

## Origin and maturity of oils in the Ukrainian Carpathians and their Mesozoic basement

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Geochemical characteristics of 25 oils collected from the Skiba Unit of the Outer Carpathians, Boryslav-Pokuttya Unit of the Carpathian Foredeep, and their Mesozoic basement in the Western Ukraine are presented in the paper. The first oil family recognized consists of almost all oils accumulated in the flysch sequence of the Outer Carpathians and the Carpathian Foredeep which have very similar geochemical characteristics. These oils were generated from Type-II or II/III kerogen deposited in clastic sediments. They are low-sulphur and migrated short distances. Slight biodegradation processes are visible only in oils accumulated in shallow deposits in the Skiba Unit. Their source rocks are the Oligocene Menilite Shales from the Boryslav-Pokuttya Unit. Oils from the Kokhanivka and Orkhovychi deposits (the Mesozoic basement of the Carpathian Foredeep) constitute the second family. These oils are extremely heavy, high-sulphur and were generated from high-sulphur Type-IIS kerogen deposited in a carbonate environment. The most probable source rocks for these oils are the Upper Jurassic strata. Oil collected from the Volia Blazhivs'ka deposit (the Boryslav-Pokuttya Unit) shows intermediate parameters between the oil families described above. It is characterized by the presence of oleanane and a high sulphur content. It was generated from the Menilite Shales containing high-sulphur kerogen. All oils were generated at an early stage or the peak of the oil window.

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### INTRODUCTION

The Ukrainian Carpathians belong to the largest petroleum provinces of Central Europe and constitute one of the oldest petroleum-producing regions in the world. Exploitation of oil began there in 1854 and natural gas production in 1921 (Vul *et al.*, 1998; Karnkowski, 1999; Fedyshyn *et al.*, 2001; Kotarba and Peryt, 2011). The study area covers the Outer Carpathians, the Carpathian Foredeep and their basement between the Polish–Ukrainian border and Ivano-Frankivs'k (Fig. 1). The Boryslav-Pokuttya Unit of the Carpathian Foredeep is the main oil-producing unit in the Western Ukraine. Of 39 fields discovered there within a wide range of depths, 37 are oil and 2 are gas-condensate. The Boryslav oil field, one of the largest onshore fields in Europe,

is located in this region. Several small oil fields have been discovered in the Skiba Unit of the Outer Carpathians. They are of small size and occur at rather shallow depths.

Three oil fields have been discovered in the Mesozoic basement of the Carpathian Foredeep. Two of them, the Kokhanivka and Orkhovychi heavy oil fields (Fig. 1), occur within the study area in Upper Jurassic carbonate reservoirs in the northwestern part of the Ukrainian Carpathian Foredeep close to the Polish–Ukrainian border, while the third one, the Lopushna oil field, occurs in Upper Jurassic carbonate as well as Cretaceous and Paleogene sandstone reservoirs in its southeastern part, close to the Ukrainian–Romanian border. The initial recoverable resources of the Western Ukraine are estimated to be 1755.7 million tons of standard fuel, including 707.1 million tons of oil and 9.7 million tons of condensate (Vul *et al.*, 1998).

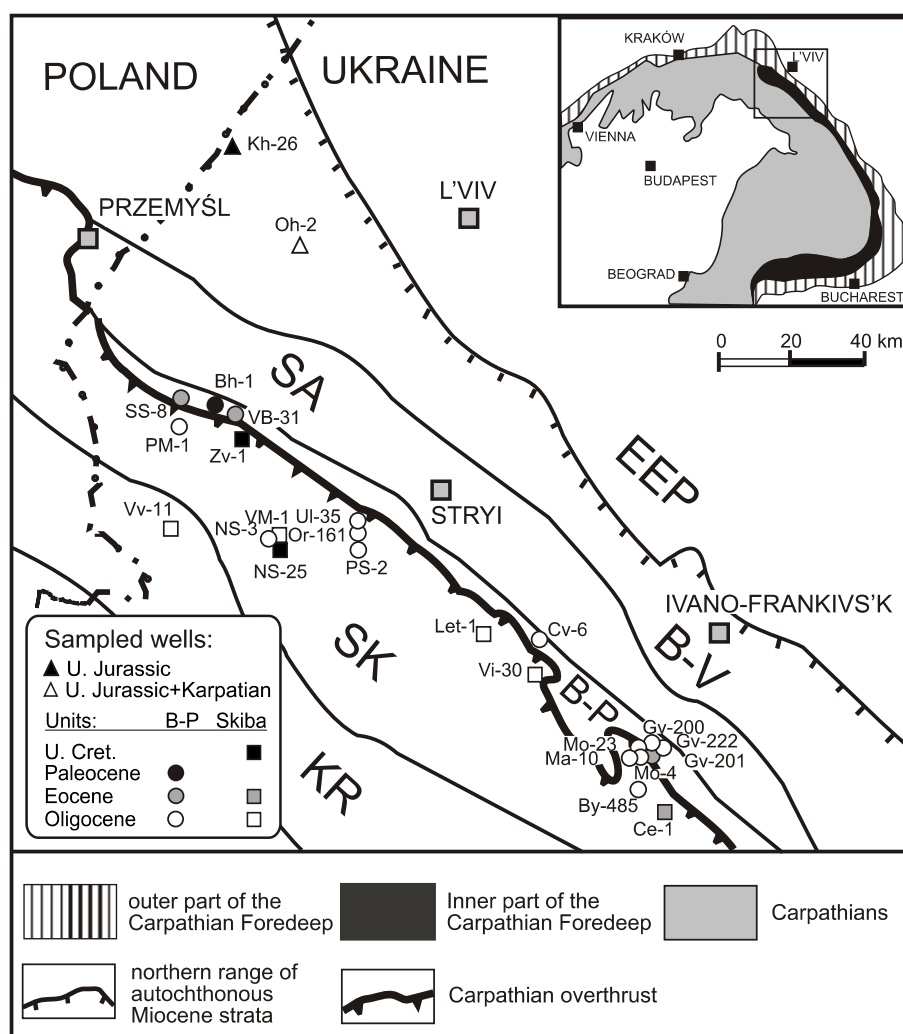


Fig. 1. Sketch geological map showing location of crude oil sampling sites

EEP – East European Platform, B-V – Bilche-Volytsia Unit, SA – Sambir Unit, B-P – Boryslav-Pokuttya Unit, SK – Skiba Unit, KR – Krosno Unit; for explanation of boreholes codes see Table 1

The Oligocene Menilite Shales are considered to be the most important source rock for Carpathian oils, representing a unique lithofacial unit of the Carpathian Flysch sequence characterized by a relatively high organic matter content of up to 20 wt.% (Koltun, 1992; Bessereau *et al.*, 1996; Krüge *et al.*, 1996; Koltun *et al.*, 1998; Köster *et al.*, 1998; Curtis *et al.*, 2004; Kotarba *et al.*, 2005, 2007; Kotarba and Koltun, 2006). Ten Haven *et al.* (1993), based on biomarker composition, did not exclude them as a source for oils accumulated in the Mesozoic basement of the Polish Carpathian Foredeep.

The main purpose of the present study is to characterize oils accumulated in the Skiba Unit of the Outer Carpathians, the Carpathian Foredeep succession (Boryslav-Pokuttya Unit) and its Mesozoic basement of the Western Ukraine (Fig. 1), as well as to identify their source rocks, maturity, migration distance and secondary processes. We would like also to revise, for the oils accumulated in the Mesozoic basement in the area studied, the concept proposed by ten Haven *et al.* (1993) for the Polish part

of the Mesozoic basement of the Carpathian Foredeep correlating all oils with the Menilite source rocks.

The primary characteristics of oils and source rock-oil correlation for the Ukrainian Outer Carpathians have been presented by Kotarba *et al.* (2005, 2007). For the Ukrainian part of the Carpathian Foredeep and its basement only basic analyses were conducted (Vul *et al.*, 1998).

## METHODS

### SAMPLING PROCEDURE

Twelve crude oil samples were collected (Table 1) from the basement of the Carpathian Foredeep (Kokhanivka 26 and Orkhovychi 2 boreholes), Boryslav-Pokuttya (Blazhiv 1, Chechva 6, Pivdenna Stynava 2, Staryi Sambir 8 and Volia Blazhivs'ka 31 boreholes) and the Skiba Units (Cherlen 1,

Table 1

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

Borehole/sample	Sample code	Reservoir rock	Reservoir age	Depth [m]	Gravity [ $^{\circ}$ API]	Sulphur [wt.%]	V [ppm]	Ni [ppm]	Fraction [wt.%]				sat./aro.	Stable carbon isotopes $^{13}\text{C}$ [‰]				
									sat.	aro.	res.	asph.		sat.	oil	aro.	res.	asph.
basement of the Carpathian Foredeep																		
Kokhanivka 26	Kh-26	carbonates	U. Jurassic	1109–1121 1130–1160	6.8	4.35	70	1.0	11.5	47.2	20.1	21.2	0.2	–30.4	–30.1	–30.2	–29.7	–30.0
Orkhovychi 2	Oh-2	carb.+sand.	U. Jur.+Karp.	1881–1915	13.4	6.5	132	37	17.0	49.0	16.2	17.8	0.3	–29.8	–29.7	–29.5	–29.4	–29.6
Carpathian Foredeep – Boryslav-Pokuttya Unit																		
Blazhiv 1	Bh-1	Yamna Beds	Paleocene	3145–3160	35.6	0.32	4.2	<0.5	62.1	25.5	8.5	3.9	2.4	–26.8	–26.5	–26.1	–26.3	–26.6
Bytkiv 485*	By-485	Menilite Beds	Oligocene	2245–2292	23.1	0.67	n.a.	n.a.	59.0	25.9	11.8	3.3	2.3	–27.7	–27.4	–27.2	–27.5	–27.1
Chevcha 6	Cv-6	Kliwa Ss	Oligocene	2232–2292	31.8	0.25	2.5	9.0	63.7	23.3	12.0	1.0	2.7	–27.1	–26.6	–26.3	–26.2	–26.6
Gvizd 200*	Gv-200	Menilite Beds	Oligocene	1524–1635	24.6	0.53	n.a.	n.a.	76.3	16.2	7.0	0.5	4.7	–29.3	–28.9	–28.4	–28.1	–27.4
Gvizd 201*	Gv-201	Vygoda Beds	Eocene	2016–2195	32.5	0.41	n.a.	n.a.	61.4	25.4	11.8	1.4	2.4	–27.1	–26.8	–26.1	–26.1	–26.4
Gvizd 222*	Gv-222	Menilite Beds	Oligocene	1586–1721	35.8	0.40	n.a.	n.a.	59.8	21.5	15.4	3.3	2.8	–26.5	–26.5	–26.4	–26.5	–26.4
Markova 10*	Ma-10	Menilite Beds	Oligocene	2147–2307	35.1	0.42	n.a.	n.a.	55.1	27.9	14.0	3.0	2.0	–27.3	–27.0	–26.7	–26.7	–26.6
Monastyrchany 23*	Mo-23	Menilite Beds	Oligocene	3486–3602	31.5	0.26	n.a.	n.a.	65.9	26.3	7.3	0.5	2.5	n.a.	n.a.	n.a.	n.a.	n.a.
Monastyrchany 4*	Mo-4	Menilite Beds	Oligocene	2292–2407	32.7	0.42	n.a.	n.a.	72.5	18.4	7.4	1.7	3.9	–26.8	–26.5	–26.2	–26.1	–26.6
Novoskhidnytsia 3***	NS-3	Boryslav Ss	Oligocene	4205–4334	35.7	0.32	n.a.	n.a.	70.7	21.3	7.5	0.5	3.3	–26.7	–26.4	–25.8	–25.9	–26.4
Oriv 161**	Or-161	Kliwa Ss	Oligocene	3090–3120	31.1	0.71	n.a.	n.a.	61.2	28.8	8.5	1.5	2.1	–27.5	–27.2	–26.5	–26.9	–27.1
Pivdenna Stynava 2	PS-2	Kliwa Ss	Oligocene	4482–4530	29.5	0.31	3.3	3.0	66.8	24.0	7.1	2.1	2.8	–27.3	–27.0	–25.8	–26.2	–26.5
Pivdennyi Monastyrchany 1**	PM-1	Kliwa Ss	Oligocene	4945–4962	22.2	0.92	n.a.	n.a.	57.7	27.6	9.8	4.9	2.1	–27.7	–27.3	–26.8	–26.9	–27.1
Staryi Sambir 8	SS-8	Vygoda Beds	Eocene	3295–3333	38.3	0.26	2.6	1.6	75.1	17.3	5.4	2.2	4.3	–26.3	–26.3	–25.9	–26.4	–26.5
Ulychno 35**	Ul-35	Kliwa Ss	Oligocene	2826–2945	31.0	0.37	n.a.	n.a.	67.0	23.0	7.9	2.1	2.9	–27.2	–26.9	–26.4	–27.0	–27.0
Volia Blazhivs'ka 31	VB-31	Vygoda Beds	Eocene	2953–3123	23.3	1.74	45	47	38.1	35.6	20.8	5.5	1.1	–29.2	–28.9	–29.2	–28.8	–28.4
Outer Carpathians – Skiba Unit																		
Cherlen 1	Ce-1	Vygoda Beds	Eocene	295–279	32.8	0.25	3.1	10	72.0	20.3	6.2	1.5	3.5	–26.7	–26.3	–25.8	–26.1	–26.2
Letsivka 1	Let-1	Kliwa Ss	Oligocene	631–915; 978–1033	35.2	0.40	3.6	6.7	68.3	20.9	10.6	0.2	3.3	–26.8	–26.6	–26.2	–26.0	–26.6
Novoskhidnytsia 25**	NS-25	Stryi Beds	U. Cret.	887–902	34.7	0.43	n.a.	n.a.	62.7	25.5	9.6	2.2	2.5	–26.6	–26.4	–25.9	–26.0	–26.5
Verkhne Maslove 1**	VM-1	Kliwa Ss	Oligocene	1296–1325	31.2	0.76	n.a.	n.a.	55.5	29.1	11.1	4.3	1.9	–27.5	–27.1	–27.0	–26.7	–26.9
Vilkhivka 30	Vi-30	Kliwa Ss	Oligocene	943–74	32.9	0.35	2.4	12	65.5	23.2	10.9	0.4	2.8	–27.3	–26.9	–26.4	–26.5	–27.1
Vovche 11	Vv-11	Golovetsko Beds	Oligocene	557–650	32.9	0.17	<0.5	<0.5	73.6	19.1	6.9	0.4	3.9	–26.3	–26.0	–25.6	–26.1	–26.6
Zvoriv 1	Zv-1	Stryi Beds	U. Cret.	949–959	36.6	0.12	<0.5	<0.5	70.2	22.4	5.6	1.8	3.1	–26.2	–26.0	–25.1	–25.3	–25.8

Ss, sand. – sandstones, carb. – carbonates, Jur. – Jurassic, Karp. – Karpatian, U. – Upper, Cret. – Cretaceous, sat. – saturated hydrocarbons, aro. – aromatics, res. – resins, asph. – asphaltenes; n.a. – not analysed, \* – data from Kotarba *et al.* (2005), \*\* – data from Kotarba *et al.* (2007)

Letsivka 1, Vilkhivka 30, Vovche 11 and Zvoriv 1 boreholes; Fig. 1). All oils were collected from producing boreholes.

Additionally, for comparative studies, eleven oils from the Boryslav-Pokuttya and two oils from the Skiba units described by Kotarba *et al.* (2005, 2007) were taken into consideration (Table 1 and Fig. 1).

#### ANALYTICAL METHODS

Oils were analysed for API gravity with an *Anton Paar DMA5300M* density meter and for sulphur content with a *Leco SR-12* analyser. The vanadium and nickel contents were determined by the inductively coupled plasma optical emission spectrometry (ICP-OES) method using a *Perkin Elmer WMA400* spectrophotometer according to the *ASTM D 5708:2002* method. Before the deasphalting, 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 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. 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 a *Finnigan Delta Plus* mass spectrometer. The stable carbon isotope data are presented in the  $\delta$ -notation relative to the V-PDB standard (Coplen, 1995), with the analytical precision estimated to be  $\pm 0.2\%$ . The elemental composition of asphaltenes was determined using a *Carlo Erba EA1108* elemental analyser.

For the whole oil analysis, high resolution gas chromatography was used. For this purpose 1  $\mu$ l of sample diluted in CS<sub>2</sub> 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 passes through a 50 m × 0.2 mm *Agilent DB1* column (0.5  $\mu$ m film thickness) using 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, and held at the final temperature 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 GC-MS for biomarker determination. The analysis was carried out with a *Agilent 7890A* gas chromatograph equipped with an *Agilent 7683B* automatic sampler, an on-column injection chamber and a fused silica capillary column (60 m × 0.25 mm i.d.) coated with a 95% methyl/5% phenylsilicone phase (DB-5MS, 0.25  $\mu$ m film thickness). Helium was used as the carrier gas. The GC oven was programmed: 80°C held for 1 min, then increased to 120°C at the rate of 20°C/min, then increased further to 300°C at the rate of 3°C/min and finally held for 35 min. The gas chromatograph was coupled with a 5975C mass selective detector (MSD). The MS was operated with an ion source temperature of 230°C, an ionization energy

of 70 eV, and a cycle time of 1 sec in the mass range from 45 to 500 Daltons.

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

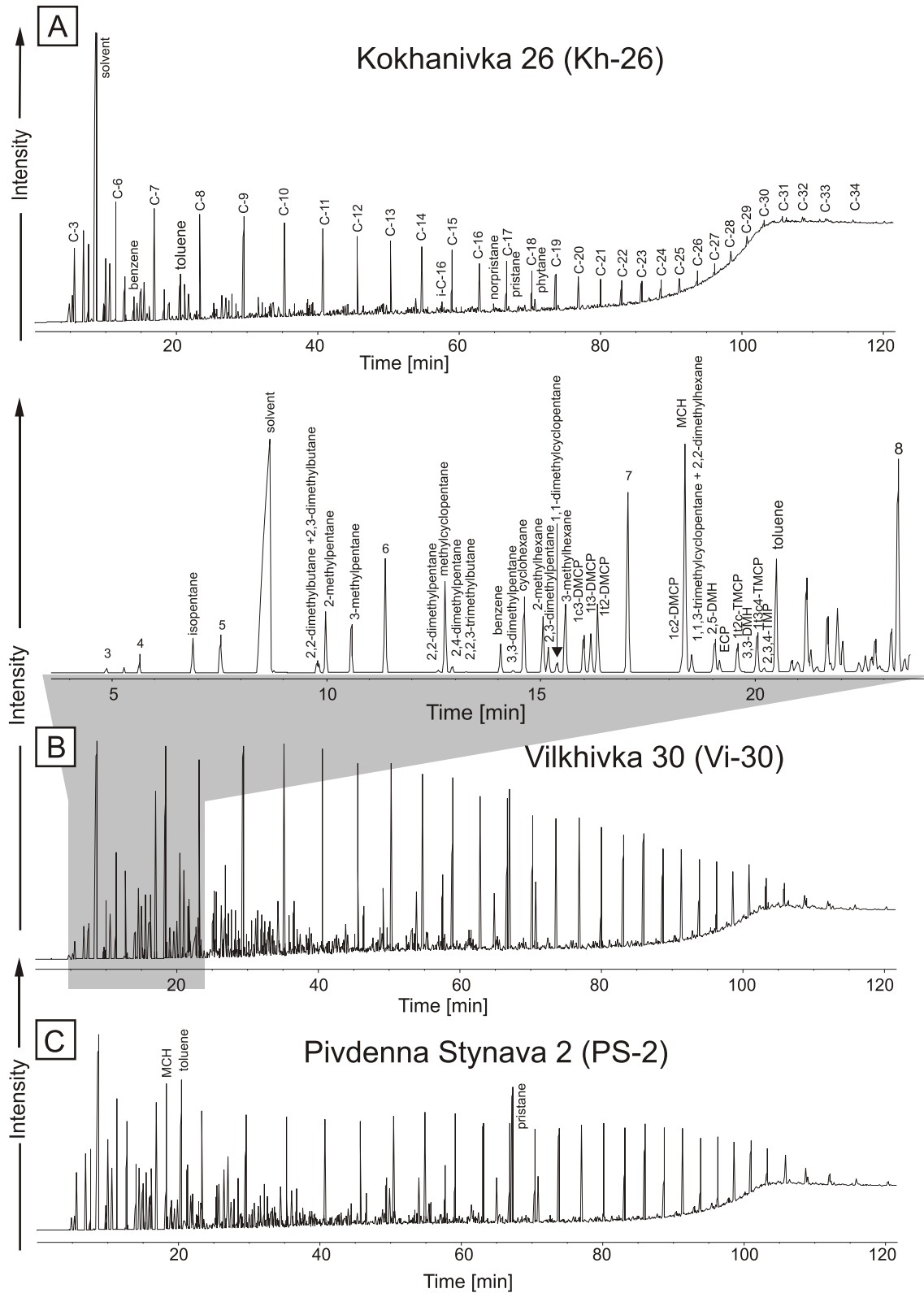
## RESULTS AND DISCUSSION

### IDENTIFICATION OF SECONDARY PROCESSES

Secondary processes, such as biodegradation, water-washing, oxidation, fractional evaporation and thermal cracking, may change properties of oil during migration or accumulation in a deposit (e.g., Blanc and Connan, 1994; Peters *et al.*, 2005).

Biodegradation is routinely recognized by an analysis of *n*-alkanes and acyclic isoprenoids in the saturated hydrocarbon fraction, or C<sub>6</sub>–C<sub>7</sub> 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, change the majority of oil geochemical parameters (e.g., Thompson, 1983, 2010; Palmer, 1984, 1993; Blanc and Connan, 1994; Masterson *et al.*, 2001; Akinlua *et al.*, 2006).

The whole oil GC analysis indicated that only in the Kokhanivka 26 and Orkhovychi 2 oils *n*-C<sub>7</sub> dominate over methylcyclohexane (MCH; Fig. 2A and 3). In the remaining oils MCH dominates (Fig. 2B, C) resulting in low values of the *n*-heptane/MCH ratio (Table 2 and Fig. 3). The values of this ratio below one, connected with a high toluene/*n*-heptane ratio, over *ca.* 0.7, indicated evaporative fractionation processes (Thompson, 1987). This took place in the oils from Pivdenna Stynava 2 and Cherlen 1 (Fig. 3). Values of Halpern's (1995) ratios show a distinction between Kokhanivka 26 and Orkhovychi 2 oils (Table 3 and Fig. 4A) and remaining oils (Fig. 4B). Biodegradation processes, showing the lowest values of TR2 to TR8 ratios were seen in the Vovche 11 oil (Table 3 and Fig. 4B). The lowest value of the TR1 ratio (Table 3 and Fig. 4B) of this oil suggests that it was also water-washed. In biodegradation processes the strong domination of isoprenoids over *n*-alkanes, is characteristic resulting in increased values of the pristane/*n*-C<sub>17</sub> and phytane/*n*-C<sub>18</sub> ratios (Table 2). The most extensive of these processes were observed in oils collected from shallow deposits in the Skiba Unit: the earlier mentioned Vovche 11 as well as Cherlen 1 and Letsivka 1 (Fig. 5). The ratios calculated based on the distribution of short-chain hydrocarbons (Table 2 and Fig. 6) and the distribution of *n*-alkanes and isoprenoids (Table 2 and Fig. 2) and values of hydrocarbon indices (Tables 2 and 3) showed that secondary processes recorded in these oils were not extensive. The chromatograms (Fig. 2) did not show the characteristic "hump" of extensive biodegradation resulting from the presence of an unresolved complex mixture (Peters *et al.*, 2005, p. 106).



**Fig. 2.** Whole oil chromatograms of samples from (A) Kokhanivka 26, (B) Vilkhivka 30 and (C) Pivdenna Stynava 2 boreholes

Numbers refer to carbon atoms in *n*-alkane chain, DMCP – dimethylcyclopentane, DMH – dimethylhexane, MCH – methylcyclohexane, ECP – ethylcyclopentane, TMCP – trimethylcyclopentane, TMP – trimethylpentane



Table 2

## Indices calculated based on whole oil GC analysis

Sample code	Reservoir age	Toluene/ <i>n</i> -C <sub>7</sub> H <sub>16</sub>	<i>n</i> -C <sub>7</sub> H <sub>16</sub> /MCH	HR	HHI	CH/ MCH	IHR	<i>n</i> -C <sub>7</sub> H <sub>16</sub> /2-MH	m-+o-+p- xylene/ <i>n</i> -C <sub>8</sub> H <sub>18</sub>	Temp [°C]	CPI <sub>17-23</sub>	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>
basement of the Carpathian Foredeep														
Kh-26	U. Jurassic	0.42	3.31	52.4	4.08	0.51	1.56	7.59	0.71	102	1.06	0.35	0.10	0.35
Oh-2	U. Jur.+Karp.	0.36	3.54	59.3	4.29	0.46	2.40	3.80	0.55	113	1.07	0.39	0.10	0.32
Carpathian Foredeep – Boryslav-Pokuttya Unit														
Bh-1	Paleocene	0.66	0.70	21.2	0.93	0.44	1.85	1.59	0.89	111	1.05	2.59	1.22	0.49
Cv-6	Oligocene	0.67	0.77	23.5	0.98	0.37	0.84	3.20	0.77	120	1.07	1.97	0.97	0.53
PS-2	Oligocene	1.22	0.84	21.4	1.11	0.39	0.77	2.83	1.18	118	1.07	2.79	1.60	0.61
SS-8	Eocene	0.63	0.69	24.7	0.91	0.42	1.58	2.86	0.87	128	1.05	2.68	1.03	0.40
VB-31	Eocene	0.40	0.72	19.7	1.02	0.27	0.59	4.43	1.17	112	1.06	1.60	1.75	1.07
Outer Carpathians – Skiba Unit														
Ce-1	Eocene	0.90	0.70	24.0	0.84	0.40	1.05	3.22	1.07	122	1.08	2.29	6.12	2.80
Let-1	Oligocene	0.61	0.72	23.0	0.87	0.32	0.85	2.97	0.80	120	1.13	2.27	3.55	1.74
Vi-30	Oligocene	0.65	0.73	24.6	0.86	0.30	0.81	3.33	0.83	118	1.05	2.22	1.30	0.63
Vv-11	Oligocene	0.45	0.42	14.0	0.45	0.56	0.69	2.91	1.12	127	n.c.	1.98	7.96	3.16
Zv-1	U. Cret.	0.43	0.66	25.3	0.87	0.35	1.72	2.68	0.80	104	1.04	2.16	0.90	0.43

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) =  $(2\text{-} + 3\text{-MH}) / (1c3\text{-} + 1t3\text{-} + 1t2\text{-DMCPs})$ ; MH – methylhexane, DMCP – dimethylcyclopentane; Temp =  $140 + 15[\ln(2,4\text{-DMP}/2,3\text{-DMP})]$  (Mango, 1997); DMP – dimethylpentane;  $\text{CPI}_{(17-23)} = [(C_{17} + C_{19} + C_{21}) + (C_{19} + C_{21} + C_{23})] / [2 \times (C_{18} + C_{20} + C_{22})]$ ; Pr – pristane; Ph – phytane; n.c. – not calculated due to lack of some hydrocarbons; for other explanations see Table 1

Table 3

Values of Halpern (1995) C<sub>7</sub> ratios

Sample code	Reservoir age	TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	C1	C2	C3	C4
basement of the Carpathian Foredeep													
Kh-26	U. Jurassic	53.1	126	43.4	16.6	60.0	1.6	14.8	1.6	0.01	0.91	0.07	0.01
Oh-2	U. Jurassic+Karp.	44.8	124	41.4	32.6	74.1	0.6	10.6	4.3	0.00	0.84	0.14	0.01
Carpathian Foredeep – Boryslav-Pokuttya Unit													
Bh-1	Paleocene	9.0	13.5	5.3	8.5	13.8	0.4	2.3	2.2	0.03	0.72	0.11	0.08
Cv-6	Oligocene	11.4	17.1	6.7	5.3	12.0	1.1	4.1	3.4	0.02	0.68	0.18	0.06
PS-2	Oligocene	20.9	17.2	7.7	6.1	13.8	1.1	5.1	2.9	0.02	0.67	0.15	0.11
SS-8	Eocene	9.0	14.4	5.5	5.0	10.6	0.7	2.1	3.2	0.03	0.55	0.24	0.08
VB-31	Eocene	6.7	16.7	8.7	3.8	12.5	2.1	5.8	6.4	0.02	0.12	0.56	0.12
Outer Carpathians – Skiba Unit													
Ce-1	Eocene	13.2	14.6	5.3	4.5	9.8	0.6	2.8	3.1	0.02	0.64	0.19	0.09
Let-1	Oligocene	9.8	16.0	6.9	5.4	12.3	0.7	4.3	3.0	0.03	0.69	0.18	0.06
Vi-30	Oligocene	12.1	18.7	7.0	5.6	12.6	1.1	4.5	3.4	0.02	0.71	0.16	0.06
Vv-11	Oligocene	2.4	5.3	2.4	1.8	4.3	0.4	2.0	2.0	0.04	0.56	0.24	0.09
Zv-1	U. Cretaceous	6.8	15.9	6.4	5.9	12.4	0.5	2.3	3.1	0.03	0.58	0.24	0.08

TR1 = toluene/1,1-DMCP (DMCP – dimethylcyclopentane); TR2 = *n*-C<sub>7</sub>H<sub>16</sub>/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; for other explanations see Table 1

Thermal cracking of oil is significant in accumulations at temperatures in the range of 150–175°C (Claypool and Mancini, 1989). However, oil accumulations occurring in reservoirs in this temperature range (e.g., Mango, 1991; Horsfield *et al.*, 1992; Pepper and Dodd, 1995) suggested the stability of

oil at these temperatures. As the oils analysed had never exceeded these temperatures under the geological conditions of the Carpathians and the Carpathian Foredeep (Kosakowski, pers. comm.), their thermal cracking has never taken place.

GENETIC TYPE AND DEPOSITIONAL ENVIRONMENT  
OF SOURCE ORGANIC MATTER

Almost all oils accumulated in the Outer Carpathians and Carpathian Foredeep have comparable values of Halpern's (1995) light hydrocarbon indices ( $C_1-C_4$ ), indicating good correlation, and only hydrocarbons deposited in the Volia Blazhivs'ka 31 and Mesozoic basement of the Carpathian Foredeep show distinctly different values of these parameters (Table 3 and Fig. 7).

Oils deposited in the Skiba Unit sequence are characterized by specific gravity in a narrow range from 31.2 to 36.6 °API (Table 1 and Fig. 8). The values of this index for oils derived from the Boryslav-Pokuttya Unit range from 22.2 (Pivdennyi Monastrets'1) to 38.3 °API (Staryi Sambir 8; Table 1). Oils collected from the deposits in the Mesozoic basement differ substantially from those in the flysch sequence. Namely, oils in the basement of the Carpathian Foredeep have very low specific gravities (below 15 °API; Table 1 and Fig. 8). The crude oils analysed from the Skiba and Boryslav-Pokuttya units are mostly low in sulphur, below 1 wt.% (with the exception of Volia Blazhivs'ka 31, where it is 1.74 wt.%), suggesting low- and normal-sulphur Type-II kerogen as their source material (Orr, 1986, 2001) deposited in a clastic environment (Moldowan *et al.*, 1985). The highest sulphur contents recorded in oils collected from the Carpathian Foredeep basement strata were 4.35 and 6.5 wt.% for the Kokhanivka and Orkhovychi deposits, respectively (Figs. 1 and 8). As in these

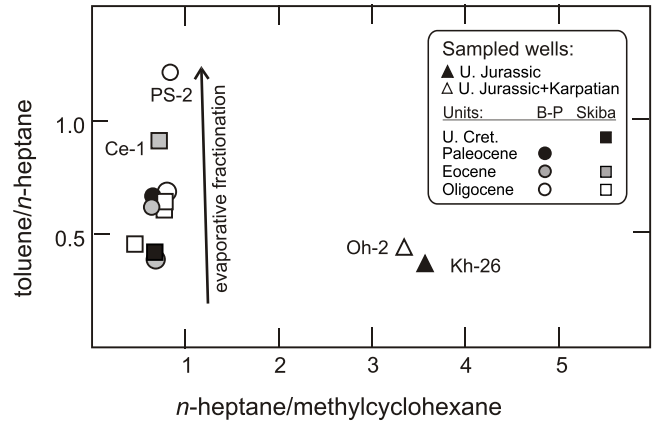


Fig. 3. Toluene/*n*-heptane ratio versus *n*-heptane/methylcyclohexane ratios

Scheme after Thompson (1987);  
for other explanations see Table 1

oils biodegradation processes have not occurred, the high sulphur content in these oils is correlated with their generation from high-sulphur, Type-IIS kerogen (Fig. 8) deposited in carbonates (Moldowan *et al.*, 1985). The high values of the *n*-heptane/MCH ratio for these oils (Table 2 and Fig. 3) also suggest generation of them from marine carbonates (Peters *et al.*, 2005). High values of the heptanes ratio (Fig. 6) might sug-

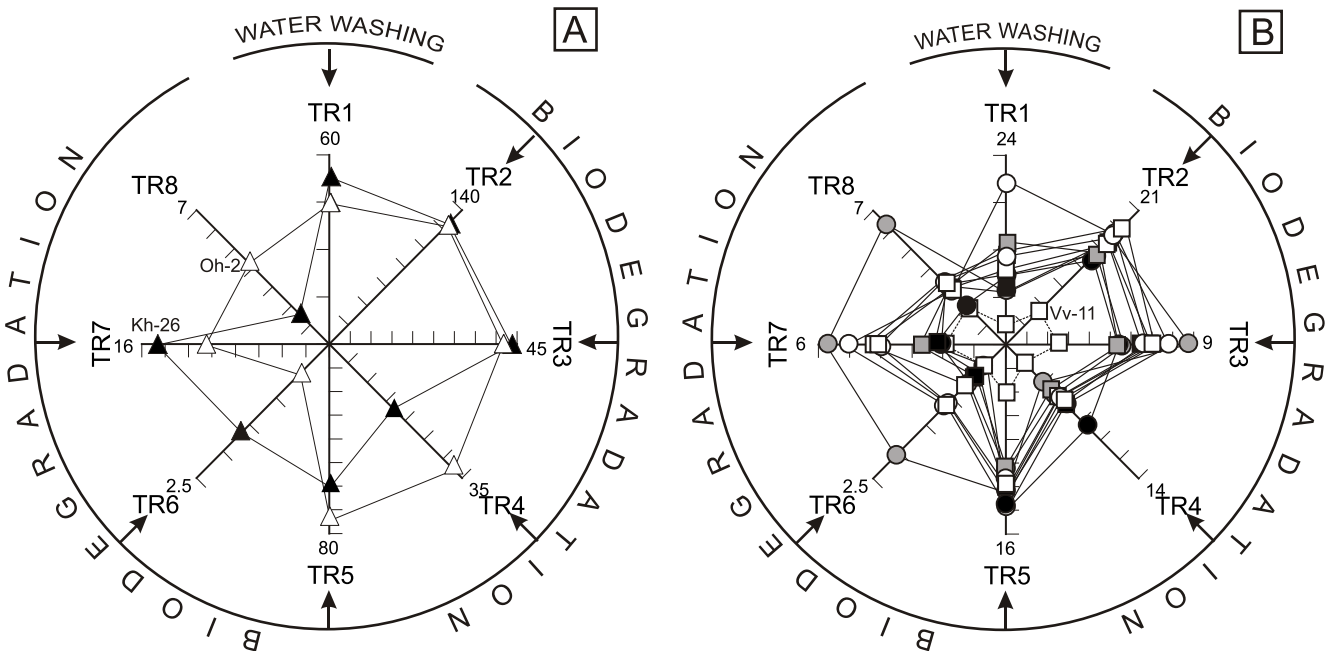


Fig. 4. Star diagram of  $C_7$  oil transformation ratios for oils from (A) Mesozoic basement and (B) Boryslav-Pokuttya and Skiba units

Scheme of star diagram after Halpern (1995); explanation of indices as in Table 3;  
for other explanations see Table 1 and Figure 3

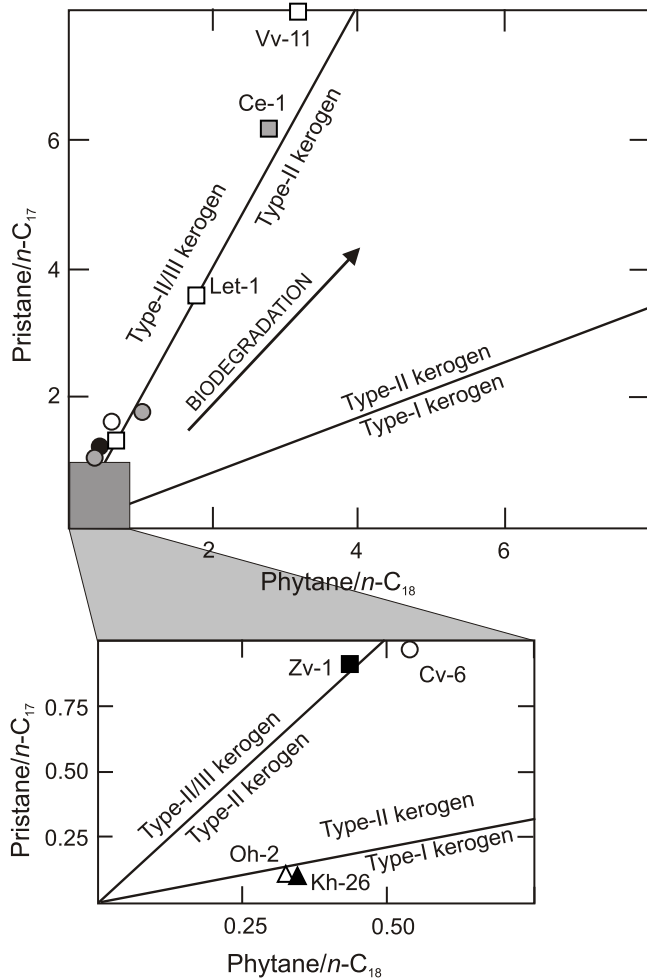


Fig. 5. Genetic characterization of oils in terms of pristane/ $n$ -C<sub>17</sub> and phytane/ $n$ -C<sub>18</sub> according to the categories of Obermajer *et al.* (1999)

Explanation of symbols as in Figure 3;  
for explanation of sample codes see Table 1

gest the presence of thermochemical sulphur reduction processes (TSR; Thompson, 1983), usually occurring in evaporates. This statement is supported by elemental analysis of asphaltenes precipitated from these oils (Table 4 and Fig. 9). High values of the S/C atomic ratio in asphaltenes, i.e. over 0.035 (Fig. 9), suggests a genetic connection of these oils with high-sulphur kerogen (Orr, 1986). The Volia Blazhivs'ka 31 oil, although characterized by an elevated sulphur content (Table 1; Figs. 8 and 9), was generated from medium-sulphur kerogen (Type-IIC according to the classification of Hunt *et al.*, 1991) or is a mixture of a high-sulphur oil (generated from kerogen Type-IIS) with a low-sulphur oil (generated from low-sulphur kerogen). These conclusions are supported by their vanadium and nickel contents (Table 1 and Fig. 10). Almost all oils (with the exception of Volia Blazhivs'ka 31) deposited in the flysch sequence were generated from organic matter deposited in conditions in which nickel and vanadium ions were available (regime II in Lewan, 1984; Fig. 10). These conditions correspond with marine and deltaic facies (kerogen

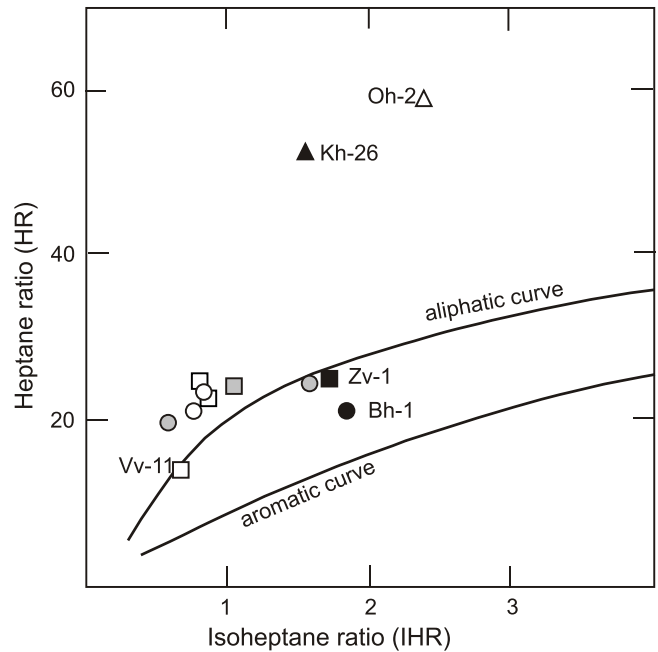


Fig. 6. Heptane ratio versus isoheptane ratio

Kerogen type curves after Thompson (1983);  
for other explanations see Figure 3 and Table 1

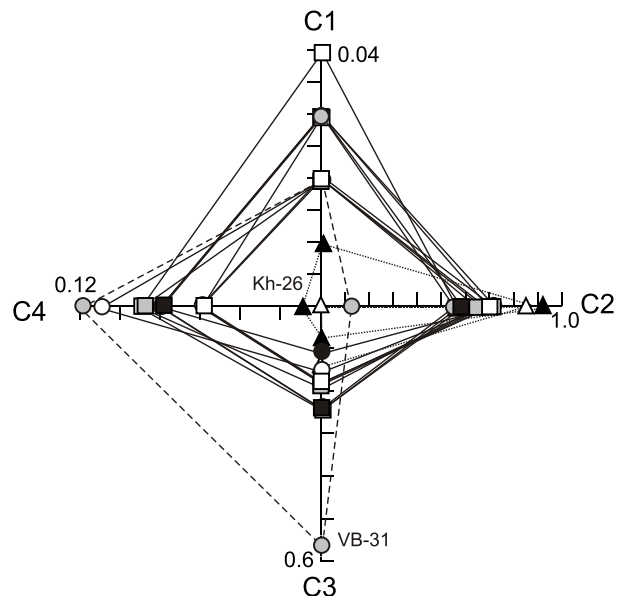


Fig. 7. Correlation of oils using star diagram of C<sub>7</sub> hydrocarbon ratios

Explanation of indices as in Table 3;  
for other explanations see Figure 3 and Table 1

Type-II and III). The oils collected from the Kokhanivka 26 and Orkhovychi 2 boreholes lie in Lewan's (1984) regime III having biogenic pelagic matter as the source rock (Fig. 10). The oil sampled from the Volia Blazhivs'ka 31 borehole is probably



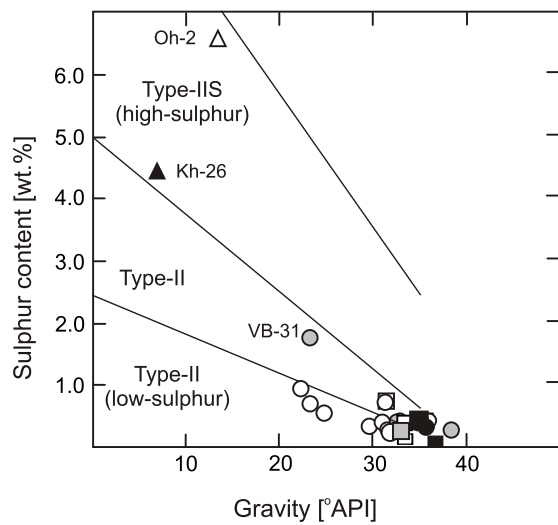


Fig. 8. Sulphur content versus gravity

Classification of source kerogen type by Orr (2001); for other explanations see Figure 3 and Table 1

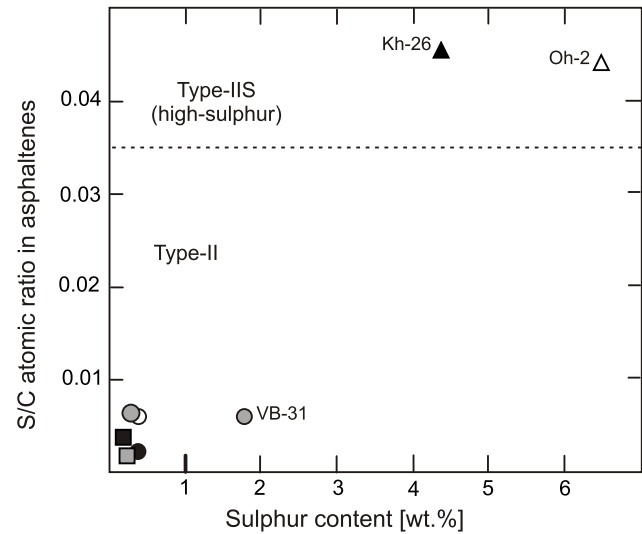


Fig. 9. S/C atomic ratio in asphaltenes versus sulphur content in oils

Classification of source kerogen type by Orr (1986); for other explanations see Figure 3 and Table 1

Table 4

#### Elemental composition of asphaltenes

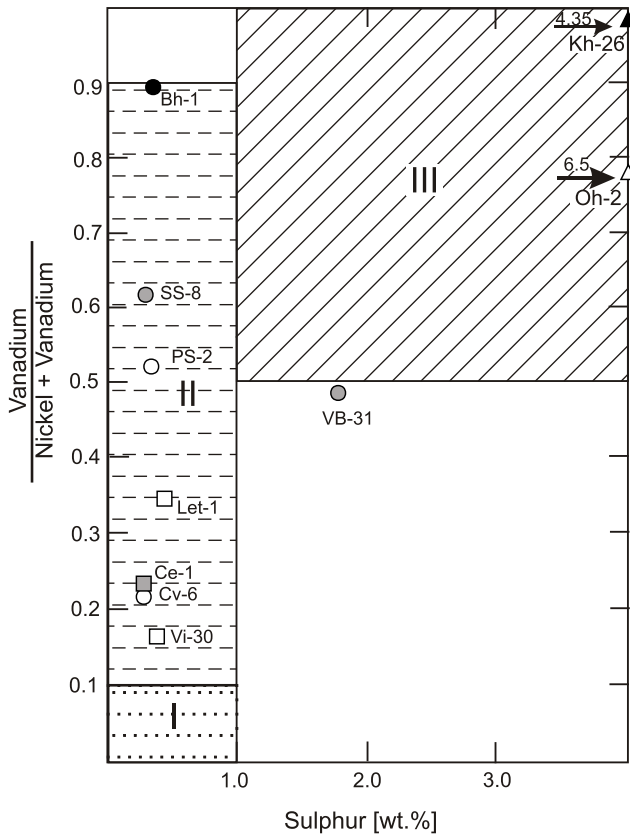
Sample code	Stratigraphy	Elemental composition [daf, wt. %]					Atomic ratio			
		C	H	O	N	S	H/C	O/C	N/C	S/C
basement of the Carpathian Foredeep										
Kh-26	U. Jurassic	76.8	8.0	5.0	1.0	9.2	1.25	0.05	0.011	0.045
Oh-2	U. Jur.+Karp.	78.8	8.5	2.6	0.9	9.1	1.29	0.02	0.010	0.043
Carpathian Foredeep – Boryslav-Pokuttya Unit										
Bh-1	Paleocene	86.8	10.4	1.4	0.9	0.5	1.44	0.01	0.009	0.002
PS-2	Oligocene	78.6	8.9	10.3	0.9	1.3	1.36	0.10	0.010	0.006
SS-8	Eocene	82.9	10.2	5.0	0.5	1.4	1.48	0.05	0.005	0.006
VB-31	Eocene	81.4	11.2	5.5	0.7	1.2	1.65	0.05	0.007	0.006
Outer Carpathians – Skiba Unit										
Ce-1	Eocene	88.3	9.4	0.7	1.2	0.4	1.28	0.01	0.012	0.002
Zv-1	U. Cret.	83.5	9.3	5.9	0.6	0.8	1.34	0.05	0.006	0.003

daf – dry, ash-free basis; for other explanations see Table 1

a mixture of hydrocarbons generated by organic matter deposited in regimes II and III (Fig. 10).

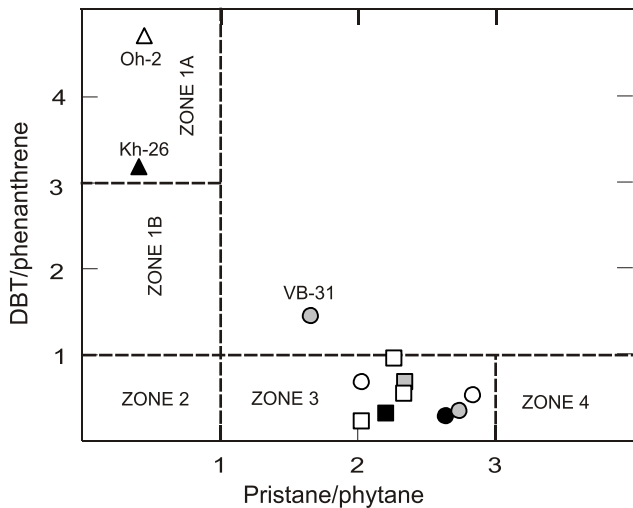
Distributions of *n*-alkanes and isoprenoids in the crude oils analysed are variable, usually monomodal, with a distinct maximum in the short-chain hydrocarbons range (Fig. 2A, B), characteristic of hydrocarbons generated from marine organic matter (e.g., Peters *et al.*, 2005). The oils with an *n*-alkanes distribution without a distinct short-chain maximum (Pivdenna Stynava 2 and Volia Blazhivs'ka 31) underwent secondary processes (e.g., evaporation). CPI values >1.0 indicate a clastic environment of source organic matter deposition (Moldovan *et al.*, 1985). This is supported by high values of pristane/phytane

(Pr/Ph) ratios, usually above unity (Table 2), indicating prevalence of sub-oxic conditions during the deposition of source rock in the Skiba and Boryslav-Pokuttya units (Didyk *et al.*, 1978; ten Haven, 1996). This concept is supported by the correlation between pristane/*n*-C<sub>17</sub> and phytane/*n*-C<sub>18</sub> indices (Fig. 5) and dibenzothiophene/phenanthrene and pristane/phytane ratios (Fig. 11). The source organic matter of the oils from the Kokhanivka 26 and Orkhovychi 2 boreholes was sedimented in different conditions. These oils were generated from marine kerogen (Type-I is not excluded) deposited in carbonates (Table 2; Figs. 5 and 11). Domination of 17 $\alpha$ (H),21 $\beta$ (H)-22R/S C<sub>35</sub> pentakishopanes over C<sub>34</sub> tetrakis-



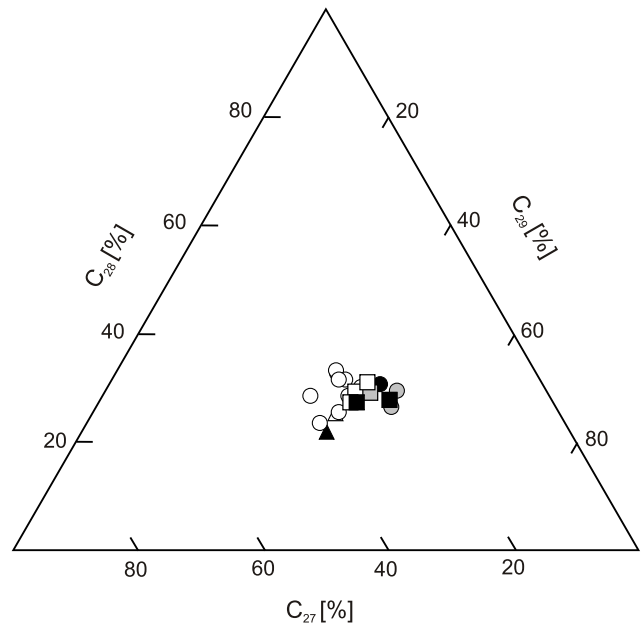
**Fig. 10. V/(V + Ni) ratio versus sulphur content in oils**

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 other explanations see Figure 3 and Table 1



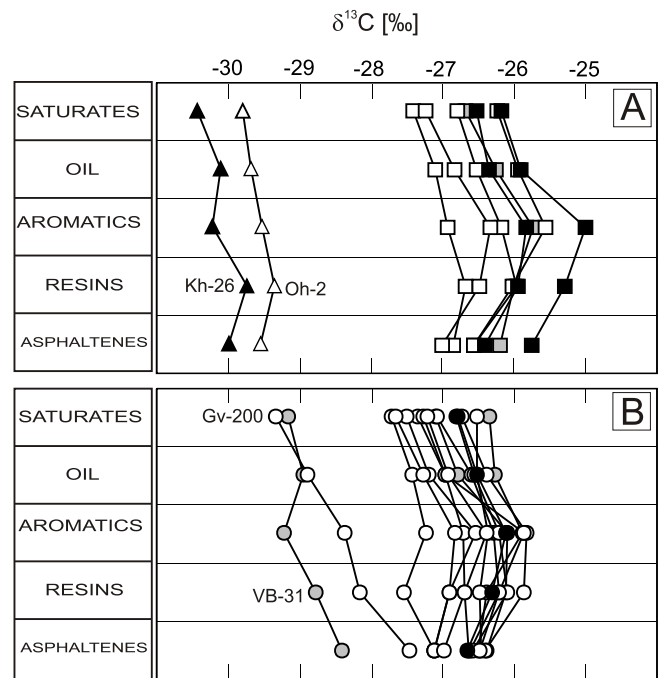
**Fig. 11. A cross-plot of the dibenzothiophene/phenanthrene ratio versus the pristane/phytane ratio**

Classification of source kerogen sedimentation conditions after Hughes *et al.* (1995); Zone 1A – marine carbonate; Zone 1B – marine carbonate or marine marl or lacustrine sulphate-rich; Zone 2 – lacustrine sulphate-poor; Zone 3 – marine shale and other lacustrine; Zone 4 – fluvial/deltaic; for other explanations see Figure 3 and Table 1



**Fig. 12. Ternary diagram of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> 5α,14α,17α(H)-20R steranes (m/z = 217)**

Abbreviations as in Figure 3



**Fig. 13. Stable carbon isotope composition of crude oils and their individual fractions of (A) oils accumulated in the Skiba Unit, the autochthonous Miocene strata and the Mesozoic basement of the Carpathian Foredeep and (B) the Boryslav-Pokuttya Unit**

Explanation of symbols as in Figure 3; for explanation of sample codes see Table 1

Table 5

## Selected biomarker characteristics

Sample code	Reservoir age	S/(S + T)	C <sub>27</sub>	C <sub>28</sub>	C <sub>29</sub>	Dia/Reg	Ol/Hop	Mor/Hop	C <sub>27</sub>	C <sub>29</sub> SR	C <sub>29</sub>	TA(I)/TA(I + II)	H <sub>31</sub> S/(S + R)	Ts/Tm	C <sub>29</sub> /C <sub>27</sub> ster	C <sub>29</sub> Ts/C <sub>29</sub> H	C <sub>35</sub> /C <sub>34</sub>
			[%]						dia/reg		ββαα						
basement of the Carpathian Foredeep																	
Kh-26	U. Jurassic	0.20	39	22	39	0.10	0.00	0.09	0.07	0.49	0.53	0.11	0.53	0.13	1.34	0.28	1.10
Oh-2	U. Jur.+Karp.	0.18	36	26	39	0.18	0.00	0.07	0.09	0.57	0.55	0.14	0.56	0.11	1.46	1.52	1.00
Carpathian Foredeep – Boryslav-Pokuttya Unit																	
Bh-1	Paleocene	0.20	26	31	43	0.96	0.18	0.15	0.41	0.46	0.47	0.15	0.55	1.09	0.83	0.07	0.92
By-485	Oligocene	0.27	32	33	35	0.3	0.12	0.19	n.d.	n.d.	n.d.	n.d.	0.52	n.d.	n.d.	n.d.	n.d.
Cv-6	Oligocene	0.29	32	34	35	0.24	0.08	0.18	0.21	0.25	0.30	0.05	0.52	0.81	0.98	0.26	0.92
Gv-200*	Oligocene	0.02	31	32	37	0.56	0.05	0.12	n.d.	n.d.	n.d.	n.d.	0.58	n.d.	n.d.	n.d.	n.d.
Ma-10*	Oligocene	0.33	32	32	36	0.33	0.13	0.21	n.d.	n.d.	n.d.	n.d.	0.51	n.d.	n.d.	n.d.	n.d.
Mo-4*	Oligocene	0.24	38	29	33	0.59	0.13	0.2	n.d.	n.d.	n.d.	n.d.	0.56	n.d.	n.d.	n.d.	n.d.
NS-3**	Oligocene	0.20	35	26	39	1.03	0.12	0.13	n.d.	n.d.	n.d.	0.24	0.57	n.d.	n.d.	n.d.	0.71
Or-161**	Oligocene	0.30	39	24	37	0.36	0.20	0.17	n.d.	n.d.	n.d.	0.1	0.56	n.d.	n.d.	n.d.	0.87
PM-1**	Oligocene	0.22	30	30	40	0.81	0.16	0.18	n.d.	n.d.	n.d.	0.09	0.55	n.d.	n.d.	n.d.	0.88
PS-2	Oligocene	0.22	29	31	40	0.62	0.09	0.14	0.31	0.46	0.44	0.10	0.55	0.51	0.97	0.73	0.76
SS-8	Eocene	0.22	26	27	47	0.59	0.22	0.21	0.46	0.39	0.39	0.10	0.53	0.81	1.21	0.58	1.21
Ul-35**	Oligocene	0.24	32	29	39	0.39	0.15	0.17	n.d.	n.d.	n.d.	0.12	0.55	n.d.	n.d.	n.d.	0.81
VB-31	Eocene	0.23	24	30	46	0.10	0.14	0.28	0.20	0.16	0.25	0.03	0.46	0.38	1.58	0.12	1.43
Outer Carpathians – Skiba Unit																	
Ce-1	Eocene	0.25	28	30	42	0.41	0.14	0.22	0.33	0.33	0.36	0.13	0.53	0.67	1.14	0.26	0.92
Let-1	Oligocene	0.34	30	30	40	0.17	0.12	0.22	0.20	0.21	0.25	0.03	0.50	0.40	1.06	0.44	0.74
NS-25**	U. Cretaceous	0.23	31	28	41	0.46	0.12	0.16	n.d.	n.d.	n.d.	0.21	0.56	n.d.	n.d.	n.d.	0.80
VM-1**	Oligocene	0.31	32	28	40	0.22	0.13	0.18	n.d.	n.d.	n.d.	0.11	0.56	n.d.	n.d.	n.d.	0.87
Vi-30	Oligocene	0.33	27	32	41	0.14	0.11	0.15	0.15	0.20	0.25	0.05	0.52	0.47	1.14	0.06	0.97
Vv-11	Oligocene	0.27	26	28	46	0.38	0.21	0.21	0.31	0.32	0.33	0.06	0.52	1.06	1.12	0.53	0.75
Zv-1	U. Cretaceous	0.50	26	28	46	0.38	0.17	0.13	0.31	0.32	0.33	0.41	0.53	0.90	1.12	0.59	0.69

S/(S + T) = all steranes/(all steranes + all terpanes), C<sub>27</sub> = C<sub>27</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes\*100, C<sub>28</sub> = C<sub>28</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes\*100, C<sub>29</sub> = C<sub>29</sub>ααα20R sterane/(C<sub>27</sub> + C<sub>28</sub> + C<sub>29</sub>)ααα20R steranes\*100, Dia/Reg = C<sub>27</sub> βα 20S diasterane/C<sub>29</sub>ααα20R sterane, Ol/Hop = oleanane/17α hopane, mor/Hop = Moretane/17α hopane, C<sub>27</sub> dia/reg = C<sub>27</sub> βα 20(S + R) diasterane/ΣC<sub>27</sub> regular steranes, C<sub>29</sub>SR = epimerisation of regular steranes C<sub>29</sub> ratio, C<sub>29</sub>ββαα = ratio of ββ-epimeres of regular steranes C<sub>29</sub> to their total quantity, TA(I)/TA(I + II) = (C<sub>21</sub> + C<sub>22</sub> triaromatic)/(C<sub>21</sub> + C<sub>22</sub> + C<sub>26-28</sub> triaromatic steroids), H<sub>31</sub>S/(S + R) = homohopane 22S/(22S + 22R), Ts/Tm = C<sub>27</sub> 18α trisnorhopane/C<sub>27</sub> 17α trisnorhopane, C<sub>29</sub>/C<sub>27</sub>ster = ΣC<sub>29</sub> regular steranes/ΣC<sub>27</sub> regular steranes, C<sub>29</sub>Ts/C<sub>29</sub>H = C<sub>29</sub> 18α norneohopane/C<sub>29</sub> norhopane, C<sub>35</sub>/C<sub>34</sub> = C<sub>35</sub> (22S + 22R) homohopanes/C<sub>34</sub> (22S + 22R) homohopanes, \* – data from Kotarba *et al.* (2005), \*\* – data from Kotarba *et al.* (2007), n.d. – not determined; for other explanations see Table 1

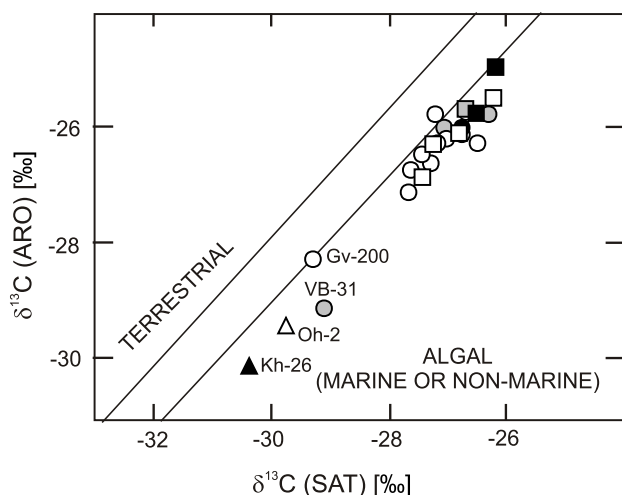


Fig. 14. Genetic characterization of oils in terms of  $\delta^{13}\text{C}$  (ARO – aromatic hydrocarbons) and  $\delta^{13}\text{C}$  (SAT – saturated hydrocarbons) according to the categories of Sofer (1984)

Explanation as in Figure 3;  
for explanation of sample codes see Table 1

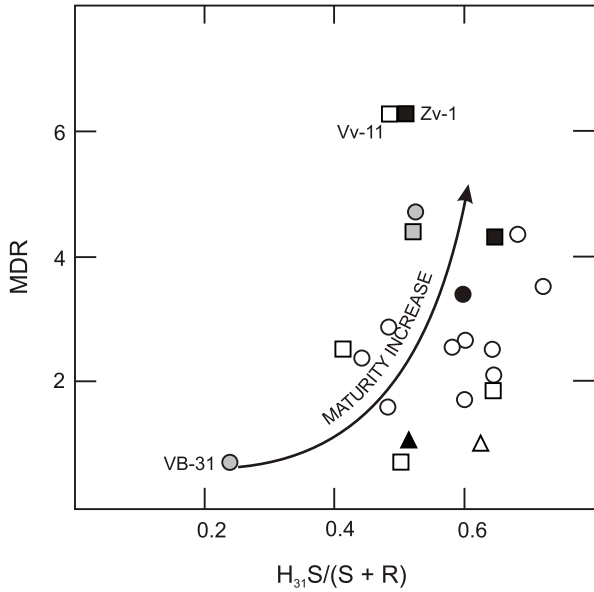
hopanes, seen in the Kokhanivka 26, Orkhovychi 2 and Volia Blazhivs'ka 31 oils (Table 5) suggests deposition of their source organic matter in carbonates (Peters and Moldowan, 1991). This thesis is supported for the Kokhanivka 26, Orkhovychi 2 oils by low values of pristane/phytane and diasterane/regular sterane ratios and for Volia Blazhivs'ka 31 oil low diasterane/regular sterane ratios (Tables 2 and 5; Peters *et al.*, 2005). Similar distribution of regular  $\alpha\alpha\alpha$  steranes in all the crude oils (Table 5 and Fig. 12) suggests a similar type of their source kerogen. The highly elevated relative abundance among the steranes of the  $\text{C}_{27}$  regular  $5\alpha,14\alpha,17\alpha(\text{H})$ -20R sterane observed in the Kokhanivka 26, Orkhovychi 2, Monastyrchany 4, Novoskhidnytsia 3 and Oriv 161 oils suggests their generation from kerogen enriched in marine plankton (Huang and Meinschein, 1979). All the oils derived from the Skiba and Boryslav-Pokuttya units contain a highly specific type of pentacyclic triterpane i.e., oleanane (Table 5). Its presence in relates to higher (angiosperm) plant input of Cretaceous or younger age (e.g., Ekweozor and Udo, 1988; Moldowan *et al.*, 1994). The most probable source rocks for these oils are the organic-rich Oligocene Menilite Shales (e.g., Kotarba *et al.*, 2005, 2007; Kotarba and Koltun, 2006), deposited in a deltaic system. Lacking specific biomarkers of this age the oils from

Table 6

Indices calculated based on phenanthrene and dibenzothiophene and their derivatives distribution

Sample code	Reservoir age	MPI 1	MPR	MPR 1	$R_{\text{cal}}$ [%]	$R_{\text{cal(MPR)}}$ [%]	DBT/P	MDR	$R_{\text{cal(DBT)}}$ [%]	$T_{\text{max(DBT)}}$ [°C]
Basement of the Carpathian Foredeep										
Kh-26	U. Jurassic	0.53	0.94	0.41	0.7	0.7	3.0	0.8	0.6	427
Oh-2	U. Jur.+Karp.	0.67	0.97	0.44	0.8	0.8	4.6	0.7	0.6	427
Carpathian Foredeep – Boryslav-Pokuttya Unit										
Bh-1	Paleocene	0.59	0.55	0.29	0.7	0.5	0.2	2.5	0.7	436
By-485	Oligocene	0.79	n.c.	n.c.	0.9	n.c.	n.c.	1.2	0.6	429
Cv-6	Oligocene	0.80	0.84	0.42	0.8	0.8	0.5	2.1	0.7	434
Gv-200*	Oligocene	0.76	n.c.	n.c.	0.9	n.c.	n.c.	2.6	0.7	436
Ma-10*	Oligocene	0.86	n.c.	n.c.	0.9	n.c.	n.c.	1.8	0.6	432
Mo-4*	Oligocene	0.84	n.c.	n.c.	0.9	n.c.	n.c.	1.9	0.7	433
NS-3**	Oligocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	3.3	0.8	440
Or-161**	Oligocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.6	0.6	431
PM-1**	Oligocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.3	0.6	430
PS-2	Oligocene	0.62	0.58	0.37	0.7	0.7	0.4	1.9	0.6	433
SS-8	Eocene	0.68	0.64	0.37	0.8	0.7	0.2	3.5	0.8	441
Ul-35**	Oligocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	2.0	0.7	433
VB-31	Eocene	0.73	0.80	0.42	0.8	0.8	1.3	0.5	0.5	426
Outer Carpathians – Skiba Unit										
Ce-1	Eocene	0.65	0.72	0.39	0.8	0.7	0.5	3.3	0.7	440
Let-1	Oligocene	0.81	0.94	0.46	0.9	0.9	0.4	1.9	0.6	433
NS-25**	U. Cret.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	3.2	0.8	439
VM-1**	Oligocene	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.4	0.6	430
Vi-30	Oligocene	0.77	0.78	0.43	0.8	0.8	0.8	0.5	0.5	426
Vv-11	Oligocene	0.90	1.01	0.50	0.9	0.9	0.1	4.7	0.9	447
Zv-1	U. Cretaceous	0.72	0.70	0.38	0.8	0.7	0.2	4.7	0.9	447

MPI 1 =  $1.5(2\text{-MP} + 3\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$ , P – phenanthrene, MP – methylphenanthrene; MPR =  $2\text{-MP} / 1\text{-MP}$ ; MPR 1 =  $(2\text{-MP} + 3\text{-MP}) / (1\text{-MP} + 9\text{-MP} + 2\text{-MP} + 3\text{-MP})$ ;  $R_{\text{cal}} = 0.60\text{MPI} 1 + 0.37$  for MPR < 2.65 (Radke, 1988);  $R_{\text{cal(MPR)}} = -0.166 + 2.242(\text{MPR} 1)$  (Kvalheim *et al.*, 1987); DBT – dibenzothiophene; MDR =  $4\text{-MDBT} / 1\text{-MDBT}$ , MDBT – methyl dibenzothiophene;  $R_{\text{cal(DBT)}} = 0.51 + 0.073\text{MDR}$ ;  $T_{\text{max(DBT)}} = 423 + 5.1\text{MDR}$ ; n.c. – not calculated; \* – data from Kotarba *et al.* (2005); \*\* – data from Kotarba *et al.* (2007)



**Fig. 15. Methylidibenzothiophene ratio versus  $S/(S + R)$  ratio of  $C_{31}$  homohopanes**

Explanation of symbols as in Figure 3;  
for explanation of sample codes see Table 1

Kokhanivka 26 and Orkhovychi 2 (Table 5) likely have their source rocks as Jurassic or older.

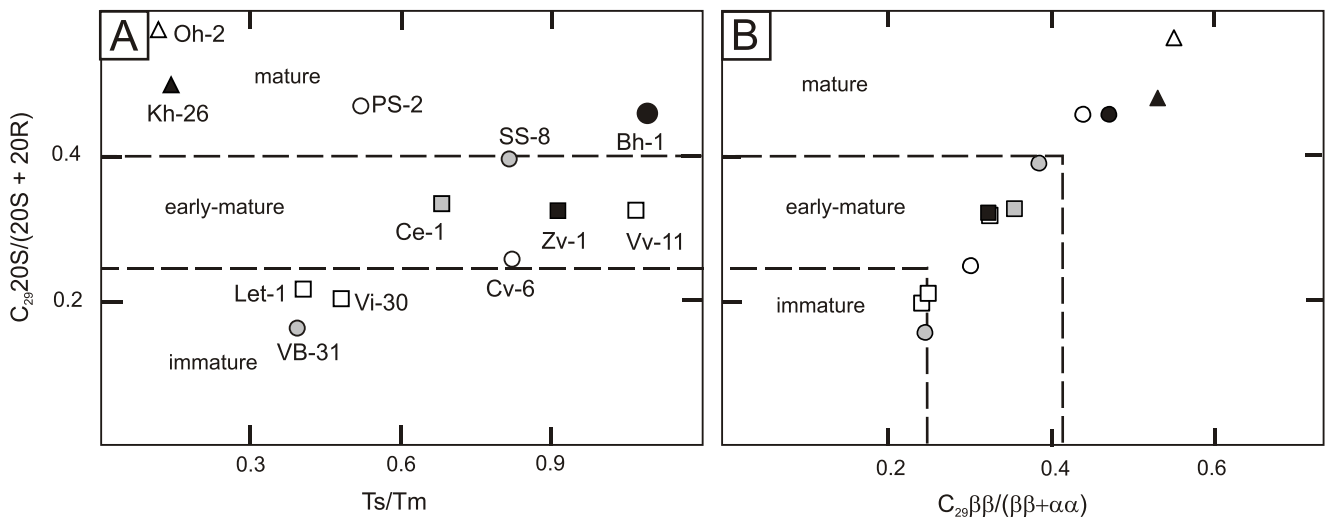
The stable carbon isotope composition of crude oils and their individual fractions (Table 1) support the biomarker data and indicate that majority of the oils that accumulated in the flysch sequence were generated probably from one common genetic type of organic matter (Figs. 13 and 14). In the majority 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 reduced oils were these processes observed on a limited scale. Some differences in the stable carbon isotope composition follow changes in source rock facies and maturity (Waples and Tornheim, 1978; Chung *et al.*, 1981; Lewan, 1983) or migration distance (Stahl, 1980). A distinct stable carbon isotope composition was detected in the oils deposited in the Jurassic strata of basement of the Carpathian Foredeep and in two oils from the Boryslav-Pokuttya Unit (Figs. 13 and 14). The Gvizard 200 oil was probably generated mainly from the same kerogen as the other oils accumulated in the flysch strata and some changes in the isotope composition may have resulted from an admixture of oil generated from isotopically light kerogen. The remaining oils were generated only from kerogen enriched with light stable carbon isotopes (Figs. 13 and 14).

Fraction composition and saturated/aromatic hydrocarbon (sat./aro.) ratios have been suggested to be influenced by migration distance. The crude oils investigated have variable contents of asphaltenes, usually over 1 wt.%, with the highest value of 21.2 wt.% in the oil from the Kokhanivka 26 borehole (Table 1). High concentrations of asphaltenes conversely correlating with low saturated-hydrocarbon content and low sat./aro. ratios (Table 1) for oils from the Kokhanivka and Orkhovychi deposits suggest they had the shortest distance of migration whereas the Gvizard 200 oil probably migrated the longest distance (Table 1). Values of this ratio can be affected by maturity and thermal cracking processes.

## MATURITY

The maturity of crude oils was determined based on the composition of light hydrocarbons (Table 2), selected



**Fig. 16. Sterane  $C_{29}20S/(20S + 20R)$  ratio versus (A)  $Ts/Tm$  and (B)  $C_{29}(\beta\beta/\beta\beta + \alpha\alpha)$  ratios**

Maturity fields after Peters and Moldovan (1993); for other explanations see Figure 3 and Table 1



biomarkers (Table 5) and indices deriving from relative concentrations of phenanthrene and dibenzothiophene and their methyl derivative distributions (Table 6).

The distribution of methylphenanthrenes shows a narrow range of maturity of the crude oils indicating their generation in the peak of the oil window ( $R_{cal}$  ca. 0.7–0.9%; Table 6). The maturity indices calculated based on methyl-dibenzothiophene distribution indicate a wider range of the oils' maturities: from 0.5 to 0.9% in the calculated vitrinite reflectance scale (Table 6 and Fig. 15). As the MPI and MPR indices were evaluated for terrestrial organic matter (e.g., Radke, 1988), while maturity described by the MDR values for the oils were generated mostly from marine Type-II kerogen, and therefore are more adequate for assessing the maturity of the oils investigated (Radke, 1988). The less mature oils were taken from the Volia Blazhivs'ka 31 (the Boryslav-Pokuttya Unit), the Vilkhivka 30 (the Skiba Unit) as well as from the Kokhanivka 26 and Orkhovychi 2 (basement of the Carpathian Foredeep) boreholes (Table 6 and Fig. 15). The most mature oils are exploited in the Vovche 11 and Zvoriv 1 boreholes (the Skiba Unit; Fig. 15). These data are supported by the relatively low sulphur, nickel and vanadium contents of these oils (Table 1). A relationship between the maturity and locality as well as depth of oil accumulation was not observed.

Biomarker distribution supports the above observation. Sterane and terpane distributions show that the oils analysed were generated from organic matter at various maturity levels (Fig. 16A, B): from immaturity, through early-mature to the mature stage. The epimerisation of steranes shows that less mature oils are in the Letsivka 1 (the Skiba Unit) and the above-mentioned Volia Blazhivs'ka 31 and Vilkhivka 30 boreholes, while the most mature are in the Orkhovychi and Kokhanivka deposits (the basement of the Carpathian Foredeep). The unusually low  $T_s/T_m$  values of the oils from the Orkhovychi and Kokhanivka deposits are a result of the carbonate depositional environment of their source rocks. This effect was described earlier by e.g., Barakat *et al.* (1997) and Moldowan *et al.* (1986).

The temperature of generation of hydrocarbons estimated from dimethylpentane homologues distribution (Mango, 1997) varies from 102°C (Kokhanivka 26) to 128°C (Staryi Sambir 8; Table 2). For the majority of oils this index varies from 110 to 130°C. The lowest temperature was calculated for high-sulphur oil generated from Type-IIS kerogen. This type of kerogen generates hydrocarbons earlier than a low-sulphur one (e.g., Hunt, 1996). The 1-D modelling of hydrocarbon generation and expulsion processes from the Upper Jurassic source rocks in this region (Kosakowski *et al.*, 2011) indicates that the main mass of liquid hydrocarbons was generated in the temperature range of 100–110°C.

## CONCLUSIONS

Almost all oils accumulated both in the flysch sequence of the Outer Carpathians and the Mesozoic basement of the Carpathian Foredeep in the Western Ukraine have very similar geochemical characteristics and were generated from one ge-

netic type of organic matter deposited under the same conditions. They are normal or heavy low-sulphur oils, that migrated short distances, with maximum concentrations of *n*-alkane distributions usually within the *n*-C<sub>9</sub>–*n*-C<sub>11</sub> range. Only in the oils accumulated in shallow deposits in the Skiba Unit is slight biodegradation visible. The marine origin (Type-II or II/III kerogen) of source organic matter dispersed in clastic sediments for the oils analysed is revealed by the distribution of *n*-alkanes, isoprenoids and biomarkers. This type of kerogen was recognized by Kotarba *et al.* (2005, 2007) in the Oligocene Menilite Shales in the Boryslav-Pokuttya and Skiba units, but only in the first unit is the organic matter dispersed there sufficiently mature to generate oil.

The second family is composed of oils from the Kokhanivka and Orkhovychi deposits in the Mesozoic basement of the Carpathian Foredeep. These oils are extremely heavy, high-sulphur and viscous and were generated from high-sulphur Type-IIS kerogen deposited in a carbonate environment. The same properties characterize oils collected from the Lubaczów 157 and Opaka 1 boreholes located in Poland about 10–20 km west of Kokhanivka (Wi law, 2011) suggesting one continuous deposit. Because of the fact that in these oils oleanane is not present, their most probable source rock are the Upper Jurassic carbonates, where the presence of Type-IIS kerogen characterized by a suitable maturity for generation of oils was detected (Kosakowski, pers. comm.). This type of organic matter was not recognized in the Polish part (Kosakowski *et al.*, 2012), so probably all oils were generated in the Ukrainian part of the Carpathian Foredeep.

Geochemical parameters and indices of the oil from the Volia Blazhivs'ka 31 borehole (the Boryslav-Pokuttya Unit) are characterized by intermediate values of these oil families (Figs. 10, 11 and 13), thus could represent a mixture of hydrocarbons generated from both the Menilite Shales and the Upper Jurassic carbonates. Organic matter characterized by such an isotope composition was found in Upper Jurassic strata in the study area (Kosakowski, pers. comm.). Also, in the Menilite Shales, in the Polish part of the Outer Carpathians, there are facies containing high- and low-sulphur organic matter with a very light isotopic signature (Curtis *et al.*, 2004; Kotarba *et al.*, 2007). Although in the Ukrainian part of the Carpathians such facies were not found, they may exist in zones where sampling was not conducted and they are the most probable source rock for this oil. All the oils were generated in the early part or at the peak of the oil window.

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