



Origin of oils accumulated in the Middle Cambrian reservoirs of the Polish part of the Baltic region

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Wi cław D., Kotarba M. J. and Kowalski A. (2010) – Origin of oils accumulated in the Middle Cambrian reservoirs of the Polish part of the Baltic region. *Geol. Quart.*, 54 (2): 205–216. Warszawa.

We have examined 21 samples of crude oils accumulated in the Middle Cambrian sandstone reservoirs from the Polish part of the Baltic region. All the crude oils have similar parameters and indices, which suggests generation from the same source rock. Evaporative fractionation and biodegradation processes were detected in oil collected from the B4-N1/01 borehole. All crude oils have high gravities and low-sulphur contents, less than 0.3 wt.%, which suggests that their source rock contained low-sulphur kerogen deposited in a clastic environment. A low asphaltene content (below 0.3 wt.%) and high saturate/aromatic hydrocarbon ratios indicate long migration distances or high thermal maturities. The longest migration distance was probably attained by oils from the arnowiec and B16 deposits. The biomarker data indicate an algal origin for the source organic matter deposited under conditions of clastic sedimentation. The stable carbon isotope data support this observation. The maturity of the oils analysed varies from *ca.* 0.75 to *ca.* 1.05% on the vitrinite reflectance scale. Unlike the B6, B16, D bki and arnowiec accumulations, oils from the B3 and B4 accumulations reveal the lowest maturity.

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Key words: Baltic region, lower Paleozoic, oil origin, biomarkers, stable carbon isotopes, oil-oil correlation.

INTRODUCTION

Distinct oil shows in the Cambrian strata from the Polish part of the Baltic region were encountered for the first time in the Olsztyn IG 2 borehole drilled in the 1960s. Since then, four small oil accumulations (arnowiec, arnowiec W, D bki and Białogóra) have been discovered in the Polish onshore area. More recently, oil inflow in the Malbork IG 1 borehole has been reported (Sikorski and Solak, 1991; Dom alski *et al.*, 2004). The first offshore oil accumulation was discovered in 1981 (B3 structure) in Middle Cambrian sandstones. Apart from this site, oil deposits: B6, B8, B16, B24 and B34 and gas-condensate deposits: B4, B6, B16 and B21 were localized in the anticlinal structures of the Łeba Block (Dom alski and Mazurek, 2003; Dom alski *et al.*, 2004). All discovered on- and offshore oil and gas accumulations are hosted in the *Paradoxides paradoxissimus* Zone of Middle Cambrian strata (Karnkowski *et al.*, 2010). Total reserves of discovered accumulations are 10 Gm³ of gas and *ca.* 30 Mt of oil (Dom alski *et al.*, 2004). The undiscovered hydrocarbons in the Polish Exclusive Economic Zone of the Baltic Sea are estimated at

ca. 100 Gm³ of gas and several hundred-million metric tonnes of oil (Dom alski *et al.*, 2004).

The main purpose of the present study is the characterization of oils accumulated in the Middle Cambrian strata of the Polish part of the Baltic region (Fig. 1), identification of their source rocks, maturity, migration distance and secondary processes.

Preliminary geochemical characteristics of oils accumulated in Middle Cambrian sandstones from the Polish part of the Baltic Sea and the adjacent onshore area have been previously reported by e.g., Reicher (1995), Schleicher *et al.* (1998), Karnkowski (1999) and Bojakowska and Sokołowska (2001). The origin of natural gases accumulated in the Middle Cambrian reservoirs in this region is discussed by Kotarba (2010). Apart from the Cambrian reservoirs, oil accumulations and shows have also been discovered in Precambrian, Ordovician, Silurian and Devonian strata in other countries of the Baltic region (Russia, Lithuania, Latvia and Sweden) (Zdanaviciute and Bojesen-Koefoed, 1997; Zdanaviciute and Lazauskiene, 2004, 2007; Pedersen *et al.*, 2006). Oils reservoired in Ordovician and younger strata have been thought to originate from a source different than the Middle Cambrian oils (Zdanaviciute and Lazauskiene, 2004).

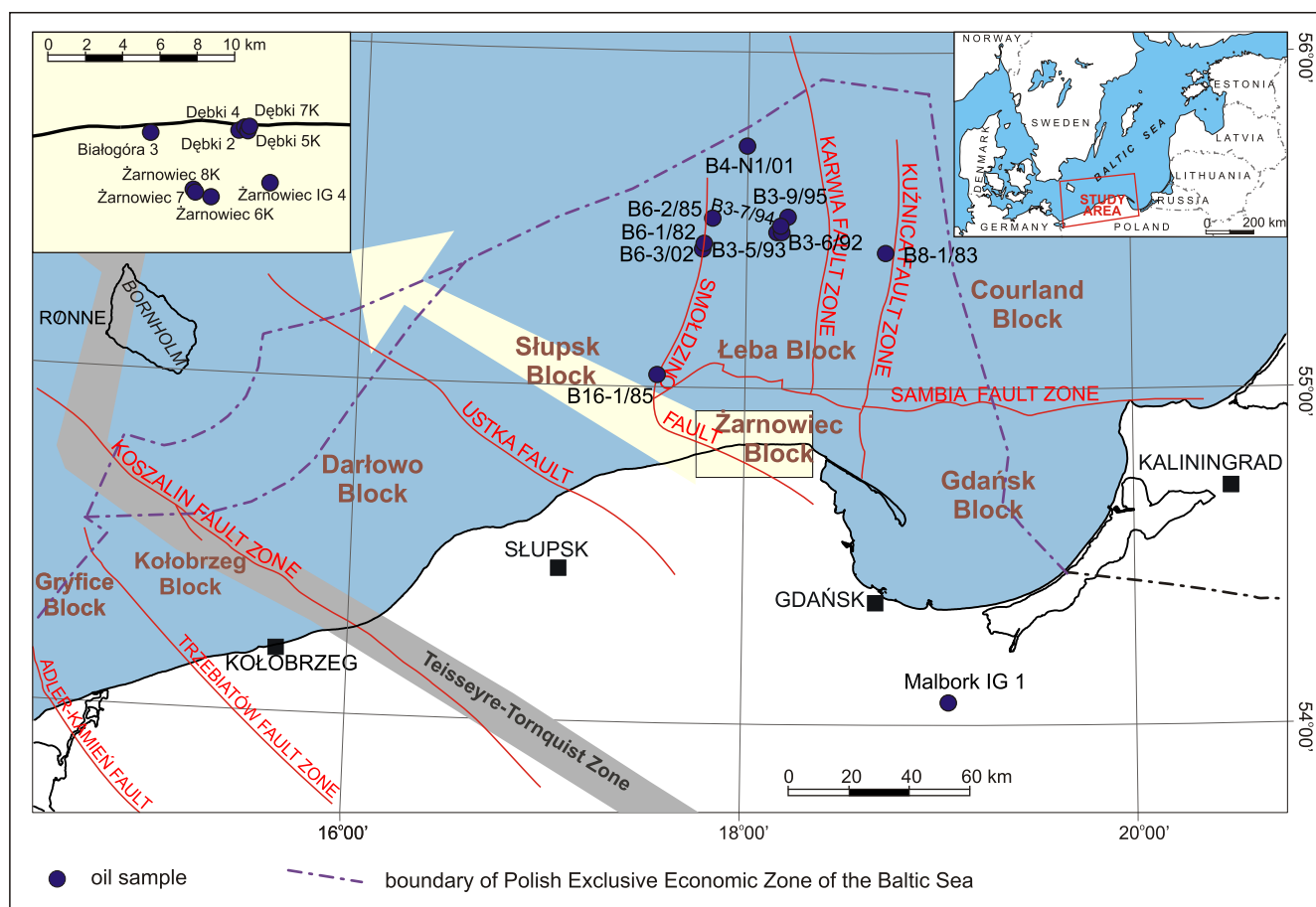


Fig. 1. Sketch map showing location of crude oil sampling sites

Fault system after Pokorski (2010)

SAMPLES AND ANALYTICAL PROCEDURES

SAMPLES

In total, 21 crude oil samples were collected (Table 1) from onshore [Białogóra 3 (Bg), Dębki (Db) 2, 4, 5K and 7K, Malbork (Mb) IG 1, Żarnowiec (Zn) 6K, 7, 8K and IG 4] and offshore [B3-5/93, B3-6/92, B3-7/94, B3-9/95, B4-N1/01, B6-1/82, B6-2/85, B6-3/02, B8-1/83 and B16-1/85 (2 samples)] boreholes (Fig. 1). All the boreholes sampled are producing except for the Malbork IG 1 borehole.

ANALYTICAL PROCEDURE

The oils were analysed for API gravity, according to the Polish Standard PN-90/C-04004, and for sulphur content with a *Leco SR-12* analyser. Before the deasphalting, samples were topped under nitrogen (5 hrs) at a temperature of 60°C. 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. For stable carbon isotope analyses the oils and their individual fractions were combusted in an on-line system. Stable carbon isotope analyses were performed using a *Finnigan Delta Plus* mass spectrometer. The stable carbon isotope data are presented in the δ -notation relative to the V-PDB standard (Coplen, 1995), at an estimated analytical precision $\pm 0.2\%$.

All the oils were analysed with high resolution gas chromatography. For this purpose 1 μ l of sample diluted in CS_2 was introduced into a split-less injector of a *Hewlett Packard 5890* series II GC held at a temperature of 300°C. From there the sample was transferred through a 50 m × 0.2 mm *Agilent DB1* column (0.5 μ m film thickness) using a constant, 0.3 ml/min flow of nitrogen as the carrier gas. The column oven was programmed to hold at 30°C for 5 minutes and then to increase to 320°C at 3°C/min, at which point it was held for 20 minutes. Components eluting the column were detected with a flame ionization detector (FID) held at 325°C.

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 μ m film thickness,

Table 1

Gravity, sulphur content, fractions and stable carbon isotope composition of crude oils reservoirised in the Middle Cambrian sandstones

Borehole/sample	Depth [m]	Gravity [°API]	Sulphur [wt.%]	Fractions [wt.%]				Sat/Aro	Stable carbon isotopes ¹³ C [‰]				
				Sat	Aro	Res	Asph		Sat	Oil	Aro	Res	Asph
B16-1/85 (1)	1876–1887	60.2	0.04	96.7	2.0	1.3	0.01	48.4	–30.3	–29.8	–28.9	–29.0	–28.2
B16-1/85 (2)	1904–1915	45.8	0.06	90.9	4.8	4.1	0.2	18.9	–29.7	–29.7	–29.0	–29.0	–29.5
B3-5/93	1714.5–1775	43.2	0.06	84.2	13.3	2.4	0.1	6.3	–30.0	–29.9	–29.4	–29.7	–29.1
B3-6/92	1389–1410, 1415–1458	60.3	0.04	79.9	17.4	2.8	0.03	4.6	–30.6	–30.3	–29.9	–29.9	–28.4
B3-7/94	1420–1424, 1428–1447	41.7	0.04	82.7	15.8	1.5	0.03	5.2	–30.5	–30.5	–29.9	–29.9	–29.3
B3-9/95	1478–1479.8	43.6	0.10	85.2	12.2	2.5	0.1	7.0	–30.0	–29.9	–29.6	–30.0	–29.7
B4-N1/01	1201–1208	47.6	0.23	78.4	13.2	8.4	0.03	6.0	–30.3	–29.9	–29.4	–29.7	–28.9
B6-1/82	1414–1480	62.1	0.05	95.4	2.5	2.1	0.05	38.9	–29.8	–29.6	–29.2	–29.3	–28.8
B6-2/85	1464–1472	43.5	0.05	88.2	8.5	3.2	0.1	10.4	–29.8	–29.7	–29.3	–29.6	–28.9
B6-3/02	1447–1476	60.2	0.05	84.2	9.3	6.6	0.03	9.1	–30.0	–29.8	–29.4	–29.5	–29.2
B8-1/83	2200–2224	41.8	0.04	79.8	16.4	3.5	0.3	4.9	–30.7	–30.4	–29.8	–29.6	–29.3
Białogóra 3	2713.4–2733	49.2	0.03	86.7	11.0	2.3	0.02	7.9	–30.9	–30.7	–30.0	–30.2	–29.1
D bki 2	2675–2723	46.3	0.03	88.1	9.7	1.8	0.4	9.1	–30.2	–30.0	–29.2	–29.3	–30.0
D bki 4	2692–2728	51.8	0.03	85.3	11.9	2.8	0.07	7.2	–30.9	–31.0	–30.6	–30.2	–30.6
D bki 5K	2826–2841	48.5	0.03	84.6	12.1	3.3	0.04	7.0	n.a.	n.a.	n.a.	n.a.	n.a.
D bki 7K	2785.5–2834	56.4	0.04	85.2	11.5	3.1	0.2	7.4	–31.0	–30.9	–30.6	–30.3	–30.9
Malbork IG 1	3234–3270	n.a.	n.a.	91.0	5.8	2.4	0.8	15.7	–30.0	–29.9	–29.4	–28.9	–29.2
arnowiec IG 4	2738.2–2771.8	47.6	0.01	92.2	6.8	1.0	0.04	13.6	–31.1	–30.7	–30.0	–30.4	–29.7
arnowiec 6K	2874–2892	48.5	0.10	97.0	2.4	0.5	0.1	40.4	–30.3	–30.2	–29.3	–29.2	–29.4
arnowiec 7	2721–2732	54.7	0.01	87.8	10.7	1.5	0.1	8.2	–30.9	–30.8	–30.5	–30.3	–30.6
arnowiec 8K	2807–2836	76.0	0.02	94.2	2.0	3.8	0.03	48.2	–30.4	–30.1	–29.2	–29.5	–28.9

Sat – saturated hydrocarbons, aro – aromatic hydrocarbons, Res – resins, Asph – asphaltenes, n.a. – not analysed

bonded phase: 14% cyanopropylphenyl – 86% dimethylpolysiloxane copolymer). The GC (gas chromatograph) was directly interfaced to a *JEOL GC-Mate* magnetic sector MS. Splitless injection was made to the injector operated isothermally at 300°C. The temperature program was as follows: 50 to 150°C at 50°C/min, 150 to 300°C at 3°C/min and 300°C hold for 9 minutes. Helium was used as a carrier gas at 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* 187.1486 (diamondoids), *m/z* 191.1800 (terpanes), *m/z* 217.1956 (steranes), *m/z* 231.1174 (triaromatic steroids) and *m/z* 253.1956 (monoaromatic steroids). Tentative peak identifications were based on elution time and confirmed in many cases with mass spectra (Philp, 1985) and MS-MS.

The aromatic hydrocarbon fractions of the oils were analysed with the GC for phenantrene and its derivatives. Analysis was carried out with an *Agilent 7890A* gas chromatograph equipped with fused silica capillary column (60 m × 0.32 mm i.d.) coated with 95% methyl/5% phenylsilicone phase (DB-5MS, 0.25 μm film thickness). Helium was used as a carrier gas. The GC oven was programmed from 40 to 300°C at a rate of 3°C min⁻¹. The gas chromatograph was coupled with a

5975C inert mass selective detector (MSD). The MS was operated at an ion source temperature of 200°C, ionisation energy of 70 eV, and a cycle time of 1 sec in the mass range from 40 to 600 Daltons.

RESULTS AND DISCUSSION

IDENTIFICATION OF SECONDARY PROCESSES

Crude oil in accumulations may undergo many secondary changes, including biodegradation, water-washing, oxidation, fractional evaporation and thermal cracking (Blanc and Connan, 1994; Peters *et al.*, 2005).

Biodegradation is usually recognized by analysis of *n*-alkanes and acyclic isoprenoids in the saturated hydrocarbon fraction, or by C₆–C₇ hydrocarbon distributions in the whole oil (Peters *et al.*, 2005). Water-washing usually coincides with biodegradation and these processes, together with oxidation and evaporation of low-boiling fractions affect most oil geochemical parameters (e.g., Thompson, 1983, 2010; Palmer, 1984, 1993; Blanc and Connan, 1994; Napitupulu *et al.*, 2000; Masterson *et al.*, 2001; Akinlua *et al.*, 2006).

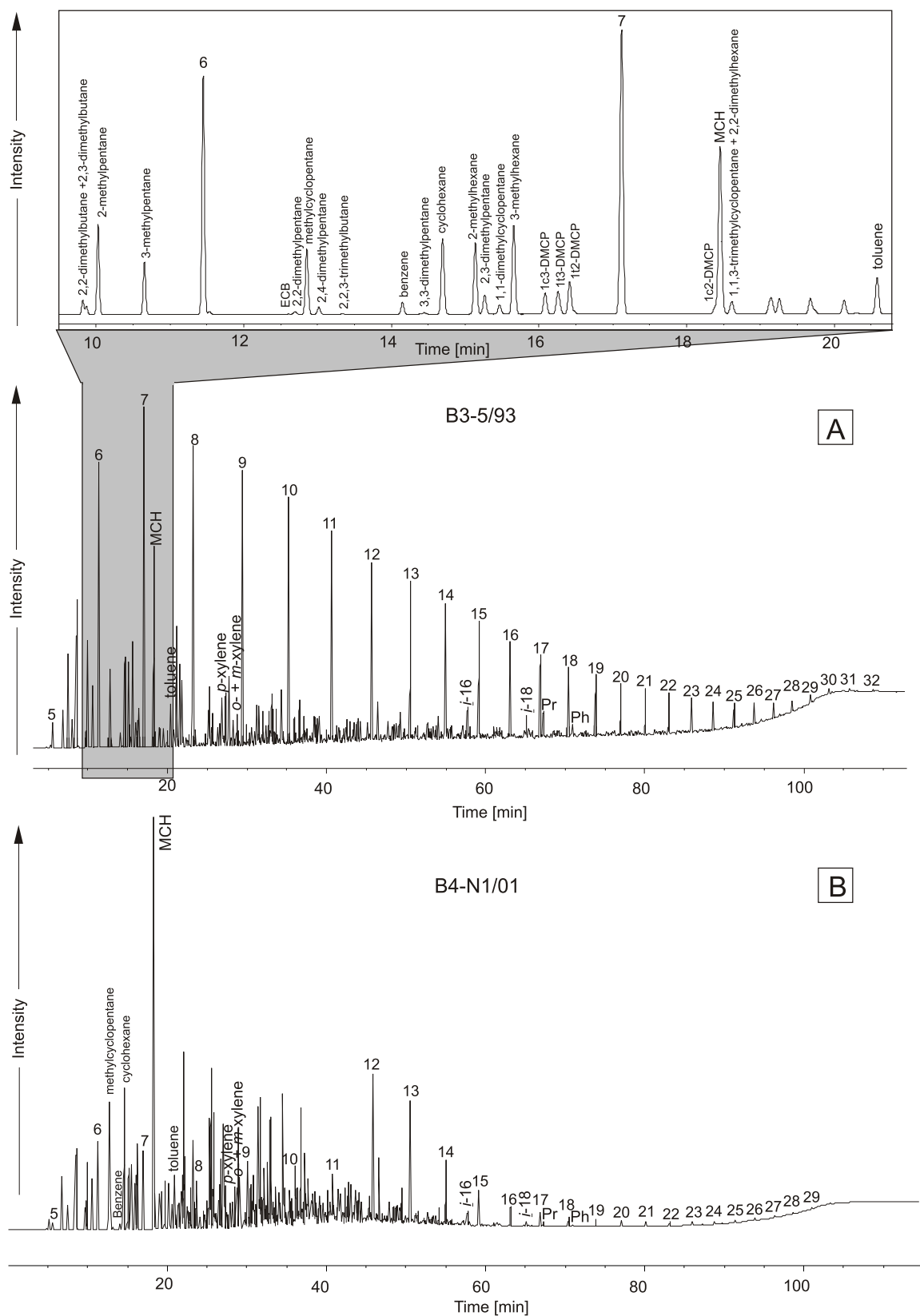


Fig. 2. Whole oil chromatogram of (A) B3-5/93 and (B) B4-N1/01 samples

Numbers refer to carbon atoms in the *n*-alkane chain, ECB – ethylcyclobutane, MCH – methylcyclohexane, DMCP – dimethylcyclopentane, Pr – pristane, Ph – phytane

Table 2

Indices calculated based on whole oil GC analysis

Borehole/ sample	Toluene/ <i>n</i> -C ₇ H ₁₆	<i>n</i> -C ₇ H ₁₆ / MCH	HR	HHI	CH/ MCH	IHR	<i>n</i> -C ₇ H ₁₆ / 2-MH	m-+o-+p- xylene/ <i>n</i> -C ₈ H ₁₈	Temp [°C]	C ₁₁ -index	CPI ₍₁₇₋₂₃₎	Pr/ Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈
B16-1/85 (1)	0.10	2.01	58.5	2.54	0.28	5.01	3.30	0.23	130	0.20	1.09	3.68	0.34	0.13
B16-1/85 (2)	0.19	1.70	68.1	1.66	0.06	0.97	6.53	0.40	116	0.18	1.05	2.16	0.35	0.21
B3-5/93	0.13	1.59	47.7	1.89	0.41	1.90	4.10	0.17	124	0.11	1.05	1.81	0.42	0.27
B3-6/92	0.13	1.58	45.1	1.99	0.45	1.96	3.88	0.34	125	0.12	1.05	2.92	0.43	0.17
B3-7/94	0.12	1.52	44.9	1.87	0.42	1.93	3.89	0.34	124	0.12	1.05	2.35	0.43	0.21
B3-9/95	0.15	1.56	44.9	1.80	0.38	1.57	4.15	0.35	123	0.12	1.05	1.96	0.43	0.25
B4-N1/01	0.34	0.17	6.9	0.25	0.29	0.48	2.57	2.01	124	0.12	1.10	2.31	0.51	0.31
B6-1/82	0.06	2.15	51.0	2.77	0.36	5.33	2.72	0.19	130	0.22	1.13	3.27	0.38	0.18
B6-2/85	0.11	1.93	52.3	2.53	0.39	5.37	3.21	0.31	128	0.13	1.04	2.97	0.34	0.13
B6-3/02	0.09	2.25	55.5	3.15	0.39	4.30	2.98	0.09	130	0.19	1.06	2.69	0.36	0.17
B8-1/83	0.15	1.33	41.5	1.65	0.41	1.44	4.14	0.38	125	0.11	1.06	2.05	0.44	0.25
Białogóra 3	0.20	1.62	46.3	2.33	0.45	2.67	3.40	0.19	132	0.11	1.05	2.61	0.37	0.16
D bki 2	0.15	1.61	47.8	2.23	0.40	2.62	3.47	0.38	131	0.12	1.03	2.00	0.36	0.20
D bki 7K	0.14	1.71	47.3	2.53	0.44	2.77	3.28	0.16	132	0.13	1.04	2.86	0.35	0.14
arnowiec IG 4	0.22	1.46	45.9	1.92	0.38	2.15	3.69	0.47	130	0.11	1.05	1.89	0.40	0.24
arnowiec 6K	0.14	1.79	65.4	2.07	0.20	3.45	4.02	0.23	129	0.20	0.97	4.23	0.38	0.11
arnowiec 7	0.14	1.69	47.0	2.45	0.39	3.52	2.86	0.15	134	0.12	1.06	2.85	0.31	0.13
arnowiec 8K	0.13	1.83	47.3	2.83	0.42	3.47	2.82	0.08	134	0.24	1.14	3.47	0.35	0.16

MCH – methylcyclohexane; HR (heptane ratio) = $100 \times n\text{-C}_7\text{H}_{16} / (\text{CH} + \text{C}_7\text{HCs})$, CH – cyclohexane, HCs – hydrocarbons; HHI = $(n\text{-C}_6\text{H}_{14} + n\text{-C}_7\text{H}_{16}) / (\text{CH} + \text{MCH})$; IHR (isoheptane ratio) = $(2\text{-} + 3\text{-MH}) / (1\text{c}3\text{-} + 1\text{r}3\text{-} + 1\text{r}2\text{-DMCPs})$, MH – methylhexane; Temp = $140 + 15[\ln(2,4\text{-DMP}/2,3\text{-DMP})]$ (Mango, 1997), DMP – dimethylpentane; C₁₁-index = $n\text{-C}_{11} / (n\text{-C}_{10} \text{ thru } n\text{-C}_{30})$ (Lewan and Buchardt, 1989); CPI₍₁₇₋₂₃₎ = $[(\text{C}_{17} + \text{C}_{19} + \text{C}_{21}) + (\text{C}_{19} + \text{C}_{21} + \text{C}_{23})] / [2 * (\text{C}_{18} + \text{C}_{20} + \text{C}_{22})]$, for other explanations see Figure 2

The whole oil GC analysis of the oils analysed indicated that in almost all samples *n*-C₆-*n*-C₇ hydrocarbons are the dominant components (Fig. 2A). Only in the oil collected from the B4-N1/01 borehole methylcyclohexane prevails (Fig. 2B). In the oil collected from the interval of 1 904–1 915 m in the B16-1/85 borehole [sample B16-1/85 (2)] the dominating component is *n*-C₁₀H₂₂. Oil sampled from the B4-N1/01 borehole has low values of *n*-heptane/methylcyclohexane, heptane (HR) and isoheptane (IHR) ratios, and increased values of the toluene/*n*-heptane ratio (Table 2; Figs. 3 and 4) indicating biodegradation processes (Thompson, 1983). Additionally, other indices of light hydrocarbons (Tables 2 and 3; Figs. 5 and 6) calculated for this oil differentiates it from the other oils studied. The Halpern C₇ hydrocarbon ratios (Halpern, 1995) (Table 3; Figs. 5 and 6) show good correlation of all oils analysed except for the previously mentioned two samples: B4-N1/01 and B16-1/85 (2). While the distinctness of the first sample was explained above the hydrocarbon composition of the second one is a typical. The very high values of almost all TR indices (Table 3 and Fig. 5) are probably the result of evaporation of light hydrocarbons from this oil during long storage.

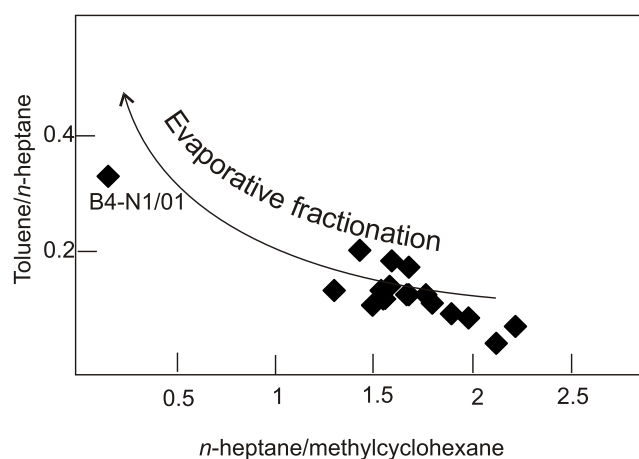


Fig. 3. Toluene/*n*-heptane ratio versus *n*-heptane/methylcyclohexane ratio

Scheme after Thompson (1987)

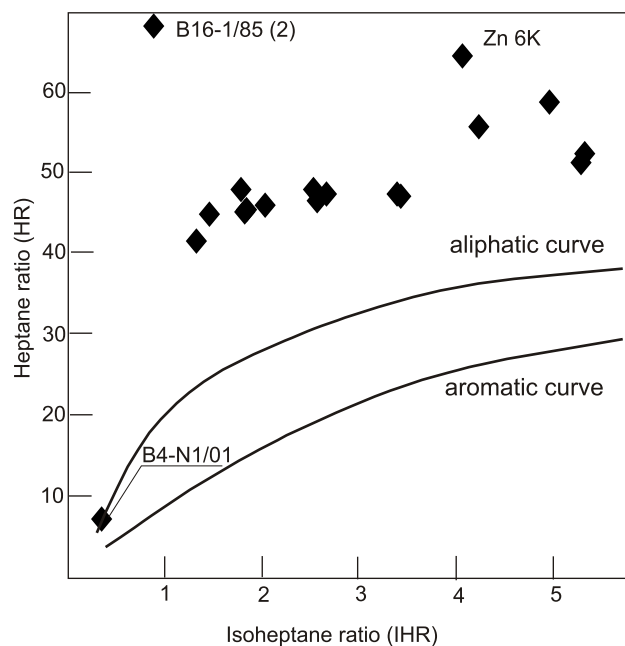


Fig. 4. Heptane ratio versus isoheptane ratio

Kerogen type curves after Thompson (1983)

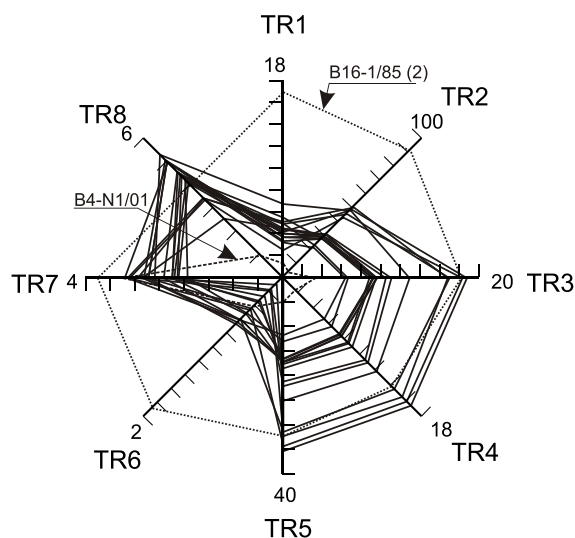


Fig. 5. Star diagram of C_7 oil transformation ratios

Scheme of star diagram after Halpern (1995);
explanation of indices as in Table 3

Table 3

Values of Halpern (1995) C_7 ratios

Borehole	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	C1	C2	C3	C4
B16-1/85 (1)	5.17	50.7	16.7	15.4	32.1	0.19	2.96	3.43	0.03	0.37	0.18	0.05
B16-1/85 (2)	17.0	91.6	18.1	14.0	32.1	1.87	3.78	4.01	0.02	0.37	0.08	0.06
B3-5/93	4.05	30.9	9.5	7.5	17.0	0.64	2.84	5.10	0.02	0.62	0.21	0.08
B3-6/92	3.73	28.4	9.2	7.3	16.5	0.67	2.74	5.02	0.02	0.62	0.23	0.06
B3-7/94	3.38	28.1	9.1	7.2	16.3	0.44	2.74	5.02	0.02	0.63	0.22	0.06
B3-9/95	4.55	31.2	9.5	7.5	17.1	0.60	2.87	2.56	0.02	0.32	0.10	0.03
B4-N1/01	1.35	4.0	3.3	1.5	4.8	0.41	3.26	0.97	0.08	0.62	0.22	0.06
B6-1/82	2.56	43.4	18.2	16.0	34.2	0.46	3.12	3.38	0.03	0.38	0.19	0.05
B6-2/85	4.97	46.1	16.9	14.4	31.3	0.61	3.17	3.46	0.02	0.38	0.17	0.05
B6-3/02	4.23	49.2	18.7	16.5	35.2	0.00	3.22	4.98	0.02	0.54	0.27	0.07
B8-1/83	3.25	21.9	6.3	5.3	11.6	0.61	2.43	4.58	0.02	0.61	0.23	0.06
Białogóra 3	5.53	28.2	8.7	8.3	17.1	0.35	2.15	4.38	0.02	0.50	0.30	0.07
D bki 2	4.54	29.3	9.0	8.4	17.5	0.52	2.26	4.55	0.02	0.53	0.28	0.07
D bki 7K	4.09	29.3	9.4	8.9	18.4	0.33	2.26	4.45	0.02	0.51	0.29	0.07
arnowiec IG 4	5.00	23.2	6.6	6.3	12.9	0.51	1.95	4.23	0.03	0.52	0.27	0.07
arnowiec 6K	6.78	48.6	12.9	12.1	25.0	0.09	2.61	5.32	0.03	0.54	0.25	0.08
arnowiec 7	4.42	31.4	11.0	11.0	22.0	0.27	2.22	4.19	0.03	0.46	0.30	0.08
arnowiec 8K	3.74	29.8	10.4	10.6	21.0	0.17	2.13	4.10	0.03	0.45	0.31	0.08

TR1 = toluene/1,1-DMCP, DMCP – dimethylcyclopentane; TR2 = $n-C_7H_{16}/1,1$ -DMCP; TR3 = 3-methylhexane/1,1-DMCP; TR4 = 2-methylhexane/1,1-DMCP; TR5 = P2/1,1-DMCP, P2 = 2-methylhexane + 3-methylhexane; TR6 = 1-*cis*-2-DMCP/1,1-DMCP; TR7 = 1-*trans*-3-DMCP/1,1-DMCP; TR8 = P2/P3, P3 = 2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 3,3-dimethylpentane + 3-ethylpentane; C1 = 2,2-dimethylpentane/P3; C2 = 2,3-dimethylpentane/P3; C3 = 2,4-dimethylpentane/P3; C4 = 3,3-dimethylpentane/P3

Table 4

Selected biomarker characteristics of crude oils

Borehole/ sample	C ₂₇	C ₂₈	C ₂₉	Gam/ Hop	Dia/ Hop	Bis/ Hop	C ₂₆ / C ₂₄	Mor/ Hop	H ₃₁ S/ (S+R)	C ₂₉ SR	C ₂₉	C ₂₉ Ts/ C ₂₉ H	Ts/ Tm	Gam/ C ₃₁ Hop	Dia/ Reg	TA(I)/ TA(I + II)	C ₂₉ ster [ppm]
B3-6/92	0.69	0.11	0.21	0.40	0.53	0.08	5.00	0.37	0.51	0.45	0.61	0.99	1.98	1.52	1.85	0.56	6.9
B3-7/94	0.74	0.07	0.19	0.58	0.55	0.00	4.85	0.28	0.56	0.45	0.62	1.07	2.36	1.77	2.51	0.64	4.2
B4-N1/01	0.63	0.12	0.25	0.24	0.48	0.15	5.09	0.14	0.60	0.47	0.62	0.78	1.52	0.81	1.97	0.48	2.1
B6-3/02	0.59	0.17	0.24	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.41	0.46	n.c.	n.c.	n.c.	2.22	n.c.	2.1
Białogóra 3	0.66	0.10	0.24	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.41	0.53	n.c.	n.c.	n.c.	2.01	0.67	6.5
D bki 7K	0.73	0.09	0.18	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.41	0.55	n.c.	n.c.	n.c.	2.98	0.67	7.1
arnowiec 7	0.52	0.18	0.30	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.41	0.43	n.c.	n.c.	n.c.	1.18	0.44	5.6

C₂₇ = C₂₇ 20R sterane/(C₂₇+C₂₈+C₂₉) 20R steranes; C₂₈ = C₂₈ 20R sterane/(C₂₇+C₂₈+C₂₉) 20R steranes; C₂₉ = C₂₉ 20R sterane/(C₂₇+C₂₈+C₂₉) 20R steranes; Gam/Hop = gammacerane/17 hopane; Dia/Hop = C₃₀ diahopane/17 hopane; Bis/Hop = 28,30-bisnorhopane/17 hopane; C₂₆/C₂₄ = C₂₆(S+R) tricyclic terpanes/C₂₄ tetracyclic terpane; Mor/Hop = (normoretane+moretane)/(norhopane+17 hopane); H₃₁S/(S+R) = homohopane 22S/(22S+22R); C₂₉SR = epimerisation of regular steranes C₂₉ ratio; C₂₉ = ratio of -epimeres of regular steranes C₂₉ to their total quantity; C₂₉Ts/C₂₉H = C₂₉ 18 α norneohopane/C₂₉ norhopane; Ts/Tm = C₂₇ 18 trisnorhopane/C₂₇ 17 trisnorhopane; Gam/C₃₁Hop = gammacerane/C₃₁ 22R hopane; Dia/Reg = C₂₇ 20S diasterane/C₂₉ 20R sterane; TA(I) = C₂₀ + C₂₁ triaromatic steroids; TA(II) = C₂₆-C₂₈ (20S+20R) triaromatic steroids; C₂₉ster = C₂₉ 20R sterane content; n.c. – not calculated due to lack or low intensity of biomarkers

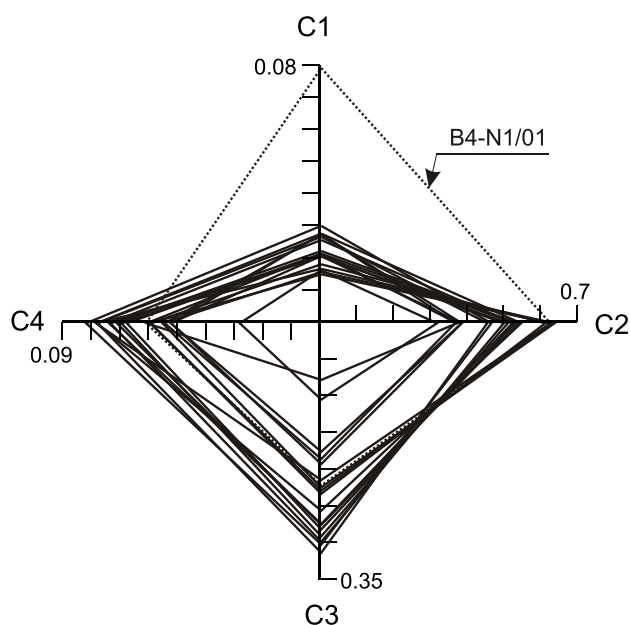


Fig. 6. Correlation of oils using star diagram of C₇-hydrocarbon ratios

Explanation of indices as in Table 3

The distribution of *n*-alkanes and isoprenoids (Fig. 2), and the values of hydrocarbon and biomarker indices (Tables 2 and 4) reveal that secondary processes detected in oil from the B4-N1/01 borehole were not extensive as the chromatogram does not show the characteristic “hump” of an unresolved complex mixture (Fig. 2; Peters *et al.*, 2005, p. 106).

The thermal cracking of oil is significant in accumulations at a temperature range of 150–175°C, as suggested by

Claypool and Mancini (1989). However, oil accumulations occurring in reservoirs under this temperature range (e.g., Mango, 1991; Horsfield *et al.*, 1992; Pepper and Dodd, 1995) indicate that oil may be thermally stable at higher temperatures, as well.

A set of organic compounds occurring in oil (condensate) that are indicative of thermal cracking are diamondoids (Peters *et al.*, 2005). The low content of 3- and 4-methyldiamantanes in the crude oils analysed (from 1.7 to 6.2 ppm; Table 5), indicates the absence of thermal cracking (Dahl *et al.*, 1999). The low concentrations of stigmastane (from 2.1 to 7.1 ppm; Table 4) that are high in uncracked oils (Dahl *et al.*, 1999) suggest that all oils are at the initial phase of thermal cracking.

GENETIC TYPE AND DEPOSITIONAL ENVIRONMENT OF SOURCE ORGANIC MATTER

The oils deposited in the Middle Cambrian sandstones show a gravity range from 41.7 to 76°API (Table 1 and Fig. 7). The lowest value of this index was found in oil collected from the B8-1/83 borehole, while oil collected from the arnowiec 8K borehole has the highest gravity (Table 1 and Fig. 7). All crude oils are very low in sulphur (below 0.3 wt.%), suggesting a low-sulphur kerogen as their source rock (Orr, 1986) and its deposition under conditions of clastic sedimentation (see Moldowan *et al.*, 1985). The highest sulphur content was measured in oil collected from the B4-N1/01 borehole (Fig. 7) where biodegradation processes took place. The most probable source-rocks for these oils, i.e. the Upper Cambrian–Tremadocian succession in the Polish part of the Baltic region, has low-sulphur kerogen (Wi claw *et al.*, 2010a, b). Although the oils analysed have too high gravities to allow direct determination of the genetic type of source kerogen (Fig. 7), the investigations of Wi claw *et al.* (2009) reveal that sulphur concentrations in oils generated during hydrous pyrolysis (HP) ex-

Table 5

Indices calculated based on phenantrene and its derivatives and diamandoids distribution and selected diamandoids concentration of crude oils

Borehole/sample	MPI1	MPR	R_{cal} [%]	3+4-MD [ppm]	MAI	MDI	DMAI1	DMDI-1	DMDI-2	$R_{cal(MDI)}$ [%]
B16-1/85 (1)	1.04	1.42	0.99	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B16-1/85 (2)	1.13	1.48	1.04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B3-5/93	0.70	0.97	0.79	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B3-6/92	0.79	0.72	0.84	6.2	0.49	0.27	0.44	0.37	0.61	1.08
B3-7/94	0.72	0.66	0.80	4.3	0.78	0.26	0.45	0.38	0.56	1.07
B3-9/95	0.66	0.77	0.77	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B4-N1/01	0.71	0.74	0.80	3.3	0.72	0.31	0.00	0.40	0.75	1.18
B6-1/82	1.01	1.36	0.98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B6-2/85	0.98	1.00	0.96	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B6-3/02	1.38	2.58	1.20	1.7	0.73	0.23	0.51	0.38	0.60	0.99
B8-1/83	0.78	1.08	0.84	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Białogóra 3	0.83	0.80	0.87	2.5	0.58	0.27	0.51	0.38	0.45	1.11
D bki 5K	0.99	1.35	0.96	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D bki 7K	1.23	1.27	1.11	2.0	0.70	0.19	0.49	0.33	0.44	0.90
arnowiec 7	1.64	2.58	1.36	2.0	0.72	0.17	0.57	0.27	0.44	0.84
arnowiec 8K	1.40	1.36	1.21	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
arnowiec IG 4	1.02	1.51	0.98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

MPI1 = $1.5(2\text{-MP}+3\text{-MP})/(P+1\text{-MP}+9\text{-MP})$, MP – methylphenantrene; MPR = $2\text{-MP}/1\text{-MP}$; $R_{cal} = 0.60\text{MPI1}+0.37$ for $\text{MPR}<2.65$ (Radke, 1988); MAI = $1\text{-MA}/(1\text{-MA}+2\text{-MA})$ (Chen *et al.*, 1996), MA – methyladamantane; MDI = $4\text{-MD}/(1\text{-MD}+3\text{-MD}+4\text{-MD})$ (Chen *et al.*, 1996), MD – methyldiamantane; DMAI1 = $1,3\text{-DMA}/(1,3\text{-DMA}+1,2\text{-DMA})$ (Zhang *et al.*, 2005), DMA – dimethyladamantane; DMDI-1 = $4,9\text{-DMD}/(3,4\text{-DMD}+4,9\text{-DMD})$ (Zhang *et al.*, 2005), DMD – dimethyldiamantane; DMDI-2 = $4,9\text{-DMD}/(4,8\text{-DMD}+4,9\text{-DMD})$ (Zhang *et al.*, 2005); $R_{cal(MDI)} = 2.4389\text{MDI}+0.4363$ (Chen *et al.*, 1996); n.a. – not analysed

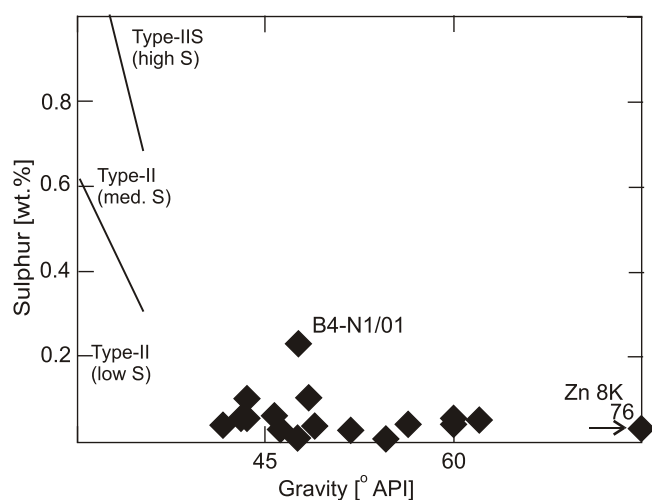


Fig. 7. Sulphur content versus gravity plot

Classification of source kerogen type after Orr (2001)

periments from low-sulphur Type-II kerogen are always below 1 wt%. By contrast, the high-sulphur (Type-IIS) kerogen always generates, independently of maturity, high sulphur oils (>2 wt.% S).

The fraction composition and saturate/aromatic (sat/aro) ratios were suggested to be influenced by migration distance. The crude oils investigated have very low contents of asphaltenes, usually below 0.2 wt.%, with the highest value of 0.8 wt.% in oil collected from oil inflow in the Malbork IG 1 (Mb IG 1) borehole (Table 1 and Fig. 8). Low concentrations of asphaltenes inversely correlate with high saturated-hydrocarbon contents and high sat/aro ratios (Table 1 and Fig. 8). Statistically, the highest values of this ratio are noted for oils from the arnowiec and B16 deposits. These oils probably migrated over the longest distance. Values of this ratio can be affected by maturity and by thermal cracking processes.

The distributions of *n*-alkanes and isoprenoids in all crude oils are similar, monomodal, with a distinct maximum in the short-chain hydrocarbons range (Fig. 2), characteristic of hydrocarbons generated from marine organic matter (e.g., Peters *et al.*, 2005). The CPI values >1.0 indicate deposition of source organic matter under conditions of clastic sedimentation

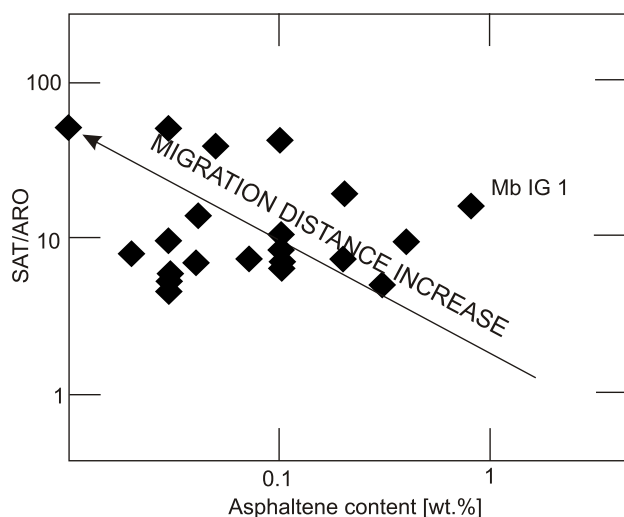


Fig. 8. A plot of saturated hydrocarbons/aromatic hydrocarbons ratio versus asphaltenes content

For explanations see Table 1

(Moldowan *et al.*, 1985). This is supported by high values of diasterane/sterane ratios and domination of tricyclic terpanes over tetracyclic terpane, and norhopane over norneohopane concentrations (Table 4; Peters *et al.*, 2005). Pristane/phytane (Pr/Ph) ratios higher than 2.0 (Table 2) indicate that sub-oxic conditions prevailed during deposition of the source rock (Didyk *et al.*, 1978; Hughes *et al.*, 1995; ten Haven, 1996). This concept is supported by correlation between pristane/ n -C₁₇ and phytane/ n -C₁₈ indices (Fig. 9). The increased values of pristane/phytane ratio (over 2.5) for some oils may reflect their high maturity (Koopmans *et al.*, 1996; Al-Arouri *et al.*, 1998).

A similar distribution of regular $\alpha\alpha\alpha$ steranes in all crude oils (Table 4 and Fig. 10) suggests their common source. According to Czochanska *et al.* (1988), these oils were generated from marine plankton. This composition correlates with bitumen extracted from the Cambrian–Tremadocian succession of the Polish part of the Baltic region (Wi cław *et al.*, 2010a).

The stable carbon isotope composition of the crude oils and their individual fractions (Table 1) corresponds to the biomarker data and indicates that a single genetic type of organic matter was the source of these oils (a maximum difference in $\delta^{13}\text{C}$ of whole oil equals to 1.4‰; Fig. 11). In some oils, asphaltenes are depleted in the ^{13}C isotope relative to resins, which is characteristic of oil generated from algal kerogen (Galimov, 1973, 1986). Although this effect can be also a result of biodegradation processes (Stahl, 1980), these processes were confirmed only in oil collected from the B4-N1/01 borehole, as noted earlier. Some differences in stable carbon isotope composition follow changes in source rock facies, changes in maturity (Waples and Tornheim, 1978; Chung *et al.*, 1981; Lewan, 1983) or migration distance (Stahl, 1980).

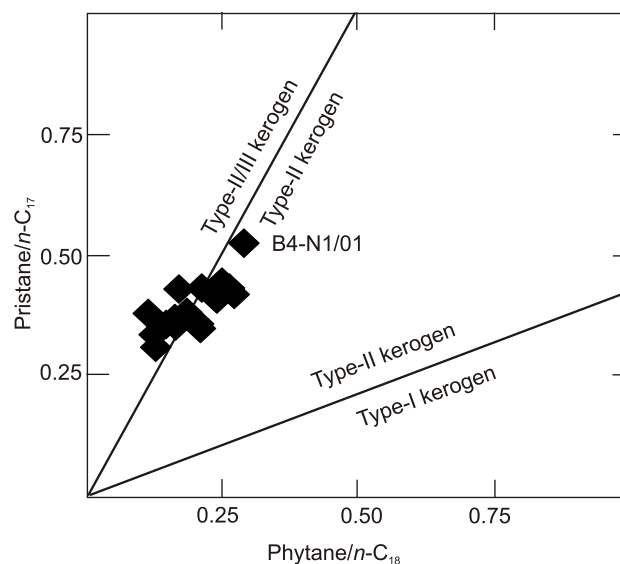


Fig. 9. Genetic characterization of oils in terms of pristane/ n -C₁₇ and phytane/ n -C₁₈, according to the categories of Obermajer *et al.* (1999)

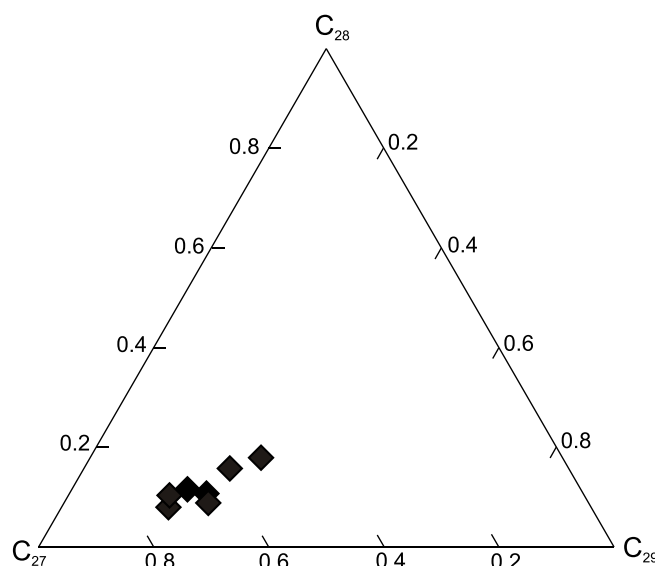


Fig. 10. Ternary diagram of C₂₇, C₂₈ and C₂₉ regular sterane composition

For explanations see Table 4

MATURITY

The maturity of crude oils was determined based on light hydrocarbons (Table 2) and biomarker distributions (Table 4), phenanthrene and its methyl derivatives as well as diamondoids (Table 5). Indirectly, oil density and n -alkane and isoprenoid distributions were also used for this purpose.

The distribution of methylphenantrenes shows variable maturities for the crude oils: oil accumulated in the B3, B4 and B8

deposits was generated during the peak of the oil window (R_{cal} about 0.75–0.8%) and samples from the B6, B16, D bki and arnowiec accumulations were generated at the late phase of the low-temperature thermogenic process (R_{cal} about 0.9–1.05%; Table 5). Biomarker distribution and values of the C_{11} – index support the above results. In oils collected from the B16, B6 and arnowiec accumulations increased quantities of condensate-range hydrocarbons were noted (Table 2) and in most oils (i.e. from the B6, Białogóra, D bki and arnowiec deposits) only traces of biomarkers indicate their high maturity. Even in the few samples (i.e. B3-5/83 and B4-N1/01), where measurable concentrations biomarkers were indicated, their amounts are low. Sterane distributions indicate that the oils analysed were generated by mature organic matter (Fig. 12) and very low concentrations of $C_{29}\alpha\alpha\alpha 20R$ sterane (stigmastane) are typical of the beginning of oil cracking (Table 4). Low densities (Table 1 and Fig. 7) and values of CPI indices

~1.0 (Table 2) are indirect indicators of the high maturity of the oils analysed (e.g., Peters *et al.*, 2005).

The values of maturity indices calculated from diamondoids distribution are ambiguous due to the low concentration of these hydrocarbons, but generally their values indicate the same maturity level as the methylphenantere and biomarker indices (Table 5 and Fig. 13A). Only the MAI values, showing very high maturity (above 1.3% R_o ; Table 5 and Fig. 13B), appear to be unreliable.

The generation temperature of hydrocarbons was estimated from dimethylpentane homologues distribution (Table 2; Mango, 1997). It varies from 123 (B3-9/95) to 134°C (arnowiec 7 and 8K). The lowest temperature calculated for oil sample B16-1/85 (2) – 116°C is probably invalid due to the secondary processes described earlier. The 1-D modelling of hydrocarbon generation and expulsion processes from the Upper Cambrian–Tremadocian source rock succession in the Polish part of the Baltic region (Kosakowski *et al.*, 2010) indicates that the main mass of the liquid hydrocarbons was generated at a temperature range of 120–140°C.

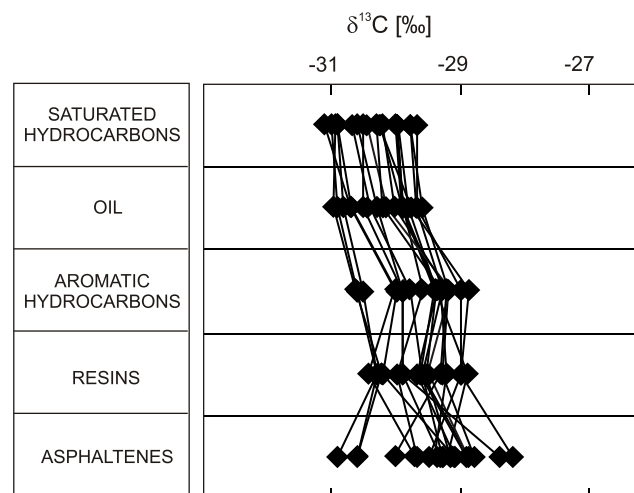


Fig. 11. Stable carbon isotope composition of crude oils and their individual fractions

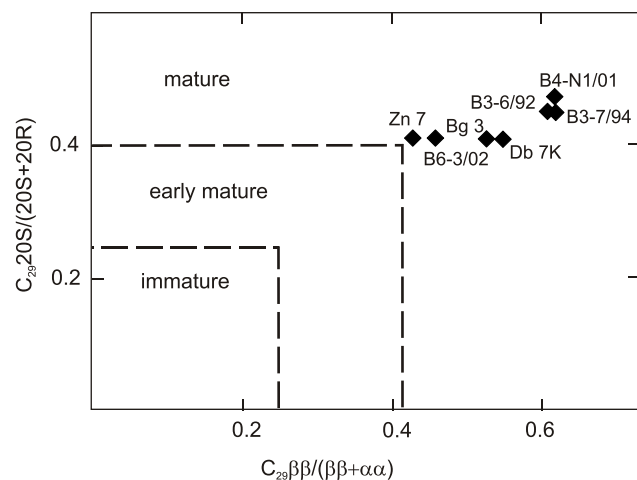


Fig. 12. Sterane $C_{29}20S/(20S+20R)$ ratio versus $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratio

Maturity fields after Peters and Moldovan (1993)

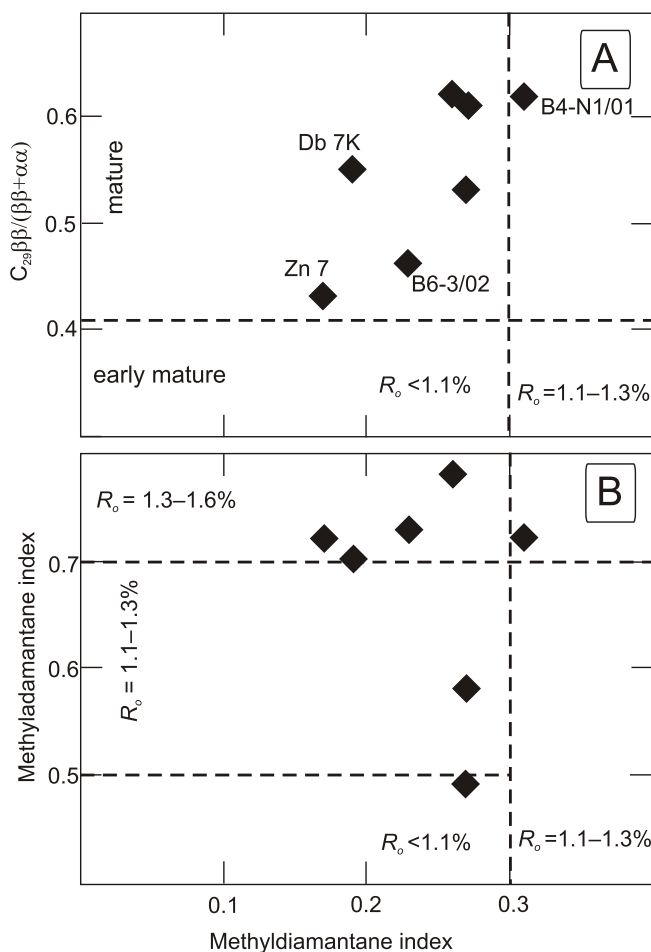


Fig. 13. Estimation of maturity of oils based on correlation of (A) $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ and (B) methyladamantane index versus methyladamantane index

Maturity ranges based on $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ after Peters and Moldovan (1993), and on methyladamantane and methyladamantane indices after Chen *et al.* (1996)

CONCLUSIONS

The oils accumulated in the Middle Cambrian sandstones from the Polish part of the Baltic region reveal very similar geochemical characteristics and were generated from a single genetic type of organic matter deposited under common conditions. These are normal or light oils with maximum concentrations of *n*-alkane distributions at *n*-C₆-*n*-C₇ hydrocarbons without a "hump" of an unresolved complex mixture. Only oil from the B4-N1/01 borehole is slightly biodegraded and fractionally evaporated.

The marine origin (Type-I or -II kerogen) of source organic matter dispersed in clastic sediments is supported by the distribution of *n*-alkanes and isoprenoids, CPI values above 1.0, high values of the diasterane/sterane ratio, domination of tricyclic terpanes over tetracyclic terpane and norhopane over norneohopane, as well as high pristane/phytane ratio values. The stable carbon isotope composition of oils and their individual fractions confirms the conclusions from biomarker distributions and indicates that a single genetic type of organic matter containing an algal component was responsible for the generation of all the oils. This type of kerogen was recognized by Wiłow *et al.* (2010a, b) in the whole lower Paleozoic sequence.

Oils accumulated in the Polish part of the Baltic region were generated at the peak and the late phase of low-temperature thermogenic processes, in a maturity range from *ca.* 0.75

to *ca.* 1.05% on the vitrinite reflectance scale. The least mature oils accumulated in the B3 and B4 deposits. The highest mature oils are in the B6, B16, D bki and arnowiec deposits and they migrated probably the longest way.

From the organic geochemistry point of view, Wiłow *et al.* (2010a) proposed the Middle Cambrian, Upper Cambrian–Tremadocian, Caradocian and Llandovery strata as the most probable source rocks. The tectonic conditions of the Polish part of the Baltic region (Poprawa *et al.*, 1999; Pokorski, 2010) indicate that all the source rocks identified may supply the Middle Cambrian reservoirs with hydrocarbons.

Acknowledgements. The research was undertaken as part of a project of the Ministry of the Environment (No. 182/2005/Wn-06/FG-sm-tx/D). J. A. Bojesen-Koefoed from the Geological Survey of Denmark and Greenland in Copenhagen, M. Fabiańska from the Silesian University in Sosnowiec, M. D. Lewan from the US Geological Survey in Denver and J. B. Curtis from the Colorado School of Mines in Golden gave very constructive remarks and comments that greatly improved the discussion and the possible consequences of the hypotheses presented in the manuscript. The authors thank M. D. Lewan and A. Warden from the US Geological Survey in Denver for biomarker analyses. Analytical work by H. Zych and T. Kowalski from the AGH University of Science and Technology in Kraków is gratefully acknowledged.

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