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Habitat and hydrocarbon potential of the lower Paleozoic source rocks in the Polish part of the Baltic region

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The quantity, genetic type and maturity of organic matter dispersed in the Lower Cambrian to the uppermost part of the Silurian (Pridoli) sequence of the Polish part of the Baltic region was determined based on the results of geochemical analyses of a total of 1377 rock samples collected from 38 onshore and offshore boreholes. The best source rocks were found in the Upper Cambrian–Tremadocian succession where present and initial total organic carbon (TOC) contents are up to *ca*. 18 and 20 wt.%, respectively. Caradocian (Ordovician) strata can be considered as an additional source of hydrocarbons. In the individual boreholes median present and initial TOC contents vary from 0.5 to 3.3 wt.% and from 1 to 6 wt.%, respectively. The Llandovery (Silurian) strata reveal moderate and locally high hydrocarbon potential of the source rocks. The present TOC content reaches locally 10 wt.% (usually 1–2 wt.%). Another source of hydrocarbons can be clayey intercalations within the Middle Cambrian strata. Their organic matter content rarely exceeds 1 wt.%, being often a result of advanced organic matter transformation. In all lower Paleozoic strata investigated from the Polish part of the Baltic region oil-prone, low-sulphur Type-II kerogen occurs, deposited in anoxic or sub-oxic conditions. The maturity of all source rocks changes from the initial phase of the low-temperature thermogenic processes in the northeastern part to the overmature stage in the southwestern part of the study area.

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Key words: Baltic region, Northern Poland, source rock, hydrocarbon potential, lower Paleozoic.

INTRODUCTION

Oil exploitation in the Polish part of the Baltic region began onshore in 1970, when a small accumulation in Żarnowiec was discovered (Strzetelski *et al*., 2004). The first offshore oil deposit (B3 structure) was discovered in 1981 (Karnkowski, 1999; Domżalski and Mazurek, 2003). All the oil and gas accumulations found in the Polish part of the Baltic region occur in anticlinal structures formed in Middle Cambrian sandstone reservoir rocks (e.g., Sikorski and Solak, 1991; Domżalski *et al*., 2004; Karnkowski *et al*., 2010). The Upper Cambrian–Tremadocian black shale succession is considered as their main source rock (e.g., Schleicher *et al*., 1998). Its thickness varies usually from 5 to 35 metres (Modliński and Podhalańska, 2010) and the total organic carbon (TOC) content is up to 12 wt.% (Górecki *et al*., 1992; Schleicher *et al*., 1998; Kosakowski *et al*., 2008). Also in the other parts of the Baltic region and its vicinity this succession is very rich in organic carbon (up to 20 wt.% TOC; e.g., Lewan and Buchardt, 1989; Buchardt and Lewan, 1990; Leventhal, 1991; Górecki *et al*., 1992; Bharati *et al*., 1992, 1995; Kanev *et al*., 1994; Schleicher *et al*., 1998; Buchardt *et al*., 1998; Pedersen *et al*., 2006). Apart from the Upper Cambrian–Tremadocian succession, Middle Cambrian, Caradocian (Ordovician) and Llandovery (Silurian) strata are also locally enriched in organic matter and, thus, are considered as source rocks (e.g., Górecki *et al*., 1992; Schleicher *et al*., 1998; Karnkowski, 2003). The lower part of the Silurian succession is the most important source rock in the eastern part of the Baltic region, particularly due to its significant thickness (up to 400 m; e.g., Ulmishek, 1990) and TOC content (up to 10 wt.%, locally up to 20 wt.%; Zdanaviciute and Bojesen-Koefoed, 1997; Zdanaviciute *et al*., 1998; Zdanaviciute and Lazauskiene 2004, 2007). The maturity of the lower Paleozoic strata in the Baltic region is variable.

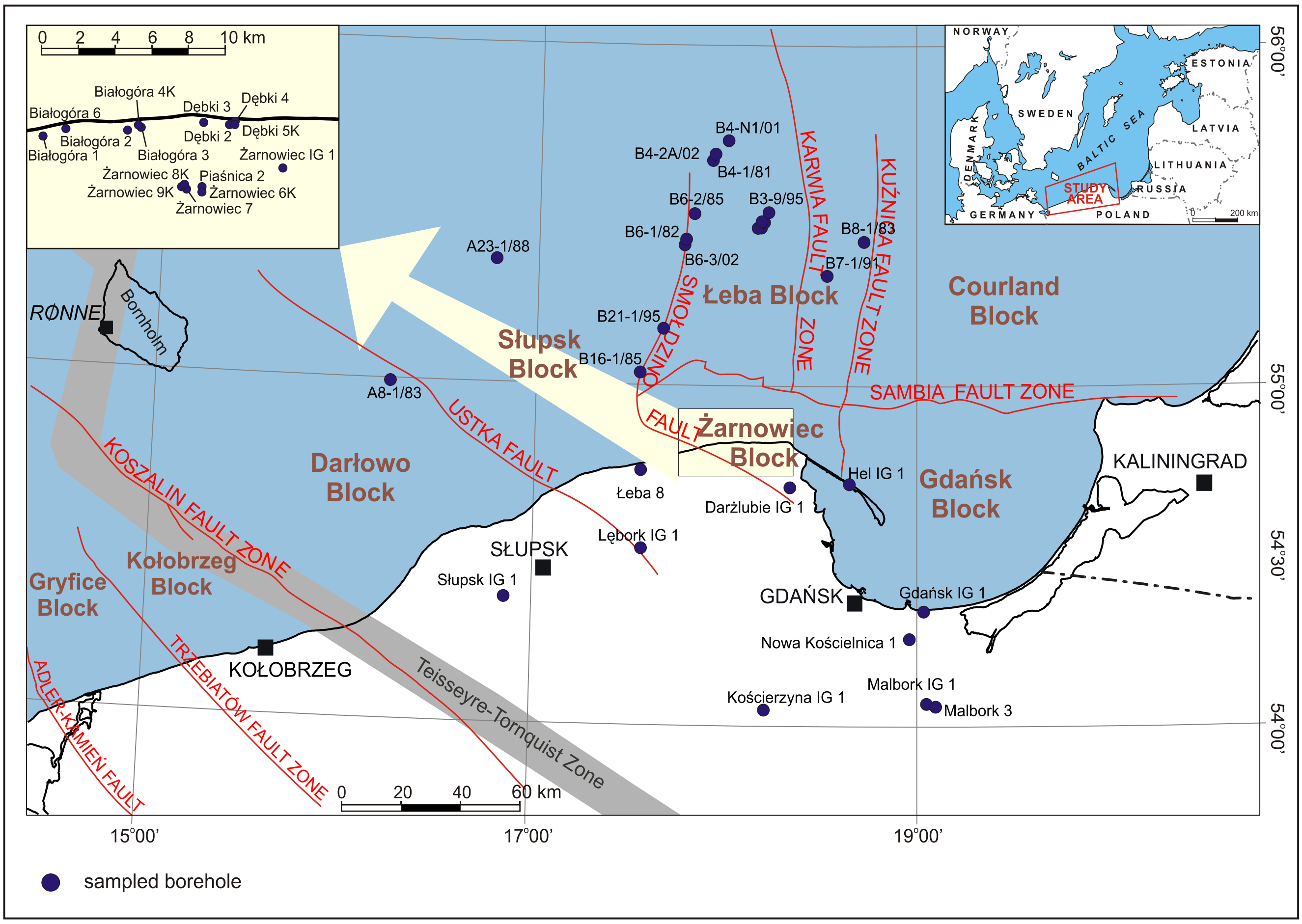

Fig. 1. Tectonic sketch map of the Polish part of Baltic region and location of sampled boreholes

Fault system after Pokorski (2010)

Previous studies carried on in the Polish part of the basin showed that the maturity of the organic matter ranges from the initial phase of the low-temperature thermogenic processes (“oil window”) up to the overmature zone (e.g., Kosakowski *et al.*, 1999; Poprawa *et al.*, 1999; Grotek, 1999, 2006; Karnkowski, 2003; Poprawa and Grotek, 2005).

The main objective of our study is to revise previous data and to define the petroleum potential of the lower Paleozoic strata in the Polish part of the Baltic region (Fig. 1). We examined the TOC content, organic matter type, thermal maturity and petroleum potential of the entire lower Paleozoic sequence. The source rock assessment was done based on geochemical criteria proposed by Peters and Cassa (1994) and Hunt (1996).

The large number of analysed samples enables us to localize the levels of the best source rocks in the lower Paleozoic strata and to estimate their initial total organic carbon (TOC_0) content in individual boreholes.

SAMPLES

The rock samples were taken from cores representing all strata recognized from the Polish part of the Baltic region. Both the onshore and offshore boreholes were sampled. Totally, 1377 core samples from 38 boreholes, weighting about 400 g each, mainly claystones and siltstones as well as marls and carbonates (Fig. 1) were collected and analysed. Table 1 shows samples collected from individual boreholes and stratigraphic levels.

METHODS

The core samples were cleaned from mud contamination and crushed to the 0.5–2 cm fraction. Then, 200 g of each sample was milled to the <0.2 mm fraction for geochemical analyses. Screening pyrolysis analyses of rock samples were carried on with a 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 a *SOXTEC™* apparatus. The asphaltene fraction was precipitated with *n*-hexane. The remaining maltenes were then separated into compositional fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography, using alumina:silica gel (2:1 v/v) columns (0.8 × 25 cm). The

Table 1

Quantity of the rock samples collected from individual boreholes

Borehole	Cambrian			Ordovician					Silurian			
	Cm1	Cm2	Cm3	Ot	Oar	Oln	Oc	Oa	Sla	Sw	Sld	Sp
A23-1/88	2	6	5	–	3	–	1	–	–	–	–	–
A8-1/83	–	4	9	4	–	–	–	–	–	–	3	–
B16-1/85	–	1	9	–	–	–	–	–	–	–	–	–
B21-1/95	–	26	28	2	3	1	7	–	2	3	6	–
B3-9/95	–	8	4	3	3	1	2	2	14	12	6	–
B4-1/81	–	2	–	5	–	–	–	–	–	–	–	–
B4-2A/02	–	6	19	–	–	–	–	–	–	–	–	–
B4-N1/01	–	3	11	–	–	–	1	–	1	–	–	–
B6-1/82	–	–	2	4	–	–	2	–	2	–	–	–
B6-2/85	–	5	–	3	1	–	–	–	–	–	–	–
B6-3/02	–	12	24	–	–	–	–	–	–	–	–	–
B7-1/91	–	–	–	15	–	–	–	–	–	–	–	–
B8-1/83	–	3	–	–	–	–	–	–	–	–	–	–
Białogóra 1	1	2	6	–	–	–	1	–	–	–	2	–
Białogóra 2	–	2	–	–	–	–	13	–	–	–	4	–
Białogóra 3	–	7	12	–	4	–	6	–	–	–	–	–
Białogóra 4K	–	1	–	–	–	–	–	–	–	–	–	–
Białogóra 6	–	5	10	–	–	–	6	–	–	–	–	–
Darżlubie IG 1	–	1	–	–	–	–	–	–	–	–	–	–
Dębki 2	–	–	2	–	–	–	–	–	–	–	–	–
Dębki 3	–	21	6	–	4	8	11	–	3	9	15	–
Dębki 4	–	26	16	–	–	–	–	–	–	–	–	–
Dębki 5K	–	2	–	–	–	–	–	–	–	–	–	–
Gdańsk IG 1	13	12	–	–	1	2	9	4	16	13	37	6
Hel IG 1	10	14	3	–	4	–	7	3	9	1	15	6
Kościerzyna IG 1	6	25	–	–	1	–	1	1	5	5	4	–
Lębork IG 1	–	–	–	–	–	–	2	1	1	10	64	1
Łeba 8	8	32	6	–	3	1	11	2	–	5	18	4
Malbork IG 1	28	29	–	–	3	–	2	4	6	7	14	8
Malbork 3	–	33	–	–	–	1	–	–	–	–	–	3
Nowa Kościelnica 1	51	27	–	–	8	1	4	–	–	–	–	–
Piaśnica 2	–	2	2	–	–	–	2	–	2	–	–	–
Słupsk IG 1	9	10	–	–	–	–	5	2	–	29	22	–
Żarnowiec IG 1	10	18	6	–	2	1	8	1	13	31	23	6
Żarnowiec 6K	–	–	8	–	2	–	9	–	3	2	–	–
Żarnowiec 7	–	4	–	–	–	–	–	–	–	–	–	–
Żarnowiec 8K	–	2	–	–	2	–	–	–	–	–	–	–
Żarnowiec 9K	–	3	–	–	–	–	–	–	–	–	–	–
TOTAL	138	354	188	36	44	16	110	20	77	127	233	34

Cm1 – Lower Cambrian, Cm2 – Middle Cambrian, Cm3 – Upper Cambrian, Ot – Tremadocian, Oar – Arenigian, Oln – Llanvirnian, Oc – Caradocian, Oa – Ashgillian, Sla – Llandovery, Sw – Wenlock, Sld – Ludlow, Sp – Pridoli 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 a *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 δ-notation relative to the V-PDB standard (Coplen, 1995). The analytical precision is estimated to be ±0.2‰.

Isolation of kerogen for elemental analysis was achieved by *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 $ZnBr_2$ 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, on a *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 difference of total and pyritic sulphur. The oxygen content was calculated as difference to 100%, taking into account C, H, N, S, moisture and ash contents.

The biomarker distributions were determined by analysing the maltene fraction on a computerized GC-mass spectrometer (MS) system using a *Hewlett Packard 6890 GC* with a DB-1701 60 m × 0.31 mm column (0.25 μm film thickness, bonded phase: 14% cyanopropylphenyl – 86% dimethylpolysiloxane copolymer) directly interfaced to a *JEOL GC-Mate* magnetic sector MS. Splitless injection was made in to the injector operated isothermally at 300°C. Temperature was programmed as follows: 50 to 150°C at 50°C/min, 150 to 300°C at 3°C/min and 300°C held for 9 minutes. Helium was used as carrier gas with a constant flow rate of 2 ml/min. Dynamic mass resolution was 3000 (50 percent valley). Multiple ion detection was accomplished by switching the accelerating voltage at a constant magnetic field. The selected ions were m/z = 191 (terpanes and gammacerane), m/z = 217 (steranes), m/z = 231 (triaromatic steroids) and m/z = 253 (monoaromatic steroids). Tentative peak identifications were based on elution time and confirmed in many cases with mass spectra (Philp, 1985) and MS-MS. Peak heights were used for measuring compound concentrations to avoid the erroneous measurement of co-eluting compounds.

The saturated hydrocarbon fractions of the extracted bitumens were analysed with the GC for *n*-alkanes and isoprenoids. Analyses were carried out with a *Hewlett Packard type 5890 Series II* gas chromatograph equipped with fused silica capillary column (25 m × 0.32 mm i.d.) coated with methyl silicone gum phase (HP-1 0.52 μm film thickness) and flame ionisation detector. Nitrogen was used as a carrier gas. The GC oven was programmed from 110 to 315°C at 5°C/min and 315°C was held for 15 minutes. The aromatic hydrocarbon fractions were analysed for phenantrene and its derivatives with the same GC, carrier gas and detector using a fused silica capillary column (60 m × 0.25 mm i.d.) coated with 95% methyl/5% phenylsilicone phase (DB-5, 0.25 μm film thickness). The GC oven was programmed from 80 to 315°C at a rate of 3°C/min.

The uranium and thorium contents in rocks were determined by instrumental neutron activation analysis (INAA) (Hoffman, 1992) at the Actlab Laboratories®, Canada.

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

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

$$TOC_0 = TOC/(1 - x) \qquad [1]$$

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

In the case of leaching directly measured elemental data, the H/C values were determined based on R_o values using the equation after Buchardt and Lewan (1990) for the Alum Shale Formation in Sweden:

$$(H/C)_{at} = (\mathrm{Log}\ R_o - 0.812)/(-1.018) \qquad [2]$$

When the direct measurements R_o or $(H/C)_{at}$ values were unavailable, the thermal maturity of the organic matter was assumed to be as in the neighbouring boreholes or based on the R_o – depth relation in individual boreholes. In the case of the Caradocian, the same maturity was assumed as for the Upper Cambrian–Tremadocian rocks due to similar burial depths of both successions (Modliński and Podhalańska, 2010).

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 a maturity level corresponding to $(H/C)_{at}$ = 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 and Cassa, 1994).

RESULTS AND DISCUSSION

HYDROCARBON POTENTIAL OF INDIVIDUAL STRATIGRAPHIC UNITS

CAMBRIAN STRATA

The source rock potential of Cambrian strata is highly variable and depends on their lithology. Potential source rocks are connected with claystones and siltstones present in all the members (lower, middle and upper), in variable proportions. The Lower Cambrian strata are developed mainly as sandstones with interbedded siltstones. In the upper part of the sequence more shales and siltstones occur (Lendzion, 1983; Modliński and Podhalańska, 2010). The Middle Cambrian strata are similar to the Lower Cambrian ones. There are black shales of the *Eccaparadoxides oelandicus* Zone and the lowermost part of the *Paradoxides paradoxissimus* Zone in the lower part of the sequence as well as sandy and silty strata of the *Paradoxides paradoxissimus* Zone in its upper part. The Upper Cambrian strata are developed as black shales with thin lenses of dark limestones. Their total thickness is up to 20 m (Modliński and Podhalańska, 2010).

The geochemical characteristics of the Cambrian strata based on Rock-Eval and *n*-alkane and isoprenoid data are presented in Table 2. The Lower Cambrian siltstones are very poor in organic matter. The measured TOC values do not exceed 0.4 wt.% and the median equals 0.09 wt.% (Table 2 and Fig. 2). Even taking into consideration the very high maturity of these strata (almost 5% reflectance of vitrinite-like macerals, Table 2; Grotek, 2006) it is necessary to recognize that this stratigraphic member did not generate significant amounts of hydrocarbons.

The results of Rock-Eval analysis of the Middle Cambrian siltstones and claystones reveal considerable variability of TOC content, from values close to zero up to nearly 6 wt.% (Table 2 and Fig. 2). The median of 0.23 wt.% calculated for a significant population of Rock-Eval results indicates the generally poor hydrocarbon potential of these strata. However, the elevated values of TOC together with S_1 and S_2 values in some samples reveal the presence of layers or lenses having good or very good source rock potential. The extractable hydrocarbon contents confirm the Rock-Eval data (Fig. 3) showing the presence of epigenetic hydrocarbons in some samples. The values of production index (PI) up to 0.65 and bitumen ratio (BR) up to 710 mg bit/g TOC are characteristic for samples containing migrating hydrocarbons (Table 2). This is not surprising because sandstone reservoir units exist within the Middle Cambrian strata (Modliński and Podhalańska, 2010; Karnkowski *et al*., 2010).

Table 2

Geochemical characteristics and hydrocarbon potential of the Cambrian strata in the Polish part of the Baltic region

Stratigraphy / Index	Lower Cambrian	Middle Cambrian	Upper Cambrian
TOC [wt.%]	0.00 to 0.36 (138) 0.09 (10)	0.01 to 5.8 (354) 0.23 (33)	0.13 to 18.4 (188) 7.8 (20)
T_{max} [°C]	no data	423 to 465 (102) 443 (24)	424 to 505 (170) 436 (20)
R_o [%]	0.89 to 4.9 (39) 1.52 (10)	0.71 to 4.1 (64) 1.31 (18)	0.55 to 2.4 (26) 1.05 (11)
S_2 [mg HC/g rock]	no data	0.05 to 7.5 (158) 0.51 (27)	0.05 to 72.0 (175) 11.3 (20)
$S_1 + S_2$ [mg HC/g rock]	no data	0.05 to 9.3 (158) 0.70 (27)	0.19 to 75.2 (175) 13.5 (20)
PI	no data	0.00 to 0.65 (158) 0.25 (27)	0.04 to 0.78 (175) 0.13 (20)
HI [mg HC/g TOC]	no data	13 to 427 (158) 147 (27)	6 to 484 (175) 209 (20)
BR [mg bit/g TOC]	110 (1)	6 to 710 (40) 78 (16)	1 to 135 (45) 14 (17)
Pristane/phytane	no data	0.48 to 1.60 (8) 1.24 (6)	0.20 to 2.65 (18) 0.74 (14)
Pristane/*n*-C_{17}	no data	0.26 to 0.58 (8)	0.16 to 0.81 (18)
Phytane/*n*-C_{18}	no data	0.18 to 0.62 (8)	0.11 to 0.95 (18)
Kerogen type	no data	II	II
Maturity	mature/overmature	mature/overmature	mature/overmature
Hydrocarbon potential	no data	poor/fair	excellent

TOC – total organic carbon, T_{max} – maximum temperature of S_2 peak, R_o – mean random reflectance of the vitrinite-like macerals, S_1 – oil and gas yield (mg HC/g rock), S_2 – residual petroleum potential, PI – production index, HI – hydrogen index, BR – bitumen ratio. Range of geochemical parameters is given as numerator, median values in denominator. In parentheses: number of samples from boreholes (numerator) and number of sampled boreholes (denominator)

The Upper Cambrian black shales show the best hydrocarbon potential within the Cambrian succession. The measured TOC contents vary from 0.13 to 18.4 wt.%, with a median value of 7.8 wt.% (Table 2 and Fig. 2). Residual hydrocarbons (S_2) and petroleum potential ($S_1 + S_2$) are also very high, up to 72 and 75.2 mg HC/g rock, respectively, with median values of 11.3 and 13.5 mg HC/g rock, respectively (Table 2 and Fig. 2). Such values document the excellent hydrocarbon potential of this stratigraphic unit. The content of extractable hydrocarbons (Fig. 3A) reveals that the Upper Cambrian shales are mainly moderate or even good source rocks. This assessment is probably invalid due to irradation of organic matter from radiogenic elements, mainly uranium. Landais (1996), Lewan and Buchardt (1989) and Court *et al*. (2006) indicated lowering of the bitumen yield caused by complexation, aromatisation and oxidation of organic matter during radiolytic decomposition.

The range of hydrogen indices values for both the Middle and Upper Cambrian strata is comparable, from 13 to 427 (me-

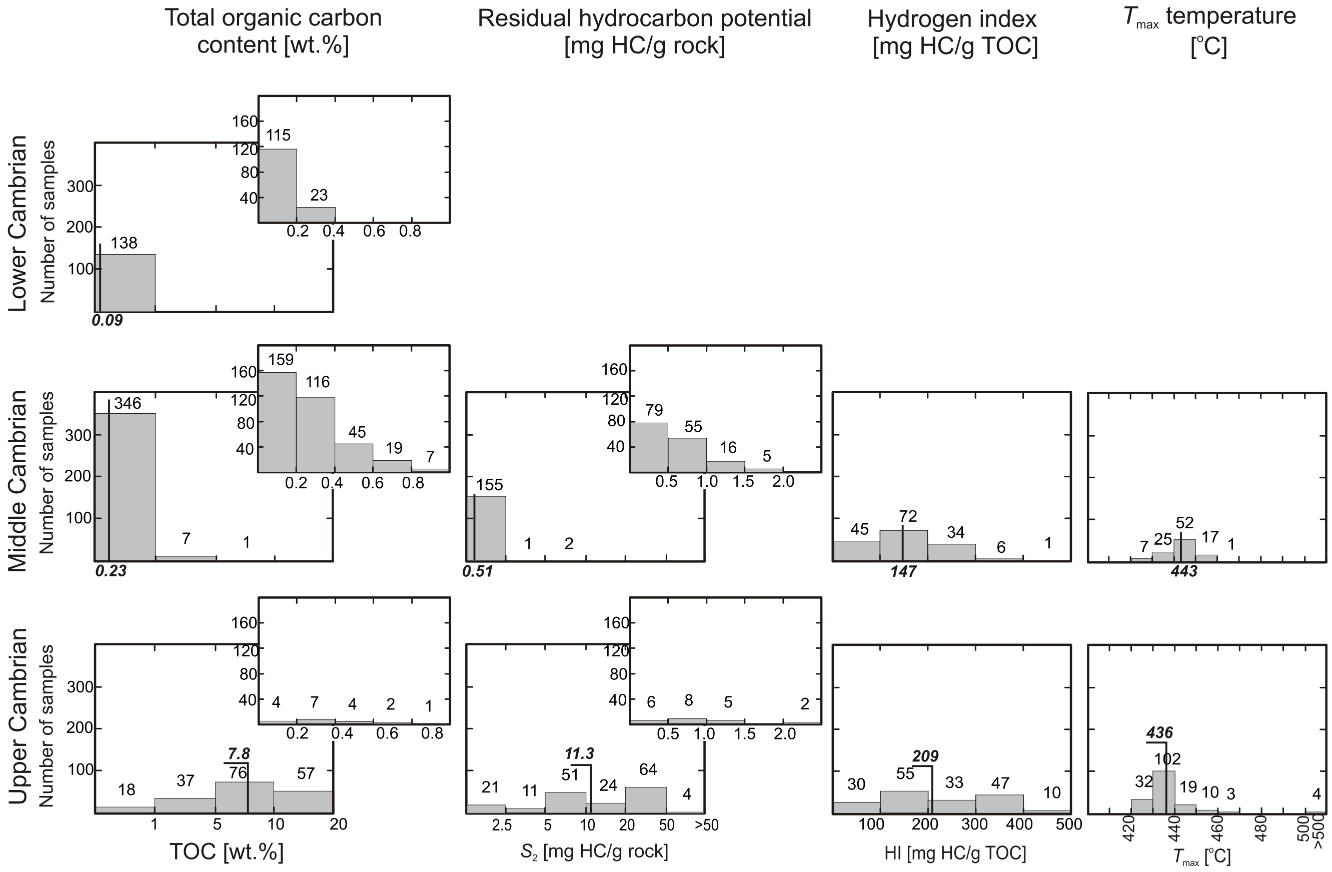

Fig. 2. Histograms of total organic carbon and residual hydrocarbon contents, hydrogen index, T_{max} temperature and median values of the individual parameters and indices for the Cambrian strata of the Polish part of Baltic region

Median parameter and index values are given in bold and italic

dian 147 mg HC/g TOC) and from 6 to 484 mg HC/ TOC (median 209 mg HC/g TOC), respectively (Table 2 and Fig. 2) indicating the varying hydrocarbon potential of both stratigraphic units.

The genetic type of dispersed organic matter in the Cambrian strata is determined by the age of the rocks and the environmental conditions of sedimentation. Here, sapropelic material derived probably from algae and bacteria is present (e.g., Riding, 2001). Taking into consideration values of pristane/phytane ratio from 0.2 to 2.65, at median value 0.74 (Table 2), it is concluded that the organic matter was deposited under reducing and sub-oxic conditions (Didyk *et al*., 1978; McKirdy and Kantsler, 1980). Results of geochemical studies: Rock-Eval data (Table 2 and Fig. 4), distribution of biomarkers (Tables 2 and 3; Fig. 5), stable carbon isotope ratios (Table 4 and Fig. 6) and elemental composition of kerogen (Table 5 and Fig. 7) point to the presence of oil-prone Type-II kerogen. Occasional low HI values, suggesting the presence of Type-III kerogen (Fig. 4A and B), were determined for samples low in TOC, where organic matter was probably partly oxidized. The *n*-alkane distribution shows maxima at 17–19 carbon atoms. Dominance of short-chain *n*-alkanes suggests their generation from algal kerogen (Peters *et al*., 2005). The large share of C_{27} regular steranes, from 0.49 to 0.64, in the regular steranes distribution (Table 3) also confirms an algal source of the extracted bitumens (Czochanska *et al*., 1988) and very high values of the diasterane/regular sterane ratio, up to 4.6 (Table 3), indicate a siliciclastic depositional environment of the organic matter (Peters *et al*., 2005).

The maturity level of the Cambrian strata was determined mainly based on the Rock-Eval data (T_{max}) and the reflectance of vitrinite-like macerals (R_o) (Table 2). For interpretation 129 results of R_o measurements were used, 111 of them from Grotek (2006). These results were verified by maturity indices calculated from distributions of biomarkers (Table 3) and aromatic hydrocarbons (Table 6). The T_{max} and R_o values show the large maturity range of the strata investigated, from the initial phase of the low-temperature thermogenic processes ("oil window") to the overmature zone (Tables 2 and 6; Figs. 2 and 4). The T_{max} values refer only to a level of maturity corresponding to the "oil window" stage, because a limitation of the applicability of this index is the sufficient residual hydrocarbons quantity. For very mature samples the T_{max} values were unreliable since only trace amounts of residual hydrocarbons (S_2 peak) were found. The measured reflectance of vitrinite-like macerals shows a maturity up to 4.9% in Lower

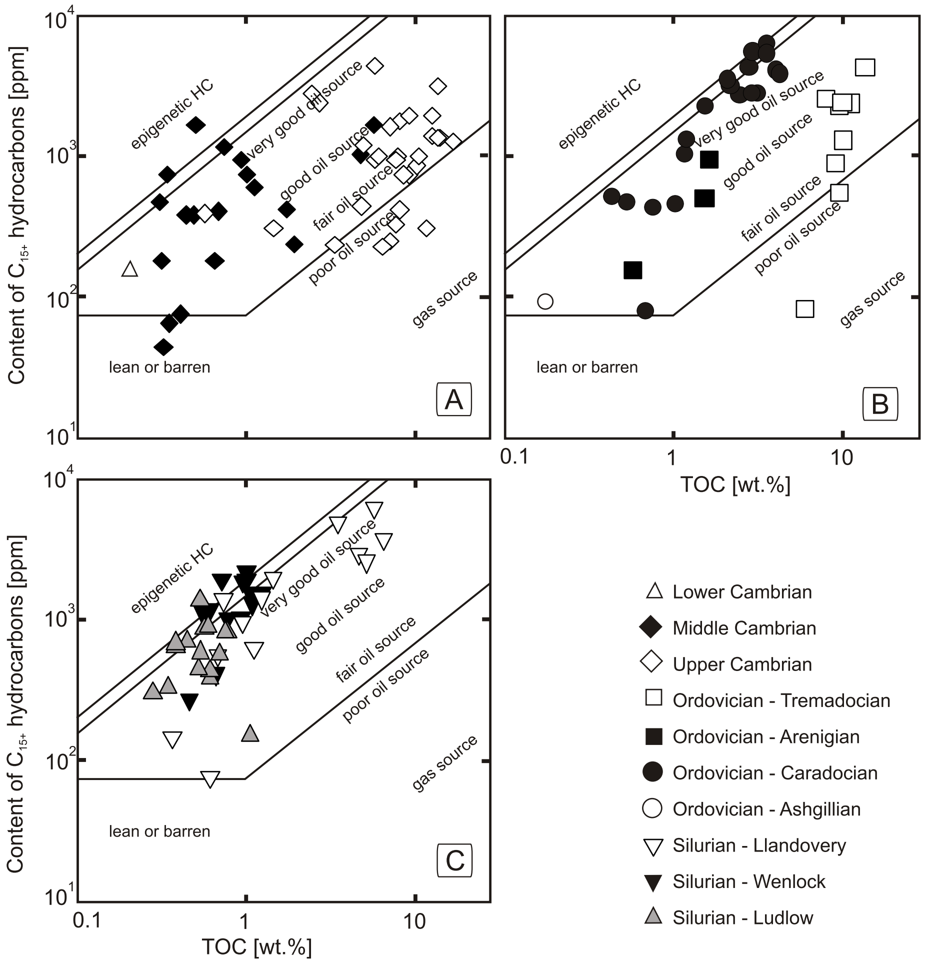

Fig. 3. Petroleum source quality diagram for organic matter of A – Cambrian, B – Ordovician and C – Silurian strata of the Polish part of Baltic region

Classification after Hunt (1979) and Leenheer (1984)

Cambrian, 4.1%, in Middle Cambrian and 2.4% in Upper Cambrian strata, respectively (Table 2). The highest maturities are noted at deepest-buried levels (over 4000 m; fig. 2 in Grotek, 2006). The biomarker (Table 3 and Fig. 8) and the aromatic hydrocarbon (Table 6) distributions confirm optical and pyrolytic measurements. Sterane and hopane isomerization indices are close to equilibrium indicating a maturity corresponding to the "oil window". The biomarker indices calculated for the Upper Cambrian shales may have been affected by radiation from radiogenic elements. Lewan and Buchardt (1989) reported that terpanes are more sensitive to uranium content then steranes. The uranium and thorium decay influenced especially the *n*-alkane and isoprenoid distributions, and led to the characteristic "hump" of unresolved complex mixture (UCM) composed of polymerized species (Lewan and Buchardt, 1989) in gas chromatograms (Fig. 9) constituting of polyaromatic hydrocarbons and oxygen-containing compounds (Court *et al*., 2006).

ORDOVICIAN STRATA

The Upper Cambrian black shales grade continuously into the lowermost part of the Ordovician strata (Tremadocian). The overlying Arenigian strata are developed as dark grey and black claystones with laminae of greyish-green claystones and limestones and marlstones above (Modliński and Podhalańska, 2010). The Llanvirnian is developed as marly limestones and locally black, dark grey and greyish-green claystones. It is overlain by black, dark grey and greyish-green claystones of Caradocian and marlstones and claystones of Ashgillian age (Modliński and Podhalańska, 2010).

The Rock-Eval pyrolysis results show that in the Tremadocian strata high amounts of organic carbon, up to 14.5 wt.%, dominate (median 9.1 wt.% TOC, Table 7 and Fig. 10). Both the residual hydrocarbon potential and the sum of hydrocarbons content (S_1 and S_2) are also very high and vary from 0.34 to 58.8 (median 27.8 mg HC/g rock) and from 0.57 to 64.2 mg HC/g rock (median 29.7 mg HC/g rock), respec-

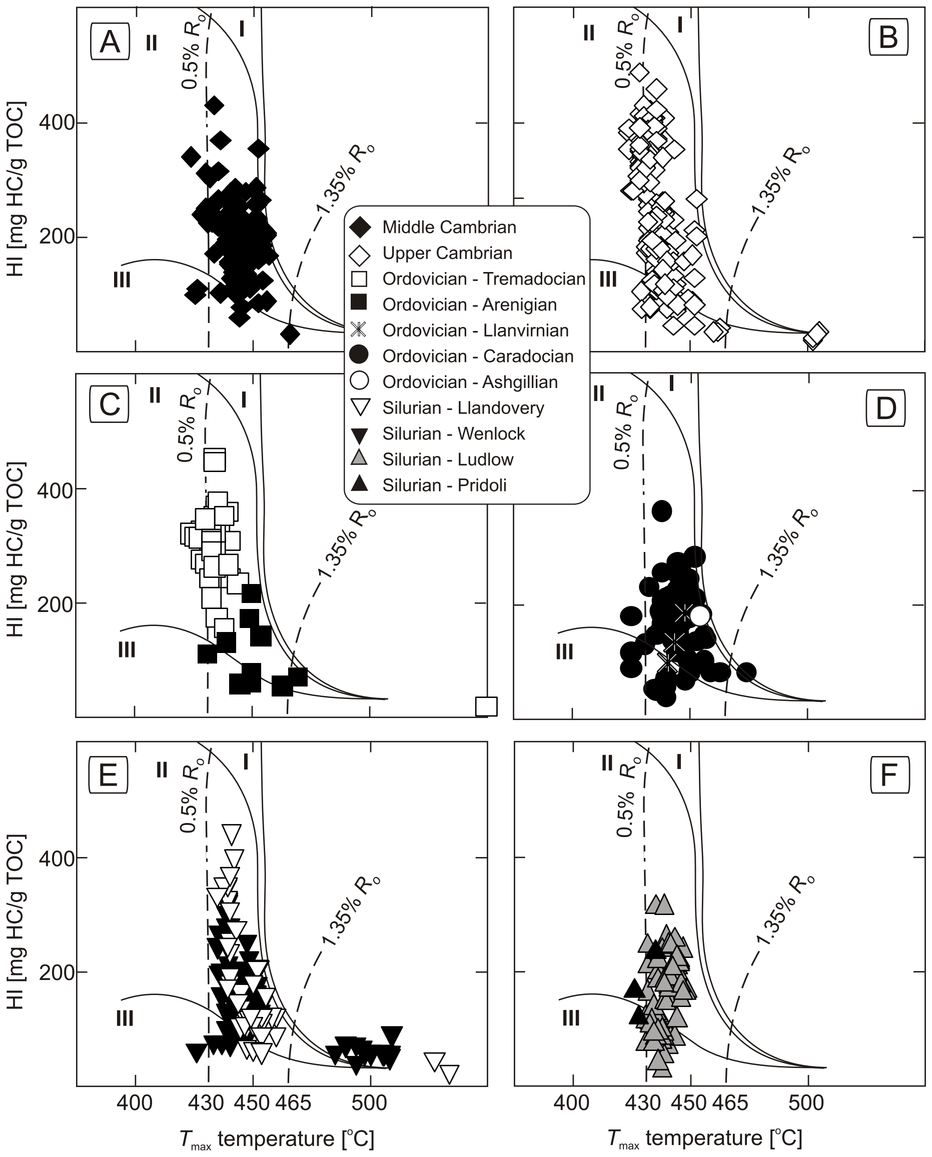

Fig. 4. Rock-Eval hydrogen index *versus* T_{max} temperature for A – Middle Cambrian, B – Upper Cambrian, C – Tremadocian and Arenigian (Ordovician), D – Llanvirnian, Caradocian and Ashgillian (Ordovician), E – Llandovery and Wenlock (Silurian) and F – Ludlow and Pridoli (Silurian) of the Polish part of the Baltic region

Maturity paths of individual kerogen types after Espitalié *et al*. (1985)

tively (Table 7 and Fig. 10). They indicate an excellent hydrocarbon potential of this unit. High hydrogen index values, mainly from 300 to 400 mg HC/g TOC (Table 7 and Fig. 10), support this thesis. The extractable hydrocarbons content, comparable to that of the Upper Cambrian due to the increased quantities of radioactive elements, show only moderate and good oil source rock potential (Fig. 3A, B). Generally, the geochemical parameters and indices of Tremadocian strata are the same as those in the Upper Cambrian. Some observed differences are only an effect of the samples population.

The clay-carbonate Arenigian strata have different geochemical characteristics than the Tremadocian rocks. The measured TOC contents are low and usually do not exceed 0.5 wt.% (Table 7 and Fig. 10). Measurable quantities of hydrocarbons were found in only 30% of samples collected from this unit. Values of all quantitative parameters and indices (S_1, S_2 and TOC) as well as the hydrogen index (mainly below 100 mg HC/g TOC) indicate the low hydrocarbon potential of these strata (Table 7 and Fig. 10). However, increased TOC and hydrocarbon contents were noted in some intervals (e.g., Łeba 8 and Żarnowiec 8K boreholes), which suggest that parts of the Arenigian strata may be considered as a supplementary source of hydrocarbons (Fig. 3B).

The Llanvirnian strata, besides their low number of representative samples, show the poorest source rock parameters. As a matter of fact, the measured TOC values vary from 0.0 to

Table 3

Selected biomarker characteristics of bitumen from the lower Paleozoic strata of the Polish part of the Baltic region

Borehole	Depth [m]	Stratigraphy	Gam/Hop	C_{27}	C_{28}	C_{29}	Dia/Hop	Bis/Hop	C_{26}/C_{24}	Mor/Hop	H_{31} S/(S+R)	H_{32} S/(S+R)	C_{29}SR	$C_{29}\beta\beta\alpha\alpha$	$C_{29}T/C_{29}H$	Ts/Tm	Gam/C_{31}Hop	Dia/Reg
Białogóra 4K	2775.2	Middle Cambrian	0.24	0.49	0.27	0.24	0.20	0.15	3.04	0.28	0.71	0.51	0.59	0.44	0.94	1.01	1.23	2.15
B16-1/85	1847.5	Upper Cambrian	0.24	0.51	0.29	0.21	0.15	0.17	2.06	0.19	0.57	0.59	0.42	0.46	0.84	1.04	0.58	2.71
B16-1/85	1857.6	Upper Cambrian	0.06	0.50	0.25	0.25	0.19	0.32	1.95	0.17	0.62	0.62	0.47	0.34	1.35	1.26	0.16	1.86
B21-1/95	1731.7	Upper Cambrian	n.c.	0.58	0.27	0.16	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.50	n.c.	n.c.	n.c.	n.c.	3.90
Dębki 3	2680.9	Upper Cambrian	0.09	0.64	0.19	0.17	0.24	0.09	1.22	0.16	0.57	0.56	0.55	0.59	0.21	0.81	0.30	4.34
B4-1/81	1103.7	O.–Tremadocian	n.c.	0.48	0.27	0.26	0.18	0.25	1.80	0.24	0.52	0.50	0.51	0.59	1.30	1.01	0.00	2.42

Gam/Hop = gammacerane/17α hopane, C_{27} = $C_{27}\alpha\alpha\alpha$20R sterane/(C_{27} + C_{28} + C_{29})$\alpha\alpha\alpha$20R steranes, C_{28} = $C_{28}\alpha\alpha\alpha$20R sterane/(C_{27} + C_{28} + C_{29})$\alpha\alpha\alpha$20R steranes, C_{29} = $C_{29}\alpha\alpha\alpha$20R sterane/(C_{27}+C_{28} + C_{29})$\alpha\alpha\alpha$20R steranes, Dia/Hop = 15α-methyl-27-*nor*-17α-hopane/17α hopane, Bis/Hop = 28.30-bisnorhopane/17α hopane, C_{26}/C_{24} = C_{26}(S + R) tricyclic terpanes/C_{24} tetracyclic terpane, Mor/Hop = (normoretane + moretane)/(norhopane + 17α hopane), H_{31}S/(S + R) = homohopane 22S/(22S + 22R), H_{32}S/(S + R) = bishomohopane 22S/(22S + 22R), C_{29}SR = epimerisation of regular steranes C_{29} ratio, $C_{29}\beta\beta\alpha\alpha$ = ratio of $\beta\beta$-epimeres of regular steranes C_{29} to sum of $\beta\beta$+$\alpha\alpha$ steranes, C_{29}Ts/C_{29}H = C_{29} 18α norneohopane/C_{29} norhopane, Ts/Tm = C_{27} 18α trisnorhopane/C_{27} 17α trisnorhopane, Gam/C_{31}Hop = gammacerane/C_{31} 22R hopane, Dia/Reg = C_{27} $\beta\alpha$ 20S diasterane/C_{29} $\alpha\alpha\alpha$ 20R sterane, n.c. – not calculated due to lack of biomarkers, O. – Ordovician

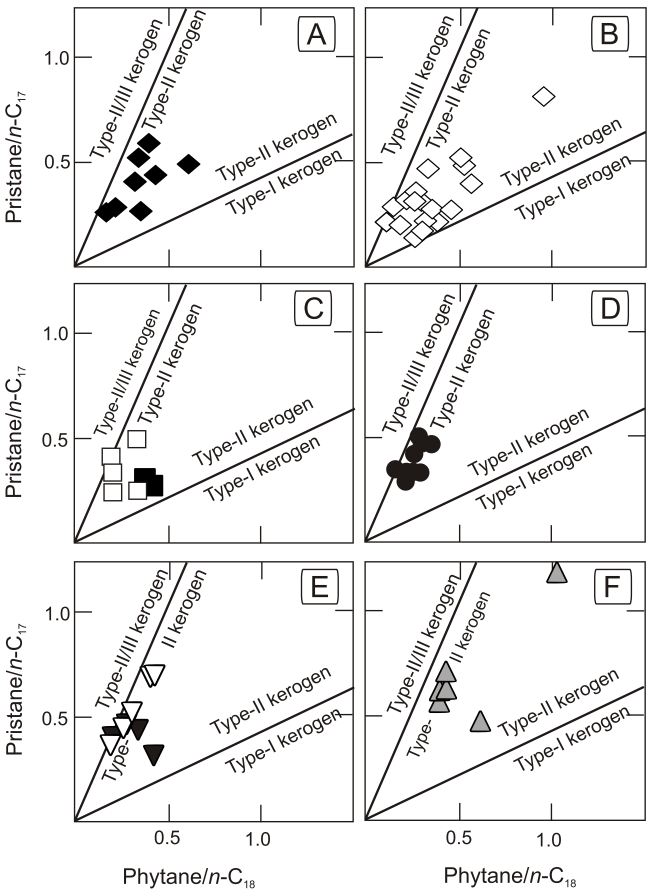

Fig. 5. Genetic characterization of bitumen from A – Middle Cambrian, B – Upper Cambrian, C – Tremadocian and Arenigian (Ordovician), D – Llanvirnian, Caradocian and Ashgillian (Ordovician), E – Llandovery and Wenlock (Silurian) and F – Ludlow and Pridoli (Silurian) of the Polish part of the Baltic region in terms of pristane/*n*-C_{17} and phytane/*n*-C_{18} according to the categories of Obermajer *et al*. (1999)

For explanation of symbols see Figure 4

1.3 wt.% (Table 7) and the median is only 0.19 wt.% (Table 7 and Fig. 10). Also the hydrocarbon content ($S_1 + S_2$) and hydrogen index values, which were determined only for *ca*. 20% of the samples, indicate the poor hydrocarbon potential of this division (Table 7).

The Caradocian claystones show favourable quantitative parameters of source rocks. The TOC content varies from 0.01 to 7.0 wt.% with median 1.9 wt.% (Table 7). The highest values were noted in the offshore part of the Łeba and Darłowo blocks (Fig. 1). The TOC content increases from the platform border to the northeastern part of the Baltic region. A high variability of residual hydrocarbon potential (S_2) and hydrocarbons content ($S_1 + S_2$) was also observed (Table 7 and Fig. 10). Values of S_2 vary from 0.05 to 10.6 mg HC/g rock with median 2.4 mg HC/g rock (Table 7 and Fig. 10), which indicates the generally good hydrocarbon potential of the Caradocian strata. The extractable hydrocarbon content supports this assessment (Fig. 3B).

Table 4

Fractions and stable carbon isotope composition of bitumen, its individual fractions and kerogen in lower Paleozoic strata

Borehole	Depth [m]	Stratigraphy	Fractions [wt.%]				$\delta^{13}C$ [‰]					
			Sat	Aro	Res	Asph	Sat	Bit	Aro	Res	Asph	Ker
A23-1/88	1321.3	Middle Cambrian	70	15	9	6	–29.9	–29.6	–29.3	–29.2	–29.8	–30.2
B3-9/95	1458.7	Middle Cambrian	53	24	16	7	–29.5	–29.2	–28.8	–29.2	–28.7	–28.4
Białogóra 4K	2775.2	Middle Cambrian	37	26	21	16	–28.5	–28.6	–28.7	–29.1	–29.5	–30.4
Dębki 4	2682.2	Middle Cambrian	62	17	11	10	–30.3	–29.9	–29.4	–29.7	–29.5	–29.6
Żarnowiec IG 1	2750.4	Middle Cambrian	58	16	13	13	–30.2	–30.1	–30.0	–29.9	–30.1	–30.6
A23-1/88	1313.4	Upper Cambrian	47	23	19	11	–27.7	–27.8	–27.8	–27.8	–28.0	–28.6
B16-1/85	1847.5	Upper Cambrian	29	33	23	15	–26.9	–27.7	–28.0	–28.2	–28.1	–29.2
B16-1/85	1857.6	Upper Cambrian	32	31	21	16	–27.8	–27.4	–27.6	–27.2	–27.2	–27.3
B21-1/95	1731.7	Upper Cambrian	39	31	20	10	–28.3	–28.4	–28.7	–28.6	–28.4	–29.4
B4-2A/02	1120.5	Upper Cambrian	22	33	24	21	–28.6	–28.7	–29.3	–28.7	–28.3	–29.3
Dębki 3	2680.9	Upper Cambrian	39	27	14	20	–27.9	–27.9	–27.9	–27.7	–27.2	–27.8
Dębki 4	2668.8	Upper Cambrian	61	19	9	11	–28.2	–28.3	–28.0	–28.0	–28.1	–28.5
Hel IG 1	3047.1	Upper Cambrian	39	36	16	9	–27.7	–28.3	–28.8	–28.8	–28.4	–30.0
Łeba 8	2730.0	Upper Cambrian	30	28	21	21	–26.6	–27.1	–26.6	–27.4	–28.0	–29.2
Żarnowiec IG 1	2723.6	Upper Cambrian	63	22	6	9	–28.6	–28.6	–28.5	–28.2	–28.9	–28.3
Żarnowiec 6K	2832.0	Upper Cambrian	66	16	6	12	–27.0	–27.2	–27.2	–27.3	–28.3	–26.6
A8-1/83	1930.5	O.–Tremadocian	29	22	40	9	–28.3	–28.3	–28.0	–28.4	–28.3	–29.6
B3-9/95	1410.5	O.–Tremadocian	43	31	15	11	–29.5	–29.3	–29.2	–28.6	–28.5	–29.5
B4-1/81	1103.7	O.–Tremadocian	23	34	25	18	–29.7	–29.5	–29.7	–29.3	–29.3	–30.0
B6-1/82	1416.15	O.–Tremadocian	34	31	26	9	–28.7	–28.9	–29.1	–29.1	–28.9	–29.8
B6-1/82	1420.0	O.–Tremadocian	33	34	25	8	–28.7	–28.9	–29.2	–29.0	–29.0	–30.1
Białogóra 2	2615.0	O.–Caradocian	78	10	9	3	–30.3	–30.2	–30.0	–29.8	–31.1	–30.4
Dębki 3	2641.0	O.–Caradocian	66	16	15	3	–31.3	–31.1	–30.9	–30.7	–30.3	–31.3
Dębki 3	2645.0	O.–Caradocian	83	10	4	3	–30.1	–30.1	–29.9	–30.0	–31.1	–30.7
Gdańsk IG 1	3105.1	O.–Caradocian	60	12	17	11	–30.3	–30.2	–29.7	–29.6	–30.0	–30.7
Hel IG 1	2990.2	O.–Caradocian	79	12	6	3	–31.1	–30.9	–30.5	–30.3	–29.8	–31.1
Łeba 8	2672.5	O.–Caradocian	85	7	6	2	–30.3	–30.2	–29.2	–29.2	–28.9	–30.9
Żarnowiec IG 1	2660.4	O.–Caradocian	74	18	6	2	–30.9	–31.0	–30.9	–30.9	–30.4	–31.6
Żarnowiec IG 1	2690.3	O.–Caradocian	74	16	6	4	–31.2	–31.0	–30.8	–30.9	–30.9	–31.8
Żarnowiec 6K	2771.0	O.–Caradocian	85	7	6	2	–30.4	–30.3	–29.2	–29.9	–30.8	–30.3
B3-9/95	1320.4	S.–Llandovery	39	27	18	16	–30.2	–29.6	–30.0	–28.9	–28.3	–28.2
B3-9/95	1324.6	S.–Llandovery	38	24	16	22	–30.5	–30.4	–30.4	–30.1	–30.1	–30.4
Żarnowiec IG 1	2639.2	S.–Llandovery	70	18	9	3	–30.1	–29.8	–29.9	–29.8	–29.9	–30.4
Gdańsk IG 1	2923.1	S.–Wenlock	65	12	12	11	–30.6	–30.7	–30.5	–30.2	–30.2	–30.7
Żarnowiec IG 1	2576.7	S.–Wenlock	68	17	9	6	–29.6	–29.5	–29.3	–29.2	–29.6	–29.9
B3-9/95	906.5	S.–Ludlow	25	26	23	26	–28.6	–28.3	–28.3	–27.8	–27.5	–27.8
Gdańsk IG 1	2471.6	S.–Ludlow	37	18	15	30	–28.1	–27.9	–28.3	–28.1	–28.0	–27.8
Żarnowiec IG 1	2201.8	S.–Ludlow	47	18	20	15	–30.3	–30.2	–30.0	–30.1	–30.0	–30.3
Żarnowiec IG 1	2408.7	S.–Ludlow	59	19	12	10	–31.0	–31.1	–31.2	–31.0	–31.2	–30.8

Sat – saturated hydrocarbons, Aro – aromatic hydrocarbons, Res – resins, Asph – asphaltenes, Bit – bitumen, Ker – kerogen, O. – Ordovician, S. – Silurian

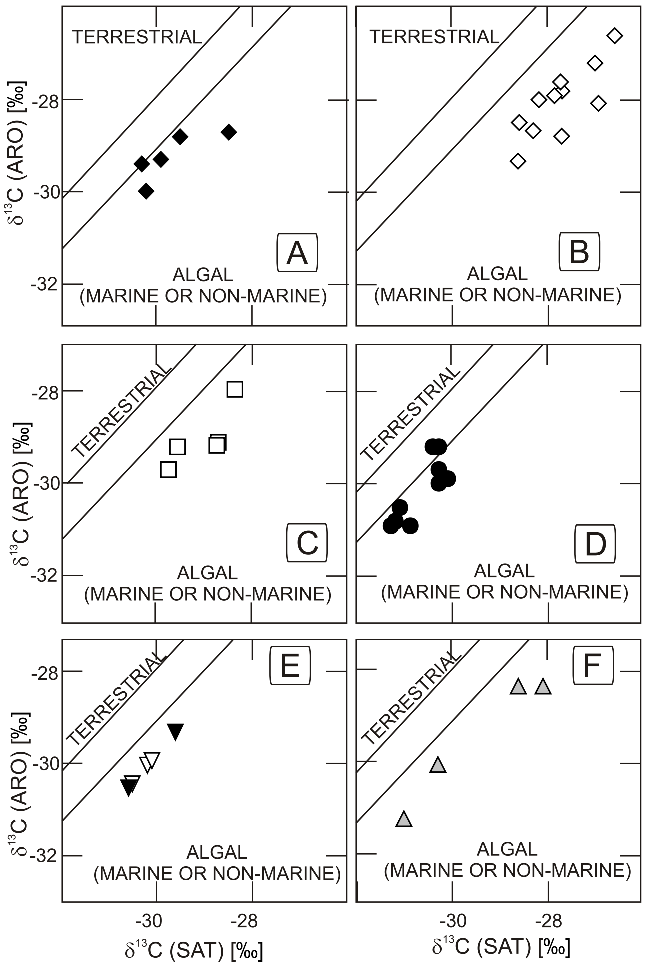

Fig. 6. Genetic characterization of bitumen from A – Middle Cambrian, B – Upper Cambrian, C – Tremadocian and Arenigian (Ordovician), D – Lanvirnian, Caradocian and Ashgillian (Ordovician), E – Llandovery and Wenlock (Silurian) and F – Ludlow and Pridoli (Silurian) of the Polish part of the Baltic region based on the stable carbon isotope composition of saturated and aromatic hydrocarbons

Genetic fields after Sofer (1984);
for explanation of symbols see Figure 4

The geochemical characteristics of the Ashgillian strata are comparable to that for the Arenigian and Llanvirnian rocks (Table 7). Low concentrations of organic carbon as well as hydrocarbons show, that these strata cannot be considered as source rocks for economic accumulations of hydrocarbons (Table 7; Figs. 3B and 10).

Similarly to the Cambrian ones, the Ordovician strata contain oil-prone Type-II kerogen. This was shown by Rock-Eval (Table 7 and Fig. 4C, D), biomarker (Tables 3 and 7; Fig. 5C, D), stable carbon isotope rations (Table 4 and Fig. 6C, D) and kerogen elemental composition (Table 5 and Fig. 7) data. The low HI values, suggesting the presence of Type-III kerogen in Arenigian and Caradocian strata (Fig. 4C, D) were determined for samples poor in organic matter, probably deposited under sub-oxic conditions. The depositional environment indicated by biomarker indices (Tables 3 and 7) was mainly anoxic and reducing. The rare values of pristane/phytane ratio over unity (Table 7) suggest sub-oxic conditions in parts of the sedimentary basin (Didyk *et al.*, 1978). An influence of radiogenic radiation on organic matter, especially observed in the Tremadocian strata (Lewan and Buchardt, 1989), cannot be excluded.

The maturity of the Ordovician strata was determined with the same methods as for the Cambrian ones (Tables 3 and 5–7). For interpretation, 41 results of R_o measurements were used, 28 of them from Grotek (2006). Both the T_{max} and R_o values show the maturity of the strata investigated from the initial phase of low-temperature thermogenic process ("oil window") up to the overmature zone (Tables 6 and 7; Figs. 4 and 10). The T_{max} values refer mainly to maturity corresponding to the "oil window" stage, because in samples showing higher transformation levels the quantities of residual hydrocarbons were insufficient to get correct T_{max} value. The measured reflectance of vitrinite-like macerals show maturity up to 2.3% in Tremadocian, 1.74%, in Arenigian, 4.2% in Caradocian and 3.9% in the Ashgillian strata (Table 7). The highest maturities are noticed in deeply buried levels (over 4000 m; fig. 4 in Grotek, 2006). The biomarker (Table 3 and Fig. 8) and the aromatic hydrocarbon (Table 6) distributions support the previous data. Sterane and hopane isomerization

Table 5

Elemental composition of kerogen from the lower Paleozoic strata

Borehole	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)
Białogóra 4K	2775.2	Middle Cambrian	83.2	5.6	4.8	2.8	3.6	0.81	0.04	0.029	0.016	0.44	0.04	0.028	0.016
B21-1/95	1731.7	Upper Cambrian	86.6	6.2	3.0	2.3	1.9	0.87	0.03	0.023	0.008	0.46	0.03	0.022	0.008
B16-1/85	1847.5	Upper Cambrian	84.7	5.2	5.2	2.6	2.3	0.74	0.05	0.026	0.010	0.42	0.04	0.025	0.010
B16-1/85	1857.6	Upper Cambrian	84.7	5.3	4.8	2.8	2.4	0.75	0.04	0.028	0.011	0.43	0.04	0.027	0.011
Dębki 3	2680.9	Upper Cambrian	82.6	5.6	6.4	2.7	2.7	0.81	0.06	0.028	0.012	0.45	0.05	0.027	0.012
B4-1/81	1103.7	O. – Tremadocian	86.0	7.2	3.4	2.5	0.8	1.01	0.03	0.025	0.004	0.50	0.03	0.025	0.004

daf – dry, ash-free basis, O. – Ordovician

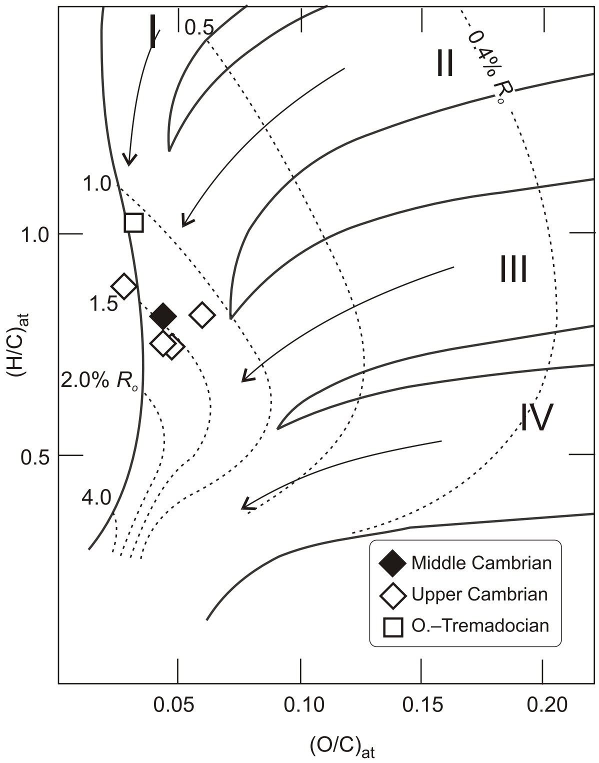

Fig. 7. Elemental composition of organic matter from Cambrian and Ordovician strata of the Polish part of the Baltic region

Fields represent natural maturity paths for individual kerogens after Hunt (1996); O – Ordovician

indices are near equilibrium and are comparable to those from the Cambrian strata. The biomarker indices calculated for the Tremadocian shales, comparable to the Upper Cambrian, could be affected by radiation from radiogenic elements (Lewan and Buchardt, 1989; Court *et al*., 2006).

SILURIAN STRATA

The Silurian strata represent a continuous succession of siltstones and claystones interbedded with thin sandstones (Szymański and Modliński, 2003). The Llandovery deposits are developed as black, dark grey and grey claystones of maximum thickness 80 m, and Wenlock strata as dark grey, grey and locally black clay- and siltstones. A lithofacial development comparable to the above described strata was observed also in the Ludlow and Pridoli; however, grey and light grey claystones dominate (Modliński and Podhalańska, 2010). The thickness of the last-mentioned unit varies from 500 to 1400 m and from 20 to 700 m, respectively.

The primary identification of the origin of free (or extractable) hydrocarbons present in the rocks investigated show, in most cases, their syngenetic nature. Only in sparse samples collected from the Llandovery, Wenlock and Ludlow strata the geochemical data (PI values, Table 8; and extractable hydrocarbons content – Fig. 3C) points to the presence of epigenetic HC. These samples were excluded from source rock characterization.

The Llandovery claystones show moderate and locally good quantitative source rock parameters and indices. The TOC content varies from 0.02 to 10.2 wt.% with median 0.77 wt.% (Table 8 and Fig. 11). Low values, below 1 wt.%, prevail but in 11 samples TOC contents over 5 wt.% were affirmed (Fig. 11). Similarly high variability is noted in the case of hydrocarbons (S_2 and $S_1 + S_2$) – from 0.12 to 40.6 (with median 1.51 mg HC/g rock) and from 0.25 to 43.7, (with median value of 2.1 mg HC/g rock), respectively (Table 8 and Fig. 11). In four samples the residual hydrocarbon potential exceeded 20 mg HC/g rock, indicating the presence of excellent source rocks (Peters and Cassa, 1994). The hydrogen index also varies over a wide range – from 8 to 436 mg HC/g TOC with a median value of 115 mg HC/g TOC (Table 8 and Fig. 11) showing the moderate hydrocarbon potential of Llandovery strata. The extractable hydrocarbon content indicates a very good oil source potential of these strata (Fig. 3C).

The Wenlock claystones show generally moderate quantitative source rock parameters and indices, but locally they are enriched in organic matter. The TOC content varies from 0.02 to 1.51 wt.% (Table 8). The median value of TOC (0.73 wt.%) is comparable to that of the Llandovery strata (Table 8 and Fig. 11). The hydrocarbons (S_1 and S_2) contents are lower there than those in the Llandovery and their sum reaches a maximum of 4.1 mg HC/g rock (Table 8). The residual hydrocarbon potential exceeds 2.5 mg HC/g rock only for four samples (Fig. 11). Hydrogen index values are comparable to those of Llandovery strata (Table 8 and Fig. 11). High contents of hydrocarbons (saturated and aromatic), up to 85% in some bitumens (Table 4), indicate there the presence of migrated hydrocarbons (Fig. 3C).

The Ludlow claystones and the Pridoli claystones and siltstones are poor source rocks. The TOC contents vary from 0.00 to 1.13 wt.% (median 0.19 wt.%) and from 0.02 to 0.52 wt.% (median 0.12 wt.%), respectively (Table 8). Low TOC values, below 1 wt.% prevail (Fig. 11). The residual hydrocarbon potential of both members never exceeds 2.5 mg HC/g rock (Table 8 and Fig. 11). The HI values are comparable to those of other Silurian stages, mainly from 100 to 200 mg HC/g TOC (Table 8 and Fig. 11). The very good oil source rock assessment of the Ludlow strata (Fig. 3C), may be invalid due to elevated hydrocarbon contents in bitumen indicating an epigenetic origin of part of them (Fig. 3C).

The pyrolytic Rock-Eval (Table 8 and Fig. 4E, F) together with the biomarker (Table 8 and Fig. 5E, F) and stable carbon isotope (Table 4 and Fig. 6E, F) data point to presence of oil-prone Type-II kerogen. The organic matter was deposited in anoxic (reduced) as well as in sub-oxic conditions, as shown by values of the pristane/phytane ratio from 0.86 to 2.41 (Table 8). The presence of Type-III kerogen (low values of HI) in some samples (Fig. 4E, F) is probably a result of partial oxidation of organic matter during deposition (Espitalié *et al*., 1985). The low HI values are noted only for organics-poor levels.

The maturity of Silurian strata was mainly based on values of T_{max} temperature and reflectance of vitrinite-like macerals (Table 8; Figs. 4 and 11) and supported by indices determined from the distribution of aromatic hydrocarbons (Table 6). For interpreta-

Table 6

Maturity indices calculated based on distribution of phenantrene and its methyl derivatives in bitumens and Rock-Eval T_{max} temperature of the lower Paleozoic strata

Borehole	Depth [m]	Stratigraphy	MPI1	MPR	MPR1	R_{cal} [%]	$R_{cal(MPR)}$ [%]	T_{max} [°C]
A23-1/88	1319.0	Middle Cambrian	1.00	0.96	0.43	0.97	0.80	n.a.
Białogóra 4K	2775.2	Middle Cambrian	0.95	1.02	0.42	0.94	0.78	447
Żarnowiec IG 1	2734.2	Middle Cambrian	0.95	1.02	0.43	0.94	0.80	441
B16-1/85	1847.5	Upper Cambrian	1.17	1.31	0.48	1.07	0.90	436
B16-1/85	1857.6	Upper Cambrian	0.98	1.05	0.42	0.96	0.77	441
B21-1/95	1731.7	Upper Cambrian	1.01	1.27	0.42	0.97	0.79	438
B4-2A/02	1120.5	Upper Cambrian	1.02	1.61	0.45	0.98	0.84	436
B6-1/82	1432.75	Upper Cambrian	1.44	2.23	0.55	1.23	1.06	431
Dębki 3	2680.9	Upper Cambrian	0.92	1.02	0.43	0.92	0.79	440
Łeba 8	2730.7	Upper Cambrian	1.96	2.33	0.64	1.55	1.28	462
Łeba 8	2734.4	Upper Cambrian	1.69	2.04	0.63	1.39	1.24	443
A8-1/83	1930.5	O.–Tremadocian	2.11	2.28	0.60	1.64	1.18	n.a.
B4-1/81	1103.7	O.–Tremadocian	0.58	0.80	0.32	0.72	0.55	440
B6-1/82	1425.0	O.–Tremadocian	1.17	1.78	0.47	1.07	0.88	434
Łeba 8	2708.8	O.–Arenigian	1.93	1.71	0.59	1.53	1.16	445
Dębki 3	2641.0	O.–Caradocian	1.02	1.12	0.45	0.98	0.84	445
Łeba 8	2666.1	O.–Caradocian	1.91	1.69	0.59	1.51	1.16	440
Łeba 8	2672.7	O.–Caradocian	1.85	1.55	0.58	1.48	1.13	448
Żarnowiec IG 1	2686.2	O.–Caradocian	1.11	1.06	0.45	1.03	0.84	445
B6-1/82	1334.75	S.–Llandovery	0.56	0.69	0.30	0.71	0.51	438
Żarnowiec IG 1	2636.1	S.–Llandovery	1.16	1.20	0.46	1.07	0.87	452

MPI1 = 1.5(2-MP + 3-MP)/(P + 1-MP + 9-MP), P – phenantrene, MP – metylphenantrene; MPR = 2-MP/1-MP; MPR1 = (2-MP + 3-MP)/(1-MP + 9-MP + 2-MP + 3-MP); R_{cal} = 0.60MPI1 + 0.37 for MPR <2.65 (Radke, 1988); $R_{cal(MPR)}$ = –0.166 + 2.242(MPR1) (Kvalheim *et al*., 1987); T_{max} – maximum temparature of the S_2 peak (Rock-Eval); n.a. – not applicable; O. – Ordovician; S. – Silurian

tion, 152 results of R_o measurements were used, 150 of them from Grotek (2006). The lowest maturities, corresponding to the initial phase of the "oil window" are noted offshore (Łeba Block) and they increase towards the south-west up to the overmature zone in the Llandovery strata in the vicinity of Lębork and Słupsk (Grotek, 2006). The lowest maturity was observed for the Pridoli strata, reaching not more then the middle phase of the "oil window" (Table 8 and Fig. 4F).

IDENTIFICATION AND CHARACTERISTICS OF THE SOURCE ROCKS WITHIN THE INDIVIDUAL STRATIGRAPHIC UNITS

The identification of source rock horizons is an essential element of petroleum system analyses of the petroleum basin in respect of calculation of the volumetric hydrocarbon potential of its structural area unit.

Results of geochemical analyses indicate that the Upper Cambrian–Tremadocian succession has the best hydrocarbon potential in the lower Paleozoic sequence in the Polish part of the Baltic region. These strata can be recognized as excellent source rocks (Tables 2 and 7). Other units, in which elevated and locally very high organic carbon contents were noted, are

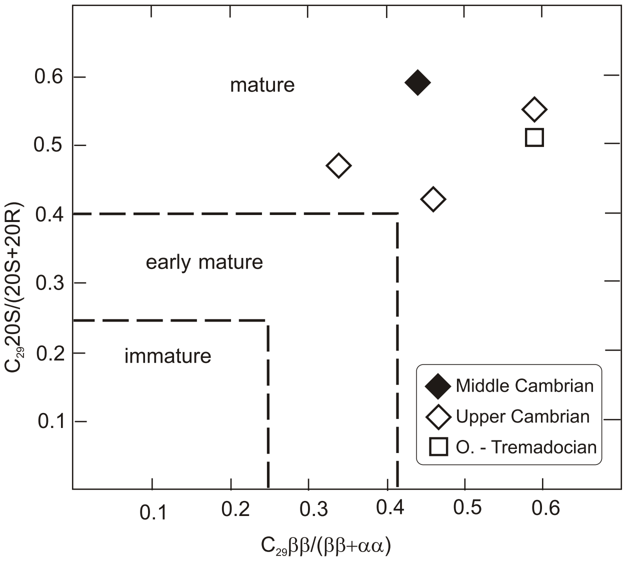

Fig. 8. Sterane C_{29} 20S/(20S + 20R) ratio *versus* C_{29} ββ/(ββ+αα) ratio for Cambrian and Ordovician strata of the Polish part of the Baltic region

Maturity fields after Peters and Moldowan (1993); O – Ordovician

Table 7

Geochemical characteristics and hydrocarbon potential of the Ordovician strata of the Polish part of the Baltic region

Stratigraphy Index	Tremadocian	Arenigian	Llanvirnian	Caradocian	Ashgillian
TOC [wt.%]	0.67 to 14.5 (36) 9.1 (7)	0.00 to 3.2 (44) 0.18 (15)	0.00 to 1.30 (16) 0.19 (9)	0.01 to 7.0 (110) 1.19 (21)	0.00 to 0.58 (20) 0.18 (9)
T_{max} [°C]	424 to 551 (36) 434 (7)	431 to 470 (10) 450 (5)	440 to 447 (3) 443 (2)	425 to 474 (74) 445 (14)	454 (1)
R_o [%]	0.72 to 2.3 (6) 0.73 (4)	0.67 to 1.74 (13) 1.15 (6)	no data	0.99 to 4.2 (15) 1.23 (11)	1.1 to 3.9 (7) 1.19 (6)
S_2 [mg HC/g rock]	0.34 to 58.8 (38) 27.8 (7)	0.21 to 4.0 (15) 0.57 (9)	0.38 to 2.4 (3) 0.76 (2)	0.05 to 10.6 (89) 2.4 (17)	0.24 to 0.79 (4) 0.41 (3)
$S_1 + S_2$ [mg HC/g rock]	0.57 to 64.2 (38) 29.7 (7)	0.29 to 5.1 (15) 0.66 (9)	0.52 to 3.6 (3) 1.31 (2)	0.06 to 13.7 (89) 3.8 (17)	0.27 to 1.57 (4) 0.74 (3)
PI	0.04 to 0.39 (38) 0.08 (7)	0.02 to 0.49 (15) 0.26 (9)	0.27 to 0.42 (3) 0.34 (2)	0.00 to 0.61 (89) 0.36 (17)	0.12 to 0.54 (4) 0.43 (3)
HI [mg HC/g TOC]	9 to 446 (38) 304 (7)	48 to 211 (15) 84 (9)	96 to 182 (3) 131 (2)	11 to 359 (89) 164 (17)	61 to 175 (4) 91 (3)
BR [mg bit/g TOC]	2 to 47 (12) 26 (6)	39 to 88 (4) 56 (3)	no data	20 to 193 (28) 112 (12)	88 (1)
Pristane/phytane	0.20 to 2.33 (6) 1.06 (6)	0.63 and 0.87 (2) 0.75 (2)	no data	0.92 to 2.36 (9) 1.43 (5)	no data
Pristane/n-C_{17}	0.24 to 1.56 (6)	0.26 and 0.27 (2)	no data	0.29 to 0.50 (9)	no data
Phytane/n-C_{18}	0.20 to 0.79 (6)	0.38 and 0.40 (2)	no data	0.17 to 0.36 (9)	no data
Kerogen type	II	II	II	II	II
Maturity	mature/overmature	mature/overmature	mature	mature/overmature	mature/overmature
Hydrocarbon potential	excellent	poor	poor	good	poor

For explanations see Table 2

clayey levels in the Middle Cambrian (Table 2), Caradocian (Table 7) and Llandovery (Table 8) strata. The other stratigraphic divisions (Lower Cambrian, Arenigian, Llanvirnian, Ashgillian, Wenlock, Ludlow and Pridoli) generally show poor hydrocarbon potential and can be omitted in the general petroleum balance of the study region.

Determination of thickness and original organic carbon content of source rocks were made for Middle Cambrian, Upper Cambrian–Tremadocian, Caradocian and Llandovery strata.

MIDDLE CAMBRIAN

The only Middle Cambrian rocks with source rock potential are black claystones occurring in the *Eccaparadoxides oelandicus* Zone and the lowermost part, and siltstone intercalations within the *Paradoxides paradoxissimus* Zone.

Precise determination of source rock thickness cannot be made on the basis of the results of geochemical analyses, due to the non-representative sampling in the individual boreholes caused by the domination of sandy facies in the Middle Cambrian strata. Therefore evaluation of source rock thickness is only an estimate.

The primary element of source rock thickness determination was the estimation of the thickness of clayey rocks. This was done based on a facial-thickness map of the Middle Cambrian strata (fig. 3 in Modliński and Podhalańska, 2010). The source rock thickness was estimated from available well data (core descriptions, well logs) taking into consideration the re-

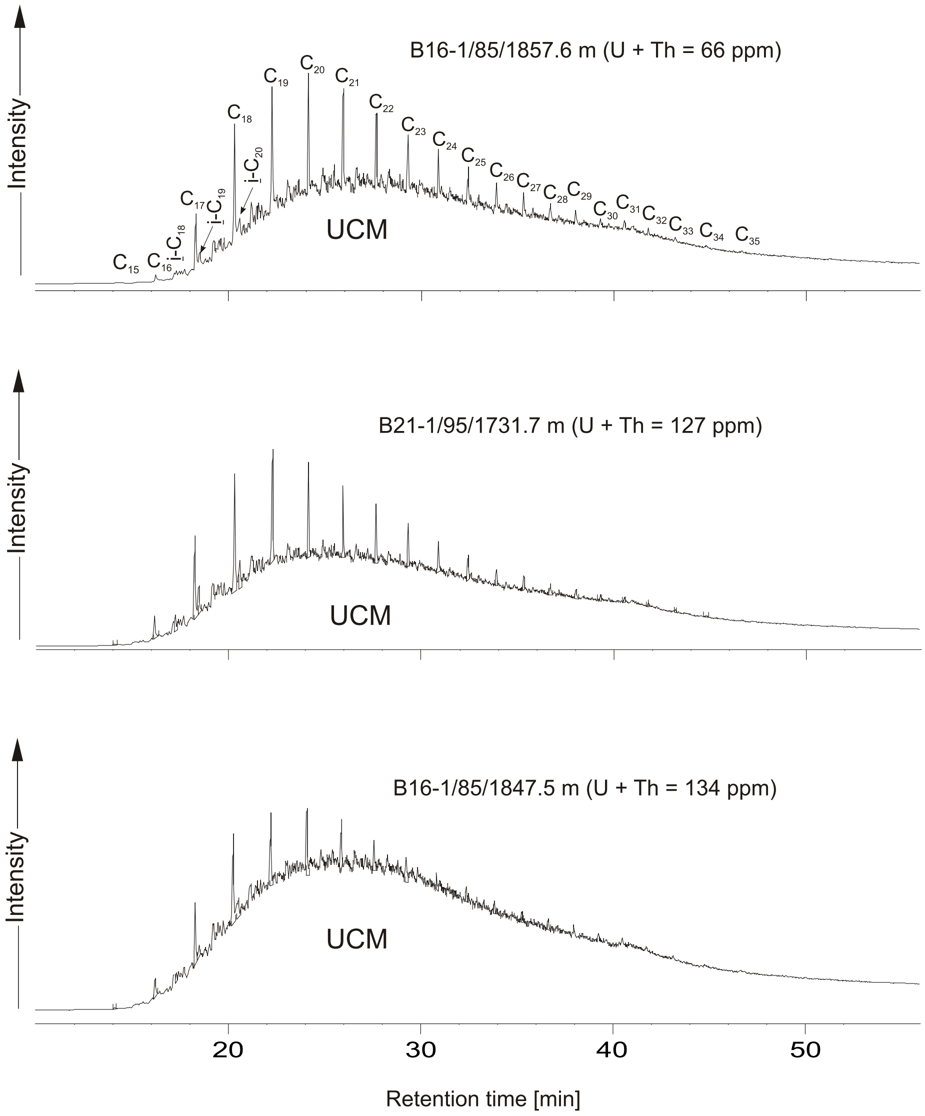

Fig. 9. Examples of *n*-alkane and isoprenoid distributions (GC-FID) in bitumen extracted from Upper Cambrian strata

Uranium and thorium contents refer to whole rock samples; UCM – unidentified complex mixture

sults of geochemical analyses of dispersed organic matter. The estimated portion of source rocks varies from 20 to 30% of the clayey succession thickness, which corresponds to 10–15% of the Middle Cambrian strata thickness.

An attempt to estimate the source rock potential was made for 26 boreholes, in which the lithology and TOC content were determined (Table 9). The estimated thicknesses usually equal 20–30 m. The highest values, *ca*. 40 m, were recorded in Białogóra 2, Hel IG 1 and Łeba 8 boreholes.

The Middle Cambrian strata generally have low dispersed organic matter contents. The highest median of present TOC content in the source rock levels was calculated in the A23-1/88 borehole (0.9 wt.%; Table 9). For the most boreholes, medians of the TOC values do not exceed 0.5 wt.%. The initial total organic carbon (TOC_0) content calculated with the method proposed by Baskin (1997) usually does not exceed 1 wt.% (Table 9). The highest values of TOC_0 were estimated in the boreholes: A23-1/88 – 1.7 wt.%, B16-1/85 – 1.2 wt.% and Białogóra 3 – 1.2 wt.% (Table 9).

It can be generally concluded that the clayey intercalations within the Middle Cambrian strata are poor and locally moderate source rocks.

UPPER CAMBRIAN –TREMADOCIAN

The Upper Cambrian and Tremadocian strata were deposited continuously. They are developed generally as bituminous shales. Their thickness varies from a few to *ca*. 35 metres (Modliński and Podhalańska, 2010).

Thickness of the source rocks and their original TOC_0 content was determined for 22 boreholes (Table 10). The average thickness of source rocks, estimated from available well data (core descriptions, well logs), is *ca*. 90% of the total thickness (Table 10).

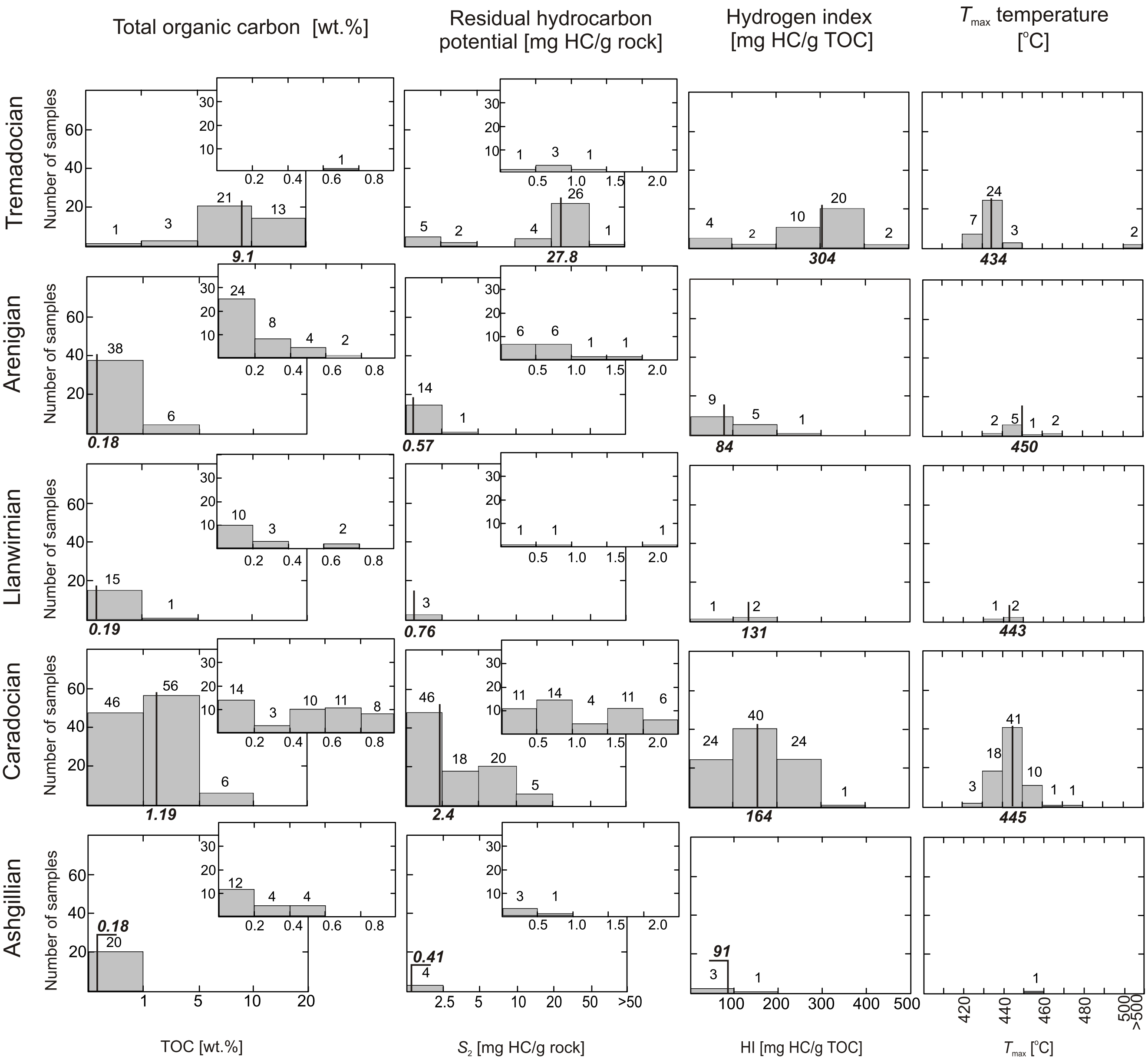

Fig. 10. Histograms of total organic carbon and residual hydrocarbons contents, hydrogen index, T_{max} temperature and median values of the individual parameters and indices for the Ordovician strata of the Polish part of the Baltic region

Median parameter and index values are given in bold and italic

The medians of the present TOC content in this succession calculated for individual boreholes always exceed 3 wt.%. The highest values, above 10 wt.%, were observed in the B3-9/95, B4-1/81, B4-2A/02, B4-N1/01, B6-1/82 and B6-3/02 boreholes (Łeba Block) (Table 10). The lower TOC contents in areas outside of the Łeba Block reveal higher maturity of the organic matter (Table 10).

The initial organic carbon content in the Upper Cambrian–Tremadocian succession was very high and usually exceeded 10 wt.% (Table 10). The highest TOC_0 values were estimated in the boreholes B6-3/02 – 20 wt.%, B4-N1/01 and B6-1/82 – 18 wt.%, and B3-9/95 – 17 wt.% (Table 10).

Generally, it can be concluded that clayey Upper Cambrian–Tremadocian succession is an excellent source rock. The highest initial organic carbon contents – up to 20 wt.% were found in the offshore area (“B” profiles) (Table 10).

CARADOCIAN

The Caradocian strata are developed mainly as black and dark grey claystones of maximum thickness *ca.* 70 m

Table 8

Geochemical characteristics and hydrocarbon potential of the Silurian of the Polish part of the Baltic region

Stratigraphy Index	Llandovery	Wenlock	Ludlow	Pridoli
TOC [wt.%]	0.02 to 10.2 (77) 0.77 (13)	0.02 to 1.51 (127) 0.73 (12)	0.00 to 1.13 (233) 0.19 (14)	0.00 to 0.52 (34) 0.12 (7)
T_{max} [°C]	435 to 534 (43) 447 (9)	425 to 509 (81) 444 (10)	430 to 448 (61) 437 (11)	426 to 435 (3) 427 (1)
R_o [%]	0.68 to 2.3 (18) 1.13 (10)	1.02 to 2.5 (36) 1.20 (9)	0.50 to 1.89 (83) 1.05 (12)	0.50 to 1.02 (15) 0.85 (7)
S_2 [mg HC/g rock]	0.12 to 40.6 (51) 1.51 (11)	0.07 to 3.5 (94) 1.07 (12)	0.08 to 2.1 (77) 0.53 (12)	0.36 to 0.53 (3) 0.37 (1)
$S_1 + S_2$ [mg HC/g rock]	0.25 to 43.7 (51) 2.1 (11)	0.13 to 4.1 (94) 1.48 (12)	0.15 to 3.2 (77) 0.74 (12)	0.42 to 0.55 (3) 0.44 (1)
PI	0.03 to 0.52 (49) 0.23 (10)	0.00 to 0.63 (90) 0.31 (12)	0.00 to 0.59 (77) 0.22 (12)	0.04 to 0.16 (3) 0.14 (1)
HI [mg HC/g TOC]	8 to 436 (51) 115 (11)	7 to 335 (94) 128 (12)	18 to 310 (77) 121 (12)	112 to 230 (3) 161 (1)
BR [mg bit/g TOC]	22 to 196 (15) 120 (5)	39 to 314 (23) 169 (8)	29 to 340 (36) 140 (10)	106 and 117 (2) 112 (1)
Pristane/phytane	1.20 to 2.41 (5) 2.14 (3)	0.86 to 2.28 (4) 1.81 (4)	0.87 to 1.97 (6) 1.62 (5)	no data
Pristane/n-C_{17}	0.37 to 0.71 (5)	0.31 to 0.46 (4)	0.47 to 1.18 (6)	no data
Phytane/n-C_{18}	0.20 to 0.44 (5)	0.20 to 0.41 (4)	0.39 to 1.02 (6)	no data
Kerogen type	II	II	II	II
Maturity	mature/overmature	mature/overmature	mature	mature
Hydrocarbon potential	fair/good	poor/fair	poor	poor

For explanations see Table 2

(Modliński and Podhalańska, 2010). The thickness of the clayey facies estimated from available well data (core descriptions, well logs) constitutes *ca*. 80% of full thickness (Table 11). This thickness was assumed as the source rock interval. Results of geochemical analyses show that *ca*. 80% of the samples have above-threshold TOC contents (Table 11).

An attempt to identify the source rock thickness was made for 18 boreholes, in which the lithology of potential source rocks has been determined and the TOC contents were available (Table 11). The estimated thicknesses were usually about 25 m. The highest one, *ca*. 45 m, was determined in the B21-1/95 borehole (Table 11).

The Caradocian strata have moderately variable organic matter contents. The highest median of the TOC present in the source rock horizons was calculated in the Białogóra 2 – 3.3 wt.%, Żarnowiec 6K – 2.9 wt.% and Żarnowiec IG 1– 2.1 wt.% (Table 11) boreholes. For most of the boreholes it varied from 0.8 to 1.8 wt.%. The estimation of TOC_0 values for the Białogóra 2 and Żarnowiec 6K boreholes indicate *ca*. 6.0 and 5.0 wt.%, respectively (Table 11). Also in two other boreholes the initial organic carbon contents are above 3 wt.% (Hel IG 1 – 3.1 wt.% and Żarnowiec IG 1 – 3.7 wt.%; Table 11).

Generally, the Caradocian claystones have good source rock parameters (TOC_0 = 1.8 wt.%, on average). The highest

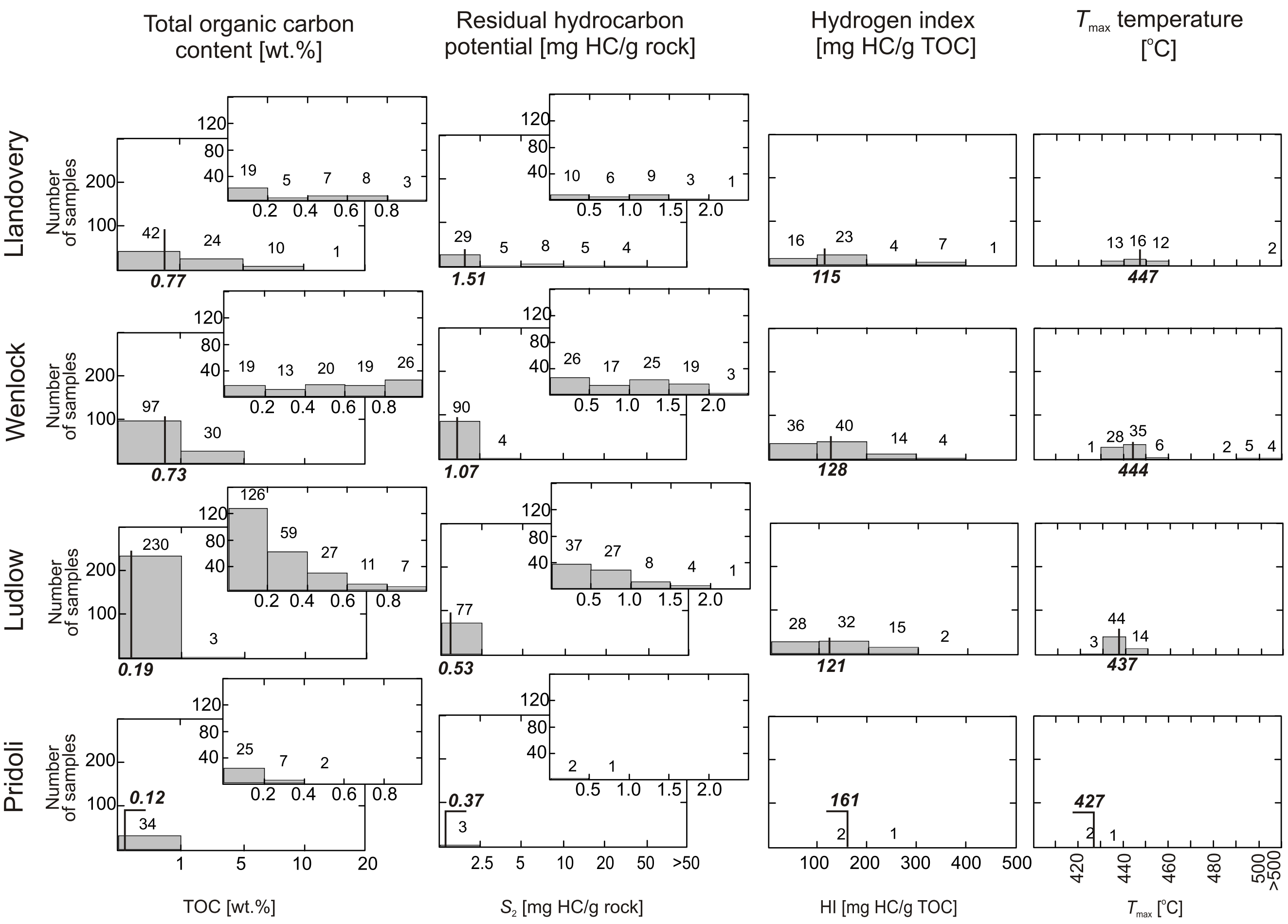

Fig. 11. Histograms of total organic carbon and residual hydrocarbons contents, hydrogen index, T_{max} temperature and median values of the individual parameters and indices for the Silurian strata of the Polish part of the Baltic region

Median parameter and index values are given in bold and italic

organic carbon contents were calculated for boreholes localized onshore in the Żarnowiec Block (Table 11 and Fig. 1).

LLANDOVERY

The Llandovery strata are developed almost entirely as clayey facies: black, dark grey and grey claystones and siltstones with a maximum thickness up to *ca*. 80 m (Modliński and Podhalańska, 2010). Results of Rock-Eval analyses reveal that *ca*. 90% of the samples have above-threshold TOC contents, so that the source rocks should constitute on average 90% of the whole thickness of this division (Table 12). Estimation of source rock thickness was made for 12 boreholes and it varies from 35 to 65 m, mainly from 50 to 60 m (Table 12).

The strata investigated have moderately variable present TOC contents. The highest median values were calculated for the Żarnowiec IG 1 – 3.9 wt.%, B3-9/95 – 3.2 wt.% and B21-1/95 – 2.5 wt.% boreholes (Table 12). For the majority of boreholes values of this index stay below 1.5 wt.% (Table 12).

The highest values of initial organic carbon content were calculated for the Żarnowiec IG 1, B3-9/95 and B21-1/95 boreholes, with TOC_0 contents of 7, 5 and 4.3 wt.%, respectively (Table 12). Generally, the clayey Llandovery strata characterize moderate and locally good source rock indices – median of TOC_0 equals to 1.7 wt.% and the highest initial organic carbon contents were affirmed in boreholes localized in the Żarnowiec and Łeba blocks (Table 12 and Fig. 1).

CONCLUSIONS

In the Polish part of the Baltic region the best source rock parameters and indices are observed for the Upper Cam-

Table 9

Estimated thickness and initial organic carbon content of identified source rocks in the Middle Cambrian strata

Borehole	Total thickness [m]	Source rock thickness [m]	TOC [wt.%]	*n*	R_o [%]	H/C	*x*	TOC_0 [wt.%]
A23-1/88	176.4	25	0.9	6	1.40	*0.65*	0.45	1.7
A8-1/83	159.5	25	0.2	2	2.40	*0.42*	0.46	0.5
B16-1/85	261.5	n.det.#	0.7	1	1.13	*0.75*	0.42	1.2
B21-1/95	241.5	35	0.3	5	0.90	*0.84*	0.40	0.5
B3-9/95	117.3 (n.d.)	20	0.4	7	no data	n.c.	*0.40*	0.6
B4-1/81	194.5	30	0.4	2	0.74	*0.93*	0.37	0.7
B4-2A/02	89 (n.d.)	30	0.4	5	no data	n.c.	*0.37*	0.7
B4-N1/01	84.1 (n.d.)	30	0.5	4	no data	n.c.	*0.37*	0.7
B6-1/82	229.5	20	*0.5*	no data	0.85	*0.87*	0.39	0.8
B6-2/85	187.0	20	0.4	3	no data	n.c.	*0.39*	0.7
B6-3/02	117 (n.d.)	20	0.6	8	no data	n.c.	*0.39*	1.0
B8-1/83	201.0	30	0.6	2	0.76	*0.91*	0.38	0.9
Białogóra 2	261.5	40	0.3	1	no data	n.c.	*0.41*	0.5
Białogóra 3	39 (n.d.)	30	0.7	1	1.01	*0.79*	0.41	1.2
Białogóra 6	275.5	30	0.3	1	no data	n.c.	*0.41*	0.5
Dębki 3	125.5	25	0.4	6	no data	n.c.	*0.43*	0.7
Dębki 4	50.5 (n.d.)	25	0.4	10	1.12	*0.75*	0.43	0.7
Gdańsk IG 1	158.7	20	0.4	7	1.38	*0.66*	0.44	0.8
Hel IG 1	238.0	40	0.4	4	1.24	*0.71*	0.43	0.7
Kościerzyna IG 1	310.7	n.det.	<0.3	0	1.78	*0.55*	n.c.	n.c.
Łeba 8	246.0	40	0.6	13	1.31	*0.68*	0.43	1.0
Malbork IG 1	193.5	30	0.3	14	1.27	*0.70*	0.43	0.6
Malbork 3	106.5 (n.d.)	20	0.3	1	no data	n.c.	*0.43*	0.5
Nowa Kościelnica 1	160.5	20	0.5	14	1.13	*0.75*	0.42	0.8
Słupsk IG 1	97.0	20	0.4	5	4.00	*0.21*	0.46	0.8
Żarnowiec IG 1	273.6	30	0.4	5	1.47	*0.63*	0.44	0.7

TOC – mean present organic carbon content in the source rock levels, *n* – quantity of above-threshold TOC measurements, R_o – reflectance of vitrinite-like macerals, H/C – hydrogen/carbon atomic ratio of kerogen, *x* – relative mass loss of TOC in relation to the maturity described by the H/C value (after Baskin, 1997), TOC_0 – initial organic carbon content, n.det. – not determined, n.d. – not drilled, n.c. – not calculated, values of H/C in italic were calculated from R_o values by the equation of Buchardt and Lewan (1990), TOC and x values in italic were used for calculations by analogy to the neighbouring boreholes, R_o values in italic were calculated from the maturity-depth relation in the individual boreholes, # – value not determined due to unrepresentative sampling

brian–Tremadocian succession. The present TOC content reaches *ca*. 18 wt.%, and, taking into consideration the maturity of these strata (0.7–0.8% R_o), the estimated initial organic carbon content might have been even about 20 wt.%. Usually, the TOC contents are at the level of several per cent. The best source rocks occur in the Łeba Block where organic matter is less transformed. Lower TOC values were observed in the remaining area but, taking into account the maturity of the organic matter, the initial TOC_0 values were also a dozen or so per cent. The Alum Shales from Southern Sweden described by Lewan and Buchardt (1989), Buchardt and Lewan (1990), Leventhal (1991), Kanev *et al*. (1994), Bharati *et al*. (1992, 1995), Schleicher *et al*. (1998) and Pedersen *et al*. (2006) are very similar to this unit.

Additional sources of hydrocarbons can be considered to be the Caradocian (Ordovician) and the Llandovery (Silurian) source rocks. The calculated mean initial organic carbon contents in the Caradocian source rocks in the specific boreholes vary from 1 to 6 wt.%, usually 1–2.5 wt.%. The best source rocks within this level occur in the Łeba and in the Żarnowiec

Table 10

Estimated thickness and initial organic carbon content of source rocks identified in the Upper Cambrian–Tremadocian succession

Borehole	Total thickness [m]	Source rock thickness [m]	TOC [wt.%]	*n*	R_o [%]	H/C	*x*	TOC_0 [wt.%]
A23-1/88	11.1	10	6.3	5	1.35	*0.67*	0.44	11
A8-1/83	18.5	16	5.2	13	2.32	*0.44*	0.46	10
B16-1/85	27.0	24	6.6	9	1.01	0.74	0.43	12
B21-1/95	34.5	30	9.3	30	no data	0.87	0.40	15
B3-9/95	4.7	4	13.2	7	no data	1.10	0.24	17
B4-1/81	6.5	5	10.8	5	0.73	1.01	0.33	16
B4-2A/02	13.5	11	10.2	19	0.74	*0.93*	0.37	16
B4-N1/01	13.4	11	11.3	11	no data	0.94	0.37	18
B6-1/82	26.5	24	10.9	6	0.84	*0.87*	0.39	18
B6-2/85	24.0	22	9.8	4	no data	0.95	0.37	16
B6-3/02	26.5	24	12.0	24	no data	0.91	0.39	20
B7-1/91	6.0	4	8.8	16	0.72	0.93	0.38	14
Białogóra 1	17.5	16	4.9	6	no data	n.c.	*0.42*	8
Białogóra 3	14.0	13	4.5	13	1.24	0.77	0.42	8
Białogóra 6	16.5	15	3.2	10	no data	n.c.	*0.42*	6
Dębki 3	12.0	11	6.0	6	1.18	0.81	0.41	10
Dębki 4	12.5	11	3.6	16	1.12	*0.75*	0.42	6
Hel IG 1	5.0	4	5.8	4	*1.15*	*0.74*	0.42	10
Łeba 8	11.5	11	7.2	6	*1.17*	*0.73*	0.42	12
Piaśnica 2	17.5	16	8.0	2	*1.22*	*0.71*	0.43	14
Żarnowiec IG 1	9.6	9	4.6	6	1.34	*0.67*	0.44	8
Żarnowiec 6K	38.5	35	7.0	8	no data	0.75	0.42	12

For explanations see Table 9

Table 11

Estimated thickness and initial organic carbon content of source rocks identified in the Caradocian (Ordovician) strata

Borehole	Total thickness [m]	Source rock thickness [m]	TOC [wt.%]	*n*	R_o [%]	H/C	*x*	TOC_0 [wt.%]
B21-1/95	54.0	45	1.2	6	no data	*0.87*	0.40	2.1
B3-9/95	37.0	30	1.7	2	no data	*1.10*	0.24	2.3
B4-N1/01	37.5	30	0.9	1	no data	*0.94*	0.37	1.4
Białogóra 2	34.5	25	3.3	12	*1.24*	*0.70*	0.43	6
Białogóra 3	35.0	25	0.8	6	*1.24*	*0.70*	0.43	1.4
Białogóra 6	32.0	25	0.8	3	*1.24*	*0.70*	0.43	1.3
Dębki 3	34.5	25	1.5	10	1.20	*0.70*	0.43	2.6
Gdańsk IG 1	13.3	10	0.9	9	*1.30*	*0.69*	0.43	1.6
Hel IG 1	25.5	20	1.8	7	1.15	*0.74*	0.42	3.1
Kościerzyna IG 1	15.0	10	0.8	1	1.72	*0.57*	0.46	1.5
Lębork IG 1	21.1	n.det.	<0.3	0	2.30	n.c.	n.c.	n.c.
Łeba 8	36.0	25	1.3	11	1.17	*0.73*	0.43	2.3
Malbork IG 1	9.5	n.det.	<0.3	0	1.23	n.c.	n.c.	n.c.
Nowa Kościelnica 1	11.0	10	0.6	3	0.99	*0.80*	0.41	1.0
Piaśnica 2	32.5	25	1.2	2	no data	n.c.	*0.43*	2.1
Słupsk IG 1	22.0	15	0.5	4	4.20	*0.19*	0.47	0.9
Żarnowiec IG 1	32.2	25	2.1	6	1.25	*0.70*	0.43	3.7
Żarnowiec 6K	34.5	25	2.9	9	no data	n.c.	*0.43*	5

Values of H/C in italic were calculated from R_o values by equation worked out by Buchardt and Lewan (1990) or, in the case of lack of R_o measurements the same values were taken as for the Upper Cambrian–Tremadocian succession; for other explanations see Table 9

Table 12

Estimated thickness and initial organic carbon content of identified source rocks in the Llandovery (Silurian) strata

Borehole	Total thickness [m]	Source rock thickness [m]	TOC [wt.%]	*n*	R_o [%]	H/C	*x*	TOC_0 [wt.%]
B21-1/95	63.0	55	2.5	2	*0.90*	*0.84*	0.42	4.3
B3-9/95	53.0	50	3.2	8	*0.70*	*0.95*	0.37	5
B4-N1/01	59.0	55	1.1	1	*0.70*	*0.95*	0.37	1.7
B6-1/82	60.5	55	1.2	3	0.82	*0.88*	0.39	2.0
Dębki 3	63.0	55	0.6	1	*1.20*	*0.72*	0.43	1.0
Gdańsk IG 1	40.0	35	1.7	12	1.27	*0.70*	0.44	3.0
Hel IG 1	49.5	45	1.1	6	0.93	*0.83*	0.40	1.8
Kościerzyna IG 1	71.0	65	0.9	5	1.69	*0.57*	0.46	1.6
Malbork IG 1	42.5	40	1.0	5	1.12	*0.75*	0.42	1.7
Piaśnica 2	66.5	60	0.4	1	*1.20*	*0.72*	0.43	0.6
Żarnowiec IG 1	63.0	55	3.9	7	1.21	*0.72*	0.43	7
Żarnowiec 6K	65.5	60	0.6	3	*1.20*	*0.72*	0.43	1.0

For explanations see Table 9

blocks, where calculated initial TOC_0 values equal usually 2–6 wt.%. The TOC_0 values of the Llandovery source rocks is usually 1–2 wt.%. The thickness of these units, usually from 20 to 30 m and from 50 to 60 m, respectively point to them as possible sources of shale gas (Poprawa and Kiersnowski, 2008).

Due to their short distance to the reservoirs, the clayey intercalations within the Middle Cambrian strata cannot be neglected as source rocks. Their TOC content is rather low and rarely exceeds 1 wt.%. These deposits are the deepest buried and, thus, have the highest maturities. This is responsible for their low present HC potential. The proximity of sandstones caused partial oxidation of organic matter present in the claystones and potential loss of their generation capabilities. Estimated initial TOC_0 values in individual boreholes do not differ significantly and vary from 0.5 to 1.7 wt.%.

Oil-prone Type-II kerogen occurs in all source rock levels of lower Paleozoic strata in the Polish part of the Baltic region. It has low organic sulphur contents (Więcław *et al*., 2010*a*) and was deposited under anoxic or sub-oxic conditions. The maturity of the strata investigated change from the initial phase of the “oil window” in both the Silurian and Ordovician strata in the northeastern part of the Łeba Block to the overmature stage in the southwestern part of the study area in the deeply buried sediments at the contact with the Teisseyre-Tornquist Zone.

From the organic geochemistry point of view all source rock units analysed have suitable parameters and indices (quantity, quality and maturity) for generation of oils and natural gases present in the Middle Cambrian sandstone reservoirs (Kotarba, 2010; Więcław *et al*., 2010*b*). Also, the tectonics of the area investigated, showing contact of the lower parts of the Silurian strata with the Cambrian strata (Poprawa *et al.*, 1999; Pokorski, 2010), do not exclude any of the source rocks identified from being sources for the Middle Cambrian reservoir sandstones. The geochemical characteristics of the oils show good correlation with source rocks occurring in entire lower Paleozoic sequence (Więcław *et al*., 2010*b*).

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