ORIGIN OF MOLECULAR NITROGEN RELATED TO HYDROCARBONS OF NATURAL GAS OF CENTRAL AND EASTERN PARTS OF THE POLISH OUTER CARPATHIANS

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Introduction

The main aim of this study is to determine the origin of molecular nitrogen occurring in natural gas both associated and non-associated with oil accumulated in the Lower Cretaceous-Oligocene reservoirs in the Silesian, Sub-Silesian and Skole nappes of the central and eastern parts of the Polish Outer Carpathians related to hydrocarbon gas origin and geological setting. For genetic interpretation we correlate isotopic composition of molecular nitrogen with stable carbon isotope composition of CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10} and C_5H_{12} and stable hydrogen isotope composition of CH_4, C_2H_6 and C_3H_8. Origin of hydrocarbon gases was discussed by Kotarba et al. (2019) and Więcław et al. (2019).

Samples and methods

26 natural gas samples were collected from the study area. Molecular compositions of natural gases (CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, CO_2, O_2, H_2, N_2, He) were analyzed in a set of columns on two Agilent 7890A GCs equipped with a gas sampling valve plumbed with a dual sample loop. The stable nitrogen isotope analyses were carried on with a Finnigan Delta Plus mass spectrometer coupled through GC combustion III with a HP series 6900 gas chromatograph. Gaseous nitrogen was separated chromatographically and transmitted to the mass spectrometer via the on-line system. The results were presented in the δ-notation (δ^{15}N, ‰) relative to the air nitrogen standard with analytical precision estimated to be ±0.4‰. Methods of stable carbon and hydrogen isotopic analyses of hydrocarbon gases is described in Kotarba et al. (2019) and Więcław et al. (2019).

Results

Natural gases accumulated within the Lower Cretaceous-Oligocene reservoirs of the of the study area are variable in their both molecular and stable isotopic ratios. Their predominant molecular components are hydrocarbon gases (Kotarba and Nagao 2008; Kotarba et al. 2019, Więcław et al., 2019). Molecular nitrogen is the second most abundant component of studied gases with concentration ranging from 0.29 vol.% in natural gas from Łodyna-75 (Lo-75) well up to 12.6 vol.% in natural gas from Jurowce-7 (Je-7). Stable nitrogen isotope composition of N_2 varies from –4.5 to 1.8‰.

Discussion and conclusions

Molecular nitrogen is a common component of natural gas from the fields of Polish Outer Carpathians, however it never prevails over hydrocarbon gases and its concentrations maximally reach 26 vol.% (e.g. Kotarba et al., 2019; Więcław et al., 2019). Isotopic composition of molecular nitrogen in natural gases may show wide variations and its usage can be limited, but recent pyrolytic studies show, that isotopic fractionation during thermal transformations of sedimentary organic matter leads to ^{15}N-enrichment in N_2 with increasing thermal maturity (Li et al., 2009). In analysed gases, molecular nitrogen is associated with hydrocarbon gases of both microbial and thermogenic origin (Kotarba et al., 2019; Więcław et al., 2019). Molecular and isotopic characteristics of discussed natural gas suggests that molecular nitrogen in the study area represents two different genetic groups. First group is mostly of organic origin, related to thermal transformations of organic matter and the second group comprises inorganic N_2, related to fixed NH_4 within illites derived from organic matter during early stages of diagenesis. N_2 origin related to thermal transformations of organic matter is supported by increasing δ^{15}N values of molecular nitrogen with N_2 concentration (Figure 1A) which represents successively higher maturity stages as consistent with increasing δ^2H values of methane (Figure 1B). N_2 related to NH_4-rich illites occurs in natural gas demonstrating the

highest $\delta^{15}N$ values of N_2, from 1.3 to 1.8‰ and showing the highest maturity, occurring as free accumulations in about 10-km long area (samples from Je-7 and Je-8 wells of Jurowce-Srogów field, Sk-1 of Sanok-Zabłotce field and Sw-2 of Strachocina field).

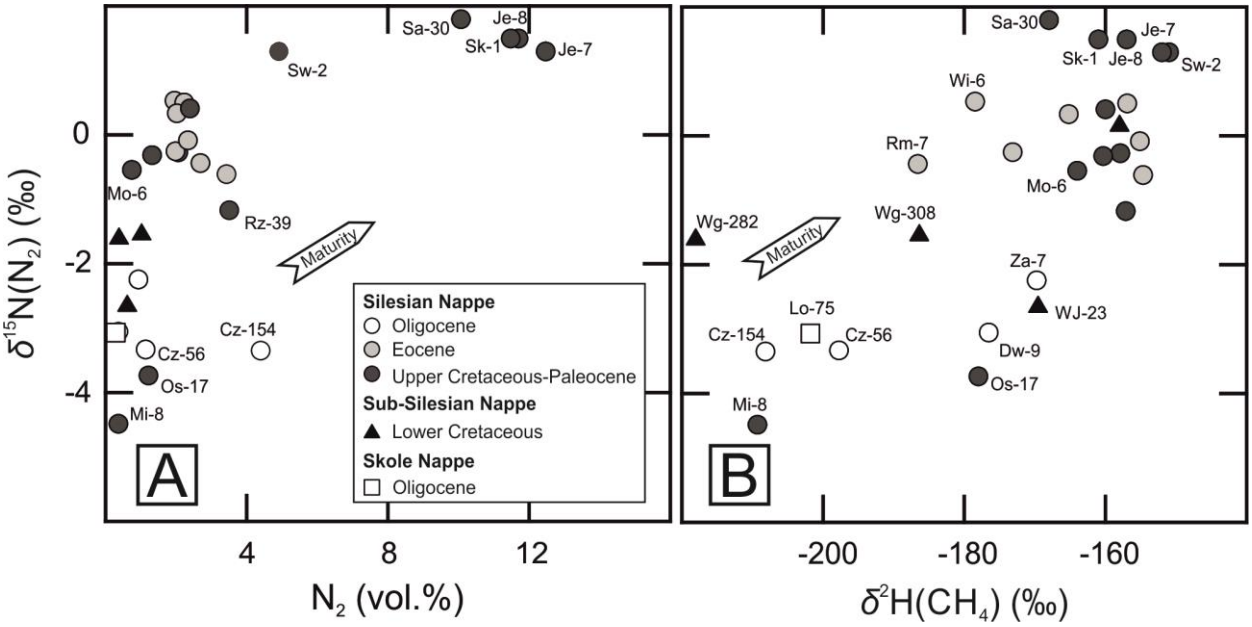

Figure 1. *$\delta^{15}N$ of molecular nitrogen versus* ***(A)*** *N_2 concentration and* ***(B)*** *$\delta^{2}H$ of methane of analysed natural gases.*

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References

Kotarba M.J., Nagao K., 2008. Composition and origin of natural gases accumulated in the Polish and Ukrainian parts of the Carpathian region: Gaseous hydrocarbons, noble gases, carbon dioxide and nitrogen. Chemical Geology 255, 426-438.

Kotarba M.J., Więcław D., Bilkiewicz E., Lillis, P.G., Dziadzio, P., Romanowski T., Kowalski A., 2019. Origin, secondary processes and migration of oil and natural gas in the central part of the Polish Outer Carpathians: geochemical and geological approach. AAPG Bulletin (in press).

Li, L., Cartigny, P., Ader, M., 2009. Kinetic nitrogen isotope fractionation associated with thermal decomposition of NH_3: Experimental results and potential applications to trace the origin of N_2 in natural gas and hydrothermal systems. Geochimica et Cosmochimica Acta 73, 6282-6297.

Więcław D., Bilkiewicz E., Kotarba M.J., Lillis, P.G., Dziadzio P., Kowalski A., Kmiecik N., Romanowski T., 2019. Origin and secondary processes in petroleum in the eastern part of the Polish Outer Carpathians. International Journal of Earth Sciences (in press).