Carbon isotopic composition of methane and its origin in natural gas from the Petišovci-Dolina oil and gas field (Pannonian Basin System, NE Slovenia) – a preliminary study

Izotopska sestava ogljika v metanu in njegov izvor v naravnem plinu na območju nafto-plinskega polja Petišovci-Dolina (Panonski bazenski sistem, SV Slovenija) – preliminarna raziskava

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Abstract

The carbon isotopic composition of methane ($\delta^{13}C_{CH4}$) in natural gas from the Petišovci-Dolina oil and gas field (NE Slovenia) was measured for the first time in August and September 2021. The gas samples from different depths were taken from three wells: Dolina-deep (Pg-6) from the depth interval 3102–3104 m, Petišovci-deep (Pg-5) from the depth interval 2772–2795 m, and Petišovci-shallow (D-5) from the depth interval 1212–1250 m. According to the available composition dataset of gas, available from the Petrol Geo d.o.o. documentation, the "deep" gases sampled from the Pg-6 and Pg-5 wells consist of 85 % methane (C1), 11 % hydrocarbons heavier than methane (C2–C6) and 4 % CO_2. The "shallow" gas from well D-5 contains more than 89 % methane, up to 11 % C2–C6 gases, while the CO_2 content is negligible. The "deep« gas from the Pg-6 and Pg-5 wells has $\delta^{13}C_{CH4}$ -36.7 ‰ and -36.6 ‰, respectively, while the "shallow" gas from the D-5 well has the $\delta^{13}C_{CH4}$ of -38.6 ‰. The methane from the "shallow" gas is slightly enriched in the lighter ^{12}C isotope. $\delta^{13}C_{CH4}$ in the range from -38.6 to -36.6 ‰ clearly indicates the thermogenic origin of methane formed during the catagenesis phase of gas formation.

Izvleček

Izotopsko sestavo metana ($\delta^{13}C_{CH4}$) v naravnem (zemeljskem) plinu naftno-plinskega polja Petišovci-Dolina (Ormoško-selniška antiklinala, NE Slovenija) smo prvič merili v avgustu in septembru 2021. Plinske vzorce smo vzorčili iz različnih globin iz treh plinskih vrtin: iz Petišovci-globoka (Pg-6) iz globine 3102–3104 m, iz Petišovci-globoka (Pg-5) iz globine 2772–2795 m in iz Dolina-plitva (D-5) iz globine 1212–1250 m. Glede na dostopne podatke o sestavi plina iz dokumentacije Petrol Geo d.o.o., so "globoki" plini iz vrtin Pg-6 in Pg-5 sestavljeni iz 85 % metana (C1), iz 11 % ogljikovodikov, težjih od metana (C2–C6) in 4 % CO_2. "Plitvi" plin iz vrtine D-5 je sestavljen iz več kot 89 % metana in do 11 % C2–C6, medtem ko je koncentracija CO_2 zanemarljiva. "Globoki" plin iz vrtin Pg-6 in Pg-5 ima $\delta^{13}C_{CH4}$ vrednost od -36.7 do -36.6 ‰, medtem ko ima "plitvi" plin iz vrtine D-5 $\delta^{13}C_{CH4}$ -38.6 ‰. "Plitvi"plin iz vrtine D-5 je obogaten na lažjem ^{12}C izotopu. Razpon $\delta^{13}C_{CH4}$ od -38.6 do -36.6 ‰ jasno kaže termogeni izvor metana, ki je nastal v fazi katageneze nastajanja plina.

Introduction

Correlation of petroleum fluids (oil and gas) with their source rocks based on their molecular and/or isotopic characteristics is an important task in fundamental and applied petroleum (and coal) studies (Milkov, 2021). Biomarkers and the carbon and hydrogen isotopic composition of compounds in petroleum fluids facilitate to clarify relations between reservoir hydrocarbons and their specific source rocks (Boreham et al., 2004;

Gratzer et al., 2011; Yang et al., 2017). Natural gases contain relatively few compounds – mostly methane to hexane (CH_4-C_6H_{14}, i.e., C1-C6), N_2 and CO_2. Such a low molecular diversification limits the ways for interpreting their sources (Whiticar, 1994). Milkov and Etiope (2018) considerably re-defined the boundaries for genetic fields of thermogenic gas, primary microbial gas from CO_2 reduction, primary microbial gas from methyl-type fermentation, secondary microbial gas and abiotic gas. Their study bases on the study of isotopic composition of carbon and hydrogen in methane and CO_2 fractions of more than 20,000 samples from different geological realms worldwide. The revised gas diagrams of Milkov and Etiope (2018) became therefore new standard tools for gas genesis interpretations (Buttitta et al., 2020; Wieclaw et al., 2020, Babadi et al., 2021). There are still ongoing debates about the definition of the exact burial depth and ultra-deep resources (Ni et al., 2021). Natural gas can form in deep parts of the sedimentary basin, migrate upwards and accumulate in the shallow layers. Studies have already shown that several factors contribute to the origin of deep gas e.g., type of organic matter, thermal maturity, oil stability (Dyman et al., 2003).

In the last 20 years, numerous theoretical and applied studies have been conducted and published on gases in the intermontane Pliocene lignite-bearing Velenje basin (Kanduč & Pezdič, 2005; Kanduč et al., 2011; Sedlar et al., 2014; Kanduč et al. 2021), about 100 km west of the PDOGF area. There, the situation is much more complicated. Reservoir "rock" in Velenje is lignite, in which the gases are very heterogeneous in composition, of different origins and a result of different processes. Especially the ratio between methane and CO_2 varies greatly, and this fact is more a risk of mining than an advantage for example for coalbed gas exploitation (see e.g., Flores 2014).

The study presented in this paper on the isotopic composition of the carbon of the gases of the PDOGF is the first such study in the Petišovci-Dolina area. This preliminary study is based on very few measurements. The aim of this paper is to publish first analysed data on isotopic composition of carbon of natural gas of the studied PDOGF, which is predominantly methane – mostly above 85 % in the deep gasses (INA Zagreb, 2019) and above 89 % (Lisjak et al., 1988; Lisjak et al., 2011;) in the "shallow" gases, and to ascertain the question of its origin at different reservoir levels.

Study area -
Petišovci-Dolina Oil and Gas Field (PDOGF)

Oil and gas in the Petišovci-Dolina area E-SE of Lendava (Figs. 1 and 2) were discovered in 1942 – as a continuation of an already known Lovászi field in neighbouring Hungary. Also in Croatia, there were operating oil and gas fields in the immediate vicinity, especially at Selnica and Peklenica, which were exploited since the mid-19th century (Pleničar, 1954). At some localities oil seeps were known, as well. The peak of oil production was reached in a very narrow time-period between 1950 and 1952, with an annual production of between 50 and 70 thousand tonnes of oil (Pleničar, 1954). In the following years, oil production decreased. On the other hand, gas production increased (Kerčmar, 2018; Internet 1).

From 1942 to 2011, a total of 145 oil and gas wells were drilled in the Petišovci-Dolina Oil and Gas Field (PDOGF) and its surroundings (Lendava, Murski Gozd, Kog) (Lisjak et al., 1988; Lisjak et al., 2011; Markič, 2014). The most numerous, 107, are the wells abbreviated as the "Pt" (Petišovci) wells, and 13 wells abbreviated as the "D" (Dolina) wells. The PDOGF is 7.5 km long and 2 km wide (Fig. 2), and the area is a flat land, between +155 and +160 m above sea level. Numerous deep seismic profiles were carried out prior to drilling (Djurasek, 1988; and confidential data).

The "Pt" and "D" wells were up to 1775 m deep and they drilled the "upper" sequence of oil- and gas-bearing horizons (Fig. 3). These horizons (from the bottom at 1750 m depth to the top at 1200 m depth) have been for a long time known as the Petišovci, Lovászi, Paka, and Ratka horizons of the Lendava Formation (Fig. 3). The later used to be "conventionally" classified as a formation of the Upper Pannonian/Pontian age (e.g., Lisjak et al., 1988). However, in the last decade, the Pontian interval - in Slovenia *sensu* Škerlj, 1985; Stevanović & Škerlj, 1985; Škerlj, 1987; Turk, 1993; Pavšič & Horvat, 2009) has been excluded from the regional stratigraphic nomenclature of the Pannonian Basin System (Pavelić & Kovačić, 2018; p. 464, and references therein). Thus, the Lendava Formation is now classified as a formation of the Upper Pannonian age (*sensu lato*). The Petišovci, Lovászi, Paka, and Ratka horizons are 50 to 90 m thick and consist of alternating impermeable marls and porous oil- and especially gas-bearing sandstones. Each horizon comprises several hydrocarbon-bearing sandstones, which are up to 3.5 m effectively thick. Their porosity is 14–16 %, saturation with water
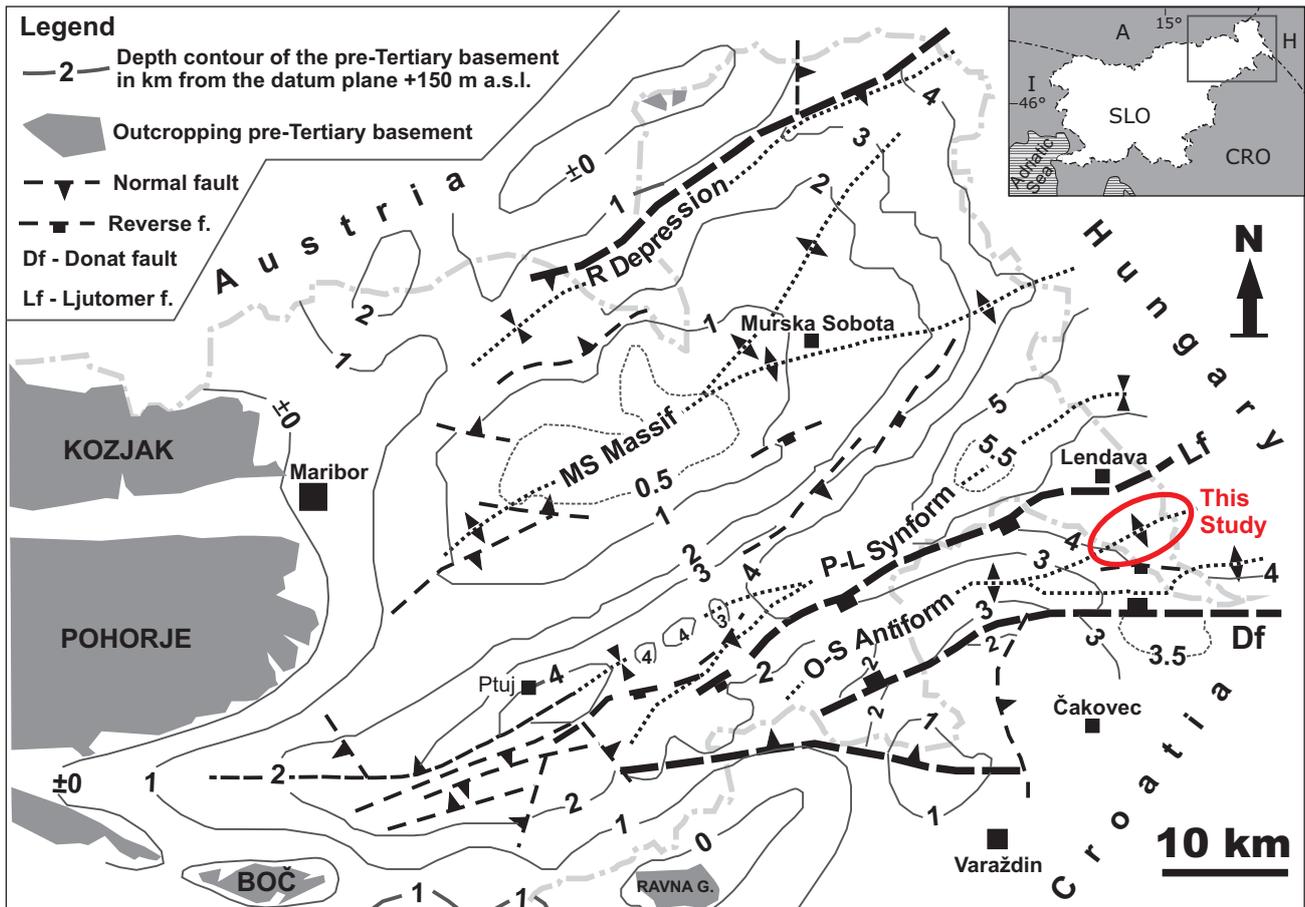
Fig. 1. Structural map of the Mura-Zala Basin. Isolines are depth contours (in km) of the pre-Tertiary basement (adopted after Djurasek, 1988; Gosar, 1994/95). Study area (PDOGF) is shown on the E of the map.

varies between 30 % and 40 % (Lisjak et al., 2011). Nowadays, the "upper" hydrocarbon-bearing reservoir sandstones are depleted – offering a possibility for storing imported gas, or for CO_2 sequestration.

In this paper, we call hydrocarbons in the "upper" sequence as the "shallow" hydrocarbons and gases, respectively.

Fig. 2. Gas sampled wells Pg-6 and Pg-5 ("deep" gasses), and D-5 ("shallow" gas) within the Petišovci-Dolina oil and gas field (PDOGF). For the cross-section see Figure 3.

In 1960, the Pg-1 well was drilled to a depth of 2977 m and encountered "deep" gas (Fig. 3). The "Pg" name means "Petišovci-globoka" (in English: "Petišovci-deep" well). Later, ten more Pg wells were drilled. The last and the deepest two were Pg-10 and Pg-11A wells from 2011, which reached a depth of 3492 m (length: 3535 m, but deviated) and 3500 m, respectively.

More than 15 gas-bearing early to middle Miocene (Karpatian to Badenian) sandstone reservoirs ("A-Q" reservoirs) were discovered by the "Pg" wells in a depth from 2200 m downwards to 3500 m (Toth & Tari, 2014; Kerčmar, 2018). Maybe there are even more reservoirs in a greater depth. The formation for "deep" gas used to be termed Murska Sobota Formation, while in the last ten years the Murska Sobota Formation is known as the Špilje Formation (e.g., Toth & Tari, 2014, Šram et al., 2015). The "deep" reservoirs are even thicker than the "shallow", but porosity is lower, 7–11 %. The "deep" Petišovci gas is characterized as the "tight gas" (Markič et al., 2016).

In the frame of the study presented in this paper, we sampled gases from three wells, from the depth intervals: 1212–1250 m (D-5), 2772–2795 m (Pg-5), and from 3102–3104 m (Pg-6) (Table 1).

Fig. 3. A "classical" cross-section along the Petišovci-Dolina oil and gas field (PDOGF) adopted after Lisjak (1988). Thicknesses of oil and gas reservoirs are somewhat exaggerated.

According to geophysical data (Djurasek, 1988), the basement rocks in the study area occur at a depth greater than 4 km (Fig. 1). Based on available data from the MG-6 well (3858 m) located in Murski Gozd few kilometres E from the PDOGF the basement rocks (only reached by the mentioned well) are composed of cataclastic breccia and shale (3732–3858 m) of "? Mesozoic" age (Brodarić, 1985). In the Mura-1 and Mura-2 wells in the Mura Depression in Croatia, the basement rocks consist of Mesozoic carbonates (Barić et al., 1996).

The PDOGF is now the only active oil and gas field in Slovenia with a small but permanent production of hydrocarbons (oil, gas, and a little of condensate). In the last 15 years, oil production varied between 150 and 365 tonnes per year and that of gas between 1.8 and 5.4 million Sm^3, with an extreme of 16 million Sm^3 in 2018 (Mineral resources in Slovenia, 2020). The highest gas production in the past was between 1988 and 1995 when it reached more than 30 million Sm^3 (1988) but dropped to 15 million Sm^3 (1995) (Kerčmar, 2018; Internet 1). This "high" production was achieved with "mechanical stimulation" of hydrocarbon-bearing strata (Fig. 9 in Kerčmar, 2018), and the same case was with a mentioned gas-peak in 2018. "Mechanical stimulation" is in general known today as "hydraulic fracturing".

Concessionaire for the exploitation and exploration of hydrocarbons in the Petišovci-Dolina oil and gas field (PDOFG) is the company Petrol Geoenergo d.o.o.

Study of source rocks and of thermal history of the Mura-Zala Basin (then called the Mura Depression) started in the late 1990s (Barić et al., 1996). A group of Slovenian and Austrian geologists initiated further investigation in the early 2000s, and two fundamental studies were published by Hasenhüttl et al. (2001) and by Sachsenhofer et al. (2001).

Geological setting

It is well known that the PDGOF is related to the Ormož-Selnica Anticline, more precisely to its northern segment, which is in Hungary named Lovászi Anticline, while the southern segment is called the Újfalu-Budafa Anticline (Toth & Tari, 2014). The northern anticline segment could be termed as the Petišovci-Lóvaszi anticline, which "bears" both oil and gas. The Újfalu Budafa anticline is hydrocarbon-bearing only in Hungary. The Ormož-Selnica Anticline, and the divided Petišovci-Lóvaszi and Újfalu Budafa anticlines are both a consequence of tectonic inversion ("up-lifting") between two regional reverse faults, the Ljutomer Fault, and the Donat Fault (Fig.1); (Djurasek, 1988; Hasenhüttl et al., 2001, Sachsenhofer et al., 2001, Toth & Tari, 2014).

The Ormož-Selnica Anticline with the PDOGF is composed of numerous alternating hydrocarbon-bearing sandstones and isolating marls (in detail Lisjak et al. 1988, Lisjak et al., 2011; and confidential data). It is a typical anticlinal hydrocarbon trap as are broadly known worldwide (e.g., Tissot & Welte, 1984; North, 1985; Ercegovac, 2002; Flores, 2014, Internet 2, and many others).

The host basin of the PDOGF is the Mura-Zala Basin (Fig. 1) situated in the SW part of the Pannonian Basin System – Central Paratethis (Placer, 1998; Fodor et al., 2002; Márton et al., 2002 Jelen et al., 2006; Pavšič & Horvat, 2009; Markič et al., 2011; Nadór et al., 2012; Šram et al., 2015; Sachsenhofer et al., 2018). Slovenian part of the Mura-Zala Basin was earlier known as the Mura Depression (Grandić & Ogorelec, 1986; Djurasek, 1988; Royden & Horváth, 1988; Gosar, 1994/1995; Mioč & Marković, 1998; Hasenhüttl et al., 2001, Sachsenhofer et al., 2001), while the Hungarian part was termed as the Zala Basin. This integration of the Mura Depression and the Zala Basin in the last twenty years was based on the above cited regional geologic, stratigraphic, tectonic, geophysical and paleomagnetic studies, and well confirmed by studying transboundary geothermal resources and management (e.g., Nadór et al., 2012). However, Mura Depression extends also to Croatia in a territory between the Mura and the Drava rivers where it is still termed as the Mura Depression (Barić et al., 1996; Saftić et al., 2003; Velić et al., 2012) and the Hrvatsko Zagorje Basin (Pavelić & Kovačić, 2018), respectively.

Tectonic structures of the Mura-Zala Basin in Slovenia characteristically consist of "antiforms" and "synforms" termed from NNW to SSE (Fig. 1): The South Burgenland Swell, Radgona Depression (or Sub-basin), Murska Sobota Massif (or High), Ptuj-Ljutomer Synform (or Ljutomer Depression), Ormož-Selnica Antiform (or Anticline) (Vončina, 1965; Djurasek, 1988; Mioč & Marković, 1998; Hasenhüttl et al., 2001, Sachsenhofer et al., 2001; Fodor et al., 2002). All these structures extend in a typical WSW-ENE direction. In the deepest "synform" structures, the thickness of Neogene sediments reaches 4 to extremely more than 5 km. A neighbouring basin to the Mura-Zala Basin is the WNW-ESE trending Drava Depression in N Slavonia in Croatia, also hosting numerous oil and gas fields (Saftić et al., 2003; Velić et al., 2012; and references therein). Along its depocenter, thickness of the Neogene sediments also reaches more than 5 km, extremely 6 km at Virovitica.

Source rocks - based on previous studies

Barić et al. (1996) studied source rocks and hydrocarbon accumulations in the Croatian part of the Mura Depression. Based on studying sediments in two wells (Mura-1 and Mura-2, about 3.8 and 4 km deep) they concluded that in the Mura Depression of Croatia source rocks for natural wet gas and condensate are Lower Miocene – Eggenburgian silty marls and limy pelites. Hydrocarbons derived from thermally altered kerogen III organic facies with hydrogen index HI < 70 mgHC/gTOC, having TOC contents mostly in a range of 0.5–1 wt % and maturity by vitrinite reflectance between 1 and 2 % R_0. The Eggenburgian source rocks being encountered at depths usually more than 3 km are up to 200 to 500 m thick. Next younger source rocks are Middle Miocene – mainly Sarmatian fine grained sediments (marlstones), but they are less spread than the Eggenburgian sediments, and up to 120 m thick. Their TOC content is 1–2 wt % and organic facies is characterized as the kerogen type II, therefore potentially gas and oil-prone. Sarmatian source rocks are in an oil window, not reaching the gas window, generating only oil.

Hasenhüttl et al. (2001) studied source rocks and generation of hydrocarbons of the whole Mura Depression in Slovenia using source rock analysis (organic carbon, Rock-Eval, gas chromatography, vitrinite reflectance) and numeric modelling techniques. They stated that most silty and marly Tertiary sediments of the Mura Depression in Slovenia ranging from Egerian/Eggenburgian to Upper Miocene host kerogen type III and are therefore gas prone. Oil-prone marly and silty sediments characterized by the kerogen type II organic matter occur in Lower Miocene (Egerian/Eggenburgian) strata in the Boč Anticline (Rogatec-1 well), in Karpatian sediments of the Radgona Depression (Šomat-1 well), and in Sarmatian sediments of the Ljutomer Depression (Ljutomer-1 well). TOC values in different hydrocarbons prone strata vary mostly in a range of < 0.5–1.5 wt %. In some strata they are somewhat greater. "Extreme" TOC contents of up to 4.1 wt % were measured in the Upper Miocene (?) brackish strata (marls, shales, sandstones, coals, coaly sediments). But these sediments are generally immature.

Hasenhüttl at al. (2001) finally concluded that the generation of hydrocarbons in different parts of the Mura Depression occurred during different time intervals. On the W (Maribor – Šomat – Benedikt – Radgona/Radkersburg – Pichla) and

on the SW (Boč), Karpatian sediments are over-mature, and hydrocarbons are interpreted to be most probably lost. Over-maturation was caused by the so-called "Karpatian heating event" in the mentioned areas with an estimated heat flow density of 375 mW/m^2 (Sachsenhofer et al., 1998) and could be a consequence of a shallow hidden pluton (Sachsenhofer et al., 2001). Also, the present heat flow density is the highest and spatially the widest in the Maribor – Šomat – Benedikt – Radgona/Radkersburg – Murska Sobota area, reaching 110–130 mW/m^2 (Rajver, 2018).

For the Ormož-Selnica Anticline, Hasenhüttl et al. (2001) measured hydrogen index (HI) to be below 130 gHC/gTOC for Lower Miocene sediments, and thus clearly showing the kerogen III type of organic matter and the gas proneness, respectively. In this area of the (present) Ormož-Selnica Anticline an early generation of hydrocarbons "probably" (Hasenhüttl et al., 2001) occurred in the Lower/Middle Miocene i.e., Karpatian/Badenian times as well, while the second hydrocarbon generation phase lasted from Middle/Late Miocene times to Early Pliocene (Hasenhüttl et al., 2001). According to the mentioned authors, the first phase of generation of hydrocarbons was probably caused by the heating event in Karpatian/Badenian (heat flow density about 150 mW/m^2), while the second one due to deep burial in Late Miocene. The heating event was the most outstanding in the previously mentioned W area, while it ceased towards the E and the Ormož-Selnica Anticline, respectively. The present heat flow density in the Petišovci area is similarly 110–130 mW/m^2 (Rajver, 2018a). From the maps of expected temperatures at different depths, it is evident that temperatures at a depth of 4 km exceed 180 °C (Rajver, 2018 b) and at 2 km depth, they exceed 100 °C (Rajver et al., 2016). Lisjak et al. (2011) cite temperature data for the upper hydrocarbon-bearing strata of the PDOGF in depths of 1240 to 1730 m in a range of 62–80 °C.

As concluded by Hasenhüttl et al. (2001), the second phase terminated in the Pliocene times because of the basin inversion between the Donat and the Ljutomer Faults (Djurasek, 1988). Inversion of the basin, giving a rise of the Ormož-Selnica Anticline, is also evident by a typically slight convex structure of the Uppermost Panonnian ("Pontian") brown coal measures in the Lendava–Benica/Petišovci–Mursko Središće area (Markič et al., 2011).

Fig. 4. Left – steel cylinder for sampling natural gas (volume 0.475 l; maximal pressure 150 bar); Right – sampling of natural gas from the Pg-5 well (gas field Petišovci, photo: Tjaša Kanduč, August 2021).

Sampling and methods – this study

Sampling of natural gas was performed in August and September 2021 at the gas station in Petišovci from wells Pg-5 and Pg-6 (deep gas) and in Dolina for well D-5 (shallow gas). Gas was collected with the use of steel cylinders (manufacturer: Swagelok, USA) as shown in Figure 4. Natural gas was sampled from the pipeline before entering the process of "cleaning" (removal of the other than methane components) under the (reduced) pressure of 5 bar. In fact (see Results and Discussion – last paragraph), also sampled with gas was condensate. Samples were then transferred to a 12 ml glass Labco ampoules fitted with a gas-tight septum using a vacuum line.

The isotopic composition of methane ($\delta^{13}C_{CH4}$) was determined using a Europa 20-20 mass spectrometer in continuous flow isotope ratio mass spectrometer with ANCA-trace gas (TG) preparation module. For CH_4 measurements, CO_2 was first removed and then the CH_4 was combusted over hot 10 % platinum CuO (1000 °C). The CH_4 completely converted to CO_2 was then analysed directly for the isotopic composition of carbon ($\delta^{13}C$). Working standard with $\delta^{13}C_{CH4}$ value of -53.4 ‰ ±0.1 ‰ calibrated to International Atomic Agency (IAEA) reference material was used with known $\delta^{13}C_{CH4}$ values. The analytical precision for carbon isotope composition is estimated to be ±0.6 ‰ for CH_4.

The relative difference of isotope ratios (also called relative isotope-ratio or delta values) has been reported using the short-hand notation $\delta^{i/j}E$. The isotope – delta value is obtained from isotope number ratios $R(^iE, \ ^jE)_p$ as follows (Brand et al., 2014):

$$\delta\big({}^{i/j}E\big) = \delta^{i/j}E = \frac{{}^{i/j}R_p - {}^{i/j}R_{Ref}}{{}^{i/j}R_{Ref}} \qquad (1)$$

Where ^{i}E denotes the higher (superscript i) and ^{j}E the lower (superscript j) atomic mass number of element E. The subscript P denotes the substance used to determine the respective values, R(^{i}E, ^{j}E)$_p$ is isotope number – ratios.

A free web-based machine learning tool (Snodgrass & Milkov, 2020) was used to determine the origin of natural gases. The input geochemical parameters are: $CH_4/(C_2H_6+C_3H_8)$, $\delta^{13}C_{CH4}$, δ^2H_{CH4}, $\delta^{13}C_{CO2}$, and δ^2H_{CH4}, and the output parameters are gas origin, confidence scores, model accuracy. In our study, the following input parameters were considered: for D-5 well C_1/C_{2+} ratio of 9.0 (90/10) and $\delta^{13}C_{CH4}$ = -38.6 ‰, for Pg-5 well C_1/C_{2+} ratio of 7.72 (85/11) and $\delta^{13}C_{CH4}$ = -36.6 ‰ and for Pg-6 well $C1/C_{2+}$ ratio of 7.72 (85/11) and $\delta^{13}C_{CH4}$ = -36.7 ‰. The coding also works with reduced number of parameters.

At this stage of our investigation, we did not perform gas composition analyses. However, we included in our study some existing gas composition data as summarized in Lisjak et al. (1988) and Lisjak et al. (2011). A more recent chromatographic analysis using HRN EN ISO 6974-5: 2014 standardization was done by Žuvela (2019) from INA Zagreb. The data were kindly provided by the Petrol Geo company in Lendava.

Results and discussion

Our results of analysed $\delta^{13}C_{CH4}$ values together with existing major gas components are summarized in Table 1. All samples are methane dominant up to 92 % (CH_4). The "deep" natural gases from the Pg wells (Pg-1, Pg-3, Pg-5–Pg-9), which provide with gas the "CPP Lek pipeline" consist of about 85 % methane (C1), 11 % hydrocarbons heavier than methane (C2–C6) and of 4 % CO_2 (Žuvela, 2019). The "shallow" gas contains more than 89 % methane, and up to 11 % C2–C6 gases, while the CO_2 content is negligible (Lisjak et al., 1988; Lisjak et al., 2011). Also, according to personal communication with engineers of the Petrol Geo company, CO_2 content is often detected (in few %) in the "deep" gases, while it is insignificant in the "shallow" gases. According to existing data, composition of gases in close hydrocarbon-bearing strata is stable. It varies within a range of around ± 1.5 % for the methane concentration. In this paper we attribute the concentrations as approximations for the isotopically studied "shallow" and "deep" gases in the wells D-5, Pg-5, and Pg-6 (Table 1).

If supposing in general a unique source rock and gas formation realm, isotope fractionation can be explained in a way that CO_2 is heavier than CH_4 which is more mobile and migrates easier upwards than CO_2. This effect quite often occurs in e. g. thick coal beds as for example in the Velenje lignite seam (Kanduč & Pezdič, 2005; Kanduč et al., 2021).

Table 1. Results of carbon isotopic composition of methane ($\delta^{13}C_{CH4}$) in D-5, Pg-5, and Pg-6 wells as measured for this study in 2021, approximate gas concentrations of methane (C1), C2-C6 gases, and carbon dioxide (CO_2) after Lisjak et al. (1988) as average for "shallow" gas-bearing layers (Petišovci, Ratka, Paka), and one available datum considered in this preliminary study for deep gas-bearing layers (the Lek pipeline) (INA Zagreb; Žuvela, 2019 - for Petrol Geo, d.o.o.), and classification into genetic typology after Snodgrass & Milkov (2020).

Well	Well-depth (m)	Gas-sampling depth (m)	Gas layer	CH$_4$ (C1)	C2-C6	CO$_2$	$\delta^{13}C_{CH4}$ (‰)	Genetic type of gas in classification after Snodgrass & Milkov (2020)
				Approximate concentrations (%)				
D-5	1575	1212–1250	"Shallow" (Paka)	89–92	< 11	< 0.1	-38.6±0.4	**Thermogenic**, confidence score: thermogenic = 84 %, secondary microbial: 14 %, abiotic: 2 %, *model accuracy: 91 %*
Pg-5	3324	2772–2795	"Deep"	85	11	4	-36.6±0.2	**Thermogenic**, confidence scores: thermogenic: 84 %, abiotic 16 %, model *accuracy: 90 %*
Pg-6	3200	3102–3104					-36.7±0.6	**Thermogenic**, confidence scores: thermogenic: 98 %, second. microb.: 2 %, model accuracy: 90 %
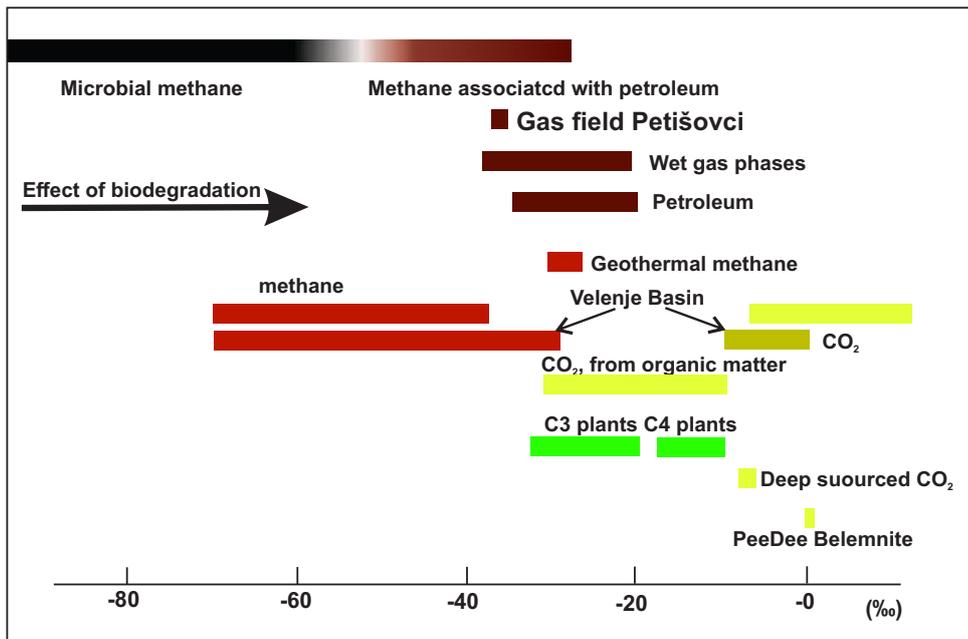
Fig. 5. Origin of methane from the Petišovci-Dolina oil and gas field (PDOGF) based on ranges of $\delta^{13}C_{CH4}$ values (‰) in diagram after Petroleum Geochemistry group CSIRO (2000).

The gas composition in terms of the methane (C1) versus all alkanes (ΣCn) ratio (from Tissot & Welte, 1984) around 0.89 (<0.98) is characteristic for both the shallow and deep wet gases generated during main stage of the catagenesis evolution.

The isotope signature of methane ($\delta^{13}C_{CH4}$) shows that the $\delta^{13}C_{CH4}$ values in the D-5, Pg-5 and Pg-6 wells range from -38.6 to -36.7 ‰. The "deep" gases from the wells Pg-5 and Pg-6 show very similar $\delta^{13}C_{CH4}$ values, -36.6 ‰ and -36.7 ‰, respectively, while the "shallow" gas around -38.6 ‰. In the diagram done by the Petroleum Geochemistry Group CSIRO (2000), the whole range of our isotopic values indicates the "methane associated with petroleum" (i.e., predominantly thermogenic origin) (Fig. 5).

Gas concentration from Table 1 and measured $\delta^{13}C_{CH4}$ were put in the "web-based machine learning tool" developed after Snodgrass and Milkov (2020) to decipher genetic type of gas (Fig. 6) The output data in Table 1 (the right-most column) are genetic type-origin of gases, confidence score and model accuracy in correspondence to revised genetic diagrams for natural gases (Milkov & Etiope, 2018). Methane to ethane plus propane ratio versus carbon isotopic composition of methane ($\delta^{13}C_{CH4}$) in the diagram after Milkov et al. (2020) (Fig. 6) shows clear thermogenic origin of investigated gas samples. Black dots refer to characterization of more than 20.000 natural gas samples all around the world from different geological habitats (Milkov & Etiope, 2018). Abbreviations CR, F, SM LMT, EMT, and OA refer to different genesis processes of gas formation – see Milkov et al. (2020). Petišovci-Dolina (PDOGH) gas fall close

to the "oil-associated (mid-mature) thermogenic gas", thus confirming their thermogenic origin.

The results show that the investigated natural gases are predominantly thermogenic in origin (Table 1). Almost entirely thermogenic is the "deep gas" from the Pg-6 well (98 % thermogenic, secondary microbial 2 %), while the deep gas from the Pg-5 is 84 % thermogenic, and 16 % abiotic. The "shallow" gas from the D-5 well is by confidence 84 % thermogenic, 14 % secondary microbial, and 2 % abiotic.
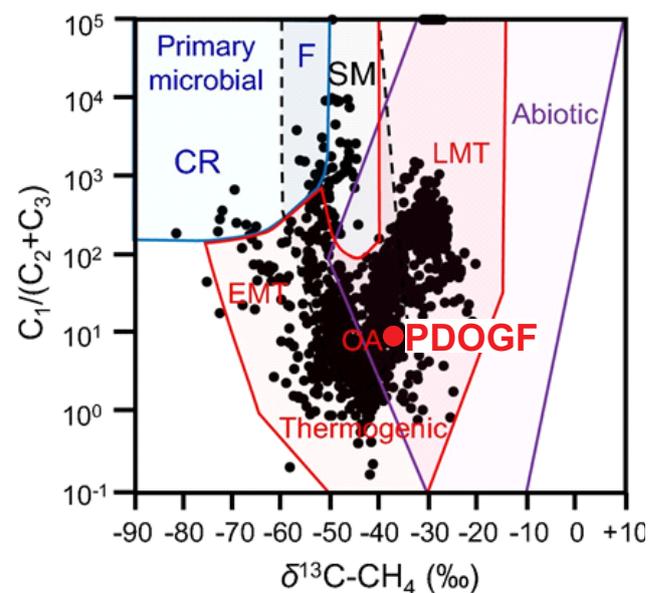
Fig. 6. Methane to ethane-plus-propane ratio (C1/C2+C3) versus carbon isotopic composition of methane ($\delta^{13}C_{CH4}$) plot after Milkov et al. (2020). Red circle (PDOGF) represents the Petišovci-Dolina gas samples. CR, F, SM LMT, EMT, and OA refer to different genesis processes of gas formation CR – CO_2 reduction (hydrogenotrophy), F – methyl-type (acetate) fermentation, SM – secondary microbial, EMT – early mature thermogenic gas, OA – oil-associated (mid-mature) thermogenic gas, LMT – late mature thermogenic gas.

At the present preliminary level of our knowledge, a question about the role and processes giving the shares of abiotic and secondary microbial gases, respectively, remains unanswered. Some artificial, un-natural effects of drilling are not excluded.

Methane from the "shallow" gas (D-5 well) has slightly more negative $\delta^{13}C_{CH4}$ value. This difference may be due to isotope fractionation due to migration from the primary reservoir, or possible mixing.

In Slovenia, based on research of natural gases and their dynamics in the last decades, it is interesting to compare results from different realms, e.g., from the Velenje lignite-bearing basin and the here studied from the PDOGF.

If we compare gas composition and $\delta^{13}C_{CH4}$ and CO_2 from the PDOGF with free coalbed gas sampled from excavation fields from the Velenje lignite-bearing basin (Kanduč et al., 2021) we can conclude that they are completely different in origin. We found out in the Velenje basin that the major coalbed gas constituents were CO_2, methane, and nitrogen, while in the PDOGF natural gas is by far predominantly composed of methane. Coalbed gas samples from excavation fields from the Velenje basin have gas concentration and isotopic values that reveal methane of biogenic origin and rarely thermogenic origin with $\delta^{13}C_{CH4}$ values of -69.4 to -29.5 ‰, $\delta^{2}H_{CH4}$ values of 301.4 to -221.9 ‰, and a fractionation factor ($\alpha_{CO2-CH4}$) of 0.998 to 1.073, suggesting that methane derives from microbial acetate fermentation and CO_2 reduction (Fig. 5). High $\delta^{13}C_{CH4}$ values (from -40 ‰ to -29.5 ‰) indicate thermogenic methane, which could be originated in shales forming pre-Pliocene basement of the Velenje Basin (Kanduč et al., 2021). The Carbon Dioxide Methane Index (CDMI) values ranged from 50 to 98.3 % and $\delta^{13}C_{CO2}$ values from -11.8 to 0.54 ‰, indicating that CO_2 is biogenic and endogenic in origin. In the PDOGF, the major gas component is methane with very low concentrations of CO_2 and higher hydrocarbons (Table 1), and $\delta^{13}C_{CH4}$ reveals methane associated with petroleum – i.e, thermogenic gas (Figs. 5 and 6).

Our study clearly revealed that the gases in the PDGOF are prevailingly thermogenic in origin.
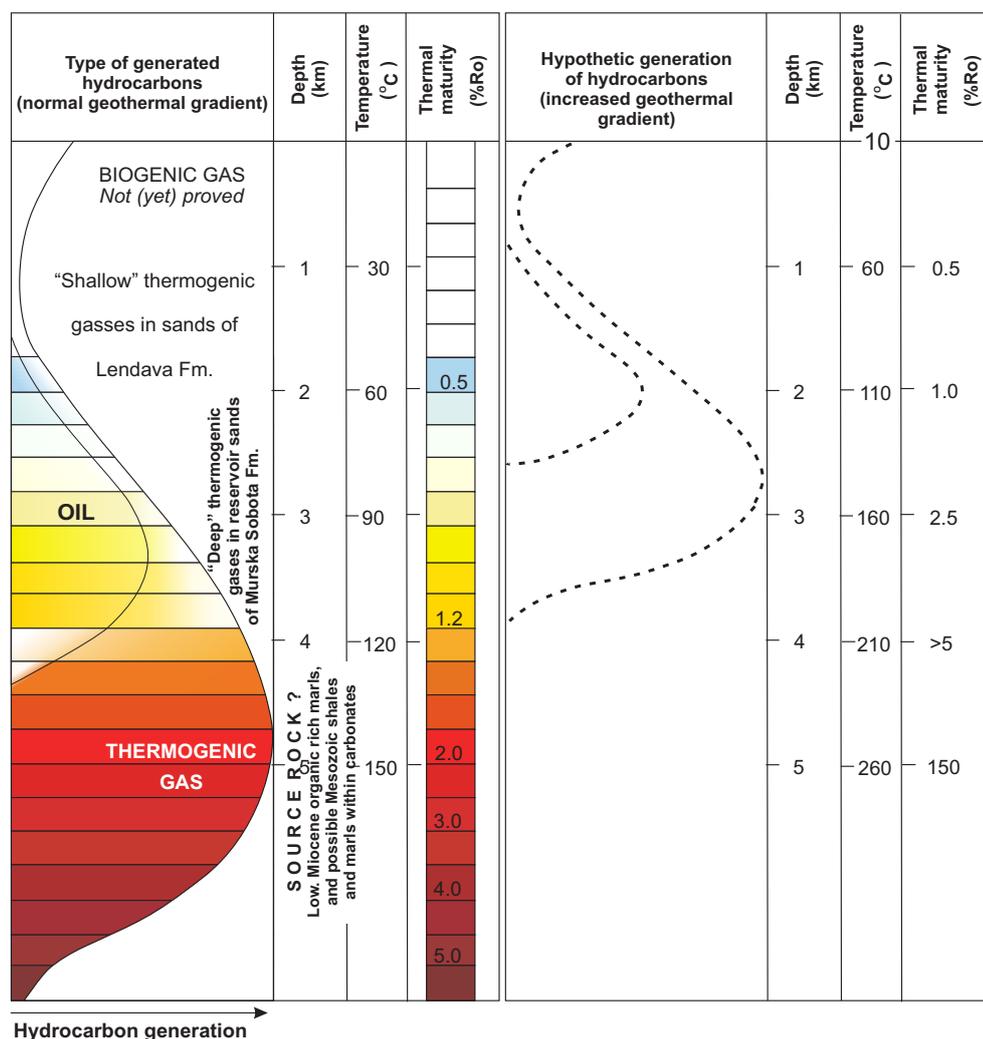
Fig. 7. Left – Generation of biogenic gas, oil, and thermogenic gas at a "normal" geothermal gradient of ca 30 °C/1km (Bjørlykke. K., 1989). Present occurrence of "shallow" thermogenic gases of the Lendava Formation (Upper Miocene) at the depth interval from 1200 to 1750 m, the "deep" thermogenic gases of the Murska Sobota Formation (Lower Miocene/Karpatian) from a depth of 2.2 km downwards to 3.5 km (and maybe more), and source of hydrocarbons are shown. Right – hypothetic generation of gases at a gradient of 50 °C/1km.

Due to increased geothermal gradient, between the normal 33 °C/km to nowadays ca. 50 °C/km (Rajver et al., 2018a, b), generation of hydrocarbons occurred at shallower depths than at normal gradients (Fig. 7). The Karpatian heat event did not most probably reach the Ormož-Selnica Anticline, and this effect of not too high maturity, and the alternation of porous and non-porous (impermeable) sediments as a trap was the reason that hydrocarbons were trapped and not lost.

According to Hasenhüttl et al. (2001), and Sachsenhofer et al. (2001) the gas was formed in the source rocks of the Lower Miocene Karpatian organic matter rich marls and shales. However, considering the source rocks studies in the Mura depression – Croatian part of Barić et al. (1996) and the Troskot-Čorbić′s study from INA Zagreb (personal communication 2022), source rocks within the PDOGF could also be older than Karpatian, i.e., of the Eggenburgian age. Further stratigraphic investigations and correlations would be welcome to clarify this question. We suppose that the generated gas did not overcome a considerable migration from deeper to younger strata. Vitrinite reflectance measurements of organic clasts in the deepest shales and marls (Karpatian) (Sachsenhofer et al., 2001) showed maturity by vitrinite reflectance of up to 1.5 %Rr (Pt-5 well), extremely to 2.0 %Rr (Mg-6) (Sachsenhofer et al. (2001), while by Barić et al. (1996) in a range of 1.3–1.5 %Rr for the Eggenburgian shales and 2 %Rr for Mesozoic shales within carbonates. At a normal geothermal gradient of 33 °C/km this indicates a depth of about 4.5–5 km (Fig. 7 - left). Nowadays accumulations in Petišovci of hydrocarbons are at a depth of 1200 to 3500 m. If an increased geothermal gradient is considered, e.g., about 50 °C/km (Rajver, 2018 b) the depths of hydrocarbons generation would be considerably shallower (Fig. 7 – right). The vitrinite reflectance of source rock indicates transition to late catagenesis and thermogenic gases associated with condensates (LMT in Milkov et al, 2020). The gases are associated with condensates according to Schoell (1980, 1983, 1988), as well.

Conclusion

Both the "deep" methane from wells Pg-5 and Pg-6 and shallow methane from the well D-5 have $\delta^{13}C_{CH4}$ values which clearly indicate thermogenic in origin. According to the Milkov's et al. (2020) diagram, the investigated gases are classified as "oil-associated (mid-mature) thermogenic gas". Because the Petišovci area was gradually lifted into antiform (Djurasek, 1988; Mioč and Mark-

ović, 1998) the initially formed gas might migrate via fractures upwards into reservoir sands termed as the "deeper" reservoirs (or "deeper" gases), and the "shallower" reservoirs (or "shallower" gases). Lower $\delta^{13}C_{CH4}$ value observed in D-5 is maybe due to migration from deeper to shallower gas reservoirs. We presume that migration paths were not very long.

Furthermore, based on available literature data, thermogenic gas in Petišovci was formed in source rocks within Lower Miocene (Karpatian or even older?) sediments composed mainly of marls and shales rich in organic matter. Measurements of the vitrinite reflectance of organic clasts in the deepest shales and marls (Sachsenhofer et al., 2001) showed maturity of up to about 1.5 %Rr, extremely to 2.0 %Rr.

If we consider a normal geothermal gradient a depth of about 4.5-5 km is inferred. The depths of hydrocarbons generation would be considerably shallower if the geothermal gradient is about 50 °C/km (Rajver, 2018 b).

During the reverse uplifting between the Donat and Ljutomer faults a system of fractures was formed enabling migration of hydrocarbons upwards from source rocks into numerous reservoir sandstones. Further study with taking more samples for isotopic (with deuterium in addition to carbon) and accompanying gas chromatographic analyses is continuing in 2022 to get better insight and more representative results of gas characterization and typology of gases generated and occurring within the Petišovci-Dolina oil and gas field.

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