GEOLOGICA CARPATHICA, 45, 6, BRATISLAVA, DECEMBER 1994
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CARBON AND HYDROGEN ISOTOPES IN FOUR NATURAL GASES FROM THE SLOVAK AND CZECH PART OF THE VIENNA BASIN

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(Manuscript received June 28, 1993; accepted October 5, 1993)

Abstract: Type and origin of four methane gases from the Neogene fill of the Vienna Basin on the Slovak and Czech territory was estimated using chemical composition and hydrogen and carbon isotopic analysis. The gas from Malacky gas field (695 m deep) is composed almost exclusively of methane (C_{2+} = 0.02 vol. %) and is evidently of biogenic origin being rich in considerably light hydrogen and carbon isotopes (δD = -194 ‰; $\delta^{13}C$ = -67 ‰). This gas is supposed to be formed in the Neogene not deeper than 1800 m. Isotopic composition of hydrogen (δD = -151 to -167 ‰) and organic carbon ($\delta^{13}C$ = -39 to -43 ‰) of the gases from the Kúty gas field, Láb and Poddvorov oil- and gas fields (1368 - 1625 m) suggests their thermogenic (catagenetic) origin in pre-Neogene formations.

Key words: Vienna Basin, natural gas, methane, carbon isotopes, hydrogen isotopes.

Introduction

Natural gas is a mixture of hydrocarbon and non-hydrocarbon gases and is often associated with petroleum. Main geochemical characteristics of the natural gases are the carbon and hydrogen isotopic ratios and "wetness", expressed by amount of higher hydrocarbon homologues - C_{2+} (Schoell 1983), $C_1/(C_2+C_3)$ ratio (Bernard et al. 1976) or $C_1/\Sigma C_n$ (Stahl 1977).

Biogenic gas (B in Fig. 3) is almost pure methane and is formed by microbial metabolic degradation of organic matter during early diagenesis (Schoell 1980). Most of biogenic gas occurs at depth less than 1000 m (Tissot & Welte 1984) or 1800 m but in rare exceptions as deep as 3350 m (Rice & Claypooll 1981). The same authors referred to the temperature of 75 °C as an upper limit for microbial activity and biogenic gas generation. Organic carbon isotopic ratio ($\delta^{13}C$) varies generally in range from -50 to -90 ‰ (Bernard et al. 1976; Hunt 1979; Schoell 1980; Deines 1980; Sacket 1980; Tissot & Welte 1984) and δD ranges from -180 to -280 ‰ (Schoell 1980, 1984).

Thermogenic (catagenetic) gas is generated from kerogen at the beginning and during the main phase of oil formation (T_o in Fig. 3), marked by vitrinite reflectance (R_o) 0.7 and 1.3 %, and that of condensate formation (T_c) at R_o from 1.3 to 2.0 %. The latter is both from kerogen and thermal cracking of erlier formed oil (Tissot & Welte 1984). Typical feature of oil-associated thermogenic gases (T_o) is the presence of high amounts of C_{2+} hydrocarbons which may be generated at temperatures ranging from 70 to 150 °C with maximum at about 120 °C (Hunt 1979). With progressive source rock maturity thermogenic methane is relatively enriched in ^{13}C and deuterium and the gas "wettness" is decreasing (Schiegel & Vogel 1970; Galimov 1973; Hunt 1979; Schoell 1980; Tissot & Welte 1984).

The aim of this paper is to present new carbon and hydrogen isotopic data of gases from the Vienna Basin as evidence of their genetic type and possible origin.

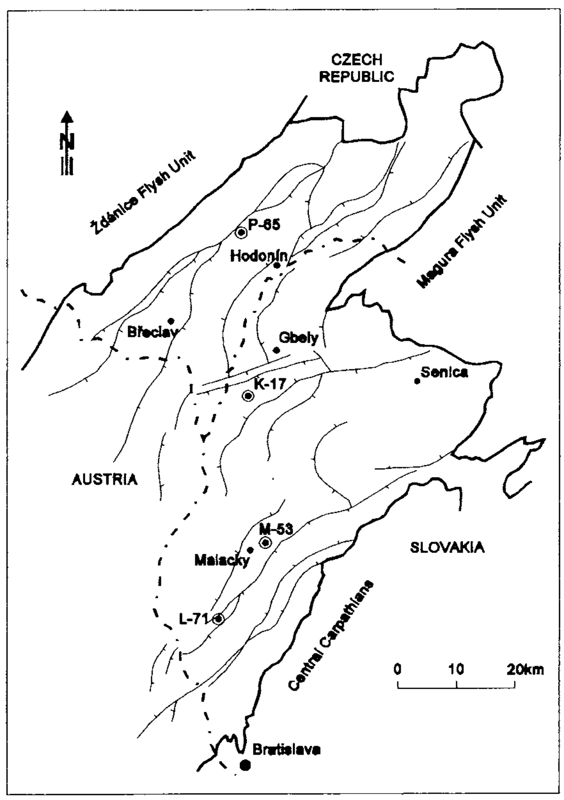

Fig. 1. Location of the studied gas samples in a simplified tectonic map of the Vienna Basin showing boundaries of the Neogene and major faults.

Table 1: Reservoir characteristics of gas samples.

Sample	Well	Stratigraphy	Perforation depth interval [m]	Reservoir temperature [°C]	Reservoir lithology	R_o [%]	T_{max} [°C]
M-53	Malacky 53	Sarmatian	693- 695	33	Fine-grained sandstone	0.25	420
L-71	Láb 17	Middle Badenian	1386-1391	65	Porous limestone with sand	0.40	425
K-17	Kúty 17	Upper Badenian	1516-1558	61	Sandstone with calcareous cement	0.40	425
P-65	Poddvorov 65	Middle Badenian	1622-1625	62	Sandstone with calcareous cement	0.40	425

Stratigraphy and lithology are after Bílek (1974) and Bílek et al. (1982). Steady state temperature data from adjacent wells in the respective gas field (Král et al. 1987). Extrapolated vitrinite reflectance (R_o) and maximum Rock-Eval pyrolysis temperature (T_{max}) are after Francû et al. (1990).

Geological characteristics of the samples

Gas samples were collected from producing wells in the Slovak and Czech part of the Vienna Basin (Fig. 1) from the Neogene reservoirs at depth ranging from 690 to 1630 m. Stratigraphy, lithology and reservoir steady state temperatures are given in Tab. 1. More details on the geology of the Vienna Basin were summarized e.g. by Bílek (1974), Gaža (1978), Wessely (1988), Jiříček & Seifert (1990).

Experimental

Gas sampling

Gases were sampled at the well head in steel cylinders and glass bottles under NaCl saturated solution.

Gas chromatography

Chemical composition of gases was analysed by gas chromatography under following conditions:

He and H_2: 280 cm column, internal diameter 0.4 cm; molecular sieve 0.5 nm; 60 °C; carrier gas Ar; TCD detection.

CO_2: 90 cm, 0.4 cm; Porapak Q; 60 °C; H_2; TCD.

Ar, O_2, N_2, CH_4, CO : capillar column PLOT, 25 m, 0.32 mm; molecular sieve 0.5 nm; 40-190 °C; H_2; TCD.

C_2-C_7: PLOT, 50 m, 0.53 mm; deactivated Al_2O_3; 40-190 °C; heating rate 5 °C/min; H_2; FID.

Analyses were carried out at the Geochemical laboratory of the Czech Geological Survey, Brno.

Carbon and hydrogen isotopic analysis

Natural CO_2 was removed from gas samples in liquid nitrogen traps. Gas was oxidized in furnace over mixture of CuO and CuO_2 at 870 °C. The resulting water was collected in a dry ice trap and CO_2 at liquid nitrogen temperature. The water was subsequently reduced to H_2 by passing over Zn at 800 °C. The isotopic composition is reported in conventional δ-notation in parts per thousand (‰). The standards for $\delta^{13}C$ and δ D are PDB and SMOW respectively (Craig 1957, 1961).

The isotopic determinations of carbon and hydrogen were carried out in the Laboratoire d'Hydrologie et de Géochimie Isotopique, Université de Paris-Sud, Orsay.

Results

The results obtained by gas chromatography and isotope analysis are presented in Tab. 2. Organic maturity at the reservoir depth is characterized by vitrinite reflectance (R_o) and maximum temperature of Rock-Eval pyrolysis (T_{max}; Tab. 1) based on data of Francû et al. (1990).

Chemical composition

The analysed samples represent methane natural gases with very low content of non-hydrocarbons. Methane is the dominant component of all studied gases, other hydrocarbons are mainly ethane and much less propane. C_4-C_7 hydrocarbons are present in trace concentrations: n.10^{-2} vol. % or they are not present (Malacky-53). The relative portion of methane to higher hydrocarbons is expressed by $C_1/(C_2+C_3)$ ratio (Tab. 2). Gases from Láb-71, Kúty-17 and Poddvorov-65 wells (L-71, K-17 and P-65) are methane gases with medium low content of higher hydrocarbons. Sample from Malacky-53 (M-53) represents almost pure methane (99.97 % CH_4 in total HC).

Nitrogen and carbon dioxide are the major non-hydrocarbon constituents (non-HC in Tab. 2). Trace amounts of helium, argon and carbon oxide were detected.

Isotopic composition

Gases L-71, K-17 and P-65 have fairly similar composition with $\delta^{13}C$ values from -39 to -43 ‰ and δD from -151 to -167 ‰. They differ significantly from the M-53 gas with much lighter carbon

Table 2: Geochemical and isotopical characteristics of the studied natural gases.

Sample	Well	R_o [%]	CH_4 [% vol.]	C_{2+} [% vol.]	Σnon HC [% vol.]	C_1/C_2+C_3	$\delta^{13}C$ [‰]	δD [‰]
M-53	Malacky 53	0.25	98.7	0.02	1.27	4935.0	-66.3	-194.4
L-71	Láb 71	0.40	95.5	2.55	1.94	64.5	-42.5	-166.6
K-17	Kúty 17	0.40	96.7	1.78	1.50	81.9	-37.5	-151.1
P-65	Poddvorov 65	0.40	94.8	4.33	0.85	26.3	-39.6	-155.7

Vitrinite reflectance (R_o) represents the maturation stage of the Neogene rocks at the reservoir depth (Francû et al. 1990). C_{2+} includes C_2 trough C_7 hydrocarbons (HC). Isotopic data are related to PDB and SMOW standards.

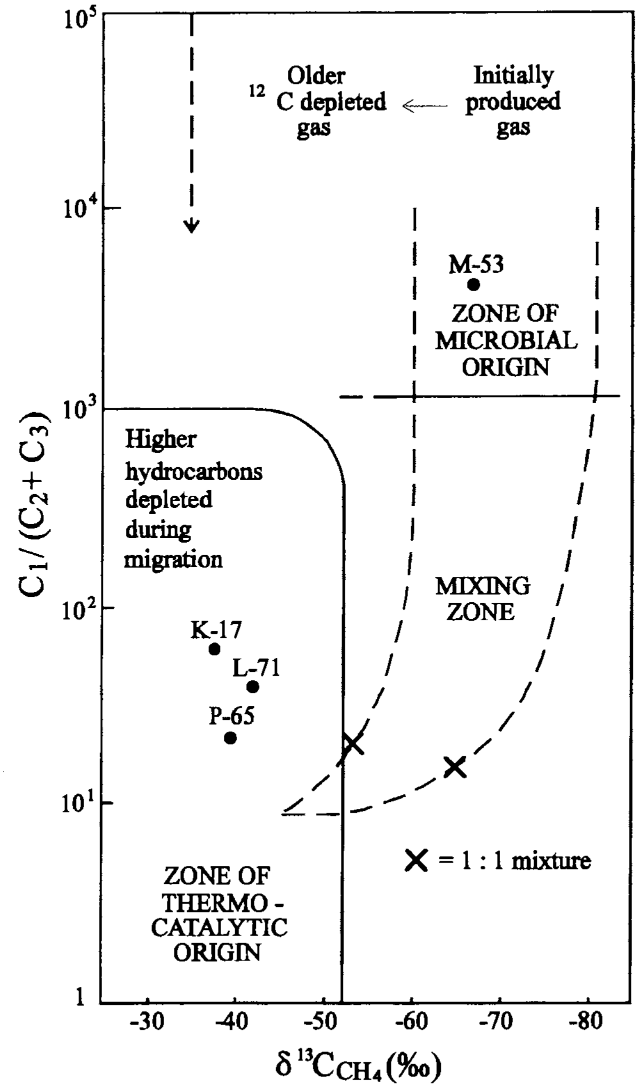

Fig. 2. Chemical and isotopic composition of the studied gases in diagram proposed by Bernard et al. (1978).

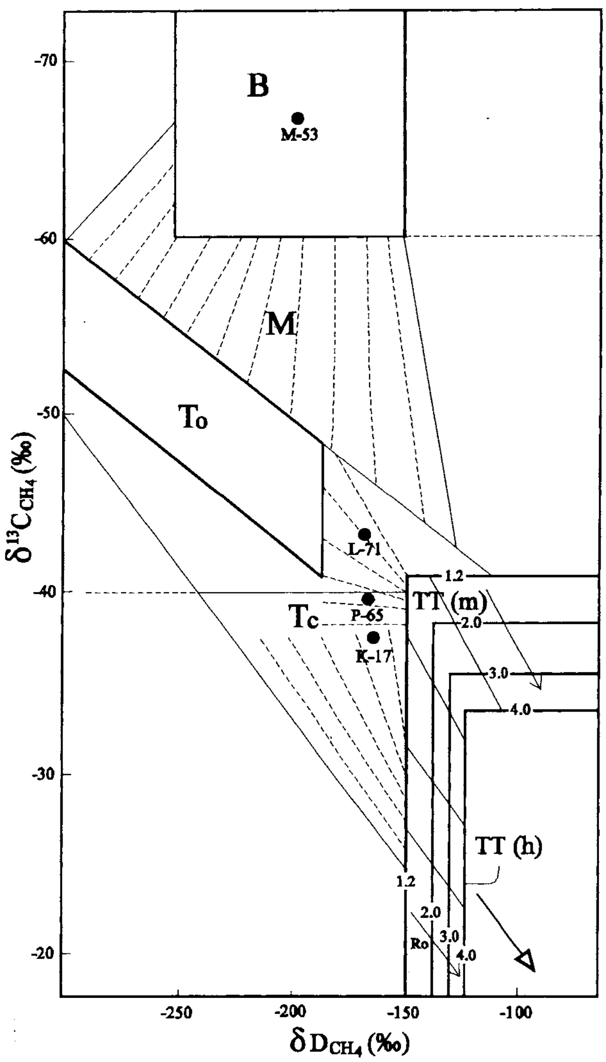

Fig. 3. Carbon and hydrogen isotopic composition of the studied methanes in Schoell's (1983) genetic diagram. **B** - biogenic gas; **T** - associated gas; **TT** - non-associated gas; **M** - mixed gas of intermediate composition; **To** - gases associated with petroleum; **Tc** - gases associated with condensate; **TT(m)** - and **TT(h)** - non-associated gasses from marine source rock and coal gases.

and hydrogen isotopes typical of biogenic origin:

$\delta^{13}C = -66.3$ ‰ and $\delta D = -194.4$ ‰.

The studied gases are shown in diagrams proposed by Bernard (1976) and Schoell (1980, 1983). They represent two genetic types - a typical biogenic gas (M-53) and thermogenic gases associated with condensate generation (L-71, K-17 and P-65; Figs. 2, 3).

Discussion

The source rocks in the Czech and Slovak part of the Vienna Basin were studied by Müller (1987), Chmelík & Müller (1987) and Francŭ et al. (1990). Using the Rock-Eval pyrolysis data and vitrinite reflectance they concluded that the Karpatian, Badenian and Sarmatian shales and marls contain owerhelmingly the humic (type III) kerogen in amount ranging from 0.5 to 1.3 % TOC. As seen from low increase of vitrinite reflectance with depth, these rather poor source rocks enter early mature zone at depth of about 3000 m. The deepest Neogene may start to generate liquid hydrocarbons but only the pre-Neogene rocks reach the peak oil generation stage. These conclusions were earlier presented by authors of maturation studies in the Austrian part of the Vienna Basin with similar geothermal conditions (Welte et al. 1982; Kratochvil & Ladwein 1984; Ladwein 1988). All the four gases studied in this paper are from reservoirs situated in the zone of immature source rocks at depth less than 1625 m.

In the Malacky gas pool the gas is produced from the Sarmatian sands at 695 m (Bílek 1974), the reservoir temperature is 33 °C. The shales adjacent to the reservoirs are immature with vitrinite reflectance lower than 0.3 %. The gas has possibly been formed at depth ranging from that of the reservoir to aproximately 1800 m, where the temperature is about 70 °C and is considered to be a limit of bacterial activity (Schoell 1984). The absence of mixing with thermogenic gas suggests that the Malacky gas pool has not been in direct contact with any deeply formed migration path.

The gases from the Láb-71, Kúty-17 and Poddvorov-65 wells are from the Middle and Upper Badenian formations. The reservoir temperature ranges from 61 to 65 °C which is typical for decreasing bacterial activity. The $\delta^{13}C$ and δD values suggest similar maturity of all three gases corresponding to thermogenic gas associated with condensate generation (T_c). Such conditions occur mainly in the pre-Neogene formations underlying the Vienna Basin (Chmelík & Müller 1987) and in the deepest Neogene basin fill. As shown in Fig. 3, L-71, K-17 and P-65 gases may have originated in source rocks with kerogen of marine-terrestrial type. This evidence supports the idea that these gases and the oils occurring in this part of the Vienna Basin have been generated in a common oil- and gas-source rock with kerogen of type II-III. In case of the Kúty and Poddvorov pools the autochthonous Malmian marls and Paleogene are the most probable candidates but some of the anoxic shales (e.g. the Menilite formation) in the Flysch units may also be considered.

The Láb pool is situated in the eastern part of the Vienna Basin, where the Neogene is underlain by the Alpine-Carpathian units. Considering the autochthonous Malmian of the Bohemian Massif as source rocks for oils and gases would be rather speculative in this area. If it occurs deeply buried under the Alpine-Carpathian units it should be in the late dry-gas zone in this area, while the Láb gas shows the maturity of the condensate stage (Fig. 3). Triassic Lunz Formation with coaly (type III) kerogen may be a contributing gas-source rock as suggested e.g. by Šimánek (1968), Schoell (1984), but other formations with more marine kerogen may be the source rocks of hydrocarbons in this part of the Vienna Basin.

Conclusions

Chemical and isotopical characteristics suggest that the isotopically light almost pure methane gas of the Malacky-53 pool situated in the Sarmatian at depth of 700 m is almost exclusively of biogenic origin. It may have been formed in the surrounding and underlying rocks to maximum depth of about 1800 m where at temperature of 70 °C the bacterial activity should cease.

Isotopically heavier gases with medium low content of ethane and propane of the Poddvorov, Kúty and Láb pools situated in the Middle and Upper Badenian at depth of about 1400 - 1600 m and temperature from 61 to 65 °C show thermogenic (catagenetic) origin associated with condensate formation from oil-prone source rock. With respect to the earlier geochemical and microscopical studies of potential source rocks and the geothermic exploration in the Vienna Basin and the underlying formations, the favorable conditions for generation of this type of gases are expected in the autochthonous Jurrasic and/or Paleogene of the Bohemian Massif, unspecified marine source rocks of the Flysch nappes, or in case of the Láb field, in the Alpine-Carpathian units.

Acknowledgements: We express our thank to the management of Gbely and Hodonín Oil Companies for permission to publish this paper. We greatly acknowledge Dr. Z. Boháček for gas chromatography analysis and Ing. M. Michalíček and Dr. M. Pereszlényi for critical comments and suggestions.

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