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Geological-geochemical assessment of occurrence and extraction of shale gas in Poland

Introduction

The idea of taking up works on shale gas at the Oil and Gas Institute had started even before the all-Poland boom for shale gas prospecting. The inspiration for these ventures were numerous discussions with American scientists and Polish-American cooperation started within the international non co-financed project executed by the Oil and Gas Institute and University of Oklahoma (*International Non Co-financed Polish American Project No 282/N-USA/2008/O*).

For many years research has been executed in the USA concerning new methods of assessment of unconventional reserves of natural gas which is considered a chance for diversification of the reserves of this precious, ecological fuel. In view of the fact that the reserves of hydrocarbons in Poland are running out and the possibilities of pointing out new prospecting areas are shrinking, it is advisable to reach for the partially known and partially utilized potential with reserves not depleted yet or not even evaluated thoroughly. For good prospecting and then extraction it is necessary, first of all, to elaborate research methods and technology which will be helpful in exploitation of unconventional deposits. The American companies which expansively enter the Polish market offer their technologies concerning the extraction itself and they hold several concessions for shale gas prospecting. However, although more and more reports of Energy Information Agency appear concerning resourcefulness of shale gas basins in Poland, the information is not based on reliable parameters and calculations but on estimations on the basis of archival data. In order to verify the news it is necessary to conduct additional research and calculations to meet the requirements of shale gas.

The common feature of '*shale gas*' and '*tight gas*' which distinguishes them at the same time from conventional accumulations of natural gas is their lack of spontaneous inflow into a drilled bore in volumes which would justify economic exploitation by traditional methods.

Clayey-mudstone complexes contain '*shale gas*' in micro pores, between laminas enriched with detritus components and also in natural crevices and micro fractures. Natural gas in shale is also absorbed by insoluble organic matter and by clayey minerals. The complexes of this type create specific hydrocarbon system in which the same rock formation is at the same time the matrix, sealing and collecting rock and hydrocarbons` migration occurs only in micro scale.

Shale gas is rated among the continuous-type accumulations, featuring large extension in space and occurring in rocks featuring low permeability and the presence of natural crevices. The forecast extraction period of such unconventional resources is estimated at 20–30 years.

These deposits are called unconventional because gas can be bound by organic matter or be absorbed by it. *Shale* gas can also be in thin layers of porous mudstone and in sandstone layer intrusions in shale series. In such cases gas is classified as free gas and it is extracted together with absorbed gas.

The significance of unconventional deposits in the world has been increasing systematically. In the United States, the country with the most developed oil industry targeted at unconventional sources of hydrocarbons, the shale gas reserves were estimated at 5÷10% of joint extracted reserves of natural gas but there are more and more discoveries which make the afore mentioned percentage likely to become much higher soon. Extraction of shale gas in 1996 reached 8.5 billion Nm^3 and in 2006 it was already three times more.

Apart from the American firms, only a few large international concerns such as BP, Total or Schlumberger can now exploit these deposits effectively [15, 16]. The obstacles are very expensive technologies which require high level of technical advancement in drilling horizontal bores at large depths (frequently exceeding 3 kilometers) as well as complicated and costly processes of hydraulic rock fracturing (creating artificial crevices) consisting in creating a system of fractures running concentrically to the borehole for even 900 m in order to connect the largest possible surface of rocks to the well.

Shale gas prospecting is mentioned more and more frequently in Poland and it has already even gained Polish terminology. However, before regular extraction is commenced it is necessary to prepare the entire geological, geochemical, engineering and deposit background which will allow the assessment of prospecting and exploitation risk. It requires interdisciplinary operations both in respect of introductory research as well as interpretation of results and then engineering decisions.

Possibilities of occurrence of unconventional deposits of natural gas in Poland and criteria for estimating its reserves

The areas in Poland which feature the largest potential of occurrence of gas in shale of large thickness and thermal maturity are related to Ordovician and Silurian formations in the Baltic and Lublin-Podlachia basins. Hence the interest in Poland which – as Pawel Poprawa of the State Geological Institute claims – has considerable extraction potential, maybe even the largest in Europe. The local shale is located at depth from 500 to 4000 m in

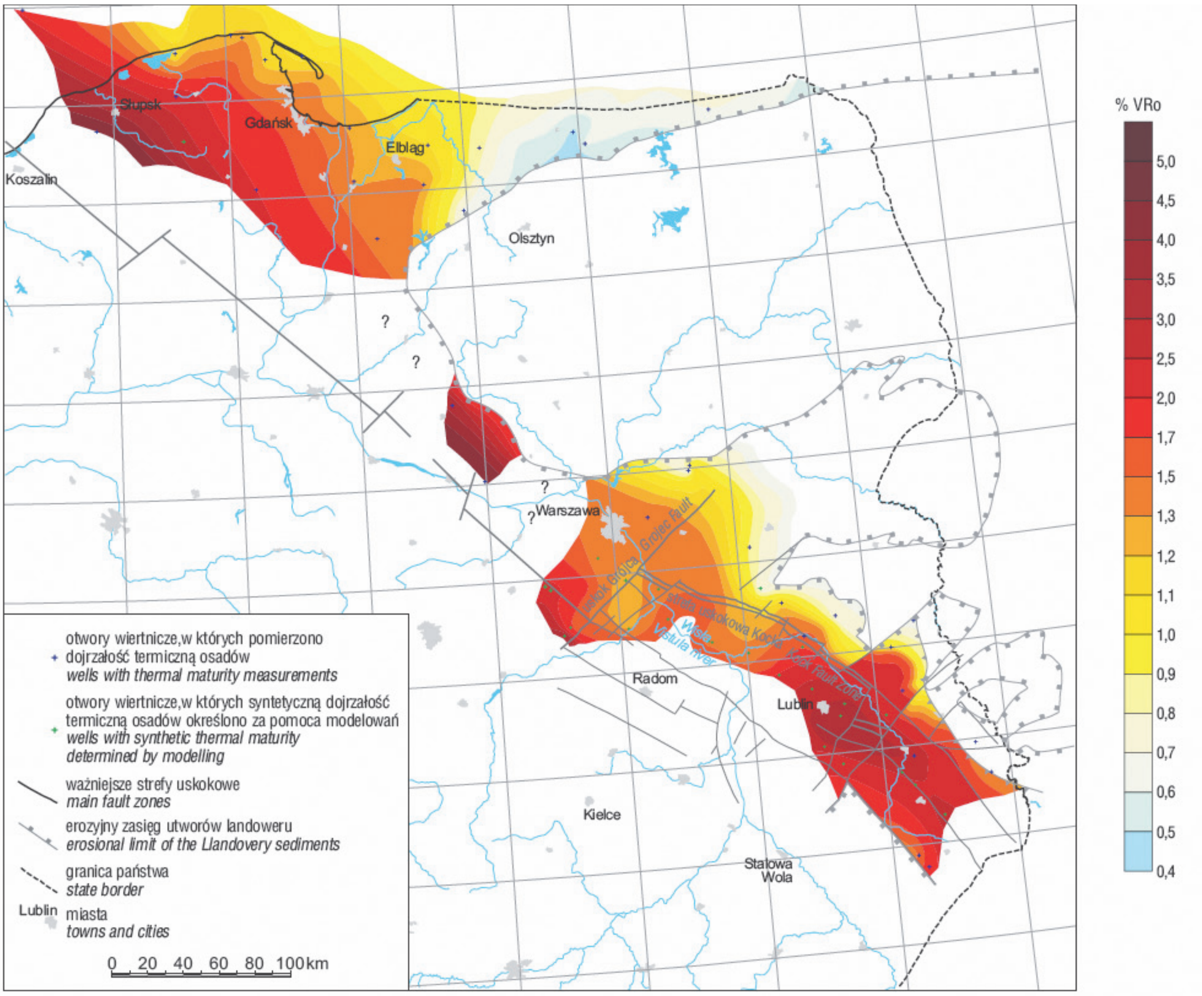


Fig. 1. Map of thermal maturity (in vitrinite reflectance % VR_o) of bores of lower Silurian (Landover) on the Western slope of the East European Craton [14]

some sedimentary basins. The most promising is the zone passing across Poland from central Pomerania to Lublin area and the area in the Sudeten Foreland.

According to preliminary geochemical prospecting, the largest potential in Poland in respect of shale gas prospecting is featured by the areas with clayey mudstone formations of large thickness, rich in organic substances featuring high level of thermal alteration. In Poland it is possible to select a few such regions where these criteria are fulfilled to larger or smaller extent [18]:

- The Baltic basin – Ordovician and Silurian formations,
- Lublin – Podlachia basin – Ordovician and Silurian formations,
- Carpathian Foredeep – Ordovician and Silurian formations,
- Carpathian Foredeep – Miocene formations,
- Wielkopolska region of Poland – Carboniferous formations.

Introductory prospecting was made for these regions to determine the content of organic substance and thermal maturity level (Fig. 1), which is crucial for selecting the sweet spot for shale gas. All these estimations were made on the basis of archival data and now they will require more detailed approach on the basis of more specific research on both archival samples as well as new ones from newly drilled bores.

Substantial limitation for the occurrence of shale gas accumulation and extraction is also, apart from geochemical criteria, lithological diversity of borehole profiles, their saturation with water and tectonic involvement of the area.

The elements which should be taken into account during the assessment of possibility and profitability of exploitation of unconventional gas deposits can be divided into four main categories according to their importance and each of these categories refers to a different set of necessary information. Figure 2 presents a list of information which should be taken into consideration during estimation of a shale gas deposit (according to George E. King, Apache).

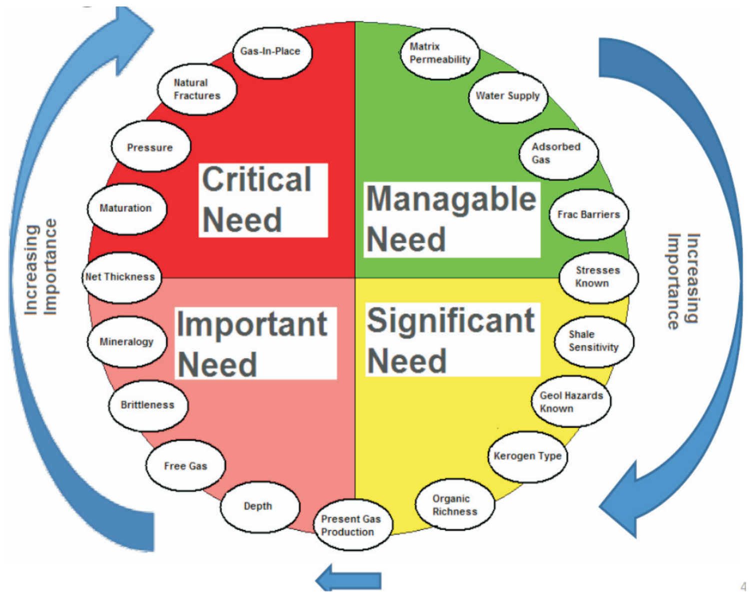


Fig. 2. Elements of characteristics in prospecting for unconventional gas deposits which should be considered according to their importance (George E. King, Apache)

This diagram shows how important the interdisciplinary approach is in operations and involvement of various laboratory research, a part of which may be adapted from research elaborated for conventional gas deposits and some of them require certain modifications resulting from specific features of shale gas.

Shale gas systems may include gas of two types: biogenic (which is rarely spoken of in Poland) or thermogenic, but this type of gas may be a mixture of the both gas types. The biogenic gas includes usually dry gas absorbed by organic matter and may be characterized by isotope content analysis.

Organic geochemical research in prospecting for unconventional gas deposits should follow two directions simultaneously – in respect of matrix rock and natural gas characteristic.

As for matrix rocks it is important to determine:

- richness in organic substance (*TOC*),
- level of thermal maturity (*VR*, T_{max}, *PI*, *TR*),
- kerogen type classification (kerogen type).

While in case of gas the following should be determined:

- gas characteristic and at which stage it has been formed,
- whether gas accompanies the oil, if it is generated at the site or it migrated; relation of free gas to adsorbed one,
- modeling of gas generation kinetics.

The condition for presence of a good system of *shale* gas type is first of all the occurrence of good quality matrix rocks with high generative potential. Equally important is the possibility of occurrence of processes of primary and secondary kerogen and residual crude oil cracking, sufficient adsorption of crude oil in the rock which undergoes cracking, increase in porosity due to destruction of organic matter and mineralogical content which provides rock brittleness properties [9, 16].

An important parameter is thermal maturity of rocks as it determines gas composition (gas quality). If the alteration is within the range from 0.7 to 1.0% R_o then we can expect deposits of gas which accompanies crude oil. While levels above 1.4% R_o we can expect continuous gas inflow. The Barnett shale is estimated to contain 30% of gas which accompanies crude oil. In rock of lower maturity at the presence of liquid hydrocarbons, the inflow of gas is considerably lower because liquids are occluded in porous space and they inhibit the gas flow. In the result, gas inflow is diminished and its extraction quickly decreases. The samples of high thermal maturity are featured by higher range of gas flow due to crude oil and kerogen cracking. The thermal conversion leads to destruction of organic matter, which indirectly increases porosity and creates convenient conditions for accumulation of larger volumes of gas. Therefore, the precise measurement of thermal maturity requires particular attention, especially in Palaeozoic formations where vitrinite macerals are absent and in case of hydrocarbon absorption the parameter T_{max} received from pyrolysis is not always reliable. In many cases it will be necessary to calibrate the value R_o for the particular type of substance with other parameters of maturity. The parameter R_o is the most popular to determine maturity and it has many advantages, such as a relatively low cost of measurement, a very wide measurement range from the diagenesis stage to metamorphism, calibration of scale with known stages of generation and bitumination, the possibility of calculating a paleothermal gradient as well as stratigraphic discontinuities. Unfortunately vitrinite reflectance has its limitations and faults which include a limited range of occurrence, redeposition of organic matter or the quality of cores taken (drilling fluid contamination, weathering of rocks). Measurement of vitrinite reflectance may be done in two ways: on isolated kerogen or on slices of the entire rock. Both of these methods are used in the Oil and Gas Institute. Marking of the thermal maturity level is important not only for determining of thermal profile but it is also connected with possibilities of recovering gas from absorbed crude oil when reservoir temperature rises. At higher temperature the adsorption ability drops substantially.

As it has been mentioned many times, gas shale is the matrix, therefore its classification is made according to principles binding in crude oil geochemistry, i.e. organic substance may be classified as one of three types of kerogen with particular maceral composition. The amount of deposited organic matter is demonstrated by % *TOC* with reference to the entire rock but quality is equally important as it determines both the volume and quality of generated hydrocarbons as well as range of generation in temperature over time scale. Meanwhile, the most popular indicator determining thermal maturity is vitrinite reflectance, i.e. the maceral originating from woody plant stems. The oil window corresponds to the range of approx. 0.5÷1.3% R_o and gas window 1.1% and above, while in the oil window generation of gas is also possible in smaller volumes.

Thus, from the geochemical point of view, for selecting the areas for prospecting for shale gas, maps of *TOC* distribution should be elaborated with maturity and transformation of organic matter and determined locations of source rocks.

In case of matrix rocks characteristic for shale gas, genetic examinations are more difficult for the lack of possibility of using biomarkers, which are usually present in extractable organic matter but only to a certain level of thermal maturity. Therefore, the only kerogen examinations that can be done are those by means of *Rock-Eval* pyrolysis, analysis of elementary and maceral composition and mineral contents. The type of kerogen as presented in Fig. 3 determines chiefly the character and proportions of produced hydrocarbons.

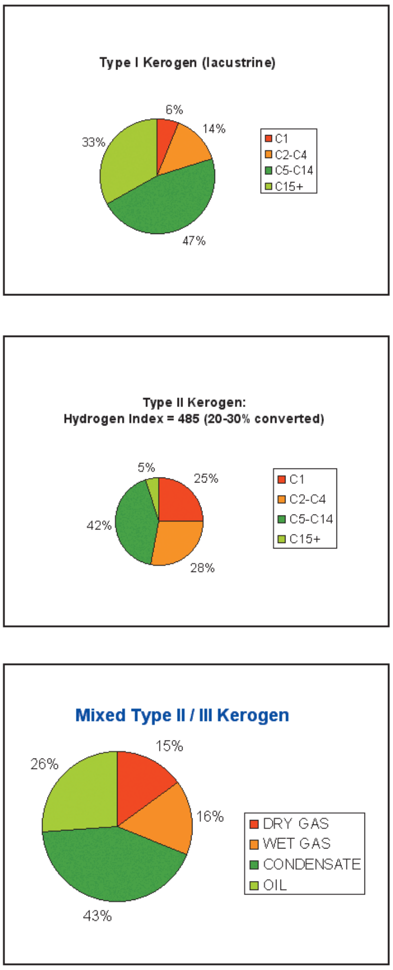


Fig. 3. Proportions of generated hydrocarbons depending on kerogen type

Of course these proportions of hydrocarbon generations for each type of kerogen undergo changes during thermal alteration of the matrix, which for the *Barnett* *shale* classified as mixed kerogen type II/III is illustrated in Fig. 4. A crucial process is cracking of generated liquid hydrocarbons to wet (46%) and dry (52%) gas at thermal maturity 1.4% in vitrinite reflectance scale. Kerogen quality has crucial meaning also in calculating primary richness in organic matter as its conversion proceeds in different degrees and so:

- type I – maximal conversion 70%,
- type II – maximal conversion 40%,
- type III – maximal conversion 20%,

Therefore, if we know the present TOC_{Ob} value and the degree of thermal conversion, we can reconstruct the initial TOC_p values,

- type I: $TOC_{present} = 1.00\%$, $TOC_{primary} = 3.33\%$,
- type II: $TOC_{present} = 1.00\%$, $TOC_{primary} = 1.67\%$,
- type III: $TOC_{present} = 1.00\%$, $TOC_{primary} = 1.25\%$.

For these primary values of $TOC_{primary}$ it is possible to calculate the primary generative potential, which later finds application in modeling of hydrocarbon generation.

The next information should concern the level of kerogen *TR* transformation, which is the function of organic facies and the level of thermal maturity.

$$TR = (HI_{\text{primary}} - HI_{present})/HI$$

For model Barnett shale samples it is assumed that initial *HI* amounted to about 434 mg *HC*/g *TOC*, which in respect of the current value *HI* = 45 mg HC/g *TOC* means that *TR* is at the level of 89%. Meanwhile, altered samples of lower degree with current value *HI* = 300 mg *HC*/g *TOC* will feature the value of conversion level *TR* = 31%, i.e. they will produce liquid hydrocarbons and smaller amounts of gas. Therefore, in *shale* gas examination the analysis determining generative potential in form of *HI* and S_2 parameters is necessary, which enables the assessment of productivity for gas (Fig. 5).

In case of research for *shale* gas and assessment of matrix rocks according to the above scheme it is possible to use partially the archival core samples or boring sam-

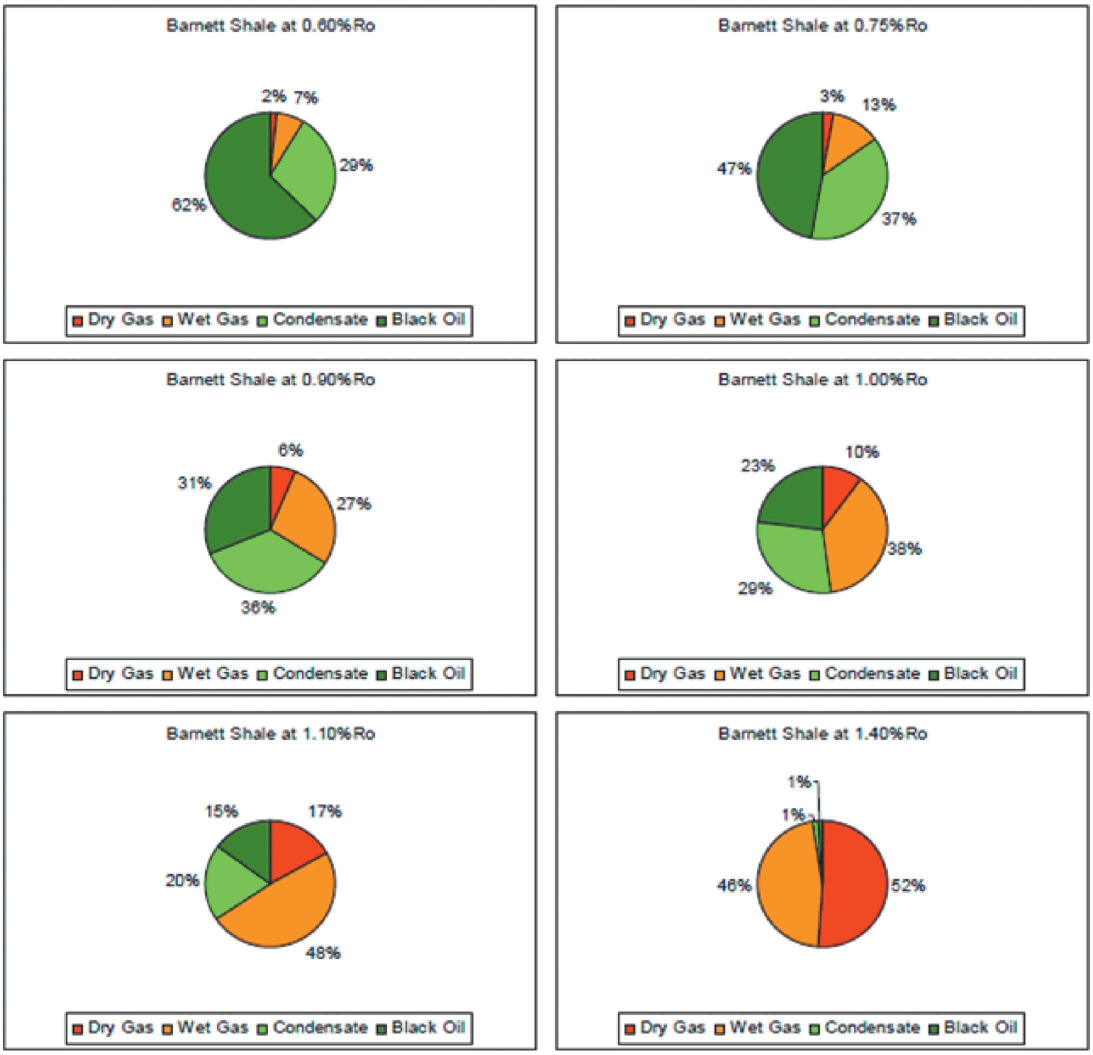


Fig. 4. Fractions of hydrocarbons generated from *Barnett Shale* at different stages of thermal alteration

ples as the time of sample storage does not influence the quality of necessary parameters. It has to be noted however that other parameters e.g. S_1 may be lowered due to loss caused by storage of samples. Such tests were conducted on selected samples of Silurian shale from various regions of Poland within the Polish-American project, which allowed to distinguish a few groups of matrix rocks differing in their abilities to generate crude oil or gas (Fig. 6).

Much of this information can be obtained from pyrolytic *Rock-Eval* analysis, which has an additional advantage that due to popularity of this method it is possible to compare different sediments examined in the world, especially those determined for *shale* gas prospecting. A very useful geochemical parameter to characterize *shale* gas concerns, as it was mentioned before, the level of thermal maturity, which can be determined also by T_{max} and recalculated into the value corresponding to vitrinite reflectance VR_o, which is the measurement of changes in chemical structure of vitrinite and its ability to reflect light. On the basis of many results of research performed for *Barnett Shale,* Jarvie elaborated a formula for recalculating R_o from T_{max} [10].

$$Cal.\%\,VR_o = 0.018 \times T_{max} - 7.16$$

For other shale kinds characterized for *shale* gas trends should be the same or similar. It turned out that the measured values R_o are usually higher than the ones calculated according to the formula elaborated by Jarvie [8, 9].

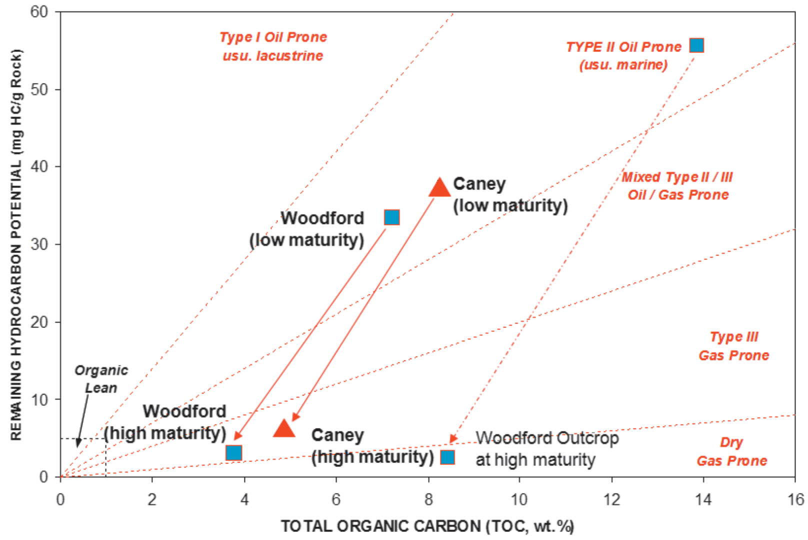


Fig. 5. Difference in S_2 parameter values for samples of low and high thermal maturity (on the basis of research in Oklahoma [15])

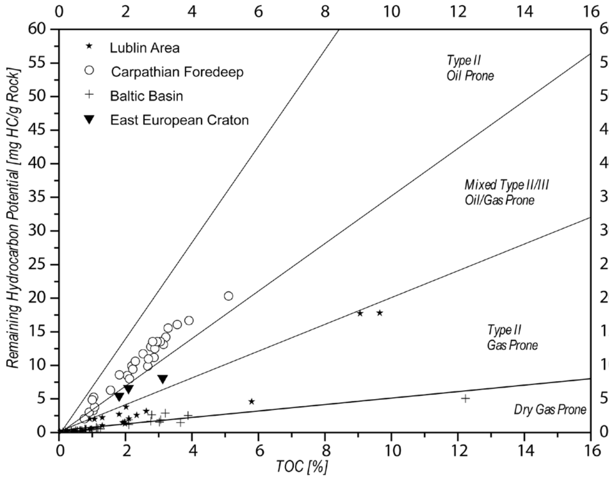


Fig. 6. Current S_2 and *TOC* values for examined Silurian shale in four basins assigned for *shale* gas prospecting in Poland

Gas characteristic – interpretation of trends of isotope fractioning of gases according to stages of generating

Natural gases are usually analyzed in two ways for requirements of *shale* gas:

1) in order to determine the molecular content, on the basis of which it is determined as follows:
   – humidity, i.e. (C_1/C_2+),
   – maturity (C_1/C_2+; and C_4/nC_4),
   – biogenic/thermogenic (on the basis of contents in relation to isotopes),
2) in order to determine isotope contents, where isotopes of carbon and hydrogen are analyzed (d13C and dD).

These two features provide information concerning the type of production and allow correlating the gas from known accumulations with the gas received from simulations of generation processes on a laboratory scale. In geochemistry it is known that most bonds in compounds included in kerogen and crude oil have bonds 12C–12C, fewer bonds 12C–13C and the fewest bonds type 13C–13C. During generation of gas the first to undergo destruction are bonds 12C–12C, which means that the gases from early generation will feature lower isotope values as they will be enriched with carbon 12C and residual crude oil and kerogen will then be isotope heavier as they will include more carbon 13C. With the increase of thermal alteration isotope contents of gas will be enriched by 13C, i.e. gases will be isotope heavier.

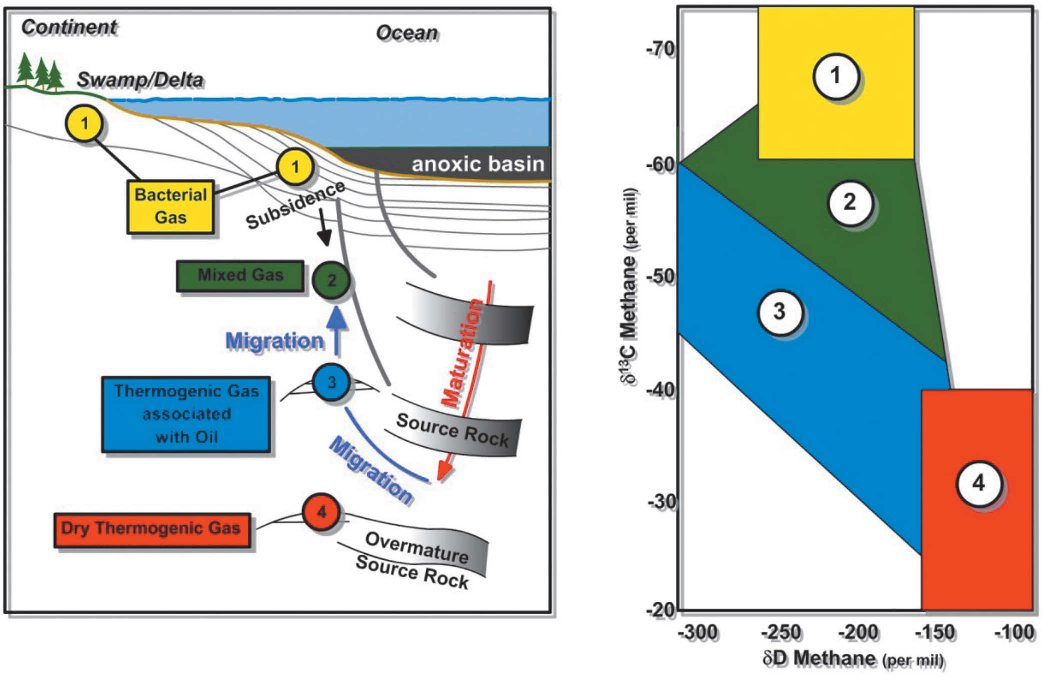


Fig. 7. Changes of isotope content depending on the origin of gas [15]

The isotope content of gas depends also on the source organic matter from which it is generated, so indirectly we can draw conclusions concerning the type of sedimentation and environment, which is illustrated by the drawing below (Fig.7).

Apart from carbon isotopes also hydrogen isotopes are determined and interpreted together with isotopes of carbon. In this way it is possible to separate groups of biogenic, thermogenic and mixed gases [1, 17].

New analytical techniques such as e.g. GCIRMS allow the isotope analysis of particular gas components and also hydrocarbons with higher number of carbon atoms, which allows to correlate gases and condensates. In case of *shale* gas it is a very important research element because one basin with high maturity contains both gases and condensates. Such analyses were made for a large number of samples for *Barnett* shale from Fort Worth Basin in Texas [7, 17] and for Polish oil systems.

Understanding the changes in isotope composition of gases generated with the increase of thermal alteration level in the shale of *Barnett Shale* type is the key for complete understanding of processes in which these gases were generated. In the first place it is necessary to differentiate if they were processes of direct cracking of kerogen or of the secondary thermal cracking of hydrocarbons generated at earlier stage. These two processes will appear at various depth levels i.e. at different thermal maturity. For *Barnett Shale* analyses were made of individual gas components and conden-

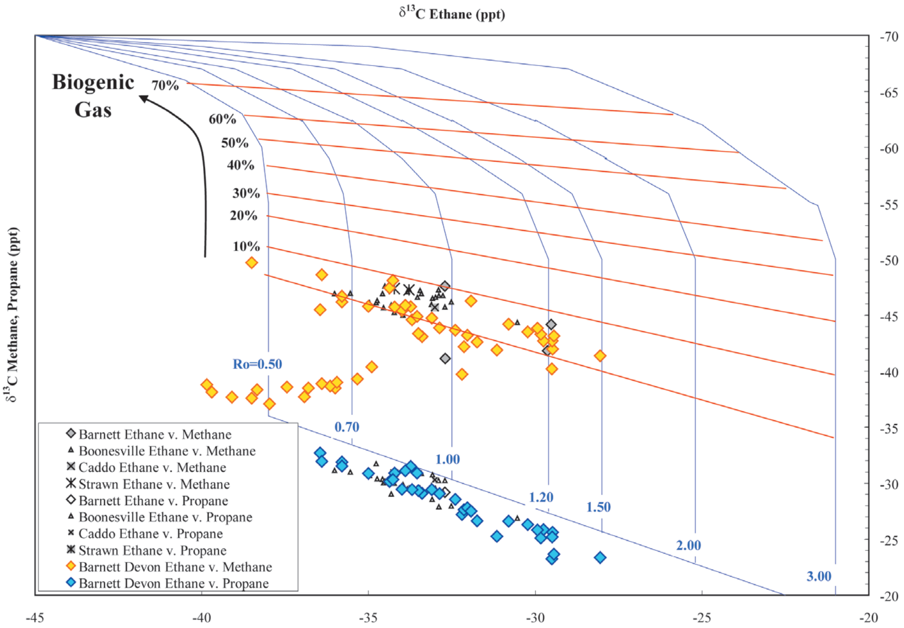
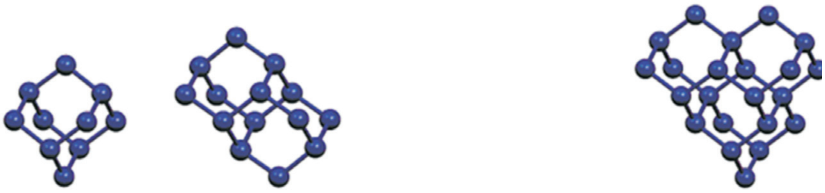
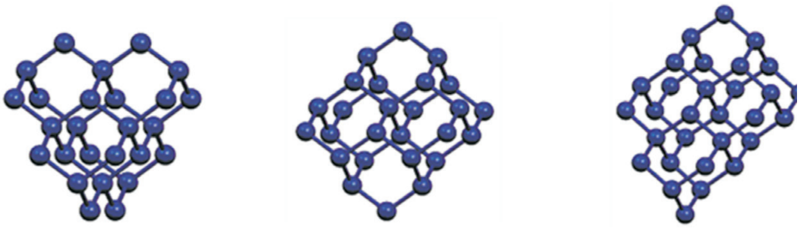


Fig. 8. Correlative diagram for predicting the stage of generating gas on the basis of isotope contents of methane, ethane and propane and vitrinite reflectance measurement [15]

sates and additionally the level of thermal maturity of condensates was determined with application of new adamantane indicators. The results of isotope research were correlated with measured vitrinite reflectance values which were measured on cores and surface samples. On this basis a method was elaborated of predicting the thermal maturity level from isotope measurements (Fig. 8). This model was then calibrated on the basis of water pyrolysis experiments made on samples – equivalents of immature *Barnett Shale* [15].



Structures of diamondoids



Structures of higher diamondoids

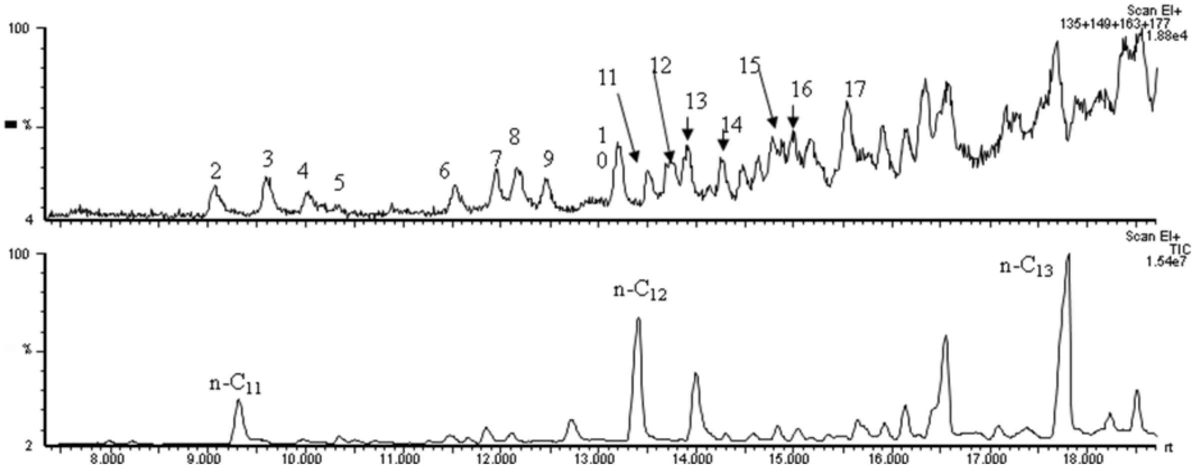


Fig. 9. Mass spectrogram of saturated fraction with extracted adamantane compounds

For examined formations of *Barnett Shale* two principal groups of gases were separated, among other things on the basis of the presence of higher hydrocarbons. Isotope content of these gases differs in the range from –37,1% to –49,7%, which is characteristic for thermogenic gases.

It means that these gases – as unconventional – are generated directly from shale ‘*in situ*’, at high level of thermal maturity of sediments but in two stages. The gases were accompanied by condensate deposits for which thermal maturity level can be determined using specific compounds – adamantanes [2, 3]. The values of methyl adamantane indicator calculated according to their content in condensates were considered equal to vitrinite reflectance measured for *Barnett Shale* [15].

Diamondoids are hydrocarbons with rigid, three dimensional structure similar to that of a diamond. They form homologous row with a generalized formula $C_{4n} + 6H_{4n+12}$ and these compounds include adamantanes, diamantanes, trimantanes, tetramantanes and higher polymantanes.

Peaks of adamantanes on a chromatogram showing record of GC/MS analysis are located between peaks of $n\text{-}C_{10}$ and $n\text{-}C_{13}$ (n-alkanes).

There are two isomers of methyl adamantane: 1 – methyl adamantane (peak no 2) and 2 – methyl adamantane (peak no 6), the first one of which is more thermally stabilized.

On the basis of decomposition of these compounds indicators are calculated, which can also be related to the vitrinite reflectance scale.

MAI = 1-MA/(1-MA + 2-MA) [%]
1-MA – 1-metyladamantane
2-MA – 2-metyladamantane
MDI = 4-MD/(1-MD + 3-MD + 4-MD) [%]
1-MD – 1-metyldiamantane
3-MD – 3-metyldiamantane
4-MD – 4-metyldiamantane

MAI [%] Methyl Adamantine Index	*MDI* [%] Methyl Diamantane Index	*Ro* [%]
50÷70	30÷40	1.1÷1.3
70÷80	40÷50	1.3÷1.6
80÷90	50÷60	1.6÷1.9
>90	>60	>1.9

Measurements of thermal maturity interpreted together with isotope contents may be then used for modeling the level of thermal maturity at which gases were generated [1, 7]. Such a model can be used for predicting the level of alteration for gas generation and thus the levels of deposition of sediments from which generation occurred but it should be calibrated individually for different matrix rocks.

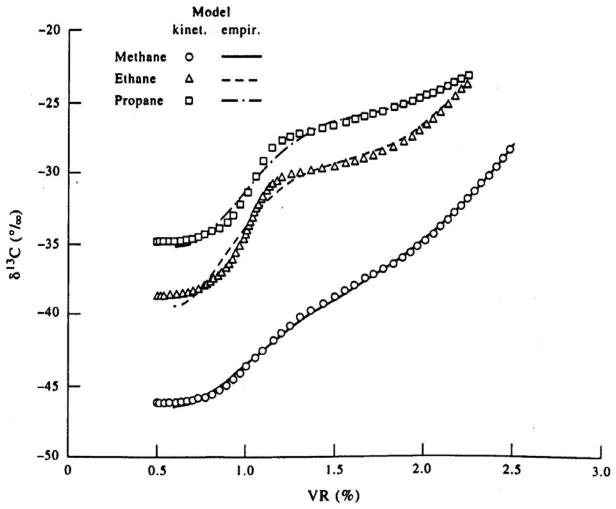


Fig. 10. Empiric models describing gas generation with algae type kerogen according to Berner's model [1]

Integration of geological analysis with results of geochemical research studies

Integration of geological-structural characteristics and facial secretions with results of geochemical research may only constitute the basis for planning prospecting and exploitation works concerning *shale* gas [4, 5, 6].

First of all, it is necessary to separate zones most suitable for prospecting, i.e.:

- separate the lithofacies which will be most productive in horizontal drilling for *shale* gas,
- define lithofacies and parasequences,
- determine organofacies,
- make a model of gas generation in laboratory conditions.

The stratigraphic, biostratigraphic, and mineralogical-petrographic analysis leads to construction of sequential model of examined basin. Conventional assessment of genetic potential of matrix levels is more general as it assumes homogeneity of matrix rocks and statistic calculations are executed there. However, matrix rocks are not in fact a homogenous sedimentation body but a heterogenic one which is caused by temporary literal and vertical changes of sedimentation facies. It is an inseparable phenomenon of history of depositing sediments of matrix rock. Therefore, if we want to determine very precisely genetic (generative) potential of a particular basin we have to devote much time to determine history of depositing and organic facies related to it. On this basis it is possible to draw maps of distribution of generative potential with consideration of all parasequences.

Such approach not only answers the question how high the genetic potential is but it also provides answers to some other questions:

- what type is the hydrocarbon potential?
- what are the petrographic facies (where the source material comes from)?
- what is thermal stability of sediments (i.e. how easy it undergoes thermal destruction)?

The above approach requires application of modeling generation and assessment of product quality (predicting the hydrocarbon composition) in regional scale. It means that each facies should be defined and examined separately.

The processes of simulation of hydrocarbon formation should determine quantitatively and qualitatively the received products formed due to cracking, which in dry pyrolysis leads finally to formation of pyrobitumen as well (Fig. 11).

Within the frames of Polish-American cooperation at the university laboratory in Oklahoma experiments of pyrolysis were conducted using a small number of samples which will be applied in assessment of unconventional deposits of *shale* gas type. These were Paleozoic samples from the Carpathian foreland where currently no prospecting works of shale gas are executed.

In anhydrous pyrolysis MSSV-Py the process is executed in closed conditions and includes reactions of cracking I and II.

On the basis of pyrolysis experiments information is obtained concerning the type of generated gases which can be correlated with gases accumulated in conventional deposits. After pyrolysis, the sample is analyzed chromatographically, which allows to attribute the particular chromatographic record to separated organic facies. Besides,

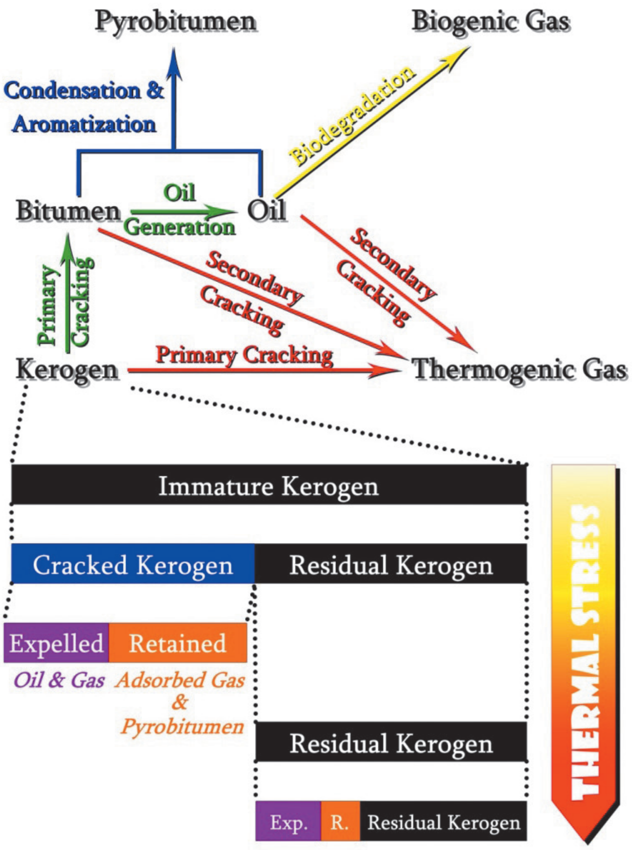


Fig. 11. Scheme of formation of hydrocarbons due to thermal alteration of kerogen [7]

these experiments provide information concerning kinetic parameters of kerosene, which is necessary for calculation of output and velocity of produced *shale* gas.

The condition for obtaining reliable results of pyrolysis MSSV-Py is introduction of non-oxidized samples featuring low thermal alteration. Recommended parameters of samples applied to determine activation energy are:

$T_{max} < 430^{\circ}\mathrm{C}$

$OI < 100\ \mathrm{mg\ CO_2/g}\ TOC$

$HI > 200\ \mathrm{mg\ HC/g}\ TOC$

$TOC > 5\%$.

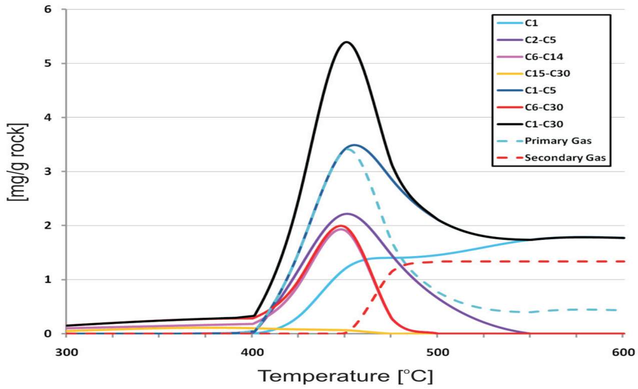


Fig. 12. Generation curves for Paleozoic formations from micropyrolysis experiments

Gas hydrocarbons are generated within the range C_1–C_5 in small amounts in the beginning of thermal degrading of kerogen but at temperature increase their share is predominant. Methane is a dominating component of gas generated at 395°C at temperature increase 1°C/hour. Similar trends were observed for immature samples and the ones with higher maturity. Output of hydrocarbons C_2–C_5 increases exponentially at higher temperature. Maximal output is achieved at temperature 423°C. At further increase of temperature cracking of hydrocarbons C_2–C_5 occurs. In pyrolysis there was a limit to certain level of maturity equaling 2.2% R_o, so the secondary cracking was much reduced. Based on pyrolysis, the output of received gases and activation energy were calculated.

As model samples for *shale* gas in works executed by the Oil and Gas Institute are shale samples belonging to *Barnett Shale* formation in Texas. At any prospecting works they serve as geochemical, lithological, facial and geological model. It is due to successful production of unconventional gas from *Barnett*, *Fayetteville* and *Woodford* shale in the USA, where only the *Barnett Shale* provides already 10% of total extraction of natural gas in 48 states. On this basis it is possible to draw a scheme of geochemical and geological research which should be performed in every basin where s*hale* gas prospecting is to be conducted.

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