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## The isotopic composition of gaseous hydrocarbons – tool for polish shale gas system evaluation

Carbon isotopic composition of individual hydrocarbons in gas samples can be used for interpretation and correlation purposes. On the basis of the  $\delta^{13}\text{C}$  values of methane, ethane and propane estimation of source rock (from which the gas was generated), thermal transformation degree can be performed. Analyses of chemical and isotopic composition were performed for gas samples from the degassing of cores, acquired during the drilling of two wells in the north (Baltic basin) and south (Lublin basin) of Poland. The isotopic composition of methane carbon from well A samples corresponds to the beginning of the oil window and from the well B samples corresponds to the gas window. Gases from the well located in northern Poland were generated on a considerably lower thermal maturity level of organic matter than gases from the well located in southern Poland. All data allow to state that polish shale formations are varied and natural gas compositional analyses can be helpful for proper shale gas system evaluation.

Key words: shale gas, chemical composition, isotopic composition,  $\delta^{13}\text{C}$ , polish shale formations, natural gas.

### Skład izotopowy gazowych węglowodorów – narzędzie ewaluacji systemu naftowego polskich formacji łupkowych

Analizy składu izotopowego węgla poszczególnych węglowodorów próbek gazowych mogą być stosowane w celach interpretacyjnych oraz korelacyjnych. Na podstawie wartości  $\delta^{13}\text{C}$  metanu, etanu i propanu można szacować stopień termicznego przeobrażenia skały macierzystej, z której gaz został wygenerowany. Analizy składu chemicznego i izotopowego zostały wykonane dla próbek gazów z degazacji rdzeni pochodzących z dwóch odwiertów z południa (basen lubelski) oraz północy (basen bałtycki) Polski. Skład izotopowy węgla w metanie próbek gazów z odwiertu A – odpowiada początkowej fazie okna ropnego, a z odwiertu B – oknu gazowemu. Gaz z odwiertu zlokalizowanego na północy Polski został wygenerowany na znacząco niższym poziomie dojrzałości termicznej substancji organicznej niż gaz z południa Polski. Pozyskane wyniki pozwalają stwierdzić duże zróżnicowanie skał łupkowych oraz przydatność tego typu analiz dla ewaluacji systemu naftowego formacji łupkowych.

Słowa kluczowe: *shale gas*, gaz z formacji łupkowych, skład chemiczny, skład izotopowy,  $\delta^{13}\text{C}$ , polskie formacje łupkowe, gaz ziemny.

### Introduction

Carbon isotopic composition of individual hydrocarbons in gas samples can be used for interpretation and correlation purposes. On the basis of the  $\delta^{13}\text{C}$  value of methane, ethane and propane estimation of source rock (from which the gas was generated) thermal transformation degree can be performed. Isotope correlation curves, which combined with n-alkanes isotopic curves, allow to perform correlations: gas–gas, gas–source rock (bitumen extract) and oil–oil and oil–source rock (bitumen extract).

Natural gas geochemistry distinguish three basic types of gases: biogenic, thermogenic and mixed. Biogenic gas (microbial) and thermogenic gas are referred to as primary gases and mixed gas as a secondary gas [17]. Biogenic gas is a product of the metabolism of microorganisms occurring in shallow, anaerobic and sulphate-free basins. Microbial gas production does not occur at great depths, since temperatures above 75°C stops microbial activity, and thus the process of methanogenesis [12]. However, there are situations where

biogenic gas occurs at great depths. This is connected with rapid seal development and subsidence. Examples are basins in the Gulf of Mexico and northern Italy [4]. It is estimated that about 20% of conventional gas reservoirs contain biogenic gas [9, 10]. Thermogenic gas is generated as a result of the kerogen and/or oil cracking due to temperature rise during basin subsidence.

The interpretation of the isotopic composition of gases, performed taking into account the chemical composition, allows to specify:

- the generation phase (gas or oil window),
- formation mechanism (biogenic or thermogenic gas),
- gas source (shallow or deep sediments),
- the type of organic matter (marine or terrestrial),
- thermal maturity level,
- gas mixing (migrated gas inflow).

The isotopic composition of the gas is dependent on the organic matter type, from which the gas was generated, so the type and environment of sedimentation can be indirectly determined. In addition hydrogen isotope composition together with carbon isotopes can be used. In this way biogenic and thermogenic gases can be distinguished, additionally the formation mechanism of biogenic gas can be determined (reduction of CO<sub>2</sub> or the acetate fermentation). Using the C<sub>1</sub>/(C<sub>2</sub> + C<sub>3</sub>) ratio and carbon isotopic composition of methane, a type of gas generation can be defined (biogenic, dry gas; wet, oil related gas; dry, thermogenic gas). Differences between δ<sup>13</sup>C of methane, ethane, and propane are used to detect the methane migration, which is important in determining the maturity of organic matter, from which the gas was generated. Isotopic correlation curves (δ<sup>13</sup>C values of subsequent hydrocarbons) can be useful for correlation with other gases, and allow to determine whether free and adsorbed gas have the same source. An additional advantage of the interpretation of the isotopic composition of gases is the possibility of recognizing gaseous artifacts (formed during drilling due to the high temperatures and the presence of hydrocarbons in the drilling fluid) [1, 17].

In gas geochemistry, most crucial is the dependence between the change of the isotopic composition of carbon and the increase of thermal maturity of source rock organic matter. δ<sup>13</sup>C of methane is increasing from approximately –100‰ in biogenic gas to –20‰ in “super mature” thermogenic gas [4].

The isotopic composition of methane, ethane and propane accurately reflects the maturity of organic matter (VR<sub>O</sub>) and the type of gas. Evaluation of the maturity of organic matter should not be made solely on the basis of the isotopic composition of carbon in methane. δ<sup>13</sup>C of ethane and propane should also be taken into account, since these compounds are more resistant to the secondary processes (oxidation) than methane. In addition, they are in traces in biogenic gases, so the mixed thermo-biogenic gas maturity level evaluated on the basis of isotopic composition of ethane and propane will be real [13, 15, 17].

In the case of gas exploration from shale formations, the isotopic composition allows to estimate the amount of gas in place and allows to recognize the so-called roll-over effect (inversion of carbon isotopic composition of methane, ethane and propane) [3]. Several studies of the stable isotopic composition of gases as a function of depth, thermal maturity, and gas wetness in unconventional shale gas accumulations have identified features described as isotope reversals/roll-overs. Such effects have been identified, for example, in Barnett, Fayetteville, Haynesville, Woodford, Appalachian and Horn River shale plays. In some cases, these features identify the most productive intervals within shale gas systems [3].

However, isotopic roll-overs and reversals are poorly defined. There are several types of reversals of stable isotopic compositions and roll-over of the isotopic composition of methane, ethane and propane with decreasing wetness and increasing depth. Generally roll-over effect is the reversion of normal δ<sup>13</sup>C values from δ<sup>13</sup>C<sub>1</sub> < δ<sup>13</sup>C<sub>2</sub> < δ<sup>13</sup>C<sub>3</sub> to δ<sup>13</sup>C<sub>1</sub> > δ<sup>13</sup>C<sub>2</sub> > δ<sup>13</sup>C<sub>3</sub>. The most common explanation for roll-over is secondary cracking in shale rock and mixing of normal, oil associated gas with a non-associated gas containing a relatively low concentration of isotopically light ethane. Another theory holds that the roll-over effect, may be a natural steam reforming reaction, where hydrocarbons in the presence of water and a ferrous catalyst at 180–200°C undergo a Fischer–Tropsch like conversion [6, 11, 14].

The aim of this work was to show the usefulness of chemical and isotopic composition analyses for the evaluation of shale gas systems, especially for the determination of the generation phase and thermal maturity level on the example of polish shale formations. Estimated shale gas and shale oil resources in Poland are significant and should be a target of detailed assessment [2, 7].

## Methods

Analysis of the chemical composition of the gas samples were made using the Agilent model 7890 A chromatographs, equipped with TCD and FID detectors. Carbon isotopic composition of individual gaseous hydrocarbons was determined

using isotope Delta V Advantage spectrometer with chromatograph Trace GC Ultra from Thermo Scientific. Column used during analysis: HP-PLOT/Q with a length of 30 meters and an inner diameter of 0.32 mm.

During the performing of the Blue Gas project “MWSSSG” Isologica software was purchased and was used for interpretation of geochemical data, especially gas chemical and isotopic composition. It is a visualization-

interpretation software with a statistical module and chart templates. The software was used for statistical analysis and interpretation of geochemical data from shale gas exploration.

**Results**

Analyses of chemical and isotopic compositions were performed for gas samples from degassing cores. A total amount of 23 samples were acquired during the drilling of two wells located in the north (well A – Baltic basin, 9 samples) and south (well B – Lublin basin, 14 samples) of Poland. Both wells were exploring Silurian and Ordovician shale formations. For well A  $\delta^{13}C$  values for methane vary from  $-50.9$  to  $-46.6\text{‰}$ , for ethane from  $-40.1$  to  $-38.4\text{‰}$  and for propane from  $-32.9$  to  $-31.7\text{‰}$ . For well B  $\delta^{13}C$  values for methane vary from  $-44.1$  to  $-36.1\text{‰}$  and for ethane from  $-39.9$  to  $-35.4\text{‰}$ . Propane amounts were insufficient for  $\delta^{13}C-C_3$  determination in most of the gas samples, only one value was acquired ( $-31.6\text{‰}$ ). Values of  $\delta D$  in methane vary from  $-212.3$  to  $-205.3\text{‰}$  for the A well and from  $-184.6$  to  $143.2\text{‰}$  for the B well.

The isotopic composition of carbon in the methane, ethane and propane, with increasing maturity of organic matter from which the gas is generated, is changing to gradually higher values. In the case of the primary cracking of the kerogen (first or second type) methane  $\delta^{13}C$  value of about  $-50\text{‰}$  is the beginning of the oil window and equals to approximately  $-40\text{‰}$  at the end of the oil window [5, 16, 17]. The isotopic composition of methane carbon from well A samples

corresponds to the beginning of the oil window and from well B samples corresponds to the gas window. In order to accurately determine the type of gas  $\delta^{13}C$  and  $\delta D$  values were plotted (Figure 1) [8]. Respective data of gases from well A

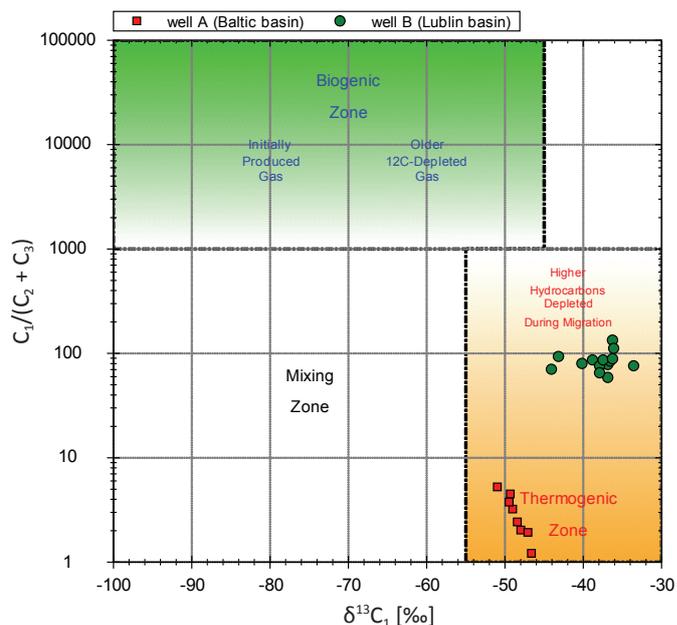


Fig. 2. Bernard diagram for two analyzed wells (Isologica chart template)

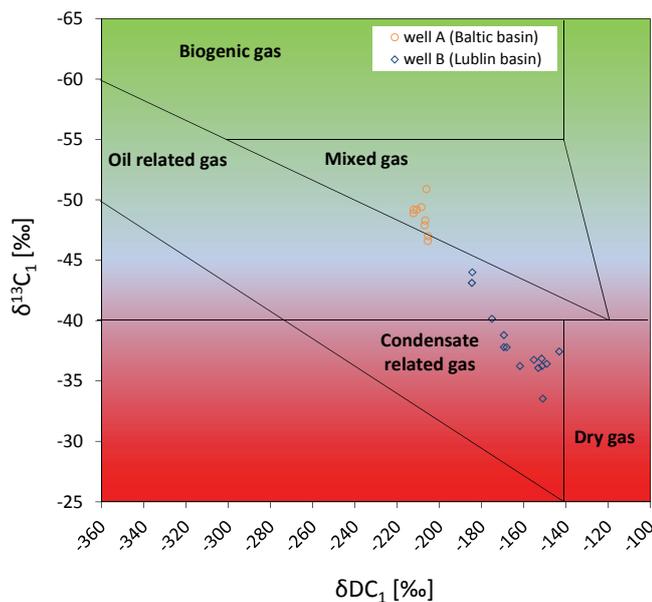


Fig. 1. Diagram indicating the type of gas, depending on the carbon and hydrogen isotopic composition of methane for two analyzed wells (modified after Peters et al., 2005) [8]

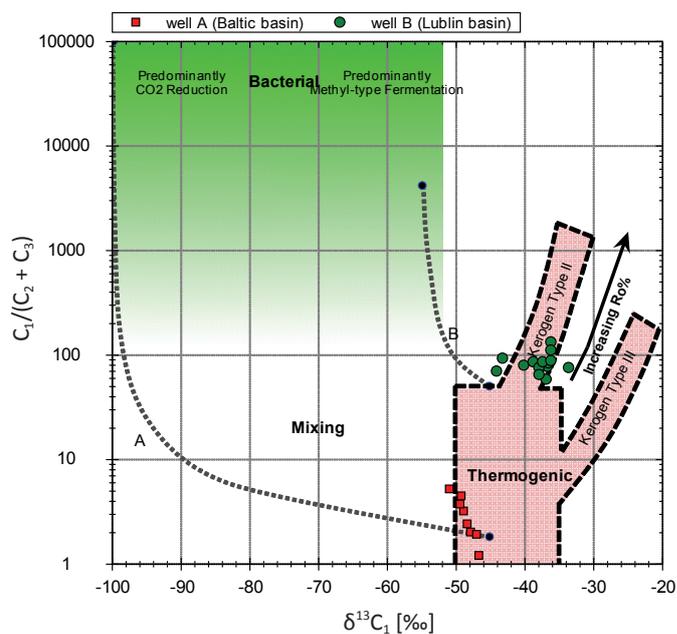


Fig. 3. Bernard/Whiticar diagram for two analyzed wells (Isologica chart template)

are located in the fields of mixed and oil related gases, while from well B they are located in the fields of condensate and oil related gases. Gases from the well located in northern Poland were generated on considerably lower thermal maturity level of organic matter than gases from the well located in southern Poland.

Chemical composition analyses allowed to calculate the wetness index, which values vary from 1.2 to 5.2 for well A and from 57.9 to 133.3 for well B. Bernard diagram (Figure 2) and modified Bernard/Whiticar diagram (Figure 3) also clearly distinguish well A and B gases. Additionally showing the difference in thermal maturity of organic matter and possible biogenic gas additive in well A gases.

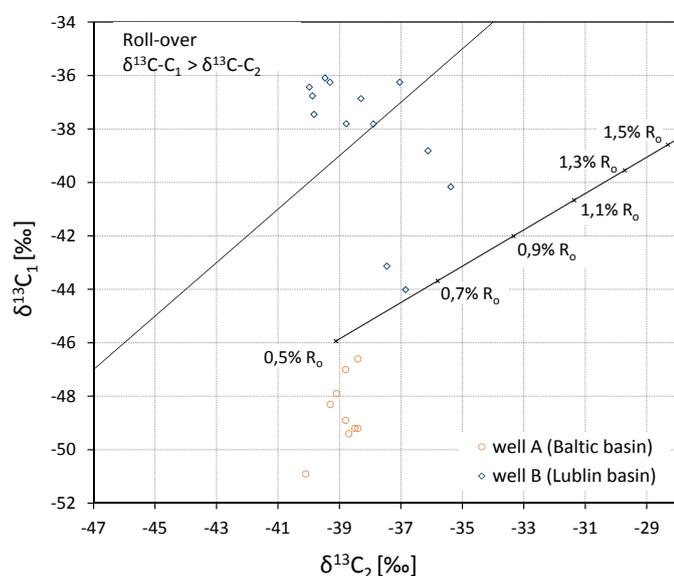


Fig. 4. Correlation between ethane  $\delta^{13}\text{C}$  and methane  $\delta^{13}\text{C}$  for two analyzed wells

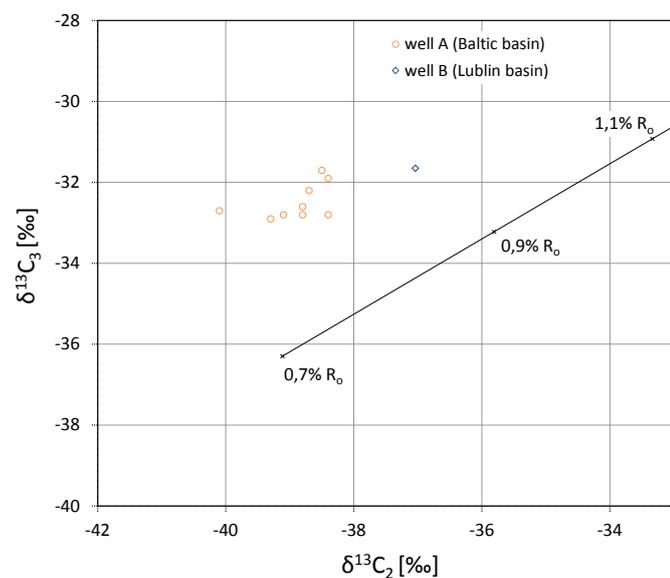


Fig. 5. Correlation between ethane  $\delta^{13}\text{C}$  and propane  $\delta^{13}\text{C}$  for two analyzed wells

The isotopic composition of methane, ethane and propane reflects the maturity of the organic matter ( $\text{VR}_o$ ) and the type of gas. These relationships are described by equations:

$$\delta^{13}\text{C}-\text{C}_1 (\text{‰}) = 15.4 \log_{(10)} \% \text{VR}_o - 41.3 \quad (1)$$

$$\delta^{13}\text{C}-\text{C}_2 (\text{‰}) = 22.6 \log_{(10)} \% \text{VR}_o - 32.2 \quad (2)$$

$$\delta^{13}\text{C}-\text{C}_3 (\text{‰}) = 20.9 \log_{(10)} \% \text{VR}_o - 29.7 \quad (3)$$

Equations 1, 2 and 3 allow to estimate maturity based on the isotopic composition of thermogenic gas (originating from the primary cracking of the kerogen type I and II) [17]. Data from the analysis of the isotopic composition of carbon in methane, ethane and propane are summarized on figures 4 and 5. Additionally, lines which are the theoretical values of the isotopic composition obtained from the above formulas, were plotted. The amounts of propane in most samples from well B were insufficient for  $\delta^{13}\text{C}$  determination, so on Figure 3 there is only one point from well B. In both graphs it can be seen that the isotopic composition of the samples, differs from the theoretical values. Ten samples from well B, have inverted isotopic composition (roll-over effect). This can result from the mixing of the gas with additional biogenic methane or the presence of gases from secondary cracking of crude oil. Additionally, differences in the degree of thermal maturity can be clearly determined.

The Isologica software chart template – marine shale model (Figure 6) allows to determine the thermal maturity of organic matter and percentage of bacterial fraction using  $\delta^{13}\text{C}$  of methane and ethane. Data from well A correspond to 0.8 to 1.0% vitrinite reflectance thermal maturity and show mixing with biogenic gas (approximately from 10 to 20%).

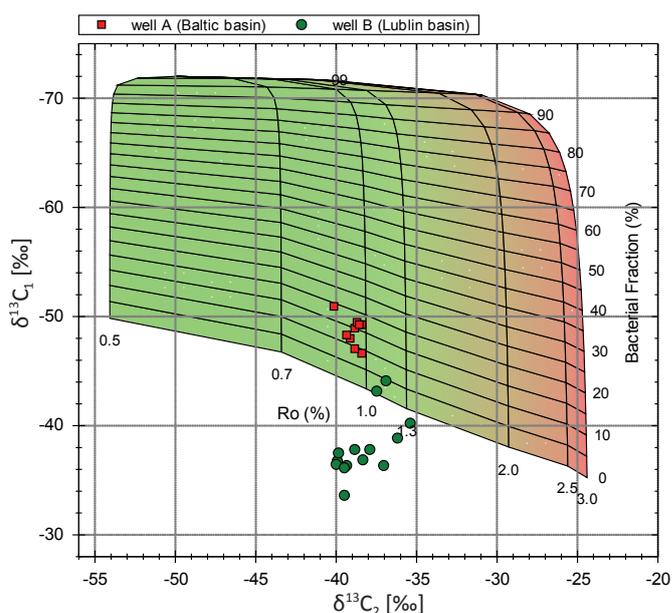


Fig. 6. Isotopic maturity – marine shale model for two analyzed wells (Isologica chart template)

From well B gas samples with roll-over effect are hard to interpret, but the other four samples correspond to 1.0 to

1.3% vitrinite reflectance thermal maturity with possible, low additive of biogenic gas in the case of two samples.

### Summary

Shale gas resource assessment needs good recognition of the mechanisms of hydrocarbons generation in shale rock. Geochemical characteristics of shale gas can be attributed to a few processes of shale gas generation:

- primary cracking of kerogen (when maturity increases, gas wetness index decreases and carbon isotope composition values of methane, ethane, propane and higher hydrocarbons increase),
- secondary cracking of different components of hydrocarbon (gas products from oil and condensate cracking have higher wetness and lighter  $\delta^{13}\text{C}$ ; but if components in gas start to crack, the gas becomes drier and the  $\delta^{13}\text{C}$  value of these components becomes heavier),
- fractionation related to expulsion (migration may cause fractionation between individual hydrocarbons with different molecular mass and structure, but this process influences isotopic fractionation slightly),
- combination or mixing products of several of the above processes (roll-over of  $\delta^{13}\text{C}_2$  can be obtained by mixing primary gas and secondary gas),
- other special processes in shale gas generation (roll-over of

$\delta^{13}\text{CO}_2$  composition in shale gas suggests water reforming and Fischer–Tropsch like reaction) [14, 15].

For the determination of all those processes analyses of chemical and isotope composition are significant and can provide very useful data. Polish shale formations (Baltic basin and Lublin basin) are varied and the chemical and isotopic compositions of natural gases acquired during shale gas exploration drillings are also diverse. The isotopic composition of methane carbon from well A samples corresponds to the beginning of the oil window and from well B samples corresponds to the gas window. Gases from the well located in northern Poland were generated on considerably lower thermal maturity level of organic matter than gases from the well located in southern Poland. Data from well A correspond to 0.8 to 1.0% vitrinite reflectance thermal maturity and from well B (four samples without roll-over effect) correspond to 1.0 to 1.3% vitrinite reflectance thermal maturity. Ten samples from well B, have inverted isotopic composition (roll-over effect). Polish shale formations are varied and natural gas composition analyses can be helpful for the correct prediction of the type and amount of natural gas in shale formations.

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