Annales Societatis Geologorum Poloniae (2011), vol. 81: 443–458.

ORIGIN OF LIQUID HYDROCARBONS ACCUMULATED IN THE MIOCENE STRATA OF THE POLISH CARPATHIAN FOREDEEP AND ITS PALAEOZOIC–MESOZOIC BASEMENT

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Więcław, D., 2011. Origin of liquid hydrocarbons accumulated in the Miocene strata of the Polish Carpathian Foredeep and its Palaeozoic–Mesozoic basement. *Annales Societatis Geologorum Poloniae*, 81: 443–458.

Abstract: Petroleum geochemical data of 34 oils and condensates accumulated in the Carpathian Foredeep and its Mesozoic and Palaeozoic basement were used to assess their origin and genetic type. The analysed liquid hydrocarbons are characterized by variable densities and sulphur contents. No relationship between these parameters and the reservoir rock age has been found. Secondary processes of evaporative fractionation and biodegradation are evidenced for some oils. These processes proceeded most intensively on the oil from Góra Ropczycka-1K well. The oils from Opaka-1, Lubaczów-157 and Góra Ropczycka-1K wells were generated from organic matter deposited in the Upper Jurassic carbonates. The oil from the inflow in Załazie-2 well originated from the Cambrian strata, but also contains biomarkers characteristic of Miocene strata. The next family, genetically connected with the Silurian and Ordovician source rocks, consists of oils accumulated in the Lower Carboniferous carbonates in Nosówka deposit and in the Upper Jurassic in the inflow into Łękawica-1 well. The condensates collected from the Miocene (Łękawica-1, Pilzno-37, Tarnów-39 and -45 wells) and Upper Jurassic strata (Łąkta-27 and Tarnów-5 wells) were generated by organic matter dispersed in the Middle Jurassic or Lower Carboniferous clastic facies. The remaining oils, from Grobla-Pławowice, Wierzchosławice, Jastrząbka Stara, Partynia-Podborze, Dąbrowa Tarnowska, Brzezówka and Zagorzyce deposits, and the inflows into Tarnów-47 and Pilzno-12 wells were generated from kerogen enriched in organic sulphur usually dispersed in carbonate rocks. Such a type of sediments occurs in the Devonian and Lower Carboniferous strata. Also, these strata as well as the underlying Silurian rocks have sufficient maturity for generation of the discussed oils. The oleanane in the discussed oils most probably originates from kerogen of the Upper Cretaceous or Miocene strata, through which these oils migrated and eluted this biomarker.

Key words: oil origin, biomarkers, stable carbon isotopes, oil-oil correlation, Palaeozoic–Mesozoic basement, Polish Carpathian Foredeep.

Manuscript received 19 May 2011, accepted 13 October 2011

INTRODUCTION

The Polish Outer Carpathians and their foredeep basin belong to the largest and oldest petroleum provinces of Central Europe. The exploitation of gas in the analysed part of the Carpathian Foredeep began in 1955 when the Niwiska gas field in the Triassic strata was discovered. Two years later the Lubaczów gas field in the Miocene and Upper Jurassic strata was discovered, and in 1958 Partynia-Podborze – the first oil deposit in the Upper Jurassic carbonates was found (Karnkowski, 2007).

So far, 26 oil, gas-condensate and gas fields have been encountered in the Mesozoic and Palaeozoic strata of the Carpathian Foredeep and the sub-Carpathian basement (Kotarba *et al.*, 2011), with booked reserves of 7.5 billion cubic metres of natural gas and 4.7 million tons of oil. The cumulative production amounts to 6.1 billion cubic metres of gas and 4.3 million tons of oil (Górka *et al.*, 2007). The geology and hydrocarbon migration and accumulation conditions of the study area are described in earlier works (*e.g.*, Karnkowski, 2001; Oszczypko *et al.,* 2006; Florek *et al.*, 2006; Laskowicz *et al.*, 2008). Historically (*e.g.*, ten Haven *et al.*, 1993), the Oligocene Menilite Shales were considered to be the most important source rock for the majority of oils accumulated in the basement of the Carpathian Foredeep. Recently, in view of the results of extended geochemical investigations and modelling of petroleum generation and accumulation processes (*e.g.*, Dudek *et al.*, 2003; Matyasik *et al.*, 2010), the Upper and Lower Palaeozoic strata have been regarded as the most probable source rocks; especially the Ordovician and Silurian strata show a high hydrocarbon potential (Więcław *et al.*, 2011; Kotarba *et al.*, 2011).

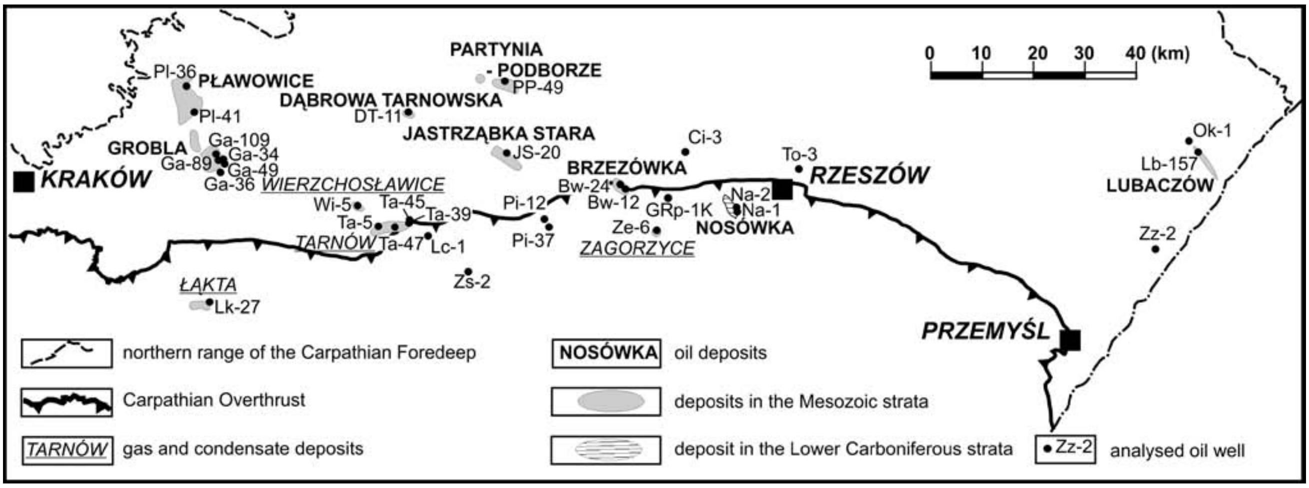

Fig. 1. Geological sketch-map showing location of crude oil sampling sites. For explanation of sample codes see Table 1

The main purpose of this study is to characterise liquid hydrocarbons (oils and condensates) accumulated in the Carpathian Foredeep succession as well as its Mesozoic–Palaeozoic basement strata in south-eastern Poland (Fig. 1), *i.e.* to identify their source rocks, maturity, migration distance and occurrence of secondary processes. Additionally, author revises the conception proposed by ten Haven *et al.* (1993) on the origin of majority of oils accumulated in the Carpathian Foredeep basement from the Oligocene Menilite Shales of the Outer Carpathians.

The primary characteristic of oils was presented by, *e.g.*, Kisielow and Wdowiarz (1967), ten Haven *et al.* (1993), Curtis *et al.* (2004), and Kotarba *et al.* (2004). This paper summarizes data from the previous works and for the first time presents the results of wide-range analyses: density, sulphur content in oil and in asphaltenes, nickel and vanadium content, whole oil GC, stable carbon isotopes, and biomarkers composition. For condensates accumulated in the Miocene molasses of the Carpathian Foredeep, such comprehensive studies are performed for the first time.

METHODS

Sampling procedure

20 crude oil and condensates were collected (Table 1): 7 from the Miocene strata of the Carpathian Foredeep (Cierpisz-3, Łękawica-1 (condensate), Pilzno-37, Tarnów-39, Tarnów-45, Zalasowa-2 and Załazie-2), 12 from the Mesozoic strata (Brzezówka-24, Góra Ropczycka-1K, Grobla-36, -89, -109, Jastrząbka Stara-20, Łękawica-1, Opaka-1, Pławowice-36, -41, Tarnów-5 and Wierzchosławice-5), and one from the Palaeozoic strata (Trzebownisko-3) (Fig. 1). Most oils and condensates were collected from producing wells. Some of them (Zalasowa-2, Załazie-2, Łękawica-1 and Opaka-1) were taken from oil inflows into the wells. The condensate from Pilzno-37 well was collected from the brine surface and the oil from Łękawica-1 well was collected from mud.

Additionally, for comparative purposes, 14 oils and condensates from the Miocene strata and the Palaeozoic–Mesozoic basement described by ten Haven *et al.* (1993), Curtis *et al.* (2004) and Kotarba *et al.* (2004) were taken into consideration (Table 1, Fig. 1).

Analytical methods

Oils were analysed for the API gravity with the use of the Anton Paar DMA5300M density meter and for sulphur content with the Leco SR-12 analyser. Vanadium and nickel contents were determined by the ICP-OES method using the Perkin Elmer WMA400 spectrophotometer according to the ASTM D 5708:2002 standard. Before the deasphalting, the oils 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 fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography, using alumina/silica gel (2:1 v/v) columns (0.8 × 25 cm). The fractions were eluted with *n*-hexane, toluene, and toluene:methanol (1:1 v/v), respectively. The oils and their individual fractions for the measurement of stable carbon isotope composition were combusted in an on-line system. The stable carbon isotope analyses were performed using the Finnigan Delta Plus mass spectrometer. The stable carbon isotope data is presented in the δ-notation relative to V-PDB standard (Coplen, 1995), with the analytical precision of ± 0.2‰. The elemental composition of asphaltenes was performed on the Carlo Erba EA1108 elemental analyser.

For the whole oil analysis, high resolution gas chromatography was used. For this purpose, 1 μl of sample diluted in CS_2 was introduced into a split-less injector of the Hewlett Packard 5890 series II GC held at a temperature of 300°C. From there, the sample passed through a 50 m × 0.2 mm Agilent DB1 column (0.5 μm film thickness) with a constant flow 0.3 ml/min 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

Table 1

Reservoir data, API gravity, sulphur, vanadium and nickel contents, fractions and stable carbon isotope composition

Well	Sample code	Reservoir		Depth (m)	Gravity (°API)	Sulphur (wt%)	V	Ni	Fraction (wt%)				sat./aro.	Stable carbon isotopes δ^{13}C (‰)				
		Lithology	Stratigraphy				(ppm)		sat.	aro.	res.	asph.		sat.	oil	aro.	res.	asph.
Brzezówka-12*	Bw-12	carb.	U. Jurassic	1,958-1,985	36.7	0.12	n.a.	n.a.	77.0	16.7	6.1	0.2	4.6	-26.9	-26.1	-25.8	-26.0	-26.1
Brzezówka-24	Bw-24			1,892-1,913	36.2	0.21	1.4	0.3	61.8	31.6	5.4	1.2	2.0	-26.6	-26.1	-25.9	-26.0	-26.2
Cierpisz-3	Ci-3	sand.	Miocene	1,346-1,330	n.a.	n.a.	n.a.	n.a.	95.1	2.7	2.2	tr.	35.2	-27.5	-27.4	-28.0	-27.6	-28.4
Dąbrowa Tarnowska-11*	DT-11	carb.	U. Jurassic	688-698	35.6	1.38	n.a.	n.a.	85.8	10.8	2.8	0.6	7.9	-25.7	-25.4	-25.1	-25.6	-25.6
Góra Ropczycka-1K	GRp-1K			2,103-2,117	25.4	0.10	1.2	1.0	89.3	9.4	1.3	0.0	9.5	-26.2	-25.5	-26.7	-28.7	n.a.
Grobla-109	Ga-109			726.5-740	39.0	0.50	1.0	0.3	78.2	16.6	4.6	0.6	4.7	-28.1	-28.4	-28.6	-28.6	-28.7
Grobla-34*	Ga-34			748-760	42.0	0.66	n.a.	n.a.	86.1	8.1	5.3	0.5	10.6	-27.6	-27.6	-27.9	-27.7	-27.4
Grobla-36	Ga-36			766-781	41.6	0.41	1.0	0.3	78.6	17.5	3.2	0.7	4.5	-28.1	-28.1	-28.3	-28.4	-28.1
Grobla-49*	Ga-49	sand.	U.Cret.	754.5-750.5	44.0	0.66	n.a.	n.a.	89.7	8.3	1.5	0.5	10.8	-27.5	-27.4	-27.6	-27.4	-27.7
Grobla-89	Ga-89	sand. +carb.	U.Jura.+ U. Cret.	700.5-662.5	43.1	0.48	1.0	3.2	78.4	16.1	4.1	1.4	4.9	-28.1	-28.1	-28.5	-28.5	-28.3
Jastrząbka Stara-6**	JS-6	sand.	U.Cretaceous	1,285-1,295	41.0	1.22	n.a.	n.a.	62.0	23.0	15.0		2.7	-25.2	-25.1	-25.1	-25.5	-26.0
Jastrząbka Stara-20	JS-20			1,294-1,288	35.4	0.80	1.0	2.9	75.2	20.2	4.2	0.4	3.7	-26.0	-26.1	-25.6	-26.0	-26.0
Lubaczów-157*	Lb-157	carb.	U.Jurassic	1,075-1,130	16.6	6.42	61	33	28.0	30.8	16.3	24.9	0.9	-28.4	-29.3	-29.5	-29.8	-30.0
Łąkta-27**	Lk-27			2,258-2,268	62.2	0.01	n.a.	n.a.	99.7	0.1	0.14	0.07	997	-26.7	-26.4	-25.5	-25.8	n.a.
Łękawica-1	Lc-1			1,992-2,000	30.4	0.38	0.9	1.5	70.3	22.2	5.8	1.7	3.2	-29.7	-29.5	-29.1	-29.0	-29.4
Łękawica-1(c.)	Lc-1(c.)	sand.	Miocene	1,830-1,835	57.2	0.40	1.0	0.3	100.0	0.0	0.0	0.0	n.c.	n.a.	-28.1	n.a.	n.a.	n.a.
Nosówka-1#	Na-1	carb.	L. Carb.	3,465-3,540	33	0.06	n.a.	n.a.	79.4	14.2	5.4	1.0	5.6	-29.5	-29.4	-28.9	-28.6	-28.8
Nosówka-2#	Na-2			3,353-3,438	n.a.	n.a.	n.a.	n.a.	81.0	13.5	4.5	1.0	6.0	-29.4	-29.3	-28.8	-28.5	-28.9
Opaka-1	Ok-1		U.Jurassic	1,007-1,057	5.3	10.10	158	71	10.1	41.6	15.8	32.5	0.2	-30.4	-29.9	-30.0	-29.7	-30.0
Partynia Podborze-49*	PP-49			817-821	34.2	0.32	n.a.	n.a.	87.3	9.7	1.9	1.1	9.0	-25.7	-25.5	-24.7	-24.5	-25.0
Pilzno-12*	Pi-12			2,189-2,233	33.0	2.31	n.a.	n.a.	85.1	12.8	1.8	0.3	6.6	-26.5	-26.4	-25.9	-25.9	-25.9
Pilzno-37	Pi-37	sand.	Miocene	1,672-1,765	n.a.	0.00	n.a.	n.a.	92.8	3.1	4.1	0.0	29.9	-28.3	-28.3	-27.9	-27.6	n.a.
Pławowice-36	Pl-36	carb.	U.Jura.	605.5-645	34.5	0.90	0.8	1.7	79.9	15.9	3.4	0.8	5.0	-28.1	-28.2	-28.5	-28.5	-28.4
Pławowice-41	Pl-41	carb. +sand.	U.Jura.+ U. Cret.	584-573	36.6	0.73	0.8	1.0	78.8	17.2	3.0	1.0	4.6	-28.0	-28.0	-28.3	-28.4	-28.1
Tarnów-39	Ta-39	sand.	Miocene	1,406-1,396	57.4	0.00	n.a.	n.a.	100.0	0.0	0.0	0.0	n.c.	n.a.	-27.3	n.a.	n.a.	n.a.
Tarnów-45	Ta-45			1,370-1,365	58.7	0.00	n.a.	n.a.	100.0	0.0	0.0	0.0	n.c.	n.a.	-27.3	n.a.	n.a.	n.a.
Tarnów-47*	Ta-47			1,488-1,492	28.6	0.55	n.a.	n.a.	80.3	13.7	4.4	1.6	5.9	-26.8	-26.5	-26.2	-25.6	-26.0
Tarnów-5	Ta-5	carb.	U.Jura.	1,650-1,662	50.9	0.24	1.2	1.4	100.0	0.0	0.0	0.0	n.c.	n.a.	-28.1	n.a.	n.a.	n.a.
Trzebownisko-3	To-3		M. Dev.	2,055-2,065	39.6	0.17	1.2	0.3	94.1	3.8	2.1	tr.	24.8	-27.4	-27.3	-26.6	-26.2	n.a.
Wierzchosławice-5	Wi-5	sand. +carb.	U.Jura.+ U. Cret.	1,450-1,486	44.9	0.12	1.2	0.3	77.1	17.7	4.7	0.5	4.4	-28.6	-28.7	-29.0	-28.8	-28.7
Zagorzyce-6*	Ze-6	carb.	U.Jurassic	2,878-2,925	27.9	1.66	1.2	1.0	67.2	20.8	10.6	1.4	3.2	-26.5	-26.2	-25.4	-26.0	-26.1
Zagorzyce-6 (c.)*	Ze-6(c.)			2,817-2,871	55.0	0.01	0.3	0.3	99.6	0.3	0.1	0.01	332	-26.3	-26.0	-25.3	-26.6	-27.4
Zalasowa-2	Zs-2	sand.	Miocene	2,959-2,973	19.4	1.37	n.a.	n.a.	46.4	22.4	27.4	3.8	2.1	-29.8	-29.4	-29.5	-28.8	-27.6
Załazie-2	Zz-2	sand.	Cm+ Miocene	2,600-2,658	46.6	0.10	0.7	1.5	80.4	16.3	3.3	0.03	4.9	-27.6	-27.0	-25.6	-25.9	-26.7

c. – condensate; sand. – sandstones; carb. – carbonates; U. – Upper; L. – Lower; M. – Middle; Cm – Cambrian; Dev. – Devonian; Jura. – Jurassic; Cret. – Cretaceous; sat. – saturated hydrocarbons; aro. – aromatics; res. – resins; asph. – asphaltenes; n.a. – not analysed; n.c. – not calculated; tr. – traces; * – data from Curtis *et al.* (2004); ** – data from ten Haven *et al.* (1993); # – data from Kotarba *et al.* (2004)

was held for 20 minutes. Components eluting from the column were detected by a flame ionization detector (FID) held at 325°C.

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

Table 2

Indices calculated based on whole oil GC analysis

Sample code	Reservoir stratigraphy	Toluene/ n-C_7H_{16}	n-C_7H_{16}/ MCH	HR	HHI	CH/ MCH	IHR	n-C_7H_{16}/ 2-MH	m-+o-+p-xylene/ n-C_8H_{18}	Temp. (°C)	CPI_{17-23}	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}
Bw-24	U.Jurassic	1.34	0.64	24.9	0.79	0.42	1.54	3.12	1.23	123	1.03	2.01	0.75	0.38
DT-11**		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.40	0.76	0.34
GRp-1K		134.8	0.06	2.2	0.07	0.66	0.20	2.08	182.1	114	n.c.	0.64	0.85	5.60
Ga-109		0.02	1.48	62.1	1.54	0.27	2.06	5.81	0.36	120	1.11	1.50	0.31	0.29
Ga-34**		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.92	0.27	0.20
Ga-36		0.02	1.62	62.1	1.80	0.33	2.13	5.56	0.35	122	1.10	1.26	0.27	0.29
Ga-49**	U.Cretaceous	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.49	0.24	0.21
Ga-89	U.Jura. +U.Cret.	0.03	1.65	59.9	1.92	0.37	2.15	5.28	0.34	123	1.12	1.31	0.27	0.29
JS-20	U.Cretaceous	0.28	0.75	28.0	0.91	0.40	1.99	2.88	0.79	125	1.03	2.27	0.62	0.30
Lk-27	U.Jurassic	0.31	1.28	39.4	1.73	0.49	2.28	3.41	0.51	126	n.d.	3.33**	0.71**	0.33**
Lc-1		n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.12	1.19	0.32	0.04
Lc-1(c.)	Miocene	0.68	1.50	56.1	1.62	0.39	2.04	5.27	0.47	123	n.c.	3.69	0.32	0.30
Na-1**	L. Carb.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.00	0.95	0.51
Ok-1	U.Jurassic	0.48	2.53	41.3	2.93	0.48	1.44	3.70	0.44	118	1.05	0.37	0.15	0.50
Pi-12**		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.89	0.75	0.41
Pi-37	Miocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.88	1.38	7.75	12.3
Pl-36	U.Jurassic	0.04	0.62	25.1	0.79	0.26	1.77	2.49	0.84	123	1.10	1.47	0.78	0.24
Pl-41	U.Jura. +U.Cret.	0.11	0.66	26.6	0.81	0.26	1.76	2.66	0.33	122	1.09	1.45	0.25	0.23
PP-49**	U.Jurassic	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.48	0.78	0.32
Ta-39	Miocene	0.63	1.51	58.2	1.56	0.34	1.84	5.66	0.43	121	n.c.	4.06	0.81	0.51
Ta-45		0.58	1.49	56.2	1.58	0.36	1.84	5.35	0.44	122	n.c.	n.c.	n.c.	n.c.
Ta-47**		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.64	0.81	0.53
Ta-5	U.Jurassic	1.18	1.12	48.3	1.18	0.38	1.70	5.87	0.89	122	n.c.	3.15	0.15	0.12
Wi-5	U.Jura. +U.Cret.	1.16	1.10	48.2	1.12	0.37	1.65	6.08	0.79	122	0.78	1.51	0.19	0.20
Zz-2	Cm+Miocene	1.72	1.25	58.9	1.14	0.35	1.91	6.47	1.21	120	1.02	3.53	0.23	0.07

c. – condensate; U. – Upper; Jura. – Jurassic; Cret. – Cretaceous; L. – Lower; Carb. – Carboniferous; Cm – Cambrian; MCH – methylcyclohexane; HR (heptane ratio) = 100x n-$C_7H_{16}/\Sigma(CH+C_7HCs)$; CH – cyclohexane; HCs – hydrocarbons; HHI = $(n\text{-}C_6H_{14} + n\text{-}C_7H_{16})/(CH+MCH)$; IHR (isoheptane ratio) = (2- + 3-MH)/(1*c*3- + 1*t*3- + 1*t*2-DMCPs); MH – methylhexane; DMCP – dimethylcyclopentane; Temp. – temperature = 140 + 15[ln(2,4-DMP/2,3-DMP)] (Mango, 1997); DMP – dimethylpentane; $CPI_{(17\text{-}23)} = [(C_{17}+C_{19}+C_{21})+ (C_{19}+C_{21}+C_{23})]/[2\ (C_{18}+C_{20}+C_{22})]$; Pr – pristane; Ph – phytane; n.c. – not calculated due to lack of hydrocarbons; n.d. – not determined; ** – data after ten Haven *et al.* (1993) – analyses of these samples were conducted on separated saturated hydrocarbon fraction

in the mass range from 45 to 500 Daltons. The aromatic hydrocarbon fractions of the oils were analysed by the GC-MS for phenanthrene, dibenzothiophene and their methyl derivatives relative concentrations. The analysis was carried out using the same equipment as for the saturate hydrocarbon fraction. The GC oven was programmed from 40 to 300°C at a rate of 3°C min^{-1}. The MS was operated with a cycle time of 1 sec in the mass range from 40 to 600 Daltons.

RESULTS AND DISCUSSION

Identification of secondary processes

Geochemical and physical properties of migrating oil or oil accumulated in a deposit may be changed by secondary processes, such as biodegradation, water-washing, oxidation, fractional evaporation and thermal cracking (*e.g.*, Blanc & Connan, 1994; Peters *et al.*, 2005; Thompson, 1983, 2010; Palmer, 1984, 1993; Holba *et al.*, 1996; Akinlua *et al.*, 2006).

The whole oil GC analysis indicated that for majority of the analysed oils and condensates in the aliphatic fraction some components dominate (Fig. 2A). In some oils, methylcyclohexane dominates over *n*-heptane resulting in low values of the *n*-heptane/methylcyclohexane ratio (Table 2, Fig. 3). The values of this ratio below one, correlated with the high toluene/*n*-heptane ratio, indicate evaporative fractionation processes (Thompson, 1987; Holba *et al.*, 1996). The most extensive evaporative fractionation proceeded on the oil collected from Góra Ropczycka-1K well (Figs 2B, 3). The values of the above-mentioned ratios strongly depend on source rock lithology (Holba *et al.*, 1996; Dzou, 2010). This is the most probable reason of the atypical, ele-

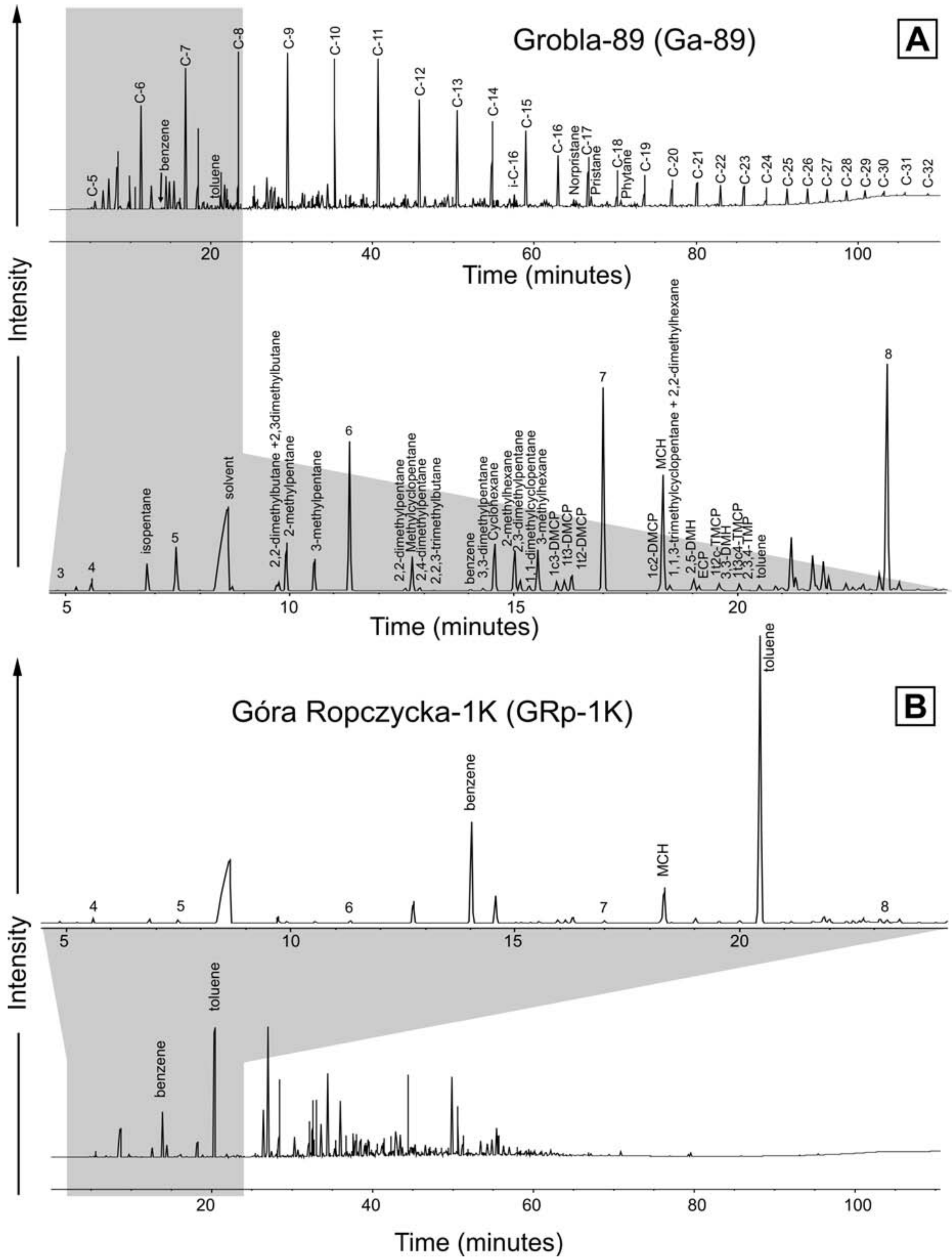

Fig. 2. Whole oil chromatogram of **(A)** Grobla-89 and **(B)** Góra Ropczycka-1K samples. Numbers refer to carbon atoms in *n*-alkane chain, DMCP – dimethylcyclopentane, MCH – methylcyclohexane, DMH – dimethylhexane, ECP – ethylcyclopentane, TMCP – trimethylcyclopentane, TMP – trimethylpentane

vated value of *n*-heptane/methylcyclohexane ratio of the Opaka-1 oil. According to the classification of Peters *et al.* (2005), this oil was generated from carbonate source rock. Biodegradation processes were evidenced by values of Halpern's (1995) ratios (Table 3, Fig. 4) and increased concentrations of isoprenoids in relation to *n*-alkanes resulting in increased values of the pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios. The advanced progress of these processes was ob-

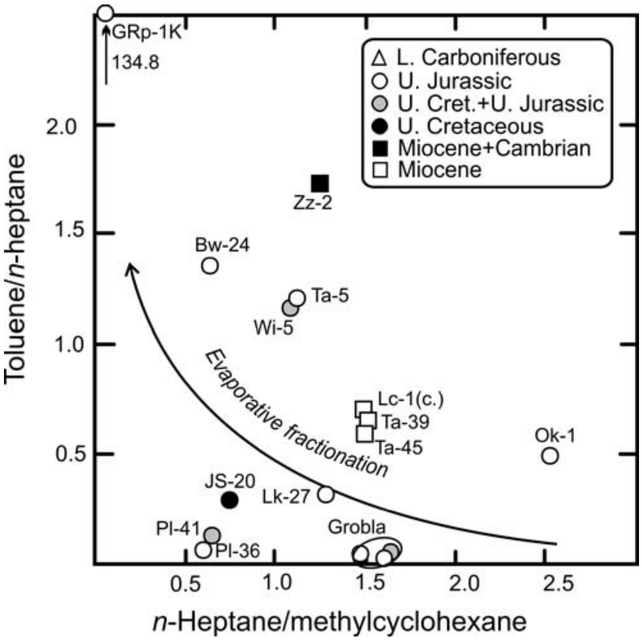

Fig. 3. Toluene/*n*-heptane ratio *versus* *n*-heptane/methylcyclohexane ratio. Scheme after Thompson (1987). For explanation of sample codes see Table 1

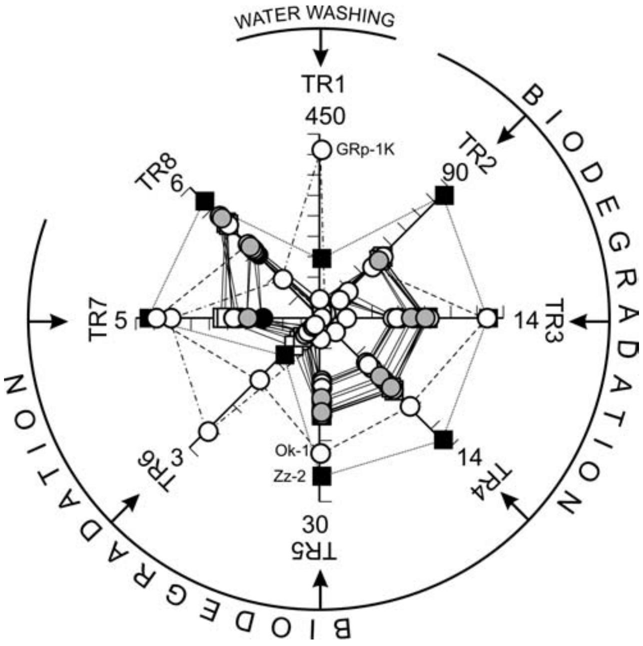

Fig. 4. Star diagram of C_7 oil transformation ratios. Scheme of star diagram after Halpern (1995). Explanation of indices as in Table 3, explanation of symbols as in Fig. 3, for explanation of sample codes see Table 1

Table 3

Values of Halpern (1995) C_7 ratios

Sample code	Reservoir stratigraphy	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	C1	C2	C3	C4
Bw-24	U.Jurassic	20.2	15.1	5.4	4.8	10.2	0.32	2.0	3.2	0.03	0.59	0.19	0.11
GRp-1K		412	3.06	1.9	1.5	3.4	2.62	4.1	1.8	0.02	0.77	0.13	0.00
Ga-109		1.0	41.4	7.8	7.1	14.9	0.38	2.3	4.7	0.03	0.60	0.16	0.15
Ga-36		0.9	42.6	8.2	7.7	15.8	0.38	2.3	4.7	0.03	0.58	0.18	0.13
Ga-89	U.Jura. + U.Cret.	1.1	39.7	7.9	7.5	15.4	0.30	2.2	4.6	0.02	0.57	0.18	0.14
JS-20	U.Cretaceous	4.0	14.4	5.6	5.0	10.6	0.32	1.6	2.9	0.04	0.55	0.20	0.11
Lk-27	U.Jurassic	5.8	18.4	6.0	5.4	11.4	0.20	1.6	3.1	0.03	0.55	0.22	0.11
Lc-1(c.)	Miocene	28.1	41.1	8.0	7.8	15.9	0.52	2.4	4.4	0.03	0.59	0.19	0.11
Ok-1	U.Jurassic	17.0	35.2	12.6	9.5	22.1	1.43	4.5	3.4	0.00	0.73	0.17	0.09
Pl-36		0.5	12.4	5.7	5.0	10.7	0.32	2.0	3.2	0.04	0.55	0.18	0.16
Pl-41	U.Jura. + U.Cret.	1.5	13.7	5.8	5.1	11.0	0.30	2.0	3.3	0.04	0.56	0.17	0.15
Ta-39	Miocene	26.7	42.4	8.1	7.5	15.6	0.64	2.7	4.4	0.02	0.63	0.18	0.10
Ta-45		23.0	39.9	8.0	7.5	15.5	0.44	2.6	4.3	0.02	0.62	0.18	0.10
Ta-5	U.Jurassic	45.7	38.8	7.0	6.6	13.6	0.16	2.4	4.3	0.03	0.59	0.18	0.11
Wi-5	U.Jura. + U.Cret.	44.3	38.3	6.8	6.3	13.1	0.37	2.4	4.3	0.03	0.60	0.18	0.12
Zz-2	Cm + Miocene	146	84.9	12.7	13.1	25.8	0.85	4.7	5.4	0.01	0.74	0.20	0.03

U. – Upper; Jura. – Jurassic; Cret. – Cretaceous; Cm – Cambrian; 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

served in condensate which contacted with brine (Pilzno-37, Fig. 5). Also, in the Góra Ropczycka-1K oil, which underwent evaporation, biodegradation process occurred (Fig. 5). In Załazie-2 oil the course of biodegradation process was mild (Fig. 4). The ratios calculated based on the distribution of short-chain hydrocarbons confirm the previous suggestion and supports evidence on biodegradation processes in the oil collected from Góra Ropczycka-1K well

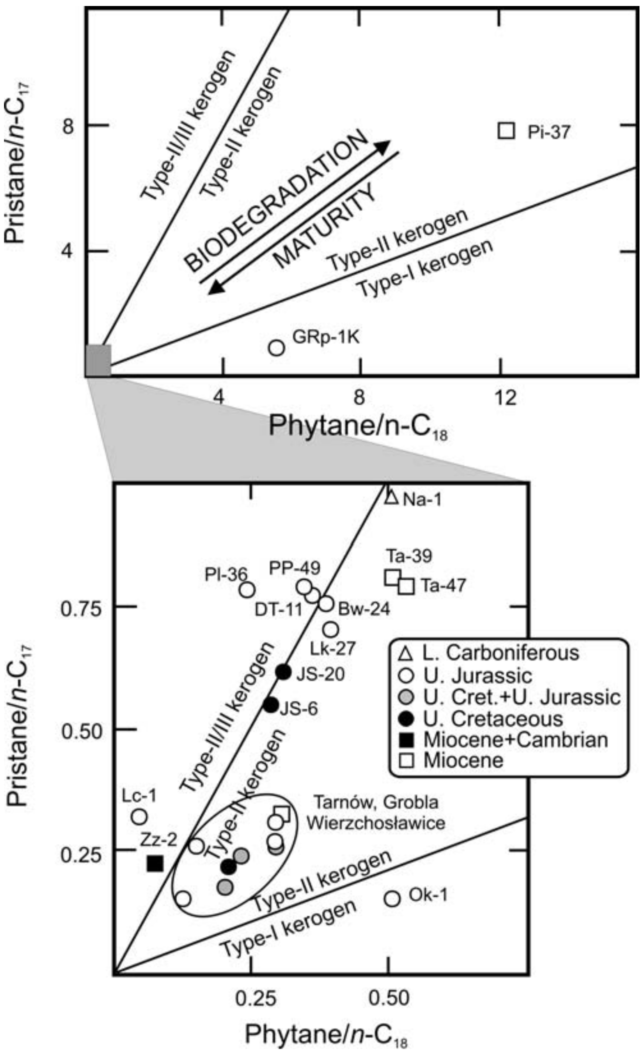

Fig. 5. Genetic characterization of oils in terms of pristane/n-C_{17} and phytane/n-C_{18} according to the categories of Obermajer *et al.* (1999). For explanation of sample codes: see Table 1

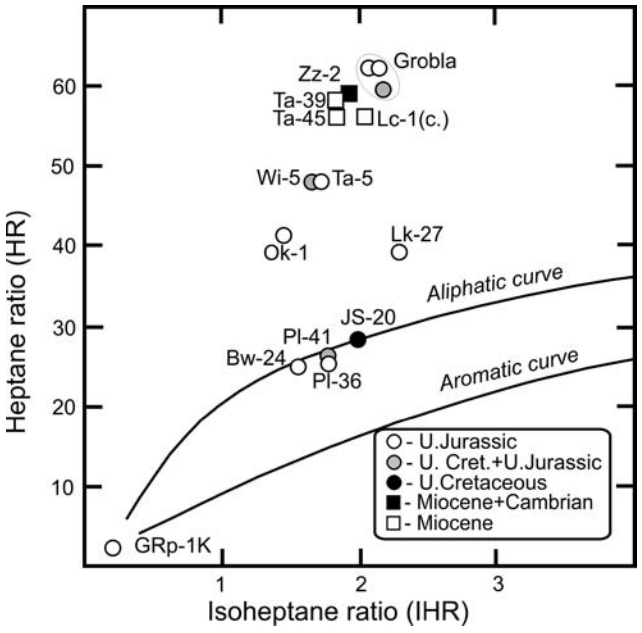

Fig. 6. Heptane ratio *versus* isoheptane ratio. Kerogen type curves after Thompson (1983). For explanation of sample codes see Table 1

(Fig. 6). The distribution of n-alkanes and isoprenoids (Fig. 2) and the values of hydrocarbon indices (Table 2) showed that secondary processes observed in the oils were not extensive. On the gas chromatogram of the most degraded sample, the characteristic of "biodegradation hump" of the unresolved complex mixture was not observed (Peters *et al.*, 2005, p. 106). Since not all n-alkanes were degraded, advancement of biodegradation is on the second degree in the ten-degree scale of Peters and Moldovan (1993).

The thermal cracking of oil, significant in accumulations at temperatures in the range of 150–175°C (Claypool & Mancini, 1989) for analysed oils had never occurred because they have never reached such temperatures under the geological conditions of the Carpathian Foredeep and its Palaeozoic–Mesozoic basin (Kosakowski & Wróbel, 2011).

Table 4

Elemental composition of asphaltenes

Sample code	Reservoir stratigraphy	Elemental composition (daf, wt%)					Atomic ratio			
		C	H	O	N	S	H/C	O/C	N/C	S/C
Bw-24	Upper Jurassic	84.7	13.6	1.0	0.3	0.4	1.93	0.01	0.003	0.002
Ga-109		75.2	8.6	8.5	0.3	7.4	1.37	0.08	0.004	0.037
Ga-36		79.3	8.8	3.9	0.2	7.7	1.34	0.04	0.002	0.036
Ga-89	Upper Jurassic + Upper Cretaceous	83.1	13.6	1.9	0.1	1.3	1.96	0.02	0.001	0.006
JS-20	Upper Cretaceous	79.2	11.7	6.2	0.2	2.8	1.77	0.06	0.002	0.013
Lc-1	Upper Jurassic	82.7	11.8	4.6	0.3	0.5	1.71	0.04	0.004	0.002
Ok-1		75.1	8.8	4.5	0.9	10.8	1.40	0.04	0.010	0.054
Pl-36		80.4	8.9	5.3	0.3	5.1	1.34	0.05	0.003	0.024
Pl-41	Upper Jurassic + Upper Cretaceous	81.7	12.3	2.2	0.2	3.6	1.80	0.02	0.002	0.016
Wi-5		76.0	7.5	8.4	0.5	7.6	1.18	0.08	0.006	0.038

daf – dry, ash-free basis

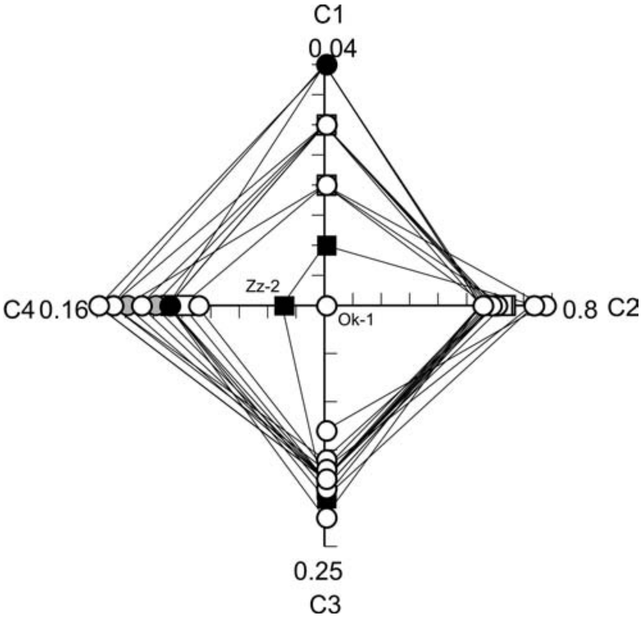

Fig. 7. Correlation of oils using star diagram of C_7 hydrocarbon ratios. Explanation of indices as in Table 3, for explanation of sample codes see Table 1

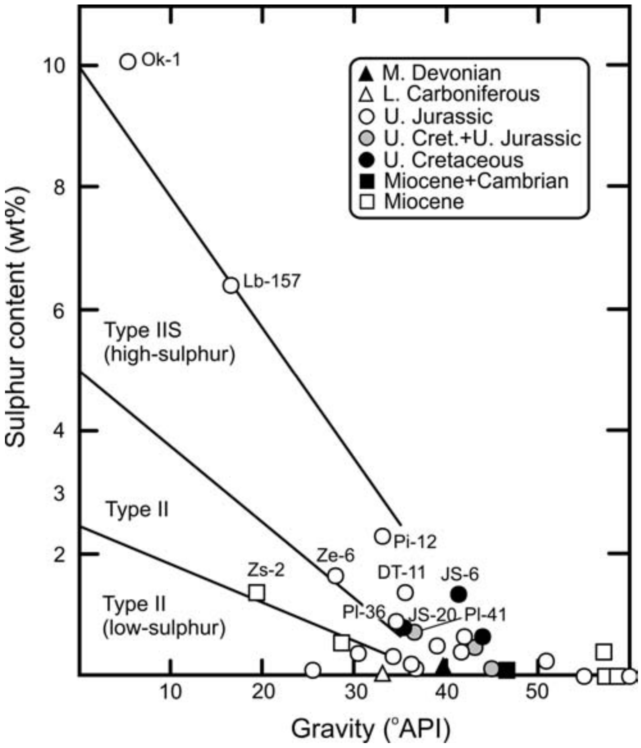

Fig. 8. Sulphur content *versus* gravity. Classification of source kerogen type by Orr (2001). For explanation of sample codes see Table 1

Genetic type and depositional environment of source organic matter

Geochemical parameters evaluated from the light hydrocarbons analyses of the oils analysed show comparable values (Table 3, Fig. 7). Only oils collected from Opaka-1 and Załazie-2 wells do differ from the other oils (Fig. 7).

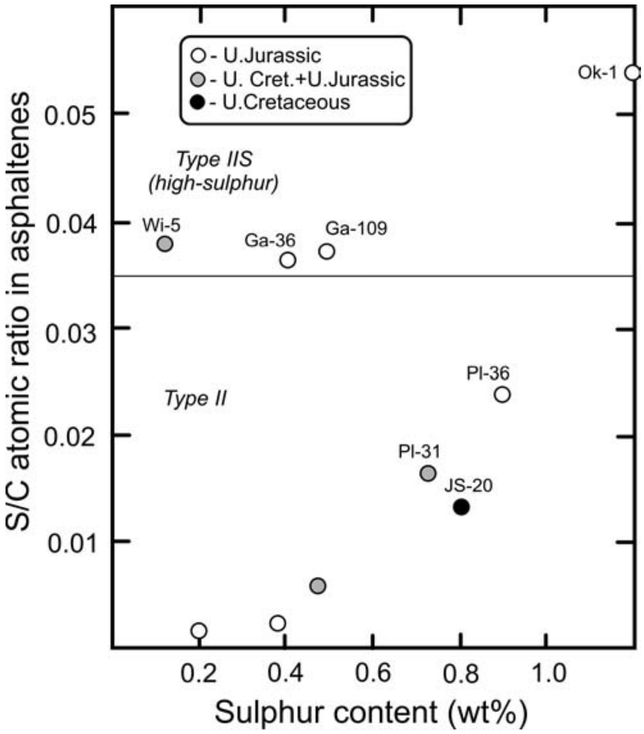

Fig. 9. S/C atomic ratio in asphaltenes *versus* sulphur content in oils. Classification of source kerogen type by Orr (1986). For explanation of sample codes see Table 1

Oils deposited in the Miocene strata as well as in the Mesozoic and Palaeozoic basement are characterized by gravity in a wide range, from 19.4 to 58.7 and 5.3 to 62.2 °API, respectively (Table 1, Fig. 8). Oils and condensates collected from the deposits in the Miocene are usually characterized by higher gravity values, over 45°API, whereas oils in the basement of the Carpathian Foredeep usually have lower gravity values (below 30°API, Table 1, Fig. 8). The crude oils with the highest sulphur content (over 2 wt%) occur only in the Upper Jurassic carbonates (Opaka-1, Lubaczów-157 and Pilzno-12, Figs 1, 8) suggesting the high-sulphur Type IIS kerogen as their source rock (Orr, 1986, 2001) deposited in carbonates (Moldowan *et al.*, 1985). Because of the fact that in these oils biodegradation processes were not observed, the reason for high sulphur content in these oils is that they were generated from the high-sulphur, Type IIS kerogen (Fig. 8). This statement is supported by the results of the elemental analysis of asphaltenes precipitated from these oils (Table 4, Fig. 9). High values of the S/C atomic ratio in asphaltenes, *i.e.* over 0.035, suggest a genetic relationship of these oils with high-sulphur kerogen (Fig. 9) (Orr, 1986). In the low-sulphur oils: Wierzchosławice-5, Grobla-36 and Grobla-109 (Table 1, Fig. 8), asphaltenes are characterized by a high content of this element (Fig. 9). It is postulated that these oils are a mixture of heavy, rich in asphaltenes high sulphur oil (generated from Type IIS kerogen) and rich in low-weight hydrocarbons light oil, generated at a higher maturity stage or from low-sulphur kerogen. The results on the vanadium and nickel content (Table 1, Fig. 10) show that the majority of oils were generated from organic matter deposited under

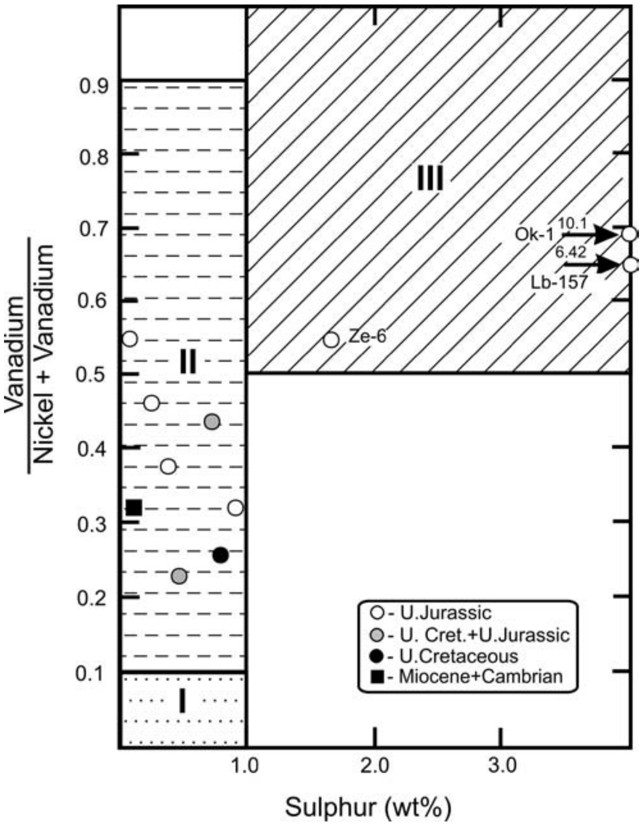

Fig. 10. V/(V+Ni) ratio *versus* sulphur content in oils. Classification of source kerogen sedimentation conditions after Lewan (1984). I – open lacustrine and playa facies; II – open marine and deltaic facies; III – biogenic pelagic facies, for explanation of sample codes see Table 1

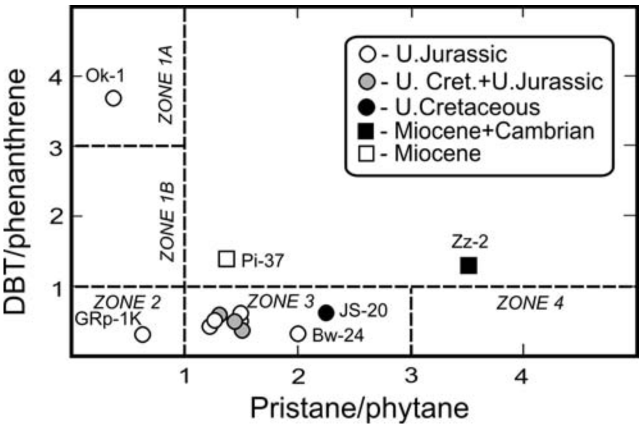

Fig. 11. A cross-plot of the dibenzothiophene/phenanthrene ratio *versus* the pristane/phytane ratio. Classification of source kerogen sedimentation conditions after Hughes *et al.* (1995). Zone 1A – marine carbonate; Zone 1B – marine carbonate or marine marl or lacustrine sulfate-rich; Zone 2 – lacustrine sulphate – poor; Zone 3 – marine shale and other lacustrine; Zone 4 – fluvial/deltaic, for explanation of sample codes see Table 1

conditions in which nickel and vanadium ions were available (regime II in Lewan, 1984) (Fig. 10), corresponding with marine and deltaic facies (the Type II and III kerogen). The oils collected from Opaka-1, Lubaczów-157 and Zagorzyce-6 wells lie in Lewan's (1984) regime III having biogenic pelagic matter as the source rock (Fig. 10).

Distributions of *n*-alkanes and isoprenoids in the analysed crude oils are variable, usually monomodal, with a distinct maximum in the short-chain range (Fig. 2A), characteristic of hydrocarbons generated from marine organic matter (*e.g.*, Peters *et al.*, 2005). The CPI values are usually above 1.0 indicating that the source organic matter was deposited mainly in clastic rocks (Moldowan *et al.*, 1985). This is supported by the high values of the pristane/phytane (Pr/Ph) ratios, usually above unity (Table 2), indicating sub-oxic conditions prevalence during the deposition of their source rock (Didyk *et al.*, 1978). Only two exceptions to these rules are observed: the CPI value of the Wierzchosławice-5 oil equals 0.78 and the Pr/Ph ratio of the Góra Ropczycka-1K oil equals 0.64 (Table 2), suggesting the domination of carbonates in the mineral composition of the source rocks of these oils. This concept is confirmed by the correlation between the pristane/n-C$_{17}$ and phytane/n-C$_{18}$ indices (Fig. 5) and the dibenzothiophene/phenanthrene and pristane/phytane ratios (Fig. 11). The elevated value of the pristane/phytane ratio, *ca.* 3.5 for the Załazie-2 oil, suggests their genetic correlation with deltaic facies of the Miocene molasses and the increased DBT/Phen ratio reveals partly the generation of this oil from a marine carbonate or marine marl. The source organic matter of the Opaka-1 oil was deposited under different conditions. This oil was generated from marine kerogen (Type I is not excluded) deposited in carbonates (Tables 2, 5, Figs 5, 11). These data are very similar to the results of the Kokhanivka-26 and Orkhovychi-2 oils collected in the Ukrainian part of the Carpathian Foredeep basement (Więcław *et al.*, in press). Interpretations of the source rock lithology of the Pilzno-37 and Góra Ropczycka-1K oils (Fig. 11) are probably invalid due to a change in their composition upon secondary processes. The distribution of regular 5α,14α,17α(H)-20R steranes in the crude oils (Table 6, Fig. 12) shows the presence of some distinct oil groups. The first group is represented by the Nosówka-1 oil, significantly different from the other oils. The second group includes oils from the Grobla and Wierzchosławice deposits, the third one – oils from the Brzezówka, Partynia Podborze, Pilzno (Jurassic), Załazie and Dąbrowa Tarnowska deposits, and the fourth one – the remaining oils (Fig. 12). Oleanane was detected in the majority of the analysed oils (Table 6, Fig. 13A). This biomarker relates to angiospermous higher plants and defines the age of the source organic matter as Cretaceous or younger (Ekweozor & Udo, 1988). As the most probable source rocks for these oils, ten Haven *et al.* (1993) and Curtis *et al.* (2004) proposed the Oligocene Menilite Shales rich in organic matter. This biomarker does not occur in oils deposited in the Palaeozoic (the Nosówka deposit) and Mesozoic basement of the Carpathian Foredeep (inflows into Opaka-1 and Łękawica-1 wells, and the Tarnów (Jurassic) and Łąkta deposits) (Table 6, Fig. 13A), nor in the Miocene strata (Tarnów, Łękawica and Pilzno deposits), thus suggesting their source rock most probably as Jurassic or older. In the other oils, oleanane is present in variable relative quantities reaching the value of (18α + 18β-oleanane)/17α hopane ratio up to 0.28 for the

Table 5

Indices calculated based on phenanthrene and dibenzothiophene and their derivatives distribution

Samplecode	Reservoir stratigraphy	MPI 1	MPR	MPR1	R_{cal} (%)	$R_{cal(MPR)}$ (%)	DBT/P	MDR	$R_{cal(DBT)}$ (%)	$T_{max(DBT)}$ (°C)
Bw-24	U.Jurassic	0.80	0.90	0.43	0.85	0.81	0.3	4.8	0.9	448
GRp-1K		0.90	1.57	0.57	0.91	1.10	0.3	1.7	0.6	432
Ga-109		0.59	0.74	0.38	0.72	0.69	0.5	4.2	0.8	444
Ga-36		0.56	0.77	0.40	0.70	0.72	0.5	3.9	0.8	443
Ga-89	U.Jura. +U.Cret.	0.61	0.77	0.39	0.74	0.71	0.6	4.0	0.8	443
JS-20	U.Cretaceous	0.78	0.83	0.42	0.84	0.77	0.6	2.4	0.7	435
Lc-1	U.Jurassic	0.75	0.90	0.45	0.82	0.84	0.4	5.1	0.9	449
Lc-1(c.)	Miocene	traces of hydrocarbons								
Ok-1	U.Jurassic	0.63	0.63	0.42	0.75	0.77	3.7	0.6	0.6	426
Pi-37	Miocene	0.42	0.76	0.42	0.62	0.77	1.4	1.2	0.6	429
Pl-36	U.Jurassic	0.56	0.65	0.37	0.70	0.66	0.6	5.2	0.9	450
Pl-41	U.Jura. +U.Cret.	0.57	0.67	0.36	0.71	0.65	0.5	4.2	0.8	444
Ta-39	Miocene	traces of hydrocarbons								
Ta-45		traces of hydrocarbons								
Ta-5	U.Jurassic	traces of hydrocarbons								
Wi-5	U.Jura. +U.Cret.	0.65	0.74	0.39	0.76	0.71	0.4	4.2	0.8	445
Zz-2	Cm+Miocene	0.66	0.87	0.46	0.77	0.86	1.3	6.0	0.9	453

U. – Upper; Jura. – Jurassic; Cret. – Cretaceous; Cm – Cambrian; 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); DBT – dibenzothiophene; MDR = 4-MDBT/1-MDBT (Radke *et al.*, 1986); MDBT – methyldibenzothiophene; $R_{cal(DBT)}$ = 0.51+0.073MDR (Radke & Willsch, 1994); $T_{max(DBT)}$ = 423+5.1MDR (Radke, 1988)

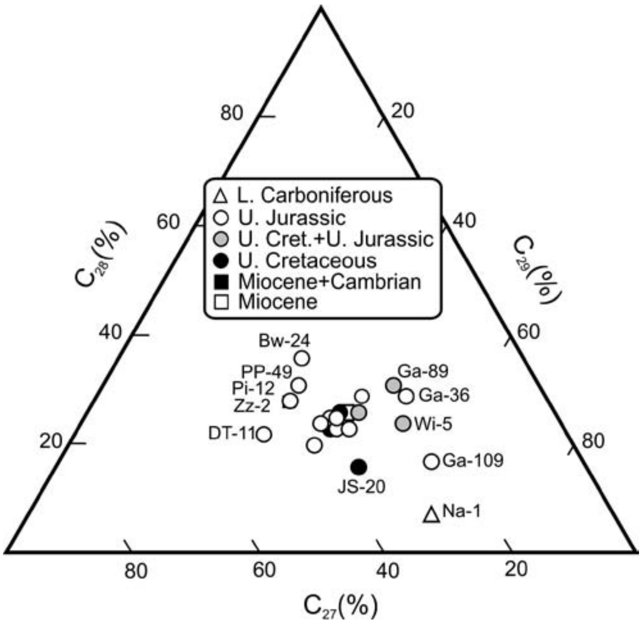

Fig. 12. Ternary diagram of C_{27}, C_{28} and C_{29} regular ααα sterane composition (m/z = 217). For explanation of sample codes see Table 1

Jastrząbka Stara-20 oil deposited in the Upper Cretaceous sandstones (Table 6, Fig. 13A).

The stable carbon isotope composition of crude oils and their individual fractions (Table 1) support the biomarker data and indicate that the analysed oils and condensates were generated from several source rocks differing in the type of organic matter (Figs 13–15). In the majority of these oils, asphaltenes are depleted in ^{13}C isotope relative to resins, which is characteristic of oil generated from algal kerogen (Galimov, 1973, 1986). This effect can also result from biodegradation processes (Stahl, 1980), but, as noted above, only in not big quantity of oils these processes were observed on a limited scale. Some differences in the stable carbon isotope composition follow changes in source rock facies and maturity (Waples & Tornheim, 1978; Chung *et al.*, 1981; Lewan, 1983) or migration distance (Stahl, 1980). A distinct stable carbon isotope composition was detected in the oils and condensates: i) deposited in the Lower Carboniferous strata (Nosówka deposit) and oil inflows in Łękawica-1 (Jurassic) and Zalasowa-2 (Miocene), ii) accumulated in the Upper Jurassic strata in the vicinity of Lubaczów (Opaka-1 and Lubaczów-157 wells), iii) accumulated in the Grobla-Pławowice, Wierzchosławice and Pilzno (Miocene) deposits, iv) inflow in Załazie-2 well, and v) the remaining oils (Figs 13–15). In a number of oils (*e.g.*, Załazie-2 and Zalasowa-2 wells) some changes in the isotope composition may result from admixture of oil generated from kerogen enriched in lighter stable carbon isotope (Figs 13–15).

The fractional composition and the saturate/aromatic hydrocarbon (sat/aro) ratios have been suggested to be influenced by migration distance. The investigated crude oils have variable contents of asphaltenes, usually below 1 wt%, with the highest value of 32.5 wt% in oil collected from Opaka-1 well (Table 1, Fig. 16). High concentrations of

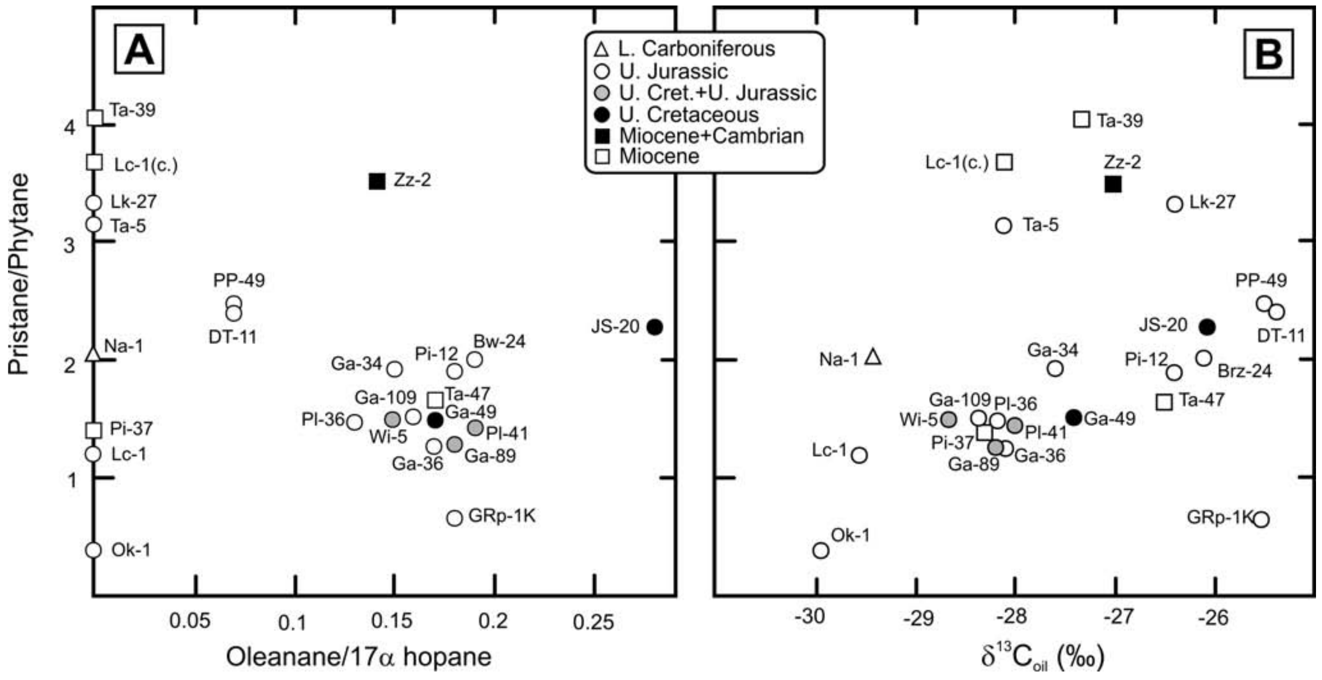

Fig. 13. Pristane/phytane ratio *versus* (**A**) oleanane/17α hopane ratio and (**B**) stable carbon isotope composition of whole oil. For explanation of sample codes see Table 1

asphaltenes conversely correlate with low saturated-hydrocarbon content and the low sat/aro ratios (Table 1, Fig. 16). The lowest values of sat/aro are noted for oils from Opaka-1, Lubaczów-157 and Zalasowa-2 wells. These oils probably migrated the shortest distance. The condensates from the Łękawica and Tarnów gas deposits probably migrated the longest distance (Fig. 16). Values of this ratio can be affected by maturity and thermal cracking processes, but the latter mentioned process was not observed here.

Maturity

The maturity of crude oils was determined based on composition of light hydrocarbons (Table 2), selected biomarkers (Table 6), and indices deriving from relative concentrations of phenanthrene and dibenzothiophene and their methyl derivatives (Table 5).

The distribution of methylphenanthrenes reveals a narrow range of maturity of oils (in condensates these hydrocarbons did not occur) indicating their generation in the initial phase and peak of the oil window (R_{cal} about 0.6–0.9%) (Table 5). The maturity indices calculated based on methyldibenzothiophenes distributions confirm the same range of the oil maturities (Table 5), but they differ for individual oils. As the MPI and MPR indices were evaluated for terrestrial organic matter (*e.g.*, Radke, 1988; Radke *et al.*, 1986), while maturity described by the MDR values for oils generated mostly from marine Type II kerogen are more adequate for assessing the maturity of investigated oils. Less mature oils, generated at *ca*. 0.6 % R_o, are accumulated in the Góra Ropczycka and Opaka (Upper Jurassic) and Pilzno (Miocene) deposits (Table 5). The remaining oils are characterised by comparable maturities (Table 5). A relationship between the maturity and locality as well as depth of oil accumulation is not observed. The biomarker distribution supports the above observation. The sterane and terpane distributions show that the analysed oils were generated from the organic matter being at variable maturity levels (Fig. 17): from immature, through the early-mature to the mature stages. The epimerisation of steranes shows that less mature oils are in the Góra Ropczycka, Partynia-Podborze and Pilzno deposits (Upper Jurassic) and the most mature oils are in the Brzezówka deposit (Upper Jurassic) and Załazie-2 well (Cambrian–Miocene) (Fig. 17). The unusually low Ts/(Ts+Tm) value of oil from Opaka-1 well is a result of carbonate depositional environment of its source rocks. This effect was earlier described by, *e.g.*, Barakat *et al.* (1997) for the oils from Gulf of Suez and Al-Ameri *et al.* (2009) for the oils accumulated in the Mishrif reservoir of the Southern Iraq, both generated from the carbonate source rocks. Also, oils from the Grobla-Pławowice, Wierzchosławice, Dąbrowa Tarnowska, Jastrząbka Stara deposits and the oil inflow into Łękawica-1 well (Upper Jurassic) show lowered values of the Ts/(Ts+Tm) ratio suggesting the presence of carbonates in their source rocks.

The temperature of generation of hydrocarbons estimated from the dimethylpentane homologues distribution (Mango, 1997) varies in a narrow range, from 114 (Góra Ropczycka-1K) to 126°C (Łąkta-27) (Table 2) indicating comparable conditions of generation of all the analysed oils and condensates.

CONCLUSIONS

The wide range of geochemical studies enabled one to evaluate detailed genetic characteristics of liquid hydrocarbons (oils and condensates) accumulated in the autochtho-

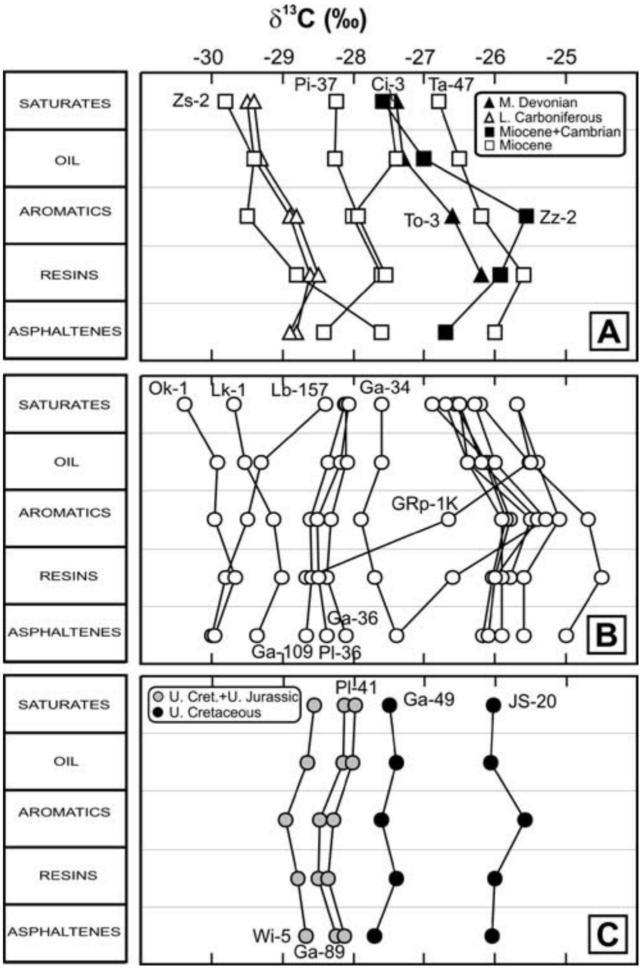

Fig. 14. Stable carbon isotope composition of crude oils/condensates and their individual fractions of (**A**) accumulated in the Cambrian, Middle Devonian, Lower Carboniferous and Miocene strata, (**B**) the Upper Jurassic strata, and **(C)** the Upper Jurassic–Upper Cretaceous and Upper Cretaceous strata. For explanation of sample codes see Table 1

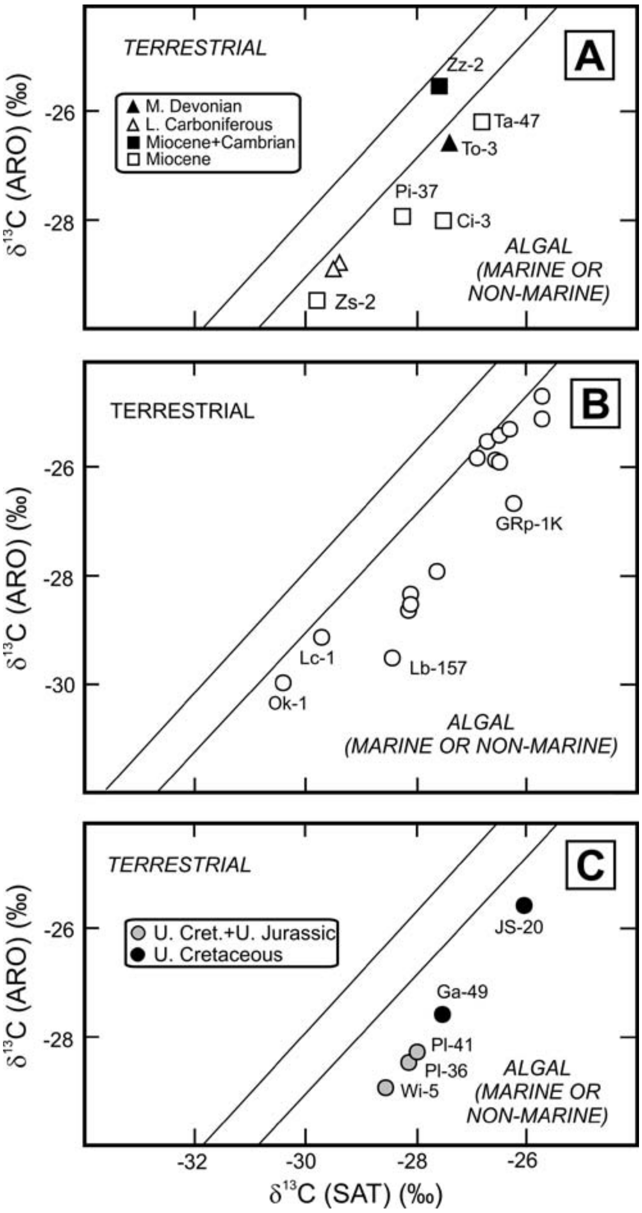

Fig. 15. Genetic characterization of oils in terms of δ^{13}C (aromatic hydrocarbons) and δ^{13}C (saturated hydrocarbons) according to the categories of Sofer (1984) of (**A**) accumulated in the Cambrian, Middle Devonian, Lower Carboniferous and Miocene strata, (**B**) the Upper Jurassic strata, and (**C**) the Upper Jurassic–Upper Cretaceous and Upper Cretaceous strata. For explanation of sample codes see Table 1

nous Miocene strata of the Carpathian Foredeep and its Mesozoic and Palaeozoic basement. For this purpose, petroleum geochemical data on 34 oils and condensates were used. The analysed oils and condensates show a wide range of gravities from 5.3 to 62.2°API and sulphur contents from 0.00 to 10.1 wt%. There is no relationship between these parameters and the reservoir rock age. The heaviest oils (Opaka-1 and Lubaczów-157) are characterized by the highest sulphur content and represent a separate group, which correlates with heavy oils in the Ukrainian territory (Vul *et al.*, 1998). These oils were generated from a high-sulphur kerogen deposited in the Upper Jurassic carbonates, recorded by Kosakowski *et al.* (in press, b), located in the Ukrainian part of the basement of the Carpathian Foredeep.

Also, oil collected from Góra Ropczycka-1K well positively correlates with organic matter deposited in the carbonates. The potential source rock levels for this oil were evidenced in the Upper Jurassic carbonates in the vicinity of Rzeszów (Kosakowski, in press, a). Geochemical indices of the Góra Ropczycka-1K oil indicate strong evaporative fractionation and biodegradation processes. This oil was generated at a very early stage of source organic matter maturity at oil window margin, the same maturity stage as the Upper Jurassic rocks in the Rzeszów area (Kosakowski & Wróbel, 2011).

The remaining oils were generated from organic matter deposited in clastic deposits (claystones, mudstones) or strata, where that type of organic matter was dominant (clayey marls). Oil collected from the inflow in Załazie-2 from the Cambrian and Miocene strata originated from the Cambrian strata and also contained biomarkers occurring in the Miocene strata. The high maturity of this oil is connected with generation of the main stream of hydrocarbons from the Lower Palaeozoic strata. The presence of the Miocene hydrocarbons is evidenced by the presence of oleanane and the high value of the pristane/phytane ratio.

The next oil group consists of oil accumulated in the Lower Carboniferous carbonates in the Nosówka deposit and the inflow into Łękawica-1 well (Upper Jurassic). The absence of oleanane and presence of a very light carbon stable isotope envelope suggests their genetic correlation with the Lower Palaeozoic source rocks (Ordovician and Silurian). These rocks in the analysed area have a very high hydrocarbon potential; they also contain oil-prone kerogen at maturity in the range for generation of liquid hydrocarbons (Więcław *et al.*, 2011). This opinion is consistent with previous studies on oils from the Nosówka deposit presented by ten Haven *et al.* (1993) and Kotarba *et al.* (2004).

The next group of oils characterized by the absence of oleanane is composed of condensates collected from the Miocene (Łękawica-1, Tarnów-39 and -45 wells) and Upper Jurassic strata (Łąkta-27 and Tarnów-5 wells). In these condensates, total absence of biomarkers is observed, caused probably by their high maturity and a long way of migration. Their origin may be determined only based on the stable carbon isotopes correlation, because the increased values of the pristane/phytane ratio, *i.e.* over 3, may reflect rather their high maturity (Koopmans *et al.*, 1996; Al-Arouri *et al.*, 1998). The Middle Jurassic or Lower Carboniferous clastic facies may be regarded as the probable source rocks of these condensates (Więcław *et al.*, 2011; Kosakowski *et al.*, in press. a). The condensate collected from Pilzno-37 well has a very similar characteristic to the above-mentioned condensates, but traces of biomarkers recorded in this sample indicate its lower maturity than the previously discussed ones.

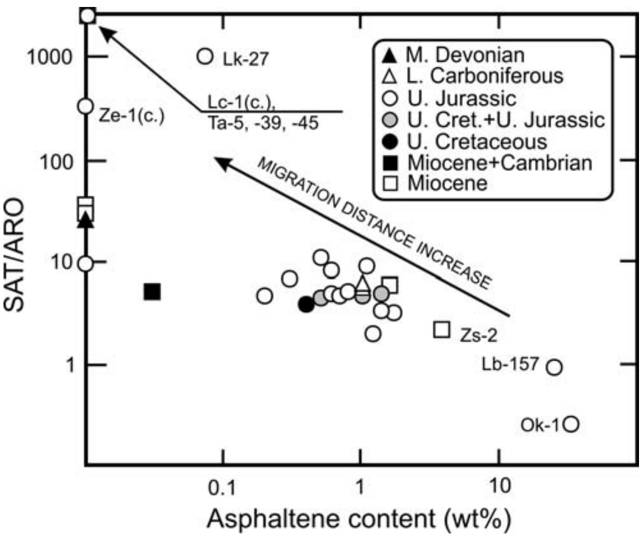

Fig. 16 Saturated hydrocarbons/aromatic hydrocarbons ratio *versus* asphaltenes content. For explanation of sample codes see Table 1

From the rest of oils, where the oleanane is present, a separate group can be distinguished, consisting of oils accumulated in the Grobla-Pławowice and Wierzchosławice deposits. They are characterized by a light stable carbon isotope envelope. Increased concentrations of sulphur in oils as well as the presence of H_2S in the accompanying gas in the Grobla-Pławowice deposit (Karnkowski, 1999) suggest that both media were generated from kerogen enriched in organic sulphur. Suitable conditions in this area occur in the Upper and Middle Devonian strata, where levels of marls with the TOC up to 2.6 wt% were observed (Więcław *et al.*, 2011). It is possible that hydrocarbons were partly generated from the Silurian strata. All the above mentioned source rocks are characterized by suitable properties (quantity, quality and maturity of organic matter) for generation of the analysed oils. The source of oleanane in the discussed

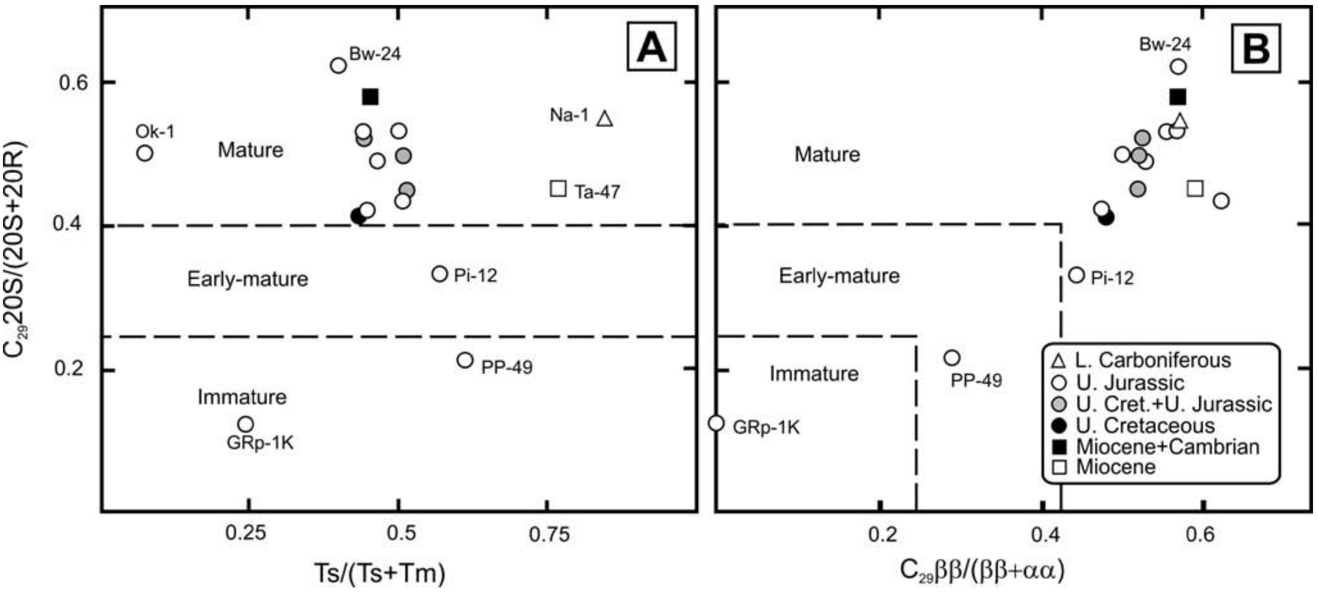

Fig. 17. Sterane C_{29}20S/(20S+20R) ratio *versus* (**A**) Ts/(Ts+Tm), and (**B**) $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$ ratios. Maturity fields after Peters and Moldovan (1993), for explanation of sample codes see Table 1

Table 6

Characteristics of selected hydrocarbon biological markers

Sample code	Reservoir strati-graphy	S/(S+T)	C_{27}	C_{28}	C_{29}	Dia/Reg	Ol/Hop	Mor/Hop	C_{27} dia/reg	C_{29} SR	C_{29} ββαα	TA(I)/TA(I+II)	$H_{31}S$/(S+R)	Ts/(Ts+Tm)	C_{29}/C_{27}ster	C_{29}Ts/C_{29}H
Bw-12*	Upper Jurassic	0.15	38	24	38	1.87	0.23	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bw-24		0.35	35	36	29	1.06	0.19	0.14	0.25	0.62	0.57	0.24	0.53	0.39	0.96	0.08
DT-11**		n.d.	48	22	30	n.d.	0.07	n.d.	1.36	0.43	0.62	n.d.	0.62	0.50	n.d.	0.29
GRp-1K		0.62	36	25	39	0.20	0.18	0.15	0.28	0.12	0.00	0.36	0.39	0.24	0.84	2.01
Ga-109		0.16	24	17	59	0.53	0.16	0.10	0.30	0.42	0.47	0.28	0.53	0.44	1.40	0.03
Ga-34*		0.09	36	23	41	0.90	0.15	0.07	0.52**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.38
Ga-36		0.16	22	29	49	0.87	0.17	0.10	0.32	0.53	0.55	0.26	0.53	0.44	1.30	0.05
Ga-49*	U.Cret.	0.09	37	23	40	1.05	0.17	0.07	0.74**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.36
Ga-89	U.Jura. + U.Cret.	0.15	24	31	46	0.71	0.18	0.10	0.28	0.52	0.52	0.28	0.51	0.44	1.24	0.08
JS-20	U.Cret.	0.28	36	17	48	0.73	0.28	0.14	0.31	0.41	0.48	0.35	0.52	0.43	0.91	0.12
JS-6*		0.12	34	26	40	1.23	0.27	0.13	0.73**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34
Lc-1	U.Jura.	0.30	35	26	40	0.83	0.00	0.08	0.32	0.49	0.53	0.33	0.55	0.46	1.02	0.11
Lc-1(c.)	Miocene	n.c.	n.c.	n.c.	n.c.	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Lb-157*	U.Jura.	0.17	41	20	39	0.56	0.06	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na-1**	L.Carbo-niferous	n.d.	29	7	64	n.d.	0.00	n.d.	1.33	0.54	0.57	n.d.	0.58	0.85	n.d.	0.62
Ok-1	U.Jura.	0.22	34	23	43	n.c.	0.00	0.09	n.c.	0.50	0.50	0.14	0.51	0.07	1.45	0.10
Pi-12**		n.d.	41	28	31	n.d.	0.18	n.d.	0.53	0.33	0.44	n.d.	0.58	0.57	n.d.	0.44
Pi-37	Miocene	n.c.	n.c.	n.c.	n.c.	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	2.05	n.c.
Pl-36	U.Jura.	0.18	29	29	42	0.88	0.13	0.08	0.32	0.53	0.57	0.26	0.57	0.49	1.22	0.08
Pl-41	U.Jura. + U.Cret.	0.17	31	26	43	0.72	0.19	0.10	0.28	0.50	0.52	0.24	0.51	0.50	1.13	0.07
PP-49**	U.Jura.	n.d.	38	31	31	n.d.	0.07	n.d.	0.27	0.21	0.29	n.d.	0.54	0.61	n.d.	0.34
Ta-39	Miocene	n.c.	n.c.	n.c.	n.c.	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Ta-45		n.c.	n.c.	n.c.	n.c.	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Ta-47**		n.d.	33	26	41	n.d.	0.17	n.d.	1.21	0.45	0.59	n.d.	0.61	0.77	n.d.	0.55
Ta-5	U.Jura.	n.c.	n.c.	n.c.	n.c.	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Wi-5	U.Jura. + U.Cret.	0.17	25	24	51	0.69	0.15	0.11	0.36	0.45	0.52	0.31	0.53	0.51	1.51	0.10
Ze-6(c.)*	U.Jura.	0	0	0	0	0	0.00	1.26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ze-6*		0.11	38	24	38	1.48	0.25	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zz-2	Cm + Miocene	0.18	41	29	31	0.33	0.14	0.08	0.14	0.58	0.57	n.c.	0.52	0.44	1.45	0.08

c. – condensate; U. – Upper; Jura. – Jurassic; Cret. – Cretaceous; L. – lower; Cm – Cambrian; S/(S+T) = all steranes/(all steranes + all terpanes); C_{27} = C_{27}αααα20R sterane/(C_{27}+C_{28}+C_{29}) ααα20R steranes*100; C_{28} = C_{28}ααα20R sterane/(C_{27}+$C2_8$+C_{29})ααα20R steranes*100; C_{29} = C_{29}ααα20R sterane/(C_{27}+C_{28}+C_{29})ααα20R steranes*100; Dia/Reg = C_{27} βα 20S diasterane/C_{29}ααα20R sterane; Ol/Hop = Oleanane/17α hopane; Mor/Hop = Moretane/17α hopane; C_{27} dia/reg = C_{27} βα 20(S+R) diasterane/ΣC_{27} regular steranes; C_{29}SR = epimerisation of regular steranes C_{29} ratio; C_{29}ββαα = ratio of ββ-epimeres of regular steranes C_{29} to their total quantity, TA(I)/TA(I+II) = (C_{21}+C_{22} triaromatic)/(C_{21}+C_{22}+$C_{26\text{-}28}$ triaromatic steroids); $H_{31}S$/(S+R) = homohopane 22S/(22S+22R); Ts/(Ts+Tm) = C_{27} 18α trisnorhopane/(C_{27} 18α trisnorhopane + C_{27} 17α trisnorhopane), C_{29}/C_{27}ster = ΣC_{29} regular steranes/ΣC_{27} regular steranes; C_{29}Ts/C_{29}H = C_{29} 18α norneohopane/C_{29} norhopane; * – data from Curtis *et al.* (2004); ** – data from ten Haven *et al.* (1993); n.d. – not determined; n.c. – not calculated due to lack of biomarkers

oils is probably the organic matter dispersed in the Upper Cretaceous rocks, from which it was eluted by the migrating oils. Such process was earlier described, *e.g.*, by Mello *et al.* (2000).

Oils from the remaining deposits and inflows (Jastrząbka Stara, Partynia-Podborze, Dąbrowa Tarnowska, Brzezówka, Zagorzyce, Tarnów-47, and Pilzno-12) have probably the same origin as the previously discussed group. Particularly high sulphur contents, up to 2.3 wt%, point to the genetic relation of these oils with the high-sulphur kerogen. Oils generated in the Silurian, Devonian and/or Lower Carboniferous carbonates have migrated through the Jurassic and/or Cretaceous strata eluting biomarkers from them. Oleanane in these oils, is most probably sourced from the Upper Cretaceous rocks and/or the Miocene strata sealing reservoirs. However, generation of these oils by the Oilgocene Menilite Shales deposited in the Outer Carpathian suite, as proposed by ten Haven *et al.* (1993), cannot be excluded.

Acknowledgements

This study was undertaken as a research project No. UKRAINE/193/2006 of the Ministry of Science and Higher Education carried out at the AGH University of Science and Technology in Kraków and the Polish Geological Institute – National Research Institute in Warsaw. Scientific work was financed from the scientific fund in the years 2007–2010. Irena Matyasik from the Oil and Gas Institute in Kraków and Franciszek Czechowski from the University of Wrocław provided very constructive reviews, which greatly improved the discussion and working hypotheses presented in the manuscript. Analytical work by Adam Kowalski, Hieronim Zych and Tomasz Kowalski from the AGH University of Science and Technology in Kraków is gratefully acknowledged.

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