Origin of hydrocarbons in the Slovak part of the Danube Basin

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Abstract: The Danube Basin is one of our largest Neogene basins in Slovakia with the highest volume of potential source rocks in active hydrocarbon generation zones. The source rocks, however, are quite poor with low hydrocarbon potential. In Blatné- and Rišňovce depressions at the northern part of the Danube Basin only early oil and oil generation window were reached below 2900 m during the Upper Miocene to Pliocene, due the lower temperature. In the southern Central Gabčíkovo Depression (CGD) that is explored by drilling only to 2700 m, all generation zones up to dry gas zone have been reached according to modelling. While the oil generation zone was reached at approximately 2800 m, dry gas is expected below 4000 m. The natural gas molecular composition and methane carbon isotopes indicate small local natural hydrocarbon gas accumulations associated mostly with oil generation that migrated to present reservoirs and mixed with biogenic methane. The carbon dioxide and partly also nitrogen here are most likely related to volcanic activity. The gasoline hydrocarbon range indicates that non biodegraded gasoline oil from the FGČ1 Čilistov well in the CGD is thermally very mature, with its origin most likely in the deeper parts of the CGD below 3500 m. In contrast, the oil trace from Sereď5 (Se5) well is strongly biodegraded and according to the sterane correlations it could have originated in any examined Neogene source reaching the oil window.
Key words: natural gas, gasoline oil, oil traces, Danube Basin, Slovakia

1. INTRODUCTION

The Danube Basin forms one of the northern promontories of the Pannonian Basin System, and it is divided into two national parts by the river Danube. While the Slovakian part retains the Danube Basin name, the Hungarian portion is known as the Little Hungarian Plain (Fig. 1). Local depressions are wedged in the Danube Basin's northern part; where the Blatné, Rišňovce, Komjatice, and Želiezovce depressions (BD, RD, KD, and ŽD) lie between the Malé Karpaty, Považský Inovec, and Tribeč core mountains and Middle Slovakian Neovolcanites, and in the southern part merge the local depressions into the Central Gabčíkovo Depression (CGD; Fig. 2).

The Danube Basin together with the Vienna- and East Slovakian Basins belongs to the prospective areas for hydrocarbon exploration in Slovakia even though that the exploration works did not bring until now the expected discoveries of liquid hydrocarbons. Oil traces and impregnations have been recorded in several core samples in BD, CGD, and ŽD depressions, while small methane deposits and accumulations are concentrated in the Blatné Depression (BD). A weak inflow of light gasoline oil is documented from the geothermal FGČ1 – Čilistov well at the south-eastern part of CGD.

Our article presents the geochemical characteristics of methane in the natural gases, selected extracts from potential source rocks and light gasoline oil and oil impregnations in the context of the source rock quality, thermal maturation zones and the hydrocarbon generation zones in the Danube Basin.

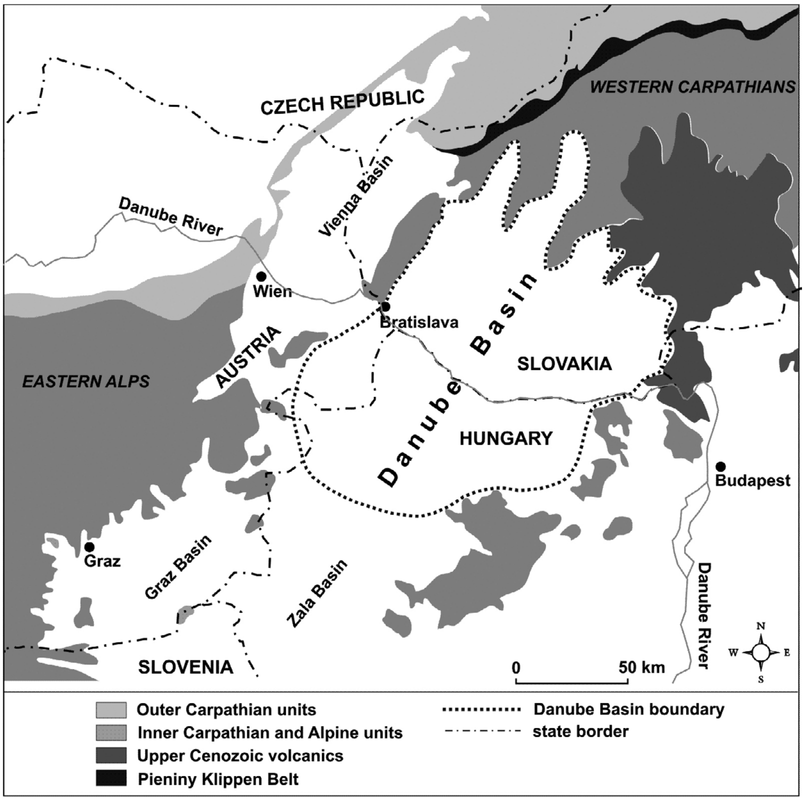

Fig. 1. Scheme of the Slovak and Hungarian parts of the Danube Basin.

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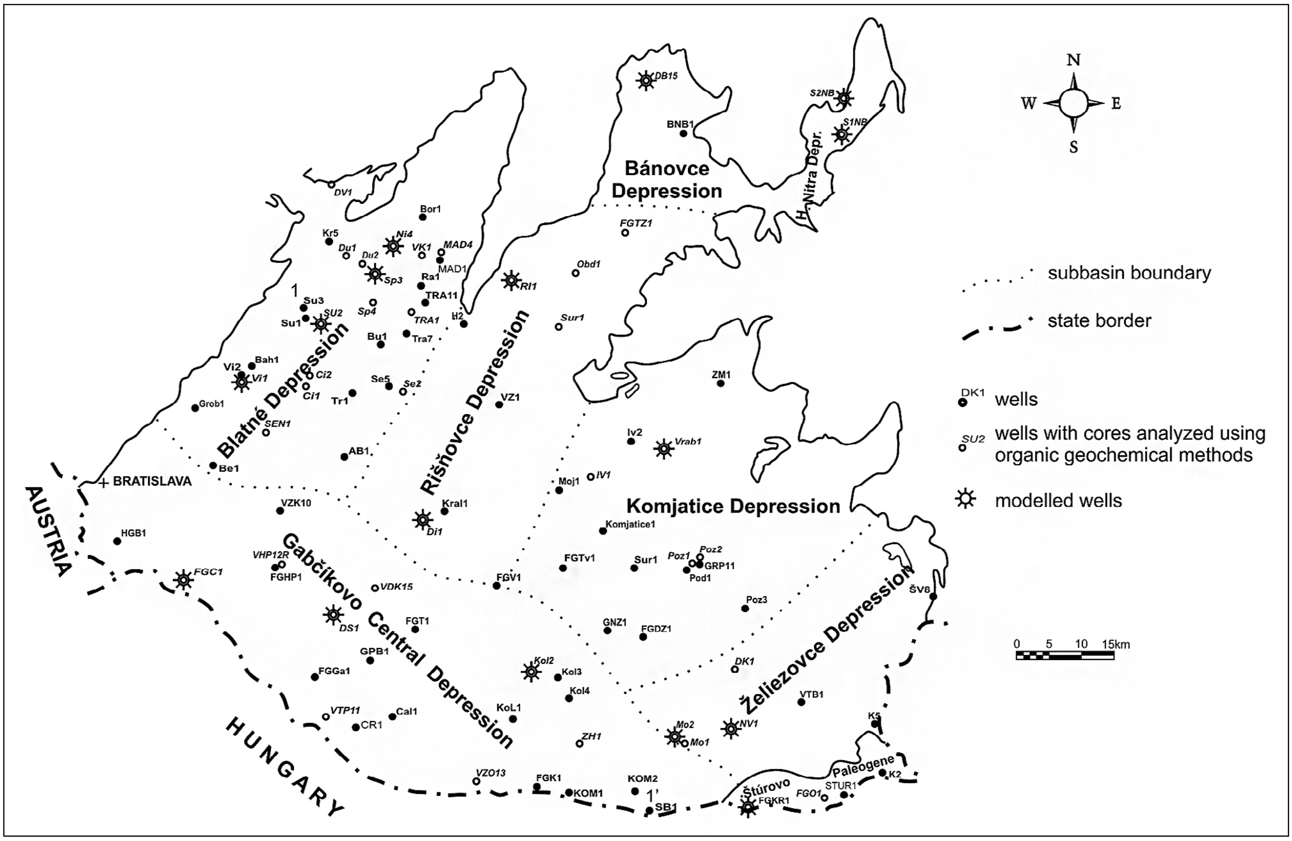

Fig. 2. Regional division of the Danube Basin (Vass et al., 1988) with location of oil- and selected geothermal wells.

2. PETROLEUM-GEOLOGICAL OUTLINE OF THE SLOVAK PART OF THE DANUBE BASIN

Hydrocarbon drilling exploration in the Slovak part of the Danube Basin was mostly performed between 1952 and 1972 and discovered small natural gas pools with prevailing methane but also other natural gas accumulations with small amount of methane and variable content of carbon dioxide and nitrogen. The exploration was renewed for a short period in the early 1990's of the last century.

Most research in this area has focused on exploitable quantities of hydrocarbon gases in the Blatné Depression (Fig. 3). Small gas deposits with 85–98.5 % methane are bound to Middle Badenian sandy horizons. This type of methane accumulations has been explored at Špačince, Krupá, Nižná, Madunice, Bučany-North and Trakovice structures. Accumulations at the southern margin and outside of the Blatné Depression contain more carbon dioxide and nitrogen than methane (Fig. 3). To these belong the Cífer with 77 % N_2 in the Middle Badenian and Sarmatian reservoirs; Sereď (52–90 % CO_2 and 2–30 % N_2) in the Middle Badenian and Pannonian sands and Golianovo with average 41 % methane plus non-combustible gases in the Lower Sarmatian reservoirs. These mixed natural gas reserves in the Lower Sarmatian deposits considerably exceed other natural gas accumulations in the Slovak portion of the Danube Basin.

Significant accumulations of crude oil in the Slovak part of the Danube Basin remain largely undetected, with only a slight inflow of light gasoline oil from the FGČ1 Čilistov geothermal well (Franko et al., 1992) and few traces of oil impregnations in wells situated on the southeastern margin of the CGD and in southern part of the ZD (Lunga, 1967; Gaža 1972, 1974, 1976, 1978; Pereszlényi et al., 1993[b]). In the Little Hungarian Plain the oil traces from wells in the Mihály High area are reported in Palcsu et al. (2014) and Vető et al. (2014).

The volume of potentially generated hydrocarbons in the Slovak part of the Danube Basin was appreciated using Waples' (1985) method based on organic-geochemical parameters and a release of 9.2 million ton of oil and 62.8 billion tons of gas was estimated (Milička et al., 2011). This volume was calculated together for all maturity zones in the area, and the calculation includes the secondary migration efficiency and the presence of buried stratovolcanoes of Badenian age in the CGD.

3. GENERAL CHARACTERISTICS OF THE POTENTIAL SOURCE ROCKS AND HYDROCARBON GENERATION ZONES IN THE DANUBE BASIN

The geochemical characteristics of potential source rocks, kerogen maturation and hydrocarbon generation zones in the Slovak part of the Danube Basin were investigated by standard organic-geochemical methods (Rock Eval, GC, GC-MS, microphotometry, stable methane carbon isotopes), and published in reports and articles by Vass et al. (1992), Pereszlényi et al. (1993[a,b]), Milička (1994) and Milička et al. (1996, 2011).

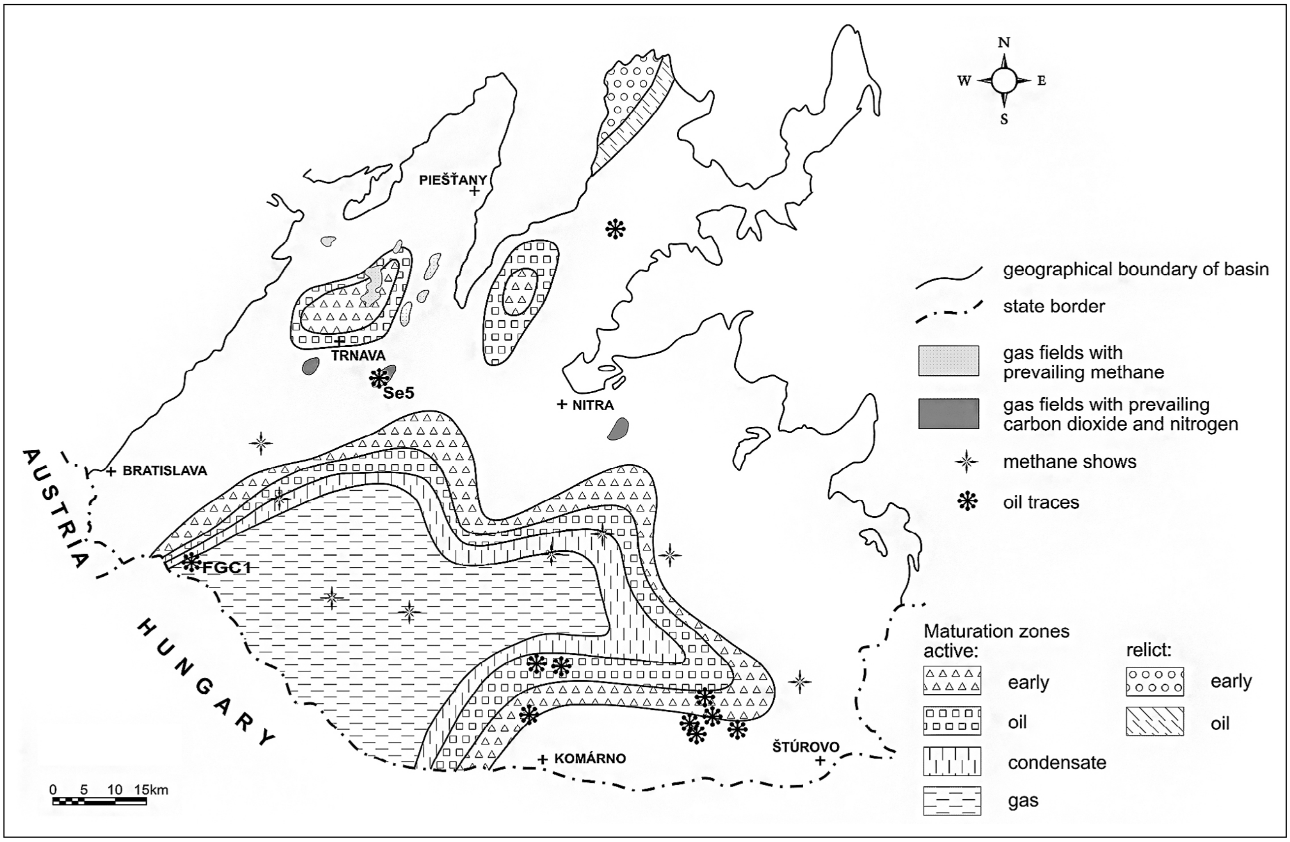

Fig. 3. Hydrocarbon generation zones, natural gas accumulations and locations of oil traces in the Danube Basin.

Sediments of the Central Western Carpathian units and Mesozoic rocks of Transdanubian Central Range in the basement of the Slovak part of the Danube Basin are very poor source rocks. The total organic carbon (TOC) maximum ranges only up to 0.6 % except for the Lunz beds in the Choč Nappe sequence in the Dobrá Voda 1 borehole where it increases up to 2 %. Although the carbonates themselves lack almost all organic matter (OM), some amount was detected in the shales between them (Milička, 1994). Similarly, the TOC content of carbonates outcropping at the northern margin of the basin in the Malé Karpaty, Považský Inovec and Tribeč mountains is generally poor, with negligible hydrocarbon (HC) potential that was exhausted probably yet before thrusting in the original sedimentary basin. Hydrocarbon generation stages of kerogen occurring in the Mesozoic basement sediments indicated by thermal maturity (Ro = 0.8–3.5 %) and modelling are passive, regarding the actual depth position.

Palaeogene sediments were evaluated almost entirely from the Štúrovo Palaeogene area; referred to as the Buda or North Hungarian Palaeogene (e.g., Nagymarosy, 1990; Vass, 2002). Source rocks with increased dispersed organic matter concentrations up to approximately 2 % were detected only in the Mo2 and NV1 wells in the Želiezovce Depression. Elevated dispersed organic matter concentrations up to 8 % detected in samples from the FGKR1 and 30 % in sample from the FGO1 wells belong to coal positions. Kerogen in the evaluated Palaeogene sediments is mostly immature with values of vitrinite reflectance Ro = 0.8 % at 3160 m; the early oil generation stage is slightly exceeded only in deepest parts of the NV1 well.

Total organic carbon distribution and the hydrocarbon source rock potential were mainly studied in Neogene well cores in Eggenburgian to Pontian sediments. The Neogene sediments are generally poor source rocks with locally fair values up to 2 % in Lower Miocene and up to 1.5 % in Middle Badenian, in Sarmatian and in Early Pannonian sediments. Gas chromatography and Rock Eval methods indicate that the most convenient source rocks with highest hydrocarbon potential occur in the Early Pannonian- and to a lesser extent in the Middle Badenian sediments.

The construction of HC generation zones was provided based on sediment burial reconstruction and kinetic HC generation modelling (Pereszlényi et al. 1993[a,b]). The most extensive active hydrocarbon generation occurred in the Central Gabčíkovo Depression from Middle Badenian to Late Pannonian shale complexes during the end of Late Miocene to Pliocene. Oil generation window was reached at approximately 2800 m in the deepest part; below 4000 m only methane generation is expected according to the modelling.

Active hydrocarbon generation zones, considerably less in area and volume, were reached in the deepest Middle Badenian sediments in the Blatné Depression and also in the Rišňovce Depression in Middle and some Upper Badenian source rocks. However, only early oil and the beginning of main oil generation phase were reached below 3000 m in this colder part of the basin from the beginning of Late Miocene to Pliocene. The Neogene sediments are maximally 3600 m thick in the deepest part of Blatné Depression.

4. METHODS

Presented study summarizes the existing organic-geochemical data from the Slovak part of the Danube Basin and is based on previous published and partly reinterpreted data. Analyzed were the potential source rocks mostly from deep hydrocarbon prospecting wells, selected rock extracts, one gasoline sample and one oil impregnation and a set of natural gases.

The clayey shales well cores from deep oil wells in the Danube Basin were analyzed by Rock-Eval I pyrolyser in Czech Geological survey Prague, branch Brno and by Rock-Eval III at the Institut Français du Pétrole in Paris by the method of Espitalié et al., (1985). The amount of 50–100 mg pulverized rock sample was firstly heated two minutes to 90 °C (degassing), than heated three minutes to 300 °C (volatilization of free hydrocarbons) followed finally by programmed heating of the sample to 600 °C by heating rate of 25 °C/min. After degassing the liberated hydrocarbons were detected by FID detector. The results of over 300 measurement are exactly published e.g. in Milička (1993). Based on these results selected samples were analyzed at IFP Paris by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) methods. The examined rocks extracts range stratigraphically from Eocene to Late Pannonian and cover all sub-basins in the Slovak part of the Danube Basin. Selected GC and GC-MS results from the analysed wells (Fig. 2) are listed in Tab. 2. All results are in detail published in l.c. (1993).

Natural gas samples from oil and geothermal wells realized between 1965 and 1990 were analyzed for chemical and isotopic composition in Czech Geological survey Prague, branch Brno. Helium, argon, oxygen, nitrogen, carbon dioxide, and the hydrocarbon gases methane to pentane (C1 to C5) were analyzed using GC-TCD, FID gas chromatography, the individual hydrocarbons in the propane to heptane groups (C1 to C7) were analyzed using capillary gas chromatography. The isotopic composition was analyzed in CGS Prague laboratories by the method of Buzek & Michalíček (1989). Analytical results of both chemical and isotopic composition are presented in Tab. 1. Genetic types of methane portion in natural gases from the Slovak part of the Danube Basin are shown in Fig. 4 proposed by Bernard et al. (1978). The basic geological-, molecular- and isotopic data are presented in Tab. 1.

Oil sample taken from FGČ1 Čilistov well was separated from water and the oil impregnation in well core from Se5/1320 m. Oil was recovered by low-temperature n-pentane extraction. Both oil and oil impregnation were analyzed using gas chromatography and oil impregnation from Se5 well also by GC-MS method at IFP Paris. The Čilistov oil was analyzed also in Maxus Energy Corporation, Dallas and in Czech Geological survey Prague, branch Brno laboratories. The results of these analyses are in tab. 2 and graphically they are presented in figs. 6 and 7.

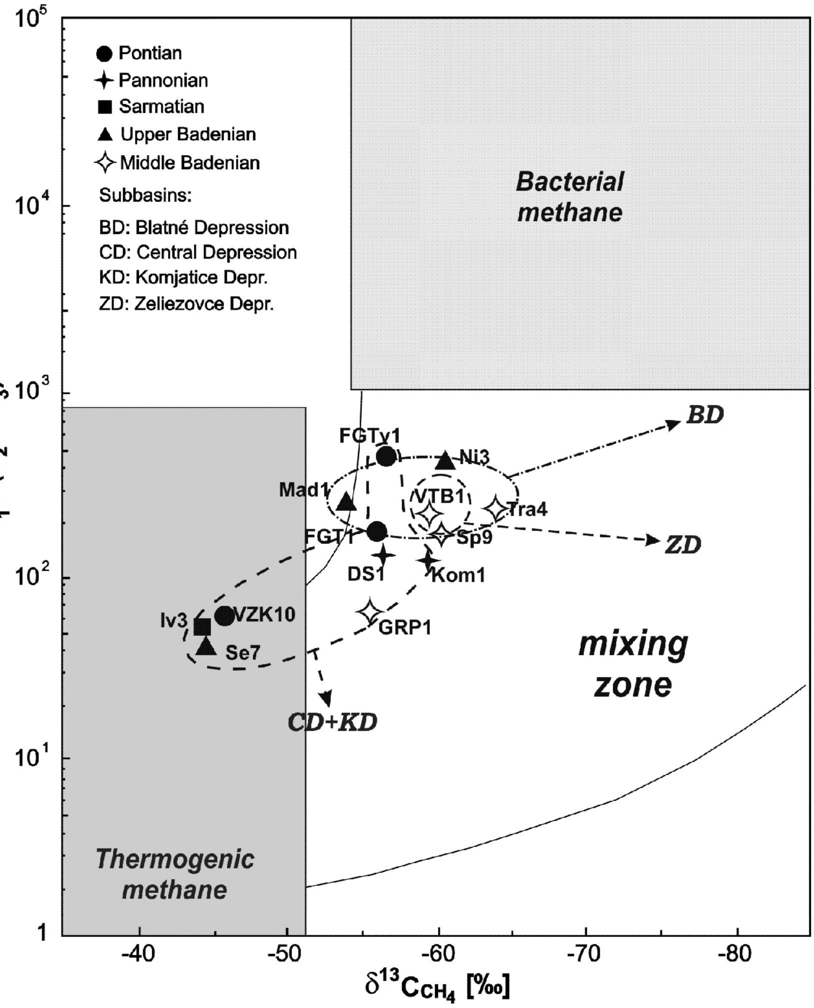

Fig. 4. Molecular and isotopic composition of the studied methane gases in the diagram proposed by Bernard et al. (1978).

5. RESULTS

5.1 Geochemical characteristics of natural gas

While hydrocarbon dominant natural gases and smaller methane deposits occur mainly in the Blatné Depression (Fig. 2,3), deposits with lower methane content and increased carbon dioxide and nitrogen concentrations in variable relations occur at the southern margins of BD depositional centre (Cífer and Sereď), and in the SW part of the Komjatice Depression (Golianovo).

Methane carbon (C_{CH4}) isotopes in analyzed set of natural gas samples indicate mixed bacterial/thermogenic methane. Relatively highest contribution of bacterial methane was detected in gases from the Ni3 and Tra1 wells area of Blatné Depression. The rock temperature in accumulation depth of these gases ranges of ~60–80 °C (Fig. 5) and enables yet the methane generation from bacteria

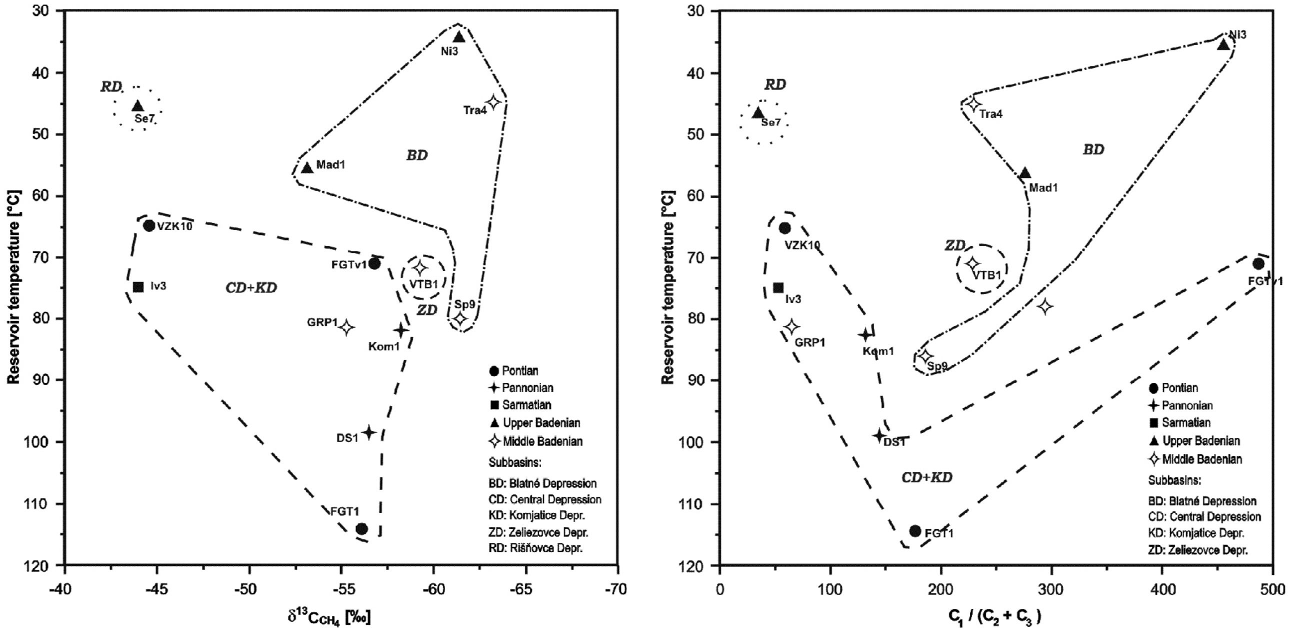

Fig. 5. Methane carbon isotopic composition and methane to higher HC gases ratio plotted versus reservoir temperature.

(Rice & Claypool, 1981; Peters et al., 2005). Relatively increased amounts of higher hydrocarbons (Tab. 1) in these gases are most probably associated with the oil generation zone in BD area.

A further group of natural gases with thermogenic methane and oil generation is indicated by their isotopic and molecular composition. The isotopically "heaviest" methane of $\delta^{13}C_{CH4}$ = –45 ‰ was detected in natural gases from the Se7, Iv3 and VZK10 wells at 1030 to 1830 m. This methane together with the other one in the sample from the GRP1-well also have the "driest" CH_4/C_{2+} composition. These gas types are mostly located in margins of the Central Gabčíkovo Depression, with assumed origin in deeper parts of CGD areas. Hydrocarbon generation modelling determined that kerogen reached here the condensate generation zone at approximately 4000 m in Neogene sediments; the dry gas generation zone is expected at the depth of 4500 m in CGD. From this zone the migration of these gases to higher positions is expected. The origin of carbon dioxide and partly also nitrogen is most likely connected with buried stratovolcanoes and subsequent post-volcanic activity.

5.2 Geochemical characteristics of rock extracts, gasoline and oil traces

Gas chromatography analysis of thirty four potential source-rock extracts in the Middle Triassic to Pannonian stratigraphical span

Tab. 1. Selected molecular and isotopic characteristics of some natural gases in the Slovak part of the Danube Basin. Molecular and isotopic data are taken from Buzek et al. (1992). SG = spontaneous gas; DG = dissolved gas.

Well code	Depth int. [m]	Reservoir stratigraphy	Reservoir temp. (°C)	CH4 (obj. %)	C2H6 (obj. %)	C3H8 (obj. %)	$\delta^{13}C_{CH4}$ [‰]	He (obj. %)	Ar (obj. %)	N2 (obj. %)	CO2 (obj. %)	Remark
Ni 3	849–853	Upper Badenian	35	73.68	0.16	0.00	-61.8	0.000	0.183	25.600	0.200	SG
Mad 1	1177–1179	Upper Badenian	56	85.01	0.28	0.02	-53.7	0.000	0.000	14.500	0.200	SG
Tra 4	932–934	Middle Badenian	45	89.08	0.34	0.05	-63.7	0.047	0.012	10.240	0.146	SG
Sp9	2144–2146	Middle Badenian	82	93.00	0.36	0.11	-61.4	0.000	0.019	6.000	0.163	SG
SE 7	1013–1029	Upper Badenian	46	17.28	0.42	0.07	-44.5	0.017	0.012	26.700	55.400	SG
Iv 3	1800–1823	Sarmatian	75	29.25	0.35	0.20	-44.4	0.073	0.036	20.800	49.100	SG
DS 1	2183–2432	Pannonian	94–104	67.40	0.39	0.08	-56.8	0.017	0.000	3.471	28.590	DG
VTB 1	1600–1905	Middle Badenian	68–75	90.15	0.37	0.03	-59.7	0.101	0.026	8.773	0.239	SG
VZK10	1331–1475	Pontian	63–67	74.98	0.92	0.36	-45.2	0.000	0.038	6.381	17.488	SG
Kom 1	1450–1780	Pannonian	75–90	90.37	0.55	0.13	-58.8	0.073	0.024	5.100	3.649	SG
GRP 1	1155–1740	Middle Badenian	73–90	2.46	0.03	0.00	-55.7	0.047	0.000	4.636	92.818	DG
FGT 1	2394–2487	Pontian	112–117	47.38	0.22	0.05	-56.6	0.029	0.000	39.020	13.260	DG
FGTv 1	1362–1637	Pontian	65–77	66.07	0.11	0.02	-57.3	0.038	0.000	21.054	12.686	DG

provided information on organic matter type and sedimentation conditions and consequently, GC-MS analyses of selected extracts were performed for correlation (Milička, 1993).

The studied kerogen is of mixed terrestrial marine type and bimodal n-alkane distribution with maxima at approximately C19 and C29. The preference of odd carbon number n-alkanes indicates immature and early mature organic matter (Ro = 0.3~0.60 %). With increasing thermal maturity toward the oil generation zone (Ro > 0,65 %) fades the area of the second n-alkane maximum. N-alkane maxima ranging from n-C25 to n-C35 reflect coaly organic matter in the Obid well (FGO1/691 m; TOC = 30.0 %), and Kravany well (FGKR1/205 m; TOC = 7.5 %) in the southern ŽD. These wells penetrated lignite layers in Štúrovo (Buda) Palaeogene sediments.

The n-alkane maxima of marine organic matter between n-C15 and n-C23 was restricted to the samples from the Trakovice well (TRA1/1452 m; Lower Badenian, BD), Suchá (SU2/2106 m; Lower Badenian, BD), Nová Vieska (NV1/858 m, Pannonian, ŽD) and also the Cífer well (CI2/1675 m; Karpatian, BD). In the first three of these extracts rather anoxic sedimentation conditions are indicated by pristane/phytane ratio (0.62–0.68).

Another samples containing marine organic matter came from well core extracts with increased free HC amounts (S1 = 0.11–0.36 mgHC/g, but negligible HC potential (S2 = 0.0–0.0X mgHC/g). These sequences belong to the Krížna- and Choč nappes comprising probably fair source rocks in the geological past – mainly the Lunz beds, carbonate- and silicaclastic shales. Although these rocks contain small amounts of residual organic carbon at 0.0X–0.56 %, most of initial organic carbon was depleted in favour of HC generation and release. Actual rock temperatures (50–90 °C), the depth position (70–2770 m) and reached thermal alteration expressed by vitrinite reflectance (Ro = 0.98–1.80 %) indicate the relict generation stage of these rocks.

Oil traces in the Slovak part of the Basin are generally very poor. The presence of benzene, toluene, and xylene detected in groundwater flowing from the FGTZ1 geothermal well in the northern part of the Rišňovce Depression are presumed to have washed out from generated fluid hydrocarbons at unknown depth.

Other oil manifestations are reported from well-core and cuttings fluorescence (Lunga, 1967; Gaža, 1974). They are mainly from the eastern part of CGD and ŽD depressions, however, without any chemical analyses at that time. On the other hand the oil impregnation in well cores penetrating the pre-Cenozoic basement in BD Dubové1 well at 2383 m (Jurassic) and 2694 m (Upper Triassic) were examined by GC. One analyzed oil impregnation comes from the Sereď5 (Se5) bottom well core at 1320 m. The well core is brecciated phyllite and belongs to the pre-Neogene basement.

Light gasoline oil from geothermal well FGČ1 (Čilistov) drilled in 1978–1979 in the SW part of the CGD is the only

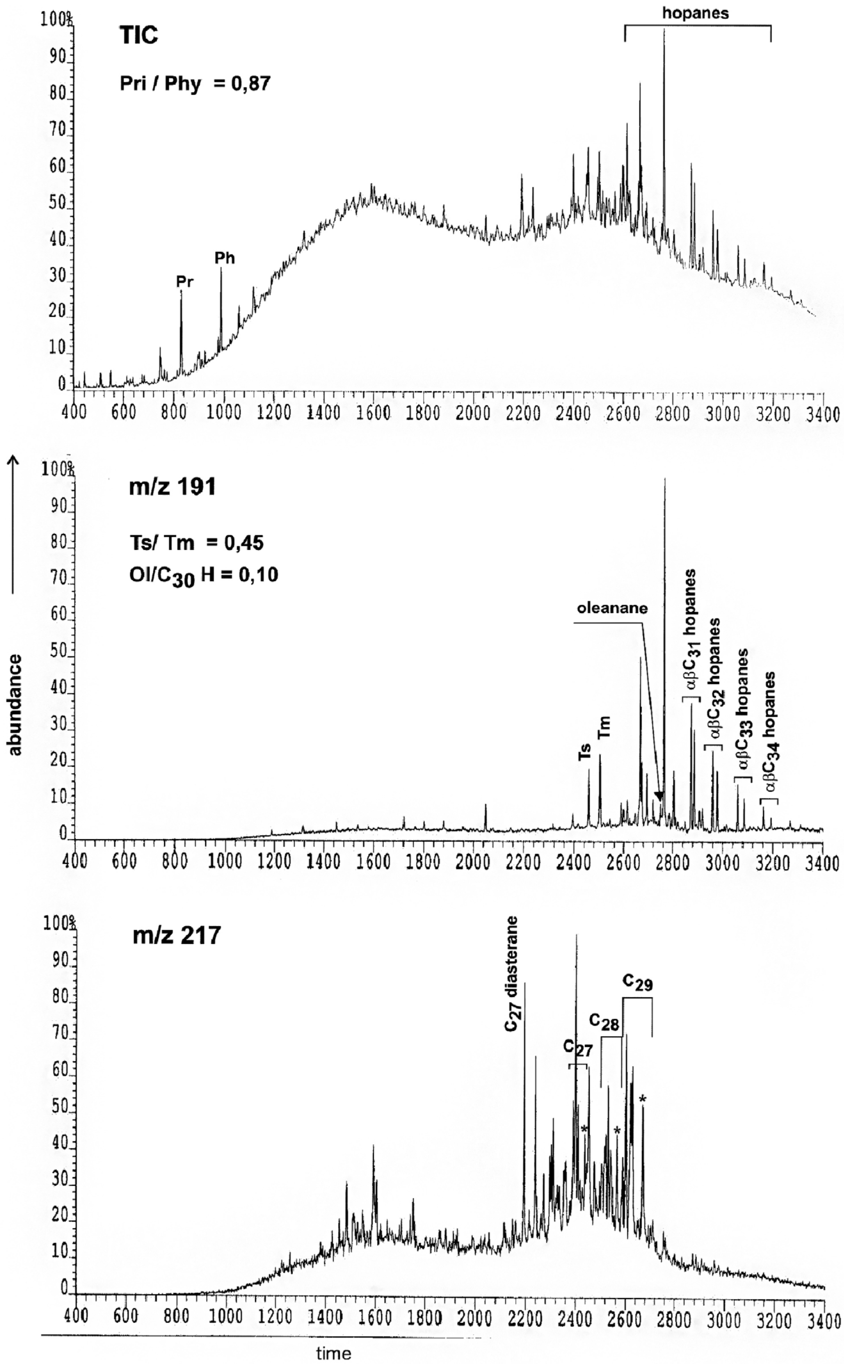

Fig. 6. Total ion chromatogram (TIC) of aliphatic fraction, triterpane (m/z 191) and sterane (m/z 217) distribution of oil impregnation from Se 5/1320m well. Ol – oleanane, H – hopane, * = aaa20R steranes.

"valid" oil found and analyzed in the Slovak part of the Danube Basin. Its geological and initial geochemical data were published by Franko et al. (1981, 1992), and lately by Milička & Pereszlényi (2012).

Oil impregnation from Sereď 5 well

Sereď 5 (Se 5) well oil impregnation was discovered at 1320 m, thus corresponding to the Neogene base, most likely to the Tatric Palaeozoic basement. Total ion chromatogram (TIC) of the aliphatic fraction, the distribution of triterpanes (m/z 191) and steranes (m/z 217) is presented in Fig. 6. The TIC confirms a strong biodegraded sample where almost all n-alkanes were consumed by bacteria; with only the more resistant molecules surviving. The rock temperature in neighbouring wells in investigated Sereď area range between 48–55 °C and do not represent a limit for bacterial attack. Analysed well core has the character of reservoir rock; the TOC amount (0.06 %) and the HC potential (S2 = 0.4 mg/g) are negligible, but the content of free HC and production index (S1 = 0.23 mg HC/g; PI = 0.85; Milička, 1994) suggests the presence of migrated free fluid hydrocarbons. The thermal maturity of this oil impregnation is indicated in this case only by trisnorhopane maturity indicator Ts/(Ts+Tm) (Moldowan et al., 1986). The Ts/(Ts+Tm) value of 0.45 is comparable to that of 0.41 in extract from the Su2/2998 m well (Tab. 2) in the centre of BD depression originating from the Middle Badenian compact shale (TOC = 0.78 %). The thermal maturity of this shale (Ro = 0.55 %) corresponds to the early oil generation stage, but in the well bottom (3500 m) reached the Neogene shales the main oil generation zone (Ro = 0.80 %; Milička, 1994). The Neogene base at BD depression centre is considered at 3700 m.

Gasoline oil from FGČ1 well

Water inflow of 11 l.s-1 together with small quantities of oil (2.4 m3 in 14 days) was detected in CGD depression in 1978–1979. The inflow came from the Upper Pannonian to lowermost Pontian sediments in FGČ1 well at 1608–1731 m. The reservoir temperature ranged from 64 to 68 °C and the dissolved gases were dominated by 91.2 % carbon dioxide, with 3.2 % nitrogen and 5.5 % methane. Detailed geological and technical information is contained in Franko et al. (1981), while Tab. 2 lists the basic GC data and Fig. 7 shows the n-alkane and isoprenoid distribution.

The investigated oil is classified as light mature at 52.2° API, and it mainly contains n-C5 to n-C24 hydrocarbons with maximum HC ranging from n-C8 to n-C11. The pristane to phytane ratio indicates oxic sedimentation conditions, and the isoprenoids to n-alkanes ratio and the biodegradation index suggest only very low biodegradation (pristane/nC17 = 0.42 to 0.47, phytane/n-C18 = 0.25 in Tab. 2 and biodegradation index 0.42 in Tab. 3). The aromaticity indexes after Thomson (1983; Tab. 3) suggest water-washing of aromatics, which agree with generally low content of aromatic HC fraction (Tab. 3). Calculated equivalent vitrinite reflectance indexes Rm(J) and Rm(V), (Schaefer & Littke, 1988) presented in Tab. 3 indicate high thermal maturity of source rocks corresponding to the late phase of condensate generation. Very high thermal maturity of the oil deduced from

Tab. 2. Basic geological and GC – GCMS characteristics of studied media. E: extract; O: oil; Ro: vitrinite reflectance; *: Rm (V) value calculated according to Schaefer and Littke (1988); Pri: pristane; Phy: phytane; CPI: carbon preference index; Ol: oleanane; DL: detection limit; na: non analyzed.

Well/ depth (m)	Analyzed medium	Stratigraphy	Ro %	ALI %	ARO %	NSO %	Pri/Fy	Pri/nC17	Fy/nC18	CPI24-34	steranes ααα 20R (%) 27	28	29	Ts/ (Ts+Tm)	Ol/ (Ol+C_{30}H)
Kol 2/2303	extract	Pannonian	0.39	24.8	13.3	61.9	1.32	1.57	0.79	2.26	22	22	56	0.17	0.27
Kol 2/2701	extract	Pannonian	0.54	47.9	10.9	41.2	1.56	0.90	0.55	1.15	41	31	28	0.65	0.00
Kol 2/2903	extract	Pannonian	0.69	28.0	10.9	61.1	4.54	2.09	0.40	1.37	28	29	43	0.71	0.16
Kol 2/3004	extract	Sarmatian	0.76	40.9	11.5	47.6	1.14	1.20	0.76	1.05	32	27	41	0.81	0.14
Vrab 1/1104	extract	Pannonian	0.42	14.2	8.0	77.8	0.91	0.77	0.79	3.80	15	22	63	< DL	Ol< DL
Vrab 1/1406	extract	Sarmatian	0.48	21.5	32.3	46.2	1.22	1.26	0.92	2.44	27	34	39	0.49	0.21
Vrab 1/1652	extract	Sarmatian	0.54	31.2	15.6	53.2	0.46	2.17	4.12	3.15	20	19	61	0.26	0.06
Vrab 1/1943	extract	GC-MS analyses of selected extracts were	0.60	20.1	38.6	41.3	0.96	1.35	0.93	1.48	24	44	32	0.31	0.08
Mad 4/1823	extract	Karpatian	0.49	23.3	11.4	65.3	0.73	0.02	1.74	1.88	24	44	32	0.31	0.08
Su 2/2106	extract	Middle Badenian	0.31	43.5	14.8	41.7	0.64	1.60	2.59	1.51	25	25	51	0.34	0.06
Su 2/2998	extract	Middle Badenian	0.55	26.5	16.5	57.0	2.93	3.13	1.01	1.55	26	26	48	0.41	0.18
Se 5/1320	oil impregnation	Ng. base/ Plz?	?	49.1	18.1	32.8	0.87	1.08	1.27	1.64	32	31	37	0.45	0.09
FGČ 1/1731–1608	gasolinic oil	Pannonian	1.72*	83.4	6.0	10.6	2.25	0.42	0.26	-	na	na	na	na	na

heptane (H) and isoheptane (I) indexes after Thomson (1983) are presented in Tab. 3. Isotopic composition of aliphatic (-25.5 ‰) and aromatic (-26.1 ‰) fractions indicates according to Sofer (1984) the marine origin of examined condensate.

6. DISCUSSION

6.1 Source rocks and hydrocarbon potential

Our study and the cited explorations confirm poor source rocks with low generation potential in the Slovak part of the Danube Basin. Shales constitute almost the only potential source rocks in the well cores and outcrops. The Inner Carpathian Mesozoic unit carbonates, with relatively fair organic matter content and residual HC potential, occur mainly at the margins in the NW part of Blatné Depression and build the pre-Neogene basement. Their HC potential is mostly exhausted in well cores at 68 to 2770 m and the maturity reaches the values in range of Ro = 0.98 to 3.50 % (Milička, 1994). Their actual depth and temperature conditions are insufficient for active HC generation (Pereszlényi et al. 1993b, Milička et al., 1996).

Central Carpathian Palaeogene Basin (CCPB) sediments are preserved in small northern parts of Blatné, Rišnovce and Bánovce depressions. Despite of the presence of partially excellent source rocks within CCPB sediments mainly in the Huty Formation (in sense of Gross et al., 1984) with S2 and IH Rock Eval parameters ranging locally up to 30 mg/g and 690 mg/g respectively (Milička, 1998), CCPB Palaeogene source rock contribution to Danube Basin HC generation is negligible. Further were examined samples from the northernmost part of the Buda-Hungarian Palaeogene in Slovakia (Štúrovo Palaeogene in Fig. 2). These Palaeogene sediments do not contain any interesting potentially source rocks besides occurrences of coaly matter. Little valuable geochemical data were obtained from the southern part of the Želiezovce Depression. Few wells (Fig. 4) penetrated locally fair source rocks in Eocene sediments e.g. in Nová Vieska (NV1) well at 2900 m; GP = 6.1 and HI = 404; Ro = 0.69 and in Modrany (Mo2) well at 2630 m; GP = 4.1 and HI = 325, Ro = 0.33 (Milička, 1994). In contrast, Kókai (1994) and Milota et al. (1995) reported the euxinic Tard- and Kiscell Clay in north Hungary as good source rocks of mostly I and II kerogen type with type III in upper part of the sequence. Milota et al. (1995) reported that the Oligocene sequence in the southern Hungarian portion of the basin is present in the oil window.

Despite their rather poor hydrocarbon potential, practically only the Neogene sedimentary sequences offer the potential HC source in the Slovak part of the Danube Basin, due to their volume and active maturation zones. The TOC, Rock-Eval and vitrinite reflectance of over 230 Neogene well cores and selected GC and GC-MS analyses (Milička, 1994) suggest the predominance of terrestrial plant derived material, i.e. the kerogen type III sensu Espitalié et al. (1985) with low hydrocarbon potential – up to 5 mgHC/g regarding the dispersed organic matter.

The terrestrial origin of the sedimentary organic matter is documented by high CPI indexes (Bray& Evans, 1961) and by the low hydrogen content in Rock Eval pyrolysis. The average

Tab. 3. Selected compounds of gasoline hydrocarbon range from Čilistov gasoline with calculated ratios according to *Thompson (1983) and **Schaefer and Littke (1988).

Nr.	Compound	Value
1	2-methylpentane	35,27
2	3-methylpentane	20,54
3	n-hexane	48,01
4	methylcyklopentane	8,41
5	2,4, dimehtylpentane	1012
6	benzene	0,98
7	cyklohexane	6,08
8	2-methylhexane	80,56
9	1,1 dimethylcyklopentane	4,88
10	3 methylhexane	78,06
11	1cis, 3-dimethylcyklopentane	7,31
12	1trans, 3-dimethylcyklopentane	7,29
13	1trans, 2-dimethylcyklopentane	11,01
14	n-heptane	189,17
15	1cis, 2-dimethylcyklopentane	-
16	methylcyklohexane	73,39
17	2,5 dimethylhexane	23,16
18	ethylcyklopentane	4,45
19	2,2,3-trimethylpentane	
20	1t, 2c, 4-trimethylcyklopentane	4,62
21	toluene	1,77

Ratios	
*aromaticity (6/3)	0,02
*aromaticity (21/14)	0,01
*I-isoheptan value (8+10)/(11+12+13)	6,19
*H heptan value (100*14)/((7+..+14)+16)	41,33
**V (14/16)	2,58
**Rm (V) 1.0 + 1.8 x log V	1,74
Biodegradation Index (2/3)	0,43

TOC content is about 0.58 wt. %. Mostly high pristane to phytane ratios of examined Neogene samples refer to prevailing oxic sedimentary conditions (Didyk et al., 1978). Kerogen thermal maturity generally increases from stratigraphically youngest to the oldest sediments, of course with respect to local structural-tectonic conditions. Minor part of examined shales contains marine or mixed marine-terrestrial kerogen occurring mostly in Middle Badenian and Lower Pannonian sediments. Mattick et al. (1996) introduce the Sarmatian and Badenian sequences as a best source rocks in the Hungarian part of the Danube Basin.

Despite previous studies, we still have no exact direct analytical knowledge about the properties of the sediments in the deepest part of the Slovak portion of the Central Gabčíkovo Depression below 2700 m, where most Neogene sediments are expected to reach the active dry-gas generation stage (Pereszlényi et al., 1993a). Considering the base of the Neogene sediments in the deepest part below 6000 m (Kilényi & Šefara, 1989), the available information from closest FGGA1 and DS1wells reaches only to 2600 m deep Pannonian sediments. Moreover, according to interpretation of seismic profiles (e.g., MXS2) a considerable portion of the sediments in the Central Gabčíkovo Depression consists of buried volcanosedimentary sequences (Milička et al., 2011).

6.2 Natural gas origin

Natural gases with prevailing hydrocarbon gases have been studied mostly in small deposits discovered by HC exploration. Many other methane shows were detected by hydrogeothermal research (Fig. 3), but they have been not systematically studied. Data from 12 gas samples are presented in Tab. 1. Based on molecular and isotopic composition of methane presented in Fig. 4, most studied methane samples have mixed thermogenic-bacterial origin. Relatively "heaviest" methane occurs at the margins of the CGD, RD and KD depressions. However, regarding their C_{2+} gas content, they are associated with oil generation that took place mostly in CGD depression and partly in BD and RD depositional centres.

The comparison of isotopic and molecular compositions of the studied natural gases and the reservoir temperature in Fig. 5 reveals no strong dependency between these parameters. Methane carbon isotopic composition and the relative "wetness" of HC gas reflect its origin in oil generation zones with bacterial contribution. Resultant methane distribution at studied reservoir temperatures and depths suggests its migration from deeper locations and admixture with bacterial methane. The conditions of formation of oil associated gas exist below 2800 m in CGD and below 3000 m in colder BD and RD depressions. No pure thermogenic or biogenic dry gas has currently been found in the Danube Basin.

The origin of CO_2 and partly also N_2, are considered to be of volcanic origin, however, inorganic gas samples including carbon dioxide have been not systematically studied on isotopic level. The origin of natural gases throughout the Pannonian Basin in Hungary is presented e.g., by Koncz (1983), Clayton & Koncz

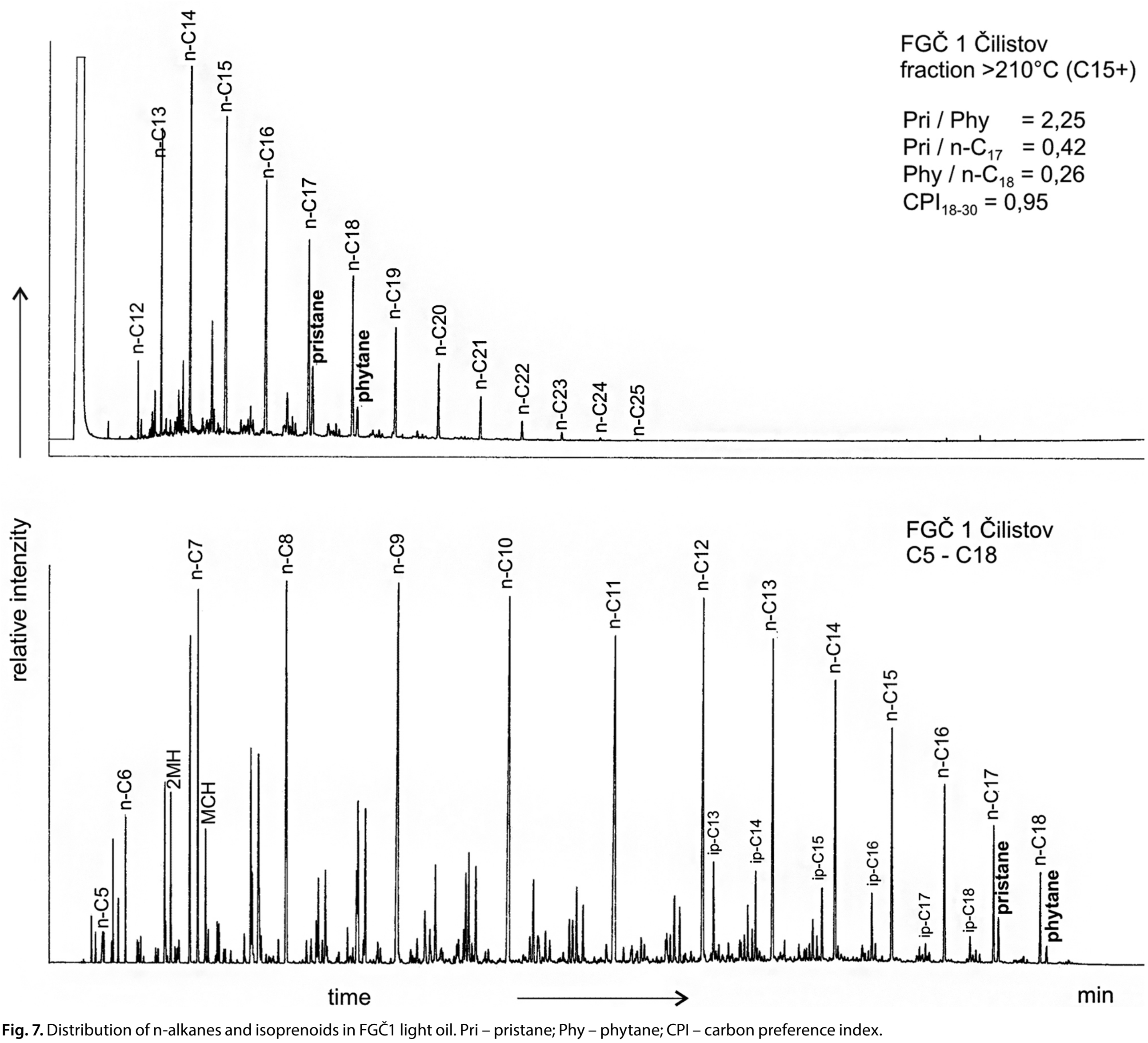

Fig. 7. Distribution of n-alkanes and isoprenoids in FGČ1 light oil. Pri – pristane; Phy – phytane; CPI – carbon preference index.

(1990), Clayton et al. (1990), Palcsu et al. (2014) and Vető et al. (2014).

6.3 Gasoline and oil traces origin

This study presents the chemical composition of two fluid media – light gasoline and biodegraded oil show. Unfortunately, the gasoline was not examined by GC-MS and therefore biomarker level correlation was not possible, and in addition, the strong biodegradation eliminated information from n-alkane distribution in oil impregnation found in the Se5 well (Fig. 6). The biodegradation differences here are most significant. The gasoline taken from FGČ1 well is almost bacterially unaltered with 0.43 3-methylpentane/n-hexane ratio (Tab. 3) and both the Pri/n-C17 and Phy/n-C18 ratios are below 0.5. The n-alkanes from the Se 5 well oil are almost entirely consumed, and isoprenoid concentration is strongly reduced (Fig. 6). A further distinction is the clear difference in pristane/phytane ratio (Tab. 2). If this ratio is considered a reliable parameter of environmental sedimentation conditions, its 2.25 value here counters the indication of rather marine origin based on isotopic composition of aliphatic (-25.5 ‰) and aromatic (-26.1 ‰) fractions according to Sofer (1984).

The oil-trace composition in sample from the Se5 well at 1320 m is comparable to that of Sarmatian and Pannonian extracts and also to middle Badenian extracts from Su2 well core situated in the BD depositional centre. This correlation is primarily based on its trisnorhopane index resemblance with the deeper Su2 sample and the extract from the Sarmatian sample taken from Vrab1/1406m well (Tab. 1; Fig. 8). The origin of

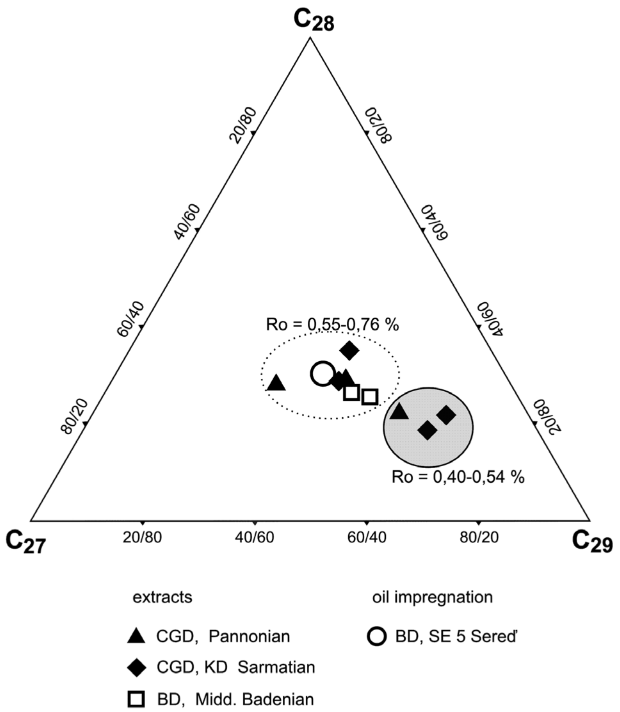

Fig. 8. Ternary diagram of C27-28-29 steranes in extracts and oil impregnation in the Danube Basin. CGD – Central Gabčíkovo Depression; BD – Blatné, KD – Komjatice depressions.

oil according to its chemical composition is possible from any examined Neogene sequence (rock extract) that reached the oil generation window.

Light molecular composition of the gasoline from the FGČ1 well indicates very high thermal maturity (Tab. 3) according to isoheptane and heptane values (Thompson, 1983). Aromaticity indexes (l.c.) suggest removal of aromatic hydrocarbons. This is supported also by very low aromatic fraction content (Tab. 2). High maturity level of generating source rock is indicated by equivalent vitrinite reflectance Rm (V) = 1.74; Tab. 3) calculated after Schaefer & Littke (1988).

Thermal conditions of such gasoline generation are expected in the CGD depression in depth range of 3500–4200 m and temperature range of 150–180 °C.

7. CONCLUSIONS

The molecular and isotopic compositions of the natural gas hydrocarbons confirmed methane with mixed thermogenic-bacterial origin. Higher HC gases (C_{2+}) suggest the origin of thermogenic portion associated with oil generation window.

Several source rocks and one oil show were analyzed by GC and GC-MS and the molecular composition within the gasoline hydrocarbon range was analyzed by whole oil gas chromatography. The gasoline and oil impregnation differ especially in biodegradation alteration and thermal maturity level. The almost non-biodegraded gasoline from FGČ1 (Čilistov) well in the Central Gabčíkovo Depression was generated at considerable temperature and depth. Such conditions are reached in the Slovak part of the Danube Basin in the Central Gabčíkovo Depression below 3500 m at temperatures of 150 °C or even higher. Based on the $C_{27\text{-}28\text{-}29}$ sterane triangle, the oil can be correlated with any examined Pannonian, Sarmatian and Middle Badenian source rocks entering the oil generation depth zone.

The HC gas and oil traces presence in both Slovak and Hungarian basin areas proved the existence of quite poor but effective source rocks that entered the active HC generation zones. Although huge volumes of Neogene sediments in the Slovak part of the Danube Basin are still to be explored, predictions of future liquid hydrocarbons discoveries remain uncertain. The known source rocks are mostly of poor quality and according to the calculation of HC expulsion for kerogen type III, the threshold value for expulsion in early and oil generation stages was not reached.

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