83	3.3	0.7	440	
Sk-5	2,977.2	0.81		0.85	0.39	0.86	0.87	4.9	0.9	448	
Zd-8K	3,326.5	0.70		0.73	0.40	0.79	0.73	0.4	0.5	425	
Zd-8K	3,332.5	0.86		0.77	0.42	0.89	0.77	0.7	0.6	427	
Zd-8K	3,335.0	0.50		0.78	0.40	0.67	0.74	1.5	0.6	430	
Ki-11*	3,671.1	L. D.		0.64	0.70	0.32	0.76	0.56	traces		
Sk-5	2,333.8	M. + U. D.		0.60	0.81	0.38	0.73	0.85	1.4	0.6	430
Be-2*	4,521.0	Lower Carboniferous (carbonates)		1.30	1.76	0.61	1.15	1.20	3.0	0.7	438
Jd-5*	2,880.0			0.90	1.66	0.52	0.91	0.99	1.1	0.6	429
Ki-12*	3,294.2			1.01	0.94	0.53	0.98	1.02	0.6	0.6	426
SWi-1*	2,865.6		1.87	1.67	0.61	1.49	1.21	13.8	n.c.	n.c.	
Be-2*	4,364.0	Lower Carboniferous (clastic)	0.70	1.00	0.42	0.77	0.77	1.3	0.6	430	
Be-2*	4,367.0		0.80	1.18	0.47	0.85	0.90	1.9	0.6	433	
Cz-1*	4,285.5		0.51	1.20	0.46	0.68	0.86	1.1	0.6	428	
Na-6*	3,698.2		0.87	1.24	0.50	0.89	0.96	0.7	0.6	426	
Na-6*	3,734.2		0.80	1.28	0.46	0.85	0.87	0.8	0.6	427	
SWi-1*	1,922.3		0.96	1.66	0.47	0.95	0.88	3.6	0.8	441	
Ze-6*	4,320.0		0.91	1.29	0.49	0.92	0.93	1.0	0.6	428	
Ze-6*	4,500.0		1.01	1.27	0.49	0.98	0.93	2.3	0.7	435	

MPI1 =  $1.5(2\text{-MP}+3\text{-MP})/(P+1\text{-MP}+9\text{-MP})$ ; P – phenanthrene; MP – methylphenanthrene; MPR =  $2\text{-MP}/1\text{-MP}$ ; MPR1 =  $(2\text{-MP}+3\text{-MP})/(1\text{-MP}+9\text{-MP}+2\text{-MP}+3\text{-MP})$ ; R<sub>cal</sub> =  $0.60\text{MPI1}+0.37$  for MPR < 2.65 (Radke, 1988); R<sub>cal(MPR)</sub> =  $-0.166+2.242\text{MPR1}$  (Kvalheim *et al.*, 1987); MDR =  $4\text{-MDBT}/1\text{-MDBT}$ ; MDBT – methyl dibenzothiophene; R<sub>cal(DBT)</sub> =  $0.51+0.073\text{MDR}$ ; T<sub>max(DBT)</sub> =  $423+5.1\text{MDR}$ ; \* – data after Kotarba *et al.* (2004); n.c. – not calculated; L. – Lower; M. – Middle; U. – Upper; D. – Devonian; explanation of well codes - see Table 1

available (Table 8). A precise determination of source rock thickness cannot be carried out on the basis of the results of geochemical analyses, due to the non-representative sampling in individual wells caused usually by not drilling the full section of the investigated strata (Table 8). Therefore, an evaluation of the source rock thickness is only an estimate, especially for the usually undrilled Lower Palaeozoic strata, where the sampling was performed for the uppermost sections only (Table 8).

The primary element of the source rock thickness determination of the Silurian strata was the estimation of the thickness 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 drilled, the thickness can be estimated from their local development (Buła & Habryn, 2011). The results of geochemical analyses were the second element determining the source rock thickness (the TOC

content). The estimated portion of source rocks was calculated as percent of samples having an up-threshold TOC content in relation to all the analysed samples.

Based on these rules, for the Ordovician strata in the vicinity of Rzeszów from 40 m (Zagorzyce-1) to 140 m (Hermanowa-1) of source rocks was estimated (Table 8) with the initial  $TOC_0$  content from 1.1 wt% (the wells near Kielanówka and Nosówka) to 2.5 wt% in the Ordovician-Silurian complex in the Zagorzyce-1 well. For the sections of Nosówka-5 and -8 and Pilzno-40 wells, where insufficient data to determine source rocks parameters were available, the thickness and the  $TOC_0$  content was taken by analogy with the neighbouring wells (Table 8). Generally, the source rocks within the Ordovician strata had initially good source rock properties.

The Silurian strata are the best source rocks in the study area. The estimated thickness varies from 40 to 80 m in the sections of Hermanowa-1, Pilzno-40 and Zawada-8K wells (Table 8). The calculated initial organic carbon content varies from 1.2 wt% in the Zawada-8K to 3.5 wt% in the Hermanowa-1 well section (Table 8). Usually, this index displays values above 2 wt% indicating generally very good initial source rock parameters of these strata (Table 8).

From the Devonian rock sequence, only in the Trzebownisko-3 well section 50 m of source rock with the initial  $TOC_0$  content of 1.2 wt% was determined (Table 8). In the other areas these rocks were very poor in organic matter or sampling was insufficient to determine source rock properties.

The Lower Carboniferous carbonates are poor source rock. The estimated source rock thickness varies from 20 to 40 m in the vicinity of Rzeszów and the initial organic carbon richness in these strata is estimated to reach from 0.5 to 0.8 wt% (Table 8). In many wells the source rock properties were not determined due to the presence of rocks poor in organic carbon or due to the fact that sampling was unrepresentative.

The estimated thickness of the source rocks in the clastic facies of the Lower Carboniferous strata varies from 50 to 210 m in the vicinity of Będzienia and Czudec (Table 8). The calculated initial  $TOC_0$  content in the vicinity of Rzeszów equals ca. 1 wt% and the best source rocks were recorded in the Strzelce Wielkie-1 well with the  $TOC_0 = 1.3$  wt% (Table 8).

## CONCLUSIONS

The results of organic geochemical analyses enable us to characterize organic matter dispersed in Ordovician, Silurian, Devonian and Lower Carboniferous strata in the basement of the Carpathian Foredeep between Kraków and Rzeszów. The Silurian strata prove to be the best source rocks, with the present total organic carbon content up to 6.6 wt% and the median value of ca. 1.5 wt%. The highest TOC content was measured in the vicinity of Rzeszów, especially in the Hermanowa-1 and Nawsie-1 wells (the median values for both of them are 3 wt%). The Ordovician, Lower Devonian, and clastic facies of the Lower Carboniferous strata with the median TOC values of 0.27, 0.56 and

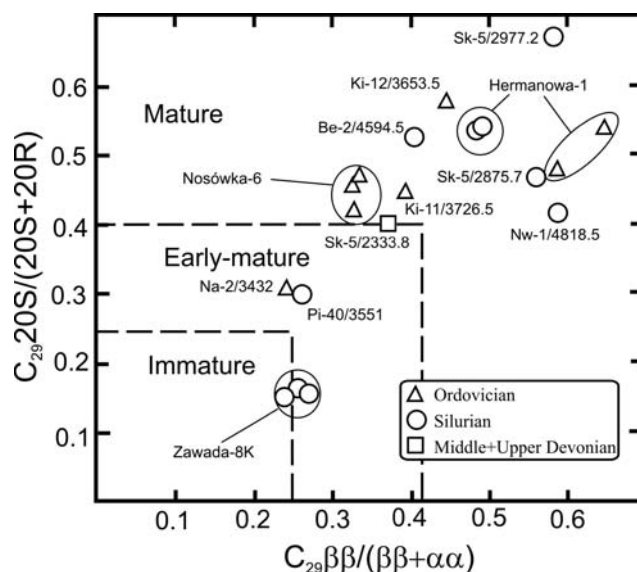


Fig. 12. Sterane  $C_{29}$  20S/(20S+20R) ratio versus  $C_{29}$   $\beta/(\beta+\alpha)$  ratio plot of the bitumen extracted from the Ordovician, Silurian, and Middle and Upper Devonian strata. Maturity fields after Peters and Moldowan (1993). For the explanation of well codes see Table 1

0.64 wt%, respectively, can be considered an additional source of hydrocarbons. The Middle and Upper Devonian strata as well as carbonate facies of the Lower Carboniferous have much lower quantities of organic carbon, but also in these strata levels with elevated TOC contents are observed. The best petroleum potential, apart from the Silurian strata, is displayed by the Ordovician and Lower Devonian sequence. In the other divisions (the Upper and Middle Devonian and the Lower Carboniferous), the quantities of pyrolysable hydrocarbons are much lower, but also there levels characterized by an increased petroleum potential do exist. The presence of the oil-prone, Type II kerogen in the Lower Palaeozoic and Lower Devonian strata was confirmed by the Rock-Eval data, and biomarker, stable isotope, elemental and maceral compositions. The high-sulphur kerogen was not observed, although due to increased maturity, especially in the Devonian and Lower Carboniferous carbonates, its earlier presence should not be excluded. In the younger strata, the gas-prone Type III kerogen dominates with local high admixtures of the Type II kerogen. The Silurian mudstones and claystones, and clastic facies (mainly mudstones) of the Lower Carboniferous strata were deposited in the normal marine conditions (reducing or sub-oxic), whereas the Ordovician, Devonian and carbonate facies of the Lower Carboniferous strata were usually deposited in the reducing or even hypersaline conditions. Most source rocks in the prevailing area are at the initial and middle phases of the low-temperature thermogenic processes. Locally, the immature (in the Lower Carboniferous carbonates in the Łąka-2 well section) or the late-mature (in the Middle and Upper Devonian strata in the Mniszów-16 well) source rocks are observed.

The initial  $TOC_0$  values of the best source level – Silurian, are changeable and vary from 1.2 wt% in the Zawada-8K well to 3.5 wt% in the Hermanowa-1 well. Also in the



Table 8

Estimated thickness and initial organic carbon content identified source rocks in the Palaeozoic strata

Well code	Stratigraphy	Thickness* (m)	Source-rock thickness* (m)	Samples	TOC (wt%)	n	R <sub>o</sub> (%)	H/C	x	TOC <sub>0</sub> (wt%)
He-1	O.	336	140	21	1.1	9	0.75	1.03	0.30	1.6
Ki-11, -12, Na-2, -6, -12		36 (n.d.)	70	51	0.75	14	0.66	1.24	0.30	1.1
Na-5, -8		28 (n.d.)	70 (s)	20	<0.5					1.1**
Pi-40		140 (n.d.)	40 (s)	6	<0.5					1.1**
Ze-1	O. + S.	41	40	4	1.85	4	0.66	1.08	0.27	2.5
Be-2	S.	34 (n.d.)	40	4	1.05	4	0.65	1.07	0.25	1.4
Be-2, Nw-1		44 (n.d.)	45	12	2.48	11	0.65	1.10	0.24	3.3
He-1		80	80	20	3.0	20	0.66	1.15	0.15	3.5
Pi-40		206	80	5	1.89	3	0.69	1.06	0.28	2.6
Zd-8K		10 (n.d.)	80	24	1.03	20	0.58	1.21	0.12	1.2
Ki-11		58	n.det.	3	0.73	1	0.98	0.75	0.08	0.8
Ne-11	L. D.	115	n.det.	3	0.56	1				
To-3		123	50	8	0.9	7	0.6	1.11	0.25	1.2
Ki-11	M. + U. D.	87	n.det.	3	<0.3					
Ne-11, Lr-2, Pu-1		499 (n.d.)	n.det.	58	0.34	1				
To-3		85	n.det.	7	0.4	1				
Be-2, Na-5	L. C. (carb.)	172	20	17	0.53	3	0.77	0.80	0.06	0.6
Be-2, Ze-1		136	40	35	0.72	12	0.77	0.80	0.06	0.8
Dc-10k		143	n.d.	5	0.89	1				
Ki-11, Na-2, -4, -6, -7, -12		149	40	38	0.46	12	0.92	0.76	0.07	0.5
Pre-2, Rd-2, Ta-19		219 (n.d.)	n.det.	8	<0.3					
SWi-1		594	n.det.#	12	0.39	5				
Be-2, Cz-1		337	210	25	0.95	16	0.65	0.84	0.05	1.0
He-1	L. C. (cl.)	308	50 (s)	22	<0.5					1.0**
Na-4, -6, -12		135	110	18	1.07	12	0.90	0.77	0.06	1.1
PW-15, LG-3		137 (n.d.)	80	6	0.53	3	0.65	1.08	0.03	0.5
SWi-1		501	n.det.#	17	1.21	12	0.95	0.76	0.07	1.3
Ze-1		143	130	38	0.85	35	0.64	0.84	0.05	0.9

\* – average thickness when at least two wells was taken into consideration; TOC – mean present organic carbon content in the source-rock levels; n – quantity of up-threshold TOC measurements; R<sub>o</sub> – vitrinite or 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.det. – not determined; n.d. – not drilled; values of H/C typed in italic were calculated from R<sub>o</sub> values by equations worked out based on data presented by Behar *et al.* (1995); R<sub>o</sub> values typed in italic were taken by analogy to the neighboring wells; (s) – synthetic thickness due to undrilling of the strata; \*\* – value taken to calculations per analogy to neighbouring wells due to unrepresentative sampling; # – value not determined due to non representative sampling; L. – Lower; D. – Devonian; M. – Middle; U. – Upper; C. – Carboniferous; cl. – clastics; O. – Ordovician; S. – Silurian; carb. – carbonates; explanation of well codes – see Table 1

Zagorzyce-1 well, in the Ordovician–Silurian section, the initial TOC<sub>0</sub> equals 2.5 wt%. The thickness of the Silurian source rocks is not high – usually 40–50 m. The highest source rock thicknesses of 100–150 m were observed in the Lower Carboniferous (clastic) and Ordovician strata. All the investigated source rock horizons are capable of generating oil and natural gas in the entire study area.

#### Acknowledgements

This research was undertaken as the research project No. UKRAINE/193/2006 of the Ministry of Science and Higher Education carried out at the AGH University of Science and Technology in Kraków and the Polish Geological Institute – National Research Institute in Warsaw. Scientific work was financed from the fund in the years 2007–2010. The detailed comments of Mo-

nika Fabiańska and an anonymous reviewer were of great assistance in our revisions of this manuscript. We also thank Mark Pawlewicz of the U.S. Geological Survey in Denver for improvement of the English text. Analytical work by Tomasz Kowalski and Hieronim Zych from the AGH University of Science and Technology in Kraków is gratefully acknowledged. The authors thank Izabella Grotek from the Polish Geological Institute – National Research Institute in Warsaw for measurements of reflectance of vitrinite-like macerals and determination of maceral composition of organic matter.

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