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EVALUATION OF HYDROCARBON POTENTIAL OF THE AUTOCHTHONOUS MIOCENE STRATA IN THE NW PART OF THE UKRAINIAN CARPATHIAN FOREDEEP

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Abstract: The quantity, genetic type, maturity and hydrocarbon potential of dispersed organic matter were determined for the complete sequence of the autochthonous Miocene ranging from the Lower Badenian Sandy-Calcareous Series to the Lower Sarmatian Upper Dashava Formation of the Bilche-Volytsia Unit. Geochemical analyses were conducted on 78 core samples collected from 11 wells in the Ukrainian Carpathian Foredeep between the Ukrainian-Polish state border and the Stryi River. The most favourable source-rock parameters characterize the Upper Badenian Kosiv Formation where the highest TOC contents, from 0.44 to 2.01 wt% (median 0.76 wt%), were found. Only slightly lower values were obtained for the Lower and the Upper Dashava formations – from 0.01 to 1.45 wt% (median 0.72 wt%) and from 0.62 to 0.77 wt% (median 0.71 wt%), respectively. In the Lower Badenian Sandy-Calcareous Series, the Lower Badenian Baraniv beds, and the Upper Badenian Tyras Formation, the TOC content is lower and varies from 0.00 to 0.77 wt%. Immature type III (terrestrial) kerogen dominates the analysed sections of the Kosiv and Dashava formations. Marine organic matter was detected sporadically, and only in the Upper Badenian Kosiv Formation in the vicinity of Kokhanivka, and in the Upper Badenian Kosiv and Tyras formations.

Key words: source rocks, hydrocarbon potential, organic geochemistry, Miocene, Bilche-Volytsia Unit, Ukrainian Carpathian Foredeep.

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INTRODUCTION

The objective of our study is to define the hydrocarbon potential of autochthonous Miocene strata of the Bilche-Volytsia Unit from the Ukrainian Carpathian Foredeep between the Ukrainian-Polish state border and the Stryi River (Fig. 1). We analysed the total organic carbon (TOC) content, organic matter type, thermal maturity and hydrocarbon potential of the Lower Badenian Sandy-Calcareous Series, Lower Badenian Baraniv beds and Upper Badenian Tyras Formation, Upper Badenian Kosiv Formation, and Lower Sarmatian Lower and Upper Dashava formations. Geochemical characterization of the potential source rocks was carried out by means of Rock-Eval analyses, bitumen content and composition, aromatic hydrocarbon and biomarkers analyses, stable carbon isotope analyses of bitumens (fractions thereof) and kerogen, and elemental analyses of kerogen.

As previous geochemical studies revealed (Kotarba *et al.*, 1987, 1998, 2005; Kotarba & Koltun, 2006 and references therein) the dispersed organic matter hosted within the autochthonous Miocene strata of the Polish Carpathian Foredeep is generally immature and of terrestrial origin, and generated almost exclusively microbial methane. To date, geochemical studies of organic matter from the Ukrainian Carpathian Foredeep included only the Rock-Eval analyses of 24 samples from the Miocene strata of the Bilche-Volytsia Unit collected from four wells in the central and south-eastern parts of the foredeep (Kotarba & Koltun, 2006). These studies showed no significant differences between geochemical parameters and indices from those of samples obtained in the Polish part of the foredeep (Kotarba *et al.*, 1998, 2005).

GEOLOGICAL SETTING AND PETROLEUM OCCURRENCE

The Ukrainian Carpathians form the central segment of the Carpathian arc located between the Polish and the Romanian Carpathians (Fig. 1) and consists of several tectonic units overthrust northeastward (Dolenko, 1962; Vialov, 1965; Glushko, 1968; Kruglov *et al.*, 1985; Ślączka *et al.*, 2006). The Carpathian Foredeep is one of the largest sedimentary basins in Europe and includes an outer and an inner sub-basin (Oszczypko, 1997). From a sedimentological point of view, the folded Sambir Unit (Stebnik Unit in Poland) and the Boryslav-Pokuttya Unit belong to the inner sub-basin of the Carpathian Foredeep but for tectonic reasons both were included in the Carpathian Overthrust. The outer sub-basin (Bilche-Volytsia Unit) is filled with autochthonous Miocene sediments (Oszczypko, 1997; Oszczypko *et al.*, 2006).

Fig. 1. Sketch map of major tectonic units of the NE part of the Ukrainian Carpathian region with the location of gas sampling sites. EEP – East European Platform, B-V – Bilche-Volytsia Unit (outer part of the Ukrainian Carpathian Foredeep). SA – Sambir (Stebnik) Unit, B-P – Boryslav-Pokuttya Unit, OC – Outer (Flysch) Carpathians

In the Ukrainian part of the Carpathian orogen, most oil and gas fields are located within the frontal tectonic units, mainly in the Carpathian Foredeep. The foredeep includes three tectonic units, which differ in geological structure and petroleum potential. The Boryslav-Pokuttya Unit is the frontal nappe of the Carpathian Outer Belt. This is the main oil-bearing unit in the Ukrainian Carpathians. It is covered by folded molasse strata belonging to the Sambir (Stebnik) Unit, in which no hydrocarbons have been found up to now. The outermost Bilche-Volytsia Unit of the Carpathian Foredeep hosts the main gas fields and its part between the Polish-Ukrainian state border and the Stryi River is the subject of this study (Fig. 1). In the southwest, the Bilche-Volytsia Unit underlies the Sambir (Stebnik) and the Boryslav-Pokuttya units, and to the northeast it covers a fragment of the East-European Platform.

The Bilche-Volytsia Unit shows diverse stratigraphic sequences and variable thickness of Miocene deposits (Shcherba *et al.*, 1987). The autochthonous Miocene strata reach their maximum thickness (over 5 km) in the Krukenychy Depression, close to the Polish-Ukrainian state border (Kurovets *et al.*, 2004). In the external, northwestern part of the unit the Miocene strata rest upon Palaeozoic and Mesozoic formations. Fourty-four gas and gas-condensate deposits and one oil deposit have been discovered in the Bilche-Volytsia Unit (Kotarba *et al.*, 2011).

In the bottom part of the Bilche-Volytsia Unit, various siliciclastic, often conglomerates and breccias, and carbonate deposits occur that are commonly regarded, in the unpublished geological documentations, as well as in the syntheses based on those documentations (*e.g.*, Vul *et al.*, 1998; Krups'kyy, 2001), to be of Karpatian and/or Palaeogene age. Based on the recent regional stratigraphic correlations and palaeogeographic reconstructions, these deposits are included into the transgressive Lower Badenian Sandy-Calcareous Series (*e.g.*, Andreyeva-Grigorovich *et al.*, 1997; Oszczypko *et al.*, 2006). In the analysed well sections these are mainly sandstones, up to several tens of metres thick. The Lower Badenian Baraniv beds, up to 80 m thick, are represented by claystones, sandstones and limestones. The Tyras Formation occurs at the base of the Upper Badenian succession (Andreyeva-Grigorovich *et al.*, 1997, 2008), which is composed mainly of evaporites, up to 50 m thick. Above this comes the Upper Badenian Kosiv Formation, up to 1,500 m thick, which comprises mainly clayey strata with sandstone intercalations. The Lower Sarmatian strata are represented by the Dashava Formation, which includes sandstone with claystone intercalations. It is subdivided into the lower part of about 3,000 m maximum thickness and the upper part, up to about 1,900 m thick (Shcherba *et al.*, 1987). The characteristic feature of the Lower Sarmatian succession is the presence of a number of sandstones extending over a vast area. These sandstones are easily identified in the well-logs and are best-correlated in the northwestern part of the Bilche-Volytsia Unit. These sandstone horizons are the gas reservoirs. Seals are provided by clayey layers. This configuration of the Lower Sarmatian succession allowed Vishniakov *et al.* (1979) to subdivide them into a number of cycles, which include sandstone horizons and embedded clayey layers. In total, 17 cycles were distin-

Table 1

Geochemical characteristics and hydrocarbon potential of the Miocene strata

Index \ Stratigraphy	L. Badenian (S.-C. Series)	L. Badenian (Baraniv Beds)	L. Badenian (Tyras Fm.)	U. Badenian (Kosiv Fm.)	L. Sarmatian (L. Dashava Fm.)	L. Sarmatian (U. Dashava Fm.)
TOC *(wt%)*	both 0.77 (2) (1)	0.00 to 0.76 (3) 0.29 (2)	0.11 to 0.65 (5) 0.27 (2)	0.44 to 2.01 (9) 0.96 [0.76] (5)	0.01 to 1.45 (51) 0.71 [0.72] (7)	0.62 to 0.77 (8) 0.70 [0.71] (2)
T_{max} (°C)	both 427 (2) (1)	429 (1)	400 to 424 (5) 410 (2)	416 to 433 (8) 425 [427] (4)	425 to 433 (48) 429 [428] (7)	423 to 430 (8) 426 [425] (2)
S_2 *(mg HC/g rock)*	0.75 and 0.90 (2) 0.83 (1)	0.56 (1)	0.36 to 0.63 (5) 0.45 (2)	0.17 to 6.7 (9) 1.76 [1.03] (5)	0.00 to 1.66 (49) 0.71 [0.69] (7)	0.67 to 0.99 (8) 0.81 [0.78] (2)
S_1+S_2 *(mg HC/g rock)*	0.84 and 0.97 (2) 0.91 (1)	0.65 (1)	0.49 to 0.71 (5) 0.57 (2)	0.24 to 7.3 (9) 1.94 [1.14] (5)	0.05 to 1.76 (49) 0.80 [0.78] (7)	0.78 to 0.11 (8) 0.92 [0.89] (2)
PI	0.07 and 0.11 (2) 0.09 (1)	0.14 (1)	0.11 to 0.27 (5) 0.21 (2)	0.08 to 0.29 (9) 0.12 [0.10] (5)	0.05 to 0.19 (48) 0.11 [0.11] (7)	0.1 to 0.14 (8) 0.12 [0.12] (2)
HI *(mg HC/g TOC)*	97 and 117 (2) 107 (1)	74 (1)	97 to 377 (5) 253 (2)	39 to 333 (9) 144 [136] (5)	68 to 149 (48) 99 [100] (7)	104 to 134 (8) 115 [109] (2)
BR *(mg bit./g TOC)*	78 (1)	64 (1)	133 and 438 (2) 286 (1)	46 to 104 (8) 74 [76] (4)	41 to 132 (20) 72 [69] (7)	61 to 75 (8) 67 [65] (2)
Kerogen type	III	III	III/(II)	III/(II)	III	III
Maturity	immature	immature	immature	immature	immature	immature
Processes	microbial	microbial	microbial	microbial	microbial	microbial
Hydrocarbon potential	good ?	fair ?	fair ?	good	good	good

S.-C. – Sandy-Calcareous, L. – Lower, U. – Upper, Fm. – Formation, TOC – total organic carbon, T_{max} – maximum temperature of S_2 peak, S_1 – oil and gas yield (mg HC/g rock), S_2 – residual petroleum potential, PI – production index, HI – hydrogen index, BR – bitumen ratio, Range of geochemical parameters is given as numerator, mean and median values in denominator. Median values in square brackets. In parentheses: number of samples (numerator) and number of sampled boreholes (denominator)

guished in the Lower Dashava Formation and another 14 were found in the Upper Dashava Formation (Kurovets *et al.*, 2004). Gas fields occur in all the sandstone horizons, except for the upper four. Moreover, gas fields were discovered in all other Miocene stratigraphic units in the Lower and Upper Badenian. Gas reservoirs in the Badenian and Sarmatian successions are sandstone and siltstone layers, usually from 0.1 to 2 m (sometimes up to 5 m) thick.

SAMPLING STRATEGY

Rock samples were taken from cores representing all recognized strata in the study area. A total of 78 core samples were collected from the following stratigraphic units: Lower Badenian Sandy-Calcareous Series – 2 samples, Lower Badenian Baraniv beds – 3 samples, Upper Lower Badenian Tyras Formation – 5 samples, Upper Badenian Kosiv Formation – 9 samples, Lower Sarmatian Lower Dashava Formation – 51 samples, and Lower Sarmatian Upper Dashava Formation – 8 samples. Cores originated from 11 wells: Bortyatyn-1 (Bn-1), Chornokuntsi-1 (Ch-1), Kokhanivka-26 (Kh-26), Kokhanivka-30 (Kh-30), Lanivka-1 (Lv-1), Moryantsi-1 (Mi-1), Pivdenne Girs'ke-1 (PG-1), Podiltsi-1 (Pt-1), Susoliv-1 (Su-1), Voloshcha-1 (Vo-1), and Yuriyiv-1 (Yu-1) (Fig. 1). All 78 samples were analysed by Rock-Eval pyrolysis (Table 1) and 13 selected samples for their biomarker distributions (Tables 2–4), elemental composition of kerogen (Table 5) and stable carbon isotope composition of bitumens and their fractions (Table 6).

ANALYTICAL METHODS

Preparation of core samples and analytical, geochemical methods as Rock-Eval, extraction, fraction analysis, stable carbon isotope analysis of kerogen, bitumens and their fractions, elemental composition (C, H, N and S) of isolated kerogen, and saturated and aromatic hydrocarbon fractions from the bitumens by GC-MS analysis were described in another paper in this volume (Więcław *et al.*, 2011).

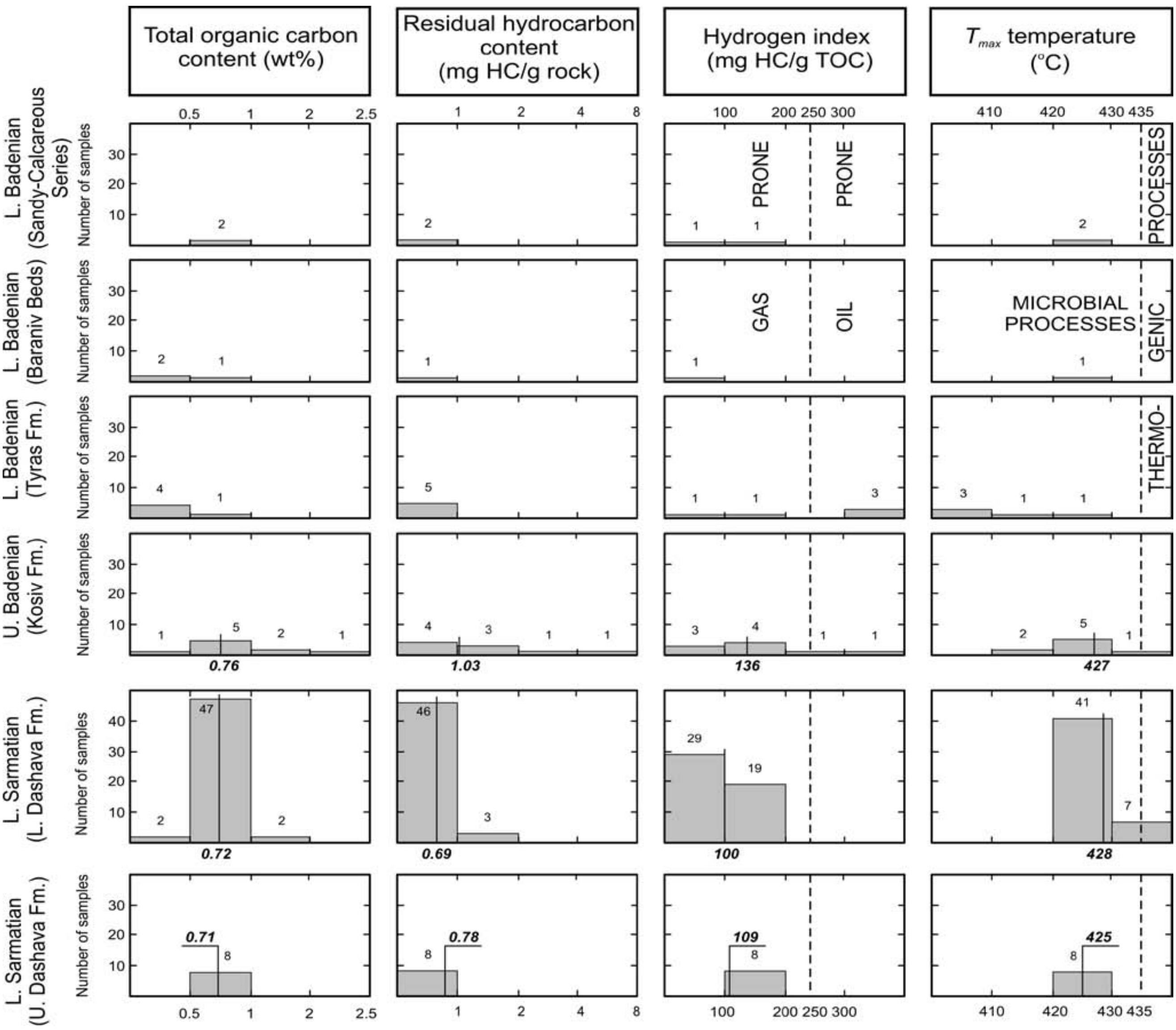

Fig. 2. Histograms of total organic carbon content, residual hydrocarbon potential, hydrogen index, T_{max} temperature; number of samples, and median values of individual geochemical parameters and indices for autochthonous Miocene strata of the Bilche-Volytsia Unit. Median values are given in bold and italics. L. – Lower, U. – Upper, Fm. – Formation

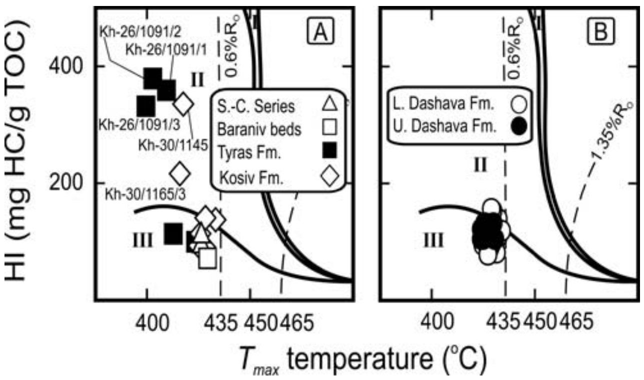

Fig. 3. Hydrogen index (HI) versus Rock-Eval T_{max} temperature for: **(A)** Sandy-Calcareous Series, Baraniv beds, Tyras and Kosiv formations (Badenian), and **(B)** Lower and Upper Dashava Formations (Sarmatian) of autochthonous Miocene strata from the Bilche-Volytsia Unit. Maturity paths of individual kerogen types after Espitalié *et al.* (1985). S.-C. – Sandy-Calcareous Series, L. – Lower, U. – Upper, Fm. – Formation

RESULTS AND DISCUSSION

In the autochthonous Miocene sequence of the Bilche-Volytsia Unit from the Ukrainian Carpathian Foredeep, the Kosiv Formation, the Lower Dashava Formation and the Upper Dashava Formation reach 1,500, 3,000 and 1,900 metres of thickness, respectively. Older Miocene rocks (Lower Badenian Sandy-Calcareous Series, Lower Badenian Baraniv beds and Upper Badenian Tyras Formation) are considerably less thick (several tens of metres) and contain much more sandstones, while the Tyras Formation also contains evaporates. Thus, these units are less interesting as potential source rocks, and far fewer samples were collected (Table 1).

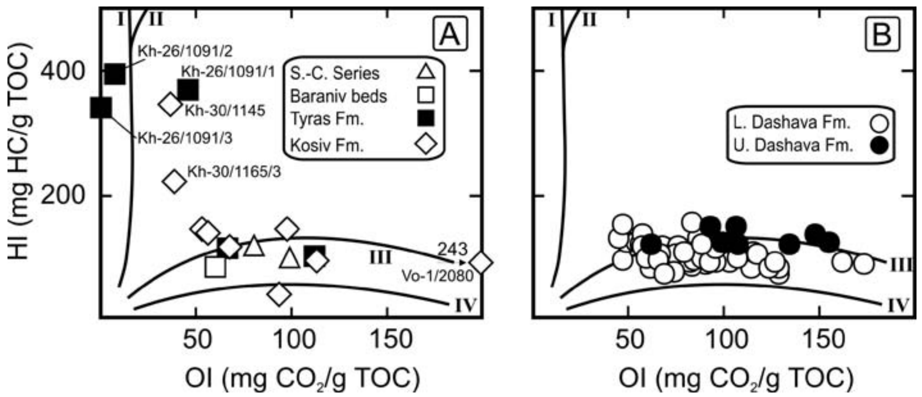

Fig. 4. Hydrogen index (HI) versus oxygen index (OI) for: **(A)** Lower Badenian Sandy-Calcareous Series and Baraniv beds, Upper Badenian Tyras and Kosiv formations, and **(B)** Lower and Upper Dashava formations (Sarmatian) of autochthonous Miocene strata from the Bilche-Volytsia Unit. Maturity paths of individual kerogen types after Espitalié *et al.* (1985). S.-C. – Sandy-Calcareous Series, L. – Lower, U. – Upper, Fm. – Formation

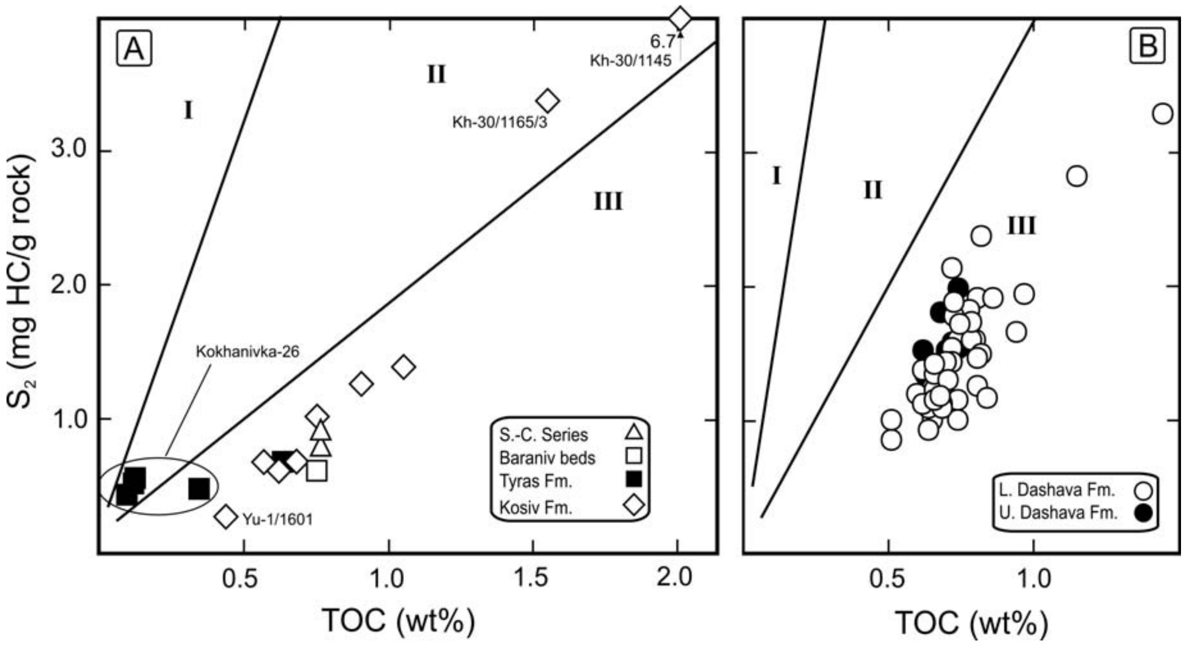

Fig. 5. Residual petroleum potential S_2 versus total organic carbon (TOC) content revealing the kerogen type in: **(A)** Lower Badenian Sandy-Calcareous Series and Baraniv beds, Upper Badenian Tyras and Kosiv formations, and **(B)** Lower and Upper Dashava formations (Sarmatian) of autochthonous Miocene strata from the Bilche-Volytsia Unit. Genetic boundaries after Langford & Blanc-Valleron (1990). S.-C. – Sandy-Calcareous Series, L. – Lower, U. – Upper, Fm. – Formation

The Lower Badenian Sandy-Calcareous Series and Baraniv beds, and the Upper Badenian Tyras Formation

In the Lower Badenian Sandy-Calcareous Series, the Lower Badenian Baraniv beds and the Upper Badenian Tyras Formation, the TOC contents range from 0.00 to 0.77 wt% (Table 1, Fig. 2). The values of Rock-Eval hydrogen index (HI), oxygen index (OI), T_{max} and residual hydrocarbon potential (S_2) (Table 1, Figs 2–6) indicate that terrestrial, gas-prone organic matter occurs in this part of the Miocene sequence. Locally, in the Tyras Formation marine, oil-prone kerogen is present.

The *n*-alkanes and isoprenoids extracted from one sample (Kokhanivka-26/1091/4) collected from the Lower Badenian Baraniv beds are dominated by short-chain hydrocarbons evidencing input of marine organic matter, while those from the Upper Badenian Tyras Formation are dominated by long-chain hydrocarbons (Fig. 7) indicating a terrestrial origin (*e.g.*, Peters *et al.*, 2005). The terrigenous/aquatic ratio (TAR_{HC}) for the single sample collected from Baraniv beds equals 1.1 (Table 2) suggesting a dominant terrigenous organic matter content (Meyers, 1997). This value is overestimated and is the result of partial evaporation of nC_{15} (Fig. 7) present in the denominator of the ratio's formula (Table 2). Taking into consideration *n*-alkanes

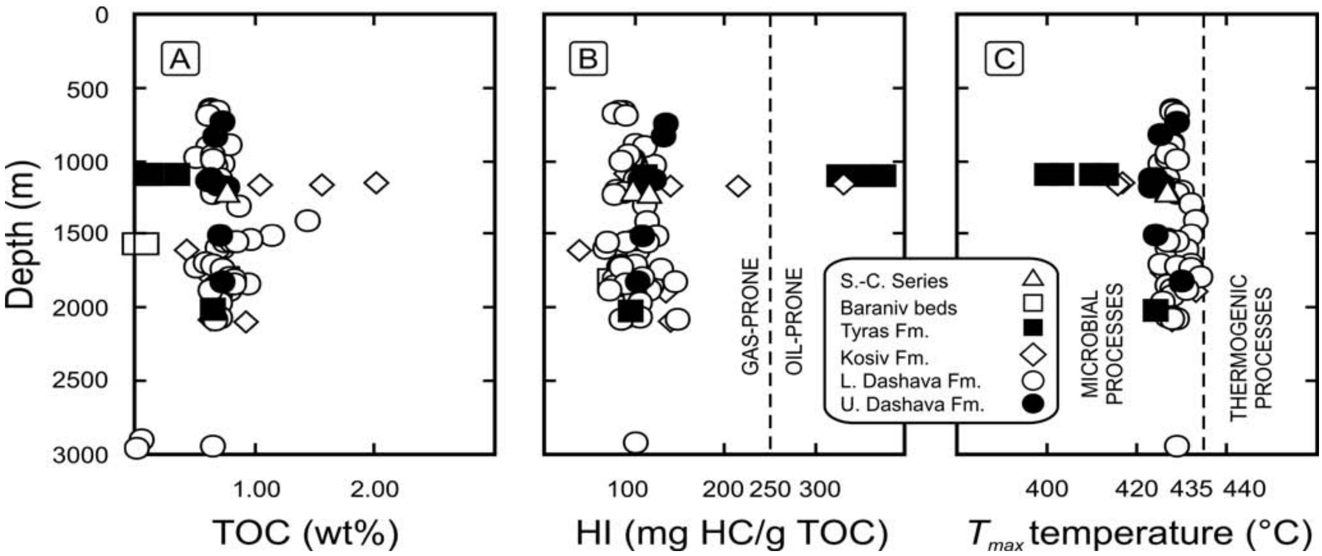

Fig. 6. (**A**) Total organic carbon content, **(B)** hydrogen index, and **(C)** T_{max} temperature versus depth in autochthonous Miocene strata from the Bilche-Volytsia Unit. S.-C. – Sandy-Calcareous Series, L. – Lower, U. – Upper, Fm. – Formation

with 17, 18 and 19 (short) and 27, 28 and 29 (long) carbon atoms in chain, respectively (Table 2), long- to-short hydrocarbon ratio (LTS_{HC}) eliminates the eventual problems of partial nC_{15} evaporation. For the sample Bortyatyn-1/1800 this ratio equals 0.7 indicating the presence of marine organic matter. A value of $CPI_{17\text{-}23}$ ratio <1 suggests deposition of source material for these compounds in evaporites (Bray & Evans, 1961). Many evaporate horizons occurring in the Badenian strata were described by, for instance, Oszczypko *et al.* (2006). Increased concentrations of phytane in the sample Kokhanivka-26/1091/4 (Fig. 7) may be connected with co-elution of crocetane (2, 6, 11, 15-tetramethylhexadecane), a biomarker of methanogenic and methanotrophic archea (Peters *et al.*, 2005). In the same sample, the presence of 2, 6, 10, 15, 19-pentamethylicosane (PMI) was recorded (Fig. 7). This isoprenoid is commonly a crocetane marker of the methanogens in the immature sediments (Noble & Henk, 1998). Elevated values of Pr/nC_{17} ratio (Table 2) and correlation of Pr/nC_{17} versus Ph/nC_{18} ratios (Fig. 8) suggest the presence of mixed, type-III/II kerogen. In some samples it was impossible to calculate short-chain-hydrocarbon indices due to their partial evaporation loss. The partial evaporation of hydrocarbons was ascertained when nC_{15}-alkane peak was non-integrable. Values of Pr/Ph ratio usually below 1 are characteristic of reducing depositional conditions over most of the study area (Didyk *et al.*, 1978); however, the above mentioned possibility of co-elution of crocetane with phytane may influence on values of this ratio. The increased concentration of hydrocarbons with odd carbon number, especially in the C_{25}-C_{31} range (Table 2, Fig. 7), evidences low maturity of the Miocene organic matter.

The distribution of regular $5\alpha(H),14\alpha(H),17\alpha(H)$ 20R steranes in analysed bitumens (Table 3, Fig. 9) evidences that in samples collected from the Tyras Formation in the Kokhanivka-26 well C_{29} steranes prevail, which suggests the presence of terrestrial organic matter (*e.g.*, Peters *et al.*, 2005). Moreover, C_{29} steranes dominate in the sample collected from the Baraniv beds (Fig. 9) indicating a significant presence of the terrigenous organic matter (Huang & Meinschein, 1976). Low values of gammacerane/17α hopane ratio (Table 3) evidence that during deposition of both series hypersalinity was not present (Sinninghe Damsté *et al.*, 1995). The results of analysis of dibenzothiophene, phenanthrene, pristane and phytane concentration in bitumens (Tables 2, 4) indicate that organic matter was deposited in marine shales (Fig. 10), but this conclusion may be invalid due to previously described co-elution of crocetane with phytane resulting in the possibility of a lower pristane/phytane ratio. Elemental composition of kerogen from the Tyras Fm. confirms previous suggestions of the presence of Type-III kerogen (Table 5, Fig. 11). Stable carbon isotope composition of bitumens, their fractions and kerogen (Table 6, Fig. 12) show the presence of two organic facies in the Tyras Fm., although samples were collected *ca*. 2 m apart from each other. One sample is enriched in a heavier isotope (^{13}C) and varies widely from all other samples (Fig. 12). Organic facies characterising comparable values of $\delta^{13}C$ of organic matter within the Upper Badenian strata in the vicinity of Rzeszów (Poland) were earlier reported by Kotarba *et al.* (2005).

The maturity of the investigated strata was determined based on the results of Rock-Eval pyrolysis (Table 1), distribution of *n*-alkanes (Table 2), steranes and hopanes (Table 3), methylphenanthrenes and methyldibenzothiophenes (Table 4), and elemental composition of kerogen (Table 5). The near immature nature of the organic matter in the sampled strata show: T_{max} values below 429°C (Table 1), high, up to 4.12 values of $CPI_{(25\text{-}31)}$ (Table 2), low values of H_{31} and H_{32} homohopanes S/(S+R), C_{29}SR and Ts/Tm ratios equalling below 0.47, 0.44, 0.15 and 0.34, respectively (Table 3). Also values of atomic ratios H/C and O/C (Table 5, Fig. 11) reveal the immature level of the organic matter present in the sample from Tyras Fm. Values of maturity in-

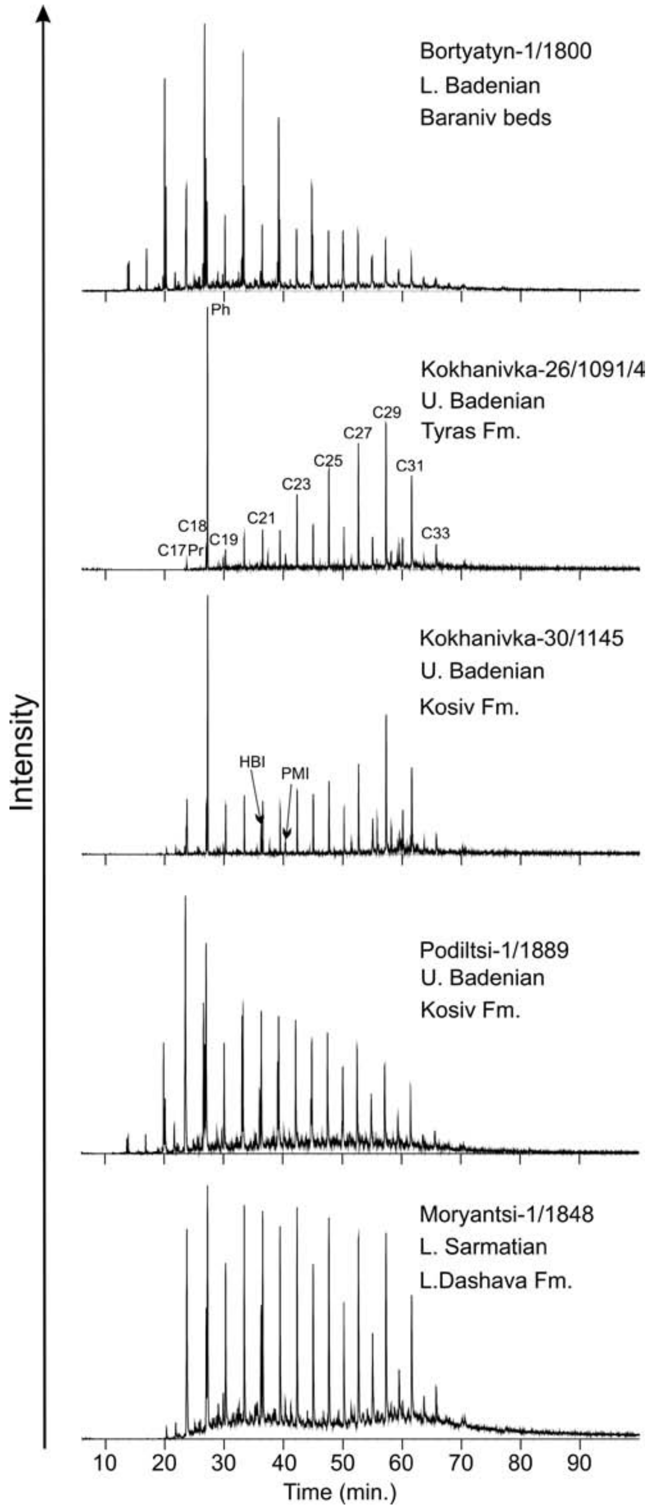

Fig. 7. Examples of ion chromatograms (m/z = 71) showing the distributions of *n*-alkanes and isoprenoids in saturated hydrocarbons of bitumens from autochthonous Miocene strata of the Bilche-Volytsia Unit. Lower, U. – Upper, Fm. – Formation, Pr – pristane, Ph – phytane, HBI – highly branched isoprenoid C_{25}, PMI – 2,6,10,15,19-pentamethylicosane

dices shown in Table 4 are probably overestimated because – according to the methylphenanthrene (MP) indices – the analysed organic matter should have reached the catage-

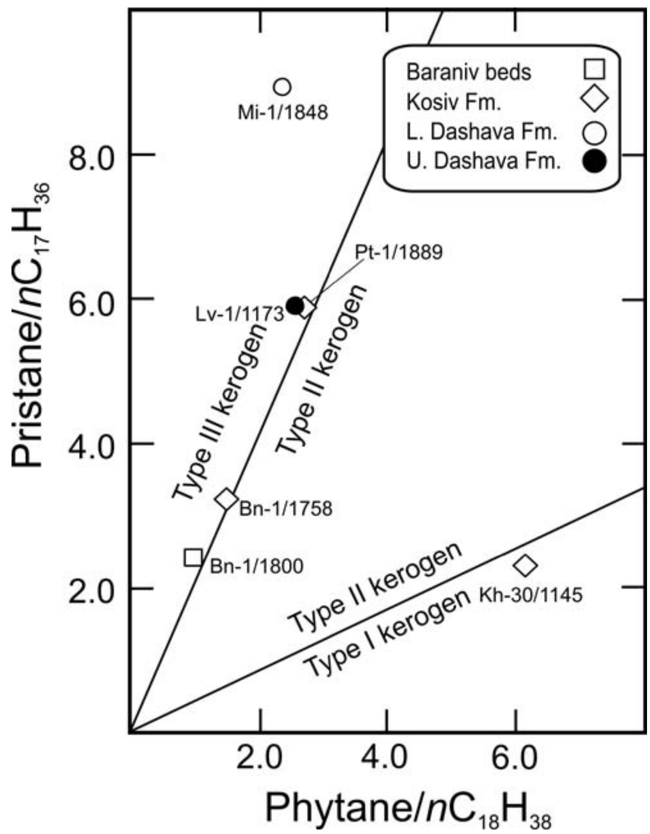

Fig. 8. Genetic characterization of bitumens in terms of pristane/$nC_{17}H_{36}$ and phytane/$nC_{18}H_{38}$ ratios for autochthonous Miocene strata of the Bilche-Volytsia Unit. Categories after Obermajer *et al.* (1999). L. – Lower, U. – Upper, Fm. – Formation

netic stage of maturation (Radke *et al.*, 1986; Radke & Welte, 1983; Radke, 1988). The MPI1 ratios were developed for organic matter being in the oil and gas window range (Radke & Welte, 1983). They are not intended for study of immature organic matter.

Generally, in the Tyras Formation both types of kerogen (III and II) are immature (Figs 2–4, 6), and thus have generated mainly microbial methane and a smaller volume of microbial ethane (Kotarba & Koltun, 2011; Kotarba *et al.*, 2011). During the microbial process one molecule of ethane is produced per one thousand molecules of methane (Oremland *et al.*, 1986). These observations were confirmed by biomarker analyses (Tables 2, 3, Figs 7–9), aromatic hydrocarbon distribution (Table 4, Fig. 10), elemental analyses of kerogen (Table 5, Fig. 11) and stable carbon isotope analyses of bitumens, and their individual fractions (Table 6, Figs 12, 13).

The Upper Badenian Kosiv Formation, the Lower Sarmatian Lower Dashava and Upper Dashava formations

The highest TOC contents from samples of the Upper Badenian Kosiv Formation measured 0.44 to 2.01 wt% (median 0.76 wt%). Slightly lower values were found in both the Lower Dashava and the Upper Dashava formations: from 0.01 to 1.45 wt% (median 0.72 wt%) and from 0.62 to

Table 2

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

Well	Sample code	Depth (m)	Strati-graphy	Lithostrati-graphy Local division	$CPI_{(17-31)}$	$CPI_{(17-23)}$	$CPI_{(25-31)}$	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	TAR_{HC}	LTS_{HC}
Bortyatyn-1	Bn-1/1800	1,800-1,810	Lower Bade-nian	Baraniv beds	1.04	0.68	1.99	1.11	2.39	0.98	1.3	0.7
Kokhanivka-26	Kh-26/1091/2	1,091-1,095	Upper Bade-nian	Tyras Fm.	n.c.	n.c.	2.94	<<1	n.c.	n.c.	31.8	16.9
	Kh-26/1091/4	1,091-1,095			n.c.	n.c.	4.12	<<1	n.c.	14.4	23.2	9.5
Bortyatyn-1	Bn-1/1758	1,758-1,768		Kosiv Fm.	1.16	0.84	2.14	1.17	3.24	1.49	1.1	0.6
Kokhanivka-30	Kh-30/1145	1,145-1,149			1.71	0.90	2.95	0.19	2.24	6.21	5.7	2.7
Podiltsi-1	Pt-1/1889	1,889-1,900			1.17	0.92	1.61	1.17	5.93	2.68	1.9	1.3
Voloshcha-1	Vo-1/2090	2,090-2,100		Kosiv Fm.?	n.c.	n.c.	2.49	<1	n.c.	2.05	3.5	2.1
Moryantsi-1	Mi-1/1848	1,848-1,853	Lower Sarma-tian	Lower Dashava Fm.	1.31	0.92	2.00	0.81	8.93	2.73	3.4	2.0
Podiltsi-1	Pt-1/1401	1,401-1,411			n.c.	n.c.	2.87	n.c.	n.c.	2.03	4.9	3.2
	Pt-1/1815	1,815-1,821			n.c.	n.c.	2.22	<1	n.c.	3.05	2.5	1.2
Susoliv-1	Su-1/2947	2,947-2,952			n.c.	n.c.	1.53	n.c.	n.c.	n.c.	3.5	3.3
Yuriyiv-1	Yu-1/1542	1,542-1,544			n.c.	n.c.	2.70	<1	n.c.	2.57	4.0	2.1
Lanivka-1	Lv-1/1173	1,173-1,178		Upper Dashava Fm.	1.36	0.77	2.71	0.34	5.85	2.56	4.7	2.2

Fm. – Formation, Pr – pristane, Ph – phytane, n.c. – not calculated, values typed in italic are estimated due to partly evaporation of hydrocarbons, $CPI_{(17-31)} = [(C_{17}+C_{19}+...+C_{27}+C_{29})+(C_{19}+C_{21}+...+C_{29}+C_{31})]/[2*(C_{18}+C_{20}+...+C_{28}+C_{30})]$, $CPI_{(17-23)} = [(C_{17}+C_{19}+C_{21})+(C_{19}+C_{21}+C_{23})]/[2*(C_{18}+C_{20}+C_{22})]$, $CPI_{(25-31)} = [(C_{25}+C_{27}+C_{29})+(C_{27}+C_{29}+C_{31})]/[2*(C_{26}+C_{28}+C_{30})]$, TARHC = $(C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$, LTSHC = $(C_{27}+C_{28}+C_{29})/(C_{17}+C_{18}+C_{19})$

0.77 wt% (median 0.71 wt%), respectively (Table 1, Fig. 2). The values of Rock-Eval hydrogen index (HI), oxygen index (OI), T_{max} temperature and residual hydrocarbon potential (S_2) (Table 1, Figs 2–6) indicate the dominance of type III (terrestrial) kerogen in these Upper Badenian and Lower Sarmatian strata. The immature, terrestrial organic matter shows Rock-Eval T_{max} temperature below 435°C (Espitalié & Bordeneve, 1993). Insignificant changes in the TOC, HI and T_{max} values (Fig. 6) suggest quite uniform depositional conditions of organic matter in the Upper Badenian and the Lower Sarmatian strata where at 3,000 metres depth only microbial methane and smaller quantities of microbial ethane were generated (Kotarba & Koltun, 2006, 2011). Marine organic matter with a hydrogen index above 200 mg HC/g TOC is present only in the Upper Badenian Kosiv Fm. in the Kokhanivka-30 borehole section (Figs 3–5). In the Polish part of the Carpathian Foredeep, comparable values were reported by Kotarba *et al.* (2005).

Long-chain *n*-alkanes dominate in almost all samples collected from the Upper Badenian Kosiv Formation and from the Lower and Upper Dashava Lower Sarmatian, formations (Fig. 7), indicating the terrestrial origin of organic matter (*e.g.*, Peters *et al.*, 2005). The terrigenous/aquatic ratio (TAR_{HC}) above one for the all samples confirms this thesis (Meyers, 1997), but the LTS_{HC} ratio of 0.6 for sample Bortyatyn-1/1758 (Table 2) indicates the presence of marine organic matter. This overestimated value of the TAR_{HC} for this sample is probably a result, like in the case of sample Bortyatyn-1/1800, of partial evaporation of nC_{15}. The LTS_{HC} ratio is close to unity also for the other two samples collected from the Podiltsi-1 borehole: Pt-1/1889 (Kosiv Fm.) and Pt-1/1815 (Lower Dashava Fm.) (Table 2, Fig. 7), suggesting addition of marine organic matter. Value of CPI_{17-23} ratio <1 suggests connection of source material for these compounds with evaporites (Bray & Evans, 1961). Increased concentrations of phytane in many samples (Fig. 7) cause low values of pristane/phytane and high values of phytane/nC_{18} ratios, respectively (Table 2). They may be connected, as in the case of previously discussed formations, with co-elution of crocetane (Peters *et al.*, 2005). Also in many samples, such as the Tyras Fm., the presence of 2, 6, 10, 15, 19-pentamethylicosane (PMI) marker of the methanogens in the immature sediments (Noble & Henk, 1998) was recorded (Fig. 7). In some samples, the highly-branched isoprenoid C_{25} [2,6,10,14-tetramethyl-7-(3-methylpenthyl) pentadecane] (HBI) was detected (Fig. 7). This biomarker, found in diatoms by Volkman *et al.* (1994, 1998), is used as an indicator of the contribution of diatoms to the organic matter. The presence of diatomites in the Miocene strata from the Polish part of the Carpathian Foredeep has already been described by Kotarba *et al.* (2005). Correlation of Pr/nC_{17} and Ph/nC_{18} ratios as well as elevated values of Pr/nC_{17} ratio (Table 2) suggest domination of Type-III kerogen (Fig. 8). In sample Kh-30/1145, the input of algal organic matter (Fig. 8) is supported the results of Rock-Eval data (Figs 3–5), composition of regular 5α(H),14α(H),17α(H) 20R steranes (Fig. 9), and the elemental composition of kerogen (Fig. 11). In some samples, such as those from the Tyras Fm., it was impossible to calculate short-chain-hydrocarbon indices due to partial evaporation loss. Values of Pr/Ph ratio usually below 1 are characteristic of reducing depositional conditions (Didyk *et al.*,

Table 3

Selected biomarker characteristics of bitumen from the Miocene strata

Sample code	Strati-graphy	Lithostratigraphy Local division	Gam/Hop	C_{27}	C_{28}	C_{29}	Ol/Hop	Mor/Hop	H_{31} S/(S+R)	H_{32} S/(S+R)	C_{29}SR	$\Sigma C_{29}/\Sigma C_{27}$ (ster)	Ts/Tm	Gam/ C_{31}Hop	Dia/Reg
Bn-1/1800	Lower Badenian	Baraniv beds	0.18	24	27	50	0.15	0.27	0.45	0.44	0.15	2.12	0.34	0.51	0.07
Kh-26/1091/2	Upper Badenian	Tyras Fm.	0.11	14	26	60	0.13	0.18	0.47	0.40	0.05	4.34	0.17	0.98	n.c.
Kh-26/1091/4			0.06	15	26	59	0.13	0.18	0.34	0.38	0.05	3.97	0.18	0.57	n.c.
Bn-1/1758		Kosiv Fm.	0.20	23	29	48	0.17	0.32	0.41	0.40	0.14	2.08	0.41	0.52	0.05
Kh-30/1145			0.04	34	22	44	0.11	0.13	0.40	0.34	0.08	1.28	0.15	0.23	n.c.
Pt-1/1889			0.20	23	29	48	0.13	0.33	0.40	0.39	0.12	2.09	0.26	0.50	0.04
Vo-1/2090		Kosiv Fm.?	0.13	19	27	54	0.18	0.26	0.44	0.46	0.14	2.78	0.38	0.43	0.06
Mi-1/1848	Lower Sarmatian	Lower Dashava Fm.	0.05	23	28	50	0.19	0.21	0.44	0.41	0.09	2.20	0.33	0.17	0.05
Pt-1/1401			0.33	21	27	53	0.29	0.37	0.32	0.43	0.10	2.55	0.33	0.44	n.c.
Pt-1/1815			0.10	23	26	51	0.19	0.24	0.44	0.47	0.09	2.25	0.38	0.35	n.c.
Su-1/2947			0.14	21	24	56	0.22	0.29	0.48	0.44	0.16	2.65	0.31	0.71	n.c.
Yu-1/1542			0.10	25	28	47	0.16	0.28	0.43	0.40	0.08	1.87	0.35	0.33	n.c.
Lv-1/1173		Upper Dashava Fm.	0.19	21	29	50	0.14	0.28	0.40	0.43	0.10	2.36	0.32	0.57	n.c.

Fm. – Formation; n.c. – not calculated due to lack of biomarkers; Gam/Hop = gammacerane/17α hopane, C_{27} = $C_{27}\alpha\alpha\alpha$20R sterane/(C_{27}+C_{28}+C_{29})$\alpha\alpha\alpha$20R steranes*100, C_{28} = $C_{28}\alpha\alpha\alpha$20R sterane/(C_{27}+C_{28}+C_{29})$\alpha\alpha\alpha$20R steranes*100; C_{29} = $C_{29}\alpha\alpha\alpha$20R sterane/(C_{27}+C_{28}+C_{29})$\alpha\alpha\alpha$20R steranes*100, Ol/Hop = leanane/17α hopane, Mor/Hop = moretane/17α hopane; H_{31}S/(S+R) = homohopane 22S/(22S+22R), H_{32}S/(S+R) = bishomohopane 22S/(22S+22R), C_{29}SR = epimerisation of regular steranes C_{29} ratio; $\Sigma C_{29}/\Sigma C_{27}$ (ster) = ΣC_{29} regular steranes/ΣC_{27} regular steranes, Ts/Tm = C_{27} 18α trisnorhopane/C_{27} 17α trisnorhopane; Gam/C_{31}Hop = gammacerane/C_{31} 22R hopane, Dia/Reg = C_{27} $\beta\alpha$ 20S diasterane/C_{29} $\alpha\alpha\alpha$ 20R sterane

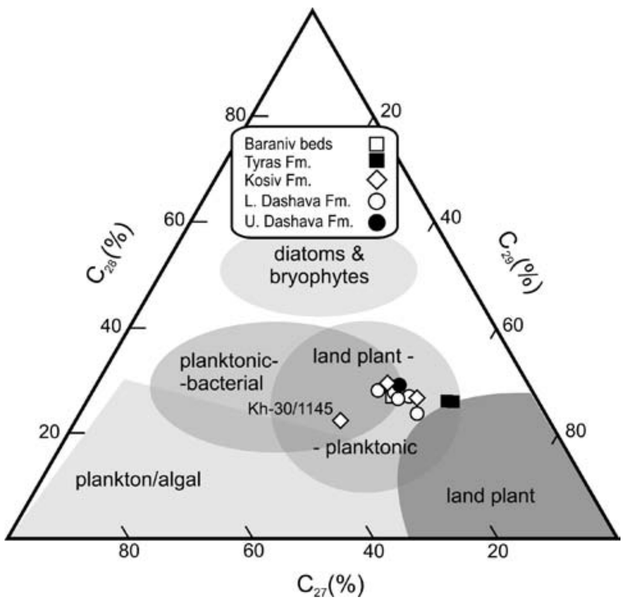

Fig. 9. Ternary diagram of distribution of regular 5α(H), 14α(H),17α(H) 20R steranes in bitumen from autochthonous Miocene strata of the Bilche-Volytsia Unit. Classification modified after Peters *et al.* (2005). L. – Lower, U. – Upper, Fm. – Formation

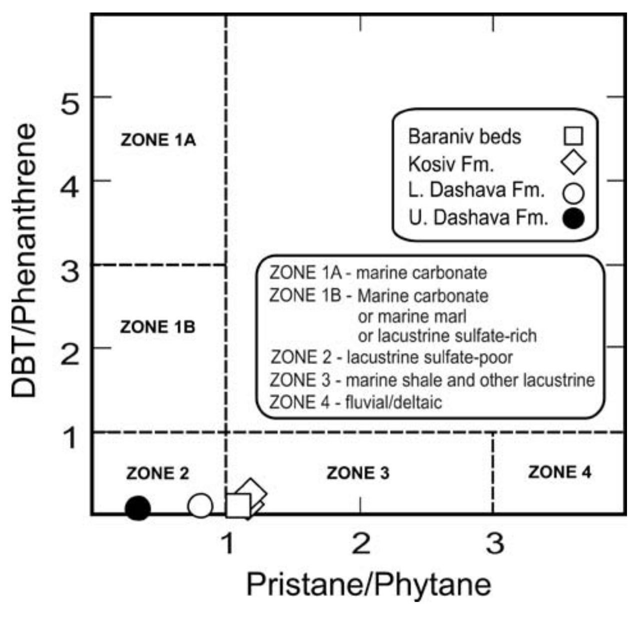

Fig. 10. Cross plot of dibenzothiophene/phenanthrene ratio versus pristane/phytane ratio for autochthonous Miocene strata of the Bilche-Volytsia Unit. Genetic scheme after Hughes *et al.* (1995). L. – Lower, U. – Upper, Fm. – Formation

1978) over most of the study area, however, the above mentioned possibility of co-elution of crocetane with phytane may influence on values of this ratio. The increased concentration of odd-carbon-hydrocarbons, especially in the C_{25}-C_{31} range (Table 2, Fig. 7), points to low maturity of Miocene organic matter accumulated in the studied strata.

The distribution of regular 5α(H),14α(H),17α(H) 20R steranes in analysed bitumens (Table 3, Fig. 9) indicates a single source of organic matter for almost all samples. C_{29} steranes dominate indicating significant share of the terrigenous organic matter (Huang & Meinschein, 1976). Only bitumen from sample Ko-30/1145 is somewhat enriched in

Table 4

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

Sample code	Stratigraphy	Lithostratigraphy Local division	MPI1	MPR	MPR1	R_{cal} (%)	$R_{cal(MPR)}$ (%)	MDR	$R_{cal(DBT)}$ (%)	$T_{max(DBT)}$ (°C)	DBT/P
Bn-1/1800	Lower Badenian	Baraniv beds	0.3	0.9	0.5	0.6	0.9	1.9	0.6	432	0.08
Kh-26/1091/2	Upper Badenian	Tyras Fm.	0.6	0.6	0.3	0.7	0.6	n.c.	n.c.	n.c.	n.c.
Kh-26/1091/4			0.7	0.7	0.3	0.8	0.6	0.2	0.5	424	n.c.
Bn-1/1758		Kosiv Fm.	0.3	1.0	0.5	0.5	0.9	3.3	0.8	440	0.08
Kh-30/1145			0.4	0.6	0.3	0.6	0.6	0.4	0.5	425	0.04
Pt-1/1889			0.4	0.9	0.5	0.6	0.9	2.2	0.7	434	0.20
Vo-1/2090		Kosiv Fm.?	0.7	0.7	0.4	0.8	0.7	1.1	0.6	429	0.28
Mi-1/1848	Lower Sarmatian	L.Dashava Fm.	0.7	0.8	0.4	0.8	0.7	1.0	0.6	428	0.06
Pt-1/1401			0.5	0.8	0.4	0.7	0.7	1.7	0.6	432	0.08
Pt-1/1815			0.6	0.8	0.4	0.7	0.8	1.5	0.6	430	0.03
Su-1/2947			0.7	0.6	0.4	0.8	0.6	0.7	0.6	427	0.00
Yu-1/1542			0.7	0.7	0.4	0.8	0.7	0.9	0.6	427	0.00
Lv-1/1173		U.Dashava Fm.	0.7	0.7	0.4	0.8	0.7	1.4	0.6	430	0.04

U. – Upper; L. – Lower; Fm. – Formation, n.c. – not calculated;
MPI1 = 1.5(2-MP+3-MP)/(P+1-MP+9-MP); P – phenanthrene; MP – methylphenanthrene; MPR = 2-MP/1-MP;
R_{cal} = 0.60MPI1+0.37 for MPR<2.65 (Radke, 1988); MPR1 = (2-MP+3-MP)/(1-MP+9-MP+2-MP+3-MP);
$R_{cal(MPR)}$ = -0.166+2.242(MPR1) (Kvalheim *et al.*, 1987); MDR = 4-MDBT/1-MDBT, MDBT - methyldibenzothiophene;
$R_{cal(DBT)}$ = 0.51+0.073MDR, $T_{max(DBT)}$ = 423+5.1MDR; DBT – dibenzothiophene

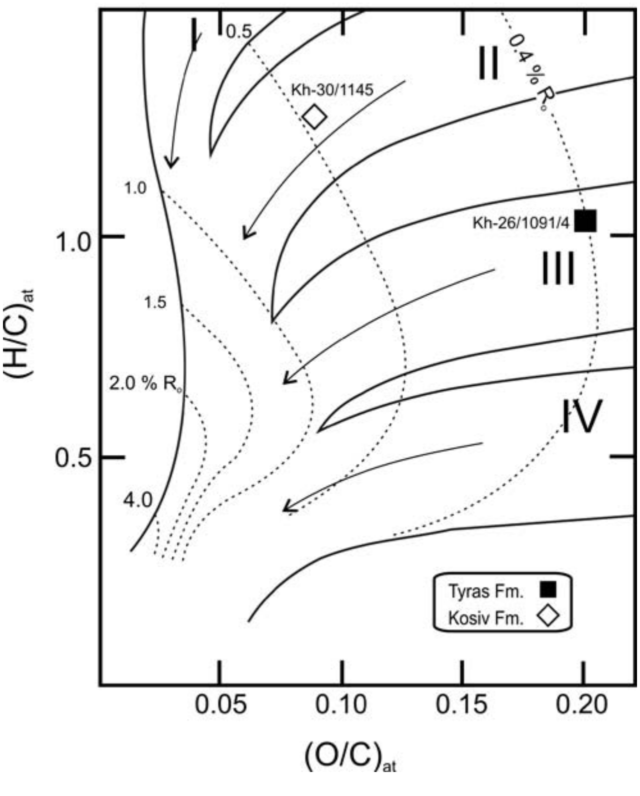

Fig. 11. Atomic hydrogen/carbon ratio versus oxygen/carbon ratio for kerogen from autochthonous Miocene strata of the Bilche-Volytsia Unit. Fields represent natural maturation trends for various kerogen types, as reported by Hunt (1996). Fm. – Formation

C_{27} steranes, in relation to other samples, which implies admixture of marine organic matter. Low values of gammacerane/17α hopane ratio (Table 3) show that during deposition of all formations hypersalinity was not present (Sinninghe Damsté *et al.*, 1995). The results of analysis of dibenzothiophene, phenanthrene, pristane and phytane concentrations in bitumens (Tables 2, 4) suggest that organic matter was deposited in marine shales or under lacustrine (fresh water) conditions (Fig. 10). However, as was above described, co-elution of crocetane with phytane may cause decreasing of values of pristane/phytane ratio. Elemental composition of kerogen dispersed in the Kosiv Formation confirm previous suggestions of the presence of Type-II kerogen in analysed samples (Table 5, Fig. 11). Stable carbon isotope composition of bitumen, their fractions and kerogen (Table 6, Fig. 12) indicate the presence in all analysed strata of one organic facies characterising comparable values of δ^{13}C of organic matter.

Like in the Baraniv beds and the Tyras Formation, the maturity of the investigated strata was determined based on the results of Rock-Eval pyrolysis (Table 1), distribution of *n*-alkanes (Table 2), steranes and hopanes (Table 3), methylphenanthrenes and methyldibenzothiophenes (Table 4) and elemental composition of kerogen (Table 5). The immature nature of the organic matter is evidenced by: T_{max} values below 433°C (Table 1), high, up to 2.95 values of $CPI_{(25-31)}$ (Table 2), low values of S/(S+R) of H_{31} and H_{32} homohopanes, C_{29}SR and Ts/Tm ratios less than 0.48, 0.47, 0.16 and 0.41, respectively (Table 3). Also H/C and O/C atomic ratios (Table 5, Fig. 11) reveal immaturity of organic matter present in the sample from Kosiv Formation. Matu-

Table 5

Elemental composition of kerogen from the Miocene strata

Sample code	Strati-graphy	Lithostrati-graphy Local division	Elemental composition (daf, wt%)					Atomic ratio				Mole fraction			
			C	H	O	N	S	H/C	O/C	N/C	S/C	H/(H+C)	O/(O+C)	N/(N+C)	S/(S+C)
Kh-26/1091/4	Upper Badenian	Tyras Fm.	68.7	5.9	18.6	1.6	5.1	1.03	0.20	0.020	0.028	0.51	0.17	0.019	0.027
Kh-30/1145		Kosiv Fm.	71.8	7.5	8.5	1.7	10.5	1.26	0.09	0.020	0.055	0.56	0.08	0.020	0.052

daf – dry, ash-free basis; Fm. – Formation

Table 6

Fractions and stable carbon isotope composition of bitumens, their individual fractions and kerogen of the Miocene strata

Sample code	Stratigraphy	Lithostratigraphy Local division	Fractions (wt%)				$\delta^{13}C$ (‰)					
			Sat	Aro	Res	Asph	Sat	Bit	Aro	Res	Asph	Ker
Bn-1/1800	Lower Badenian	Baraniv beds	20	16	34	30	-27.4	-27.4	-28.6	-26.7	-27.4	-24.9
Kh-26/1091/2	Upper Badenian	Tyras Fm.	9	11	62	18	-23.9	-22.3	-22.4	-21.6	-23.7	-21.6
Kh-26/1091/4			12	9	50	29	-27.9	-26.4	-26.9	-25.7	-27.0	-24.5
Bn-1/1758		Kosiv Fm.	20	15	33	32	-27.7	-27.4	-28.0	-27.3	-27.0	-24.8
Kh-30/1145			16	10	54	20	-27.4	-26.3	-26.5	-25.9	-26.4	-24.7
Pt-1/1889			12	13	33	42	-27.7	-26.6	-27.4	-26.9	-25.8	-25.2
Vo-1/2090		Kosiv Fm.?	12	11	46	31	-27.8	-26.6	-26.6	-26.5	-26.3	-24.8
Mi-1/1848	Lower Sarmatian	L.Dashava Fm.	12	10	35	43	-27.6	-26.2	-26.8	-26.3	-25.6	-24.4
Pt-1/1401			14	13	34	39	-27.8	-26.8	-26.9	-26.8	-26.4	-25.4
Pt-1/1815			18	9	36	37	-28.4	-26.8	-27.0	-26.7	-26.1	-24.8
Su-1/2947			11	10	39	40	-29.1	-27.4	-27.7	-27.5	-26.9	-25.0
Yu-1/1542			14	12	33	41	-28.1	-26.5	-26.9	-26.5	-25.7	-24.8
Lv-1/1173		U.Dashava Fm.	14	7	43	36	-27.9	-26.7	-26.9	-26.8	-26.0	-24.7

U. – Upper; L. – Lower; Fm. – Formation; Sat – saturated hydrocarbons; Aro – aromatic hydrocarbons; Res – resins; Asph – asphaltenes; Bit – bitumen; Ker – kerogen

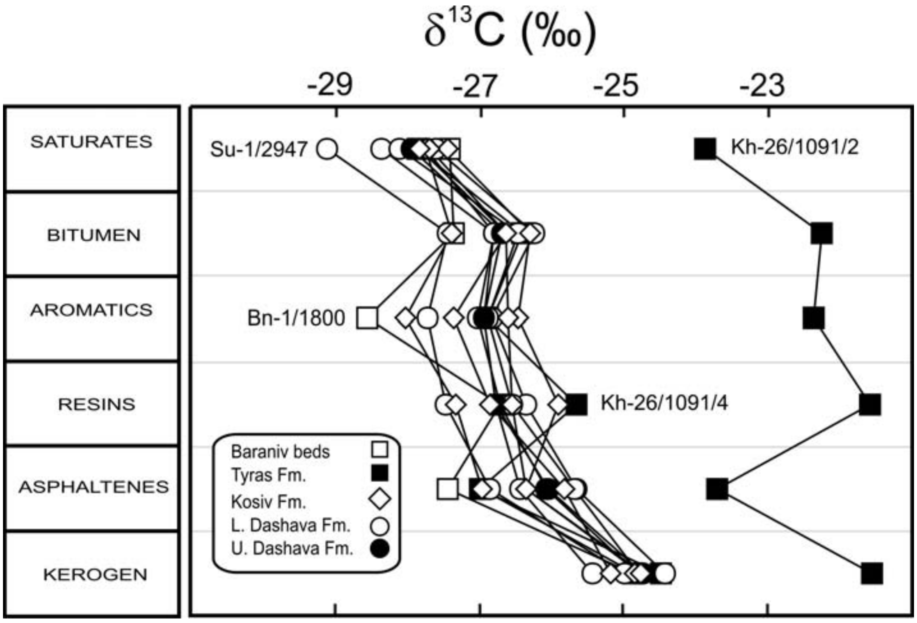

Fig. 12. Stable carbon isotope composition of bitumens and their individual fractions extracted from autochthonous Miocene strata of the Bilche-Volytsia Unit. S.-C. – Sandy-Calcareous Series; L. – Lower; U. – Upper

rity indices shown in Table 4, for the same reason as for previously discussed Baraniv beds and Tyras Formation, are probably overestimated.

Generally, in the Kosiv and Lower and Upper Dashava formations kerogen, independently of its type, is immature (Figs 2–4, 6), and thus has generated mainly microbial methane and less volumes of microbial ethane (Kotarba & Koltun, 2011; Kotarba *et al.*, 2011).

CONCLUSIONS

The geochemical studies of organic matter dispersed in the autochthonous Miocene sequence of the Bilche-Volytsia Unit between Ukrainian-Polish state border and the Stryi lead to the following conclusions:

1) the best source-rock parameters are from the Upper Badenian Kosiv Formation where the higher TOC contents (from 0.44 to 2.01 wt%, median 0.76 wt%) were detected;

2) slightly lower TOC contents were found in the Lower and Upper Dashava formations. These range from 0.01 to 1.45 wt% (median 0.72 wt%) and from 0.62 to 0.77 wt% (median 0.71 wt%), respectively;

3) the immature, terrestrial (gas-prone) type III kerogen dominates in the Upper Badenian Kosiv Formation and Lower Sarmatian Dashava formations;

4) in the Lower Badenian Sandy-Calcareous Series, the Lower Badenian Baraniv beds, and the Upper Badenian Tyras Formation the TOC contents are low and range from 0.00 to 0.77 wt%;

5) marine organic matter occurs sporadically in the Upper Badenian Kosiv Formation in the vicinity of Kokhanivka;

6) in the Lower Badenian Baraniv beds and in the Upper Badenian Tyras Formation an input of marine organic matter was disclosed.

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