

Sergii Vakarchuk

SE Naukanaftogaz – Research Institute of Oil & Gas Industry, NJSC Naftogaz of Ukraine

# Main stratigraphic levels of carbonate rocks and their connection with the possibilities of unconventional hydrocarbons deposits development in the Paleozoic sedimentary basins in Ukraine

The paper deals with the unconventional petroleum potential of the Paleozoic carbonate sedimentary rocks in the petroleum basins of Ukraine. The study is based on tectonic-structural, petrophysical, geochemical and production data analysis for the carbonate and calcareous shale Paleozoic rocks. Such parameters as lithological composition, TOC values, type of dispersed organic matter and its thermal maturity, porosity and permeability, as well as thickness and depth to prospective intervals or units were analyzed. Based on this study several prospective lithostratigraphic units to search for such unconventional hydrocarbon accumulations in the Paleozoic formations of the Dnieper-Donets intracratonic, Volyn-Podillya pericratonic, and Dobrogea foredeep basins were identified.

Key words: carbonate rocks, unconventional source of gas, shale gas, tight gas.

## Główne poziomy stratygraficzne skał węglanowych i możliwości występowania w nich niekonwencjonalnych nagromadzeń węglowodorów w paleozoicznych basenach sedymentacyjnych Ukrainy

W artykule omówiono perspektywy występowania niekonwencjonalnych nagromadzeń węglowodorów w skałach węglanowych i ilasto-węglanowych w obrębie paleozoicznych basenów naftowych Ukrainy. Studium oparte jest na wynikach analiz strukturalno-tektonicznych, petrofizycznych oraz geochemicznych badaniach formacji węglanowych i ilasto-węglanowych. Analizowane były takie parametry jak: wykształcenie litologiczne, zawartość TOC, typ rozproszonej materii organicznej i stopień jej dojrzałości termicznej, porowatość, przepuszczalność, miąższosć i głębokości zalegania obiecujących horyzontów. Na podstawie przeprowadzonych badań zidentyfikowano kluczowe poziomy stratygraficzne oraz rozprzestrzenienie skał węglanowych perspektywicznych dla poszukiwań niekonwencjonalnych złóż węglowodorów w paleozoicznych basenach Dnieprowsko-Donieckim, Wołyńsko-Podolskim i Zapadlisku Przeddobrudzkim.

Słowa kluczowe: skały węglanowe, niekonwencjonalne złoża gazu, gaz związany.

## Introduction

An analysis of recent developments and trends of oil and gas exploration and production in Ukraine testifies, that at recent conditions the achievement of substantial growth in oil and gas production, is only possible by the development of so-called unconventional hydrocarbon (HC) sources. First of all, to such sources most researchers attribute shale gas and tight gas to arenaceous rocks (basin-centered gas systems).

At the same time, the practice of developing unconventional resources in North America, demonstrates that other lithological types, namely carbonates and calcareous shales, have quite similar hydrocarbon potential when compared to black shales and arenaceous rocks. For example, over 30% of annual unconventional oil and gas production in the USA, comes from carbonates and shale carbonate sedimentary rocks

Era	System	Series	Stage	Boundary dates, Ma	Stratigraphic levels			
					Dnieper-Donets basin	Volyn-Podillya basin	Dobrogean foredeep	
Paleozoic	Permian	Lopingian	Changhsingian	252.17 ±0.06				
			Wuchiapingian	254.14 ±0.07				
		Guadalupian	Capitanian	259.8 ±0.4				
			Wordian	265.1 ±0.4				
			Roadian	268.8 ±0.5				
			Kungurian	272.3 ±0.5				
		Cisuralian	Artinskian	283.5 ±0.6				
			Sakmarian	290.1 ±0.26				
			Asselian	295.0 ±0.18				
			Gzhelian	298.9 ±0.15				
Paleozoic	Carboniferous	Pennsylvanian	Kasimovian	303.7 ±0.1				
			Moscovian	307.0 ±0.1				
		Mississippian	Bashkirian	315.2 ±0.2				
			Serpukhovian	323.2 ±0.4				
			Visean	330.9 ±0.2				
			Tournaisian	346.7 ±0.4				
			Famennian	358.9 ±0.4				
		Upper	Frasnian	372.2 ±1.6				
			Givetian	382.7 ±1.6				
Paleozoic	Devonian	Middle	Eifelian	387.7 ±0.8				
			Emsian	393.3 ±1.2				
		Lower	Pragian	407.6 ±2.6				
			Lochkovian	410.8 ±2.8				
			Pridoli	419.2 ±3.2				
			Ludlow	423.0 ±2.3				
			Gorstian	425.6 ±0.9				
			Homerian	427.4 ±0.5				
			Sheinwoodian	430.5 ±0.7				
		Llandovery	Telychian	433.4 ±0.8				
Paleozoic	Silurian		Aeronian	438.5 ±1.1				
			Rhuddanian	440.8 ±1.2				
			Hirnantian	443.8 ±1.5				
	Upper	Katian	445.2 ±1.4					
		Sandbian	453.0 ±0.7					
	Middle	Darriwilian	458.4 ±0.9					
		Dapingian	467.3 ±1.1					
	Lower	Floian	470.0 ±1.4					
		Tremadocian	477.7 ±1.4					
Paleozoic	Ordovician	Furongian	Stage 10	485.4 ±1.9				
			Jiangshanian	~ 489.5				
		Series 3	Paibian	~ 494				
			Guzhangian	~ 497				
		Series 2	Drumian	~ 500.5				
			Stage 5	~ 504.5				
		Terreneuvian	Stage 4	~ 509				
			Stage 3	~ 514				
		Terreneuvian	Stage 2	~ 521				
			Fortunian	~ 529				
				541.0 ±1.0				
Cambrian	Cambrian							

Fig. 1. Stratigraphic complexes prospective for unconventional hydrocarbons in the Paleozoic tight carbonate and shale carbonate reservoirs in Ukraine

(except of coalbed methane). Besides, there are some advantages in developing unconventional hydrocarbons from carbonate and shale carbonate rocks or successions, in comparison with their arenaceous equivalents. For instance, the carbonate sequences can be positively identified through seismic data, that increases the reliability of prospective areas delineation and depth of their occurrence. This significantly facilitates prospecting efforts, to find plays with high a density of recoverable resources (sweetspots) and increases economic viability of new wells drilling. It is also known,

that the effectiveness of fracking jobs for carbonate rocks, is higher than for terrigenous ones [7]. The above without doubt, speaks about the significant potential of tight carbonate rocks in the search for unconventional hydrocarbon accumulations and the need, to conduct a comprehensive study for them, along with black shales and arenaceous tight rocks. This study is focused on the carbonate sedimentary rocks of the Paleozoic basins in Ukraine, the Dnieper-Donets (DDB), Volyn-Podillya (VPB), and Dobrogean Foredeep (DFB) basins (Figure 1).

### **Criteria to evaluate hydrocarbon potential**

Nowadays, more than a dozen petroleum-prone basins in North America are producing from unconventional hydrocarbons reservoirs, carbonates and calcareous shales. All of them practically coincide with well known prolific conventional petroleum basins with conventional hydrocarbon traps. In terms of stratigraphy, the majority of known commercial unconventional accumulations are attributed to the Paleozoic and to a lesser extent to Mesozoic formations. Lithologically, the producing rocks are represented by limestones, dolostones, shaly limestones, clayey dolostones, calcareous shales, cherty marls, as well as marls and chalks for younger formations. Dry gas, wet gas with condensate and light tight oil (LTO) are main varieties of unconventional hydrocarbons due to their phase state.

Generalization and ranging of geological, geophysical and production data on tight carbonate reservoirs petroleum potential in the abovementioned provinces in Ukraine have allowed the formulation of the main criteria to evaluate un-

conventional hydrocarbon prospecting potential, taking into account specific peculiarities of the carbonate formations in the Paleozoic basins. These main criteria are as follows:

- by lithology – clayey limestones, massive limestones, clayey dolostones and dolostones,
- TOC content in the carbonates and related shales should exceed 1%,
- optimal rock maturity range is 0.8÷2.5%  $R_r$  for unconventional gas, and 0.60÷0.80%  $R_r$  for unconventional oil (and higher in some cases depending on organic matter type),
- minimal rock porosity for gas is 1% and 2% for oil,
- minimal values of permeability is 0.009 mD for gas and 0.1 mD for oil,
- minimal thickness of prospective interval should be at least 25 m for oil and 40 m for gas,
- maximal depth to prospective interval is limited to 4500 m below the surface.

### **Primary data and the technique**

At present, an evaluation of the prospecting potential for unconventional hydrocarbons in the Paleozoic carbonate rocks is at the initial stage in Ukraine [4]. Some theoretical and practical aspects of petroleum potential related to tight carbonate reservoirs, were preliminary elucidated in the monograph *Unconventional sources of hydrocarbons in Ukraine* [6]. No special studies on this issue were practically done prior to the last couple of years. This study is based on 1456 analyses for petrophysical rock properties, 1192 for thermal maturity, 286 measurements for TOC content, 282 analyses for X-ray diffraction rock investigation and over 1680 core description from 1027 deep wells in total. The majority of those analytical measurements were done

by Ukrainian industrial laboratories and research organizations and enterprises, namely Chernigiv Naftogaz Geologia, Poltava Naftogaz Geologia, Zakhid UkrGeologia, Ukrainian State Geo-Prospecting Institute, Ukrainian Research Institute for Natural Gases, Institute of Geological Sciences, and Institute of Geology and Geochemistry of Fossil Fuels, while exploring for the conventional oil and gas. An integral interpretation of well-log data from 135 wells to identify the tight reservoirs intervals prospective for unconventional hydrocarbons and total organic matter content (TOC) evaluation was performed by applying commercial and original techniques. For several stratigraphic units the Rock-Eval data were employed [1, 2, 3, 5].

### **Prospective lithostratigraphic complexes**

Eleven stratigraphic levels of tight carbonate and shale carbonate rocks, most promising for unconventional hydrocarbons

have been identified applying the above defined criteria and the results of an integral analysis of geological, geophysical,

and production data on tight carbonate reservoirs in the Paleozoic formations of the DDB, VPB, and DFB (Figure 2).

## Dnieper-Donets basin

The study reveals five tight carbonate levels prospective for unconventional hydrocarbons in the DDB.

1. The upper part of Lower Frasnian sub-stage (Sargaev and Semiluky horizons) of late Devonian complex. It is represented by re-crystallized biogenic limestones, dolomitized limestones and dolostones with interbeds of shales. The carbonate varieties are characterized by TOC at 0.1÷0.3% and at 0.6÷2.9% for shale interbeds. Kerogen type – II (HI – 198÷300 mg HC/g TOC). Generation potential ( $S_1 + S_2$ ): 3.4÷5.3 mg HC/g. Thermal maturity of the formation penetrated by wells is changed from 0.7%  $R_r$  (vitrinite reflection ratio) to 1.55%  $R_r$ . Open porosity value is at 3.5÷4.5% and permeability is less than 0.5 mD. Average prospective interval depth ranges from 2500 to 3800 m as revealed by the deep wells. The thickness of individual formation units is up to 40÷50 m. It is envisaged that unconventional accumulations will be represented mostly by LTO.
2. Lower part of Lower Famennian sub-stage (Zadonsk horizon) of Late Devonian complex. The prospective interval is represented by limestones, biogenic grainstones, re-crystallized, sometimes dolomitized and clayey alternated with shale beds. TOC of the carbonates is of 0.8÷2.8% with

1.2÷3.5% for shaly varieties (up to 5.8% in some cases). Kerogen type is of II-III type (HI – 86÷220 mg HC/g TOC). Generation potential ( $S_1 + S_2$ ): 2.4÷5.6 mg HC/g. Thermal maturity of the rocks is changed from 0.55% to 1.50%  $R_r$ . The formation is characterized by average open porosity of 4.0÷5.0% and permeability is at 0.05÷0.1 mD. The thickness of prospective units is up to 90 m. Average prospective interval depth ranges from 2800 to 3200 m. It is expected that these carbonate rocks will be favorable for unconventional oil and gas.

3. Tournaisian sub-stage of Early Carboniferous complex. It is represented by clastic re-crystallized and dolomitized limestones with shale beds, rarely by siltstones and calcarenites. TOC for these carbonates 0.1÷2.2%, and 0.8÷5.2% for shale beds. Kerogen type – II-III and III (HI – 56÷260 mg HC/g TOC). Generation potential ( $S_1 + S_2$ ) – 0.5÷13.5 mg HC/g. Thermal maturity of these rocks is 0.50%  $R_r$  till 2.0%  $R_r$ . Average values of open porosity are at 3÷4%, and permeability ranges from 0.01 to 0.5 mD. Improved values of porosity (up to 16÷18%) and permeability (140÷180 mD) are related only to the rocks making the core parts of biohermal bodies and localized as usual within the positive structures. A number of conventional hydrocarbon fields are related to those structures. The thickness of prospective units is up to 90÷110 m. Average prospective interval depth ranges from 2900 to 3900 m. It is expected that these tight carbonate



Fig. 2. Petroleum provinces of Ukraine prospective for unconventional hydrocarbons in carbonate rocks

rocks will be favorable, mainly for unconventional gas with high condensate content, and the subordinate share will belong to dry unconventional gas and oil.

4. Lower Visean sub-stage of Early Carboniferous complex. It is represented by re-crystallized and of different shale content, biogenic grainstones with beds of dark-gray and black shales. TOC for pure limestones is 0.01÷1.5% and 8.5÷11.2% for shaly beds. Kerogen type is of II-III type and II (HI – 70÷267 mg HC/g TOC). Generation potential ( $S_1 + S_2$ ): 2.3–12.5 mg HC/g. Average values of open porosity are at 4–5%, and permeability ranges from 0.05 to 0.1 mD. Localization of the areas with improved reservoir properties (to 22% for porosity and to 146 mD for permeability) is similar to the Tournasian sediments and related to various biohermal bodies. Thermal maturity of these rocks varies from  $R_r = 0.45\div2.36$  till the depth of 4500 m with  $R_r = 0.45\div1.55$ . The thickness of prospective units is up to 120 m. Average prospective interval depth ranges from 2800 to 3200 m. It is expected that tight carbonates of the Lower Visean sub-stage are mainly prospective for unconventional wet gas with high gas condensate content.
5. Lower Bashkirian sub-stage of Middle Carboniferous complex. By its lithology the prospective rocks are represented by limestones of different facies (mainly by wackestones and packstones, fine grainstones and mudstones) of different clay content, sometimes dolomitized with pyritization. TOC of carbonate varieties is 0.1÷2.5% while for shale ones is 0.5÷5.2%. Kerogen type: II-III and II (HI – 74÷275 mg HC/g TOC). Generation potential: ( $S_1 + S_2$ ) – 0.7÷3.1 mg HC/g. Thermal maturity of these rocks varies from 0.4% to 2.1%  $R_r$  till the depth 4500 m. The formation is characterized by average open porosity of 3÷6% and permeability at 0.1÷0.5 mD. The thickness of prospective units is up to 40-50 m. Average prospective interval depth ranges from 3000 to 3500 m. It is expected that tight carbonates of the Lower Bashkirian sub-stage are mainly prospective for unconventional oil.

### **Dobrogean Foredeep basin**

An integral study reveals four stratigraphic levels in the Dobrogean foredeep prospective for unconventional hydrocarbons in tight carbonate and shaly carbonate sedimentary rocks:

1. Silurian system complex. The prospective units are represented by dolostones and limestones with beds of shales and marls. The limestones are composed mainly of biogenic packstones and mudstones, usually re-crystallized, sometimes lumpy. In some places biomorphic limestones occur. TOC for limestones is 0.1÷0.6% and 1.0÷2.0% for dolostones and 0.3÷4.2% for shales. Kerogen type is of II type. Open porosity varies broadly from 0.5% to 7.5% av-

eraging to 2.5÷3.0%. Average permeability is 0.01÷0.1 mD. Thermal maturity of these rocks within the central part of the foredeep is 1.6÷2.2%  $R_r$  while its northern flank (Lower Dniester depression and Moldova monocline) is characterized by 0.35÷1.6%  $R_r$  [1]. The thickness of prospective units is up to 50 m. Average prospective interval depth in the central part of the foredeep is 3000 to 3500 m, but lowers in its northern flank to 2000÷2400 m. It is expected that tight carbonates of the Silurian system in the central part of the foredeep will be favorable for unconventional dry gas in the central part of the foredeep and for unconventional oil within its northern flank.

2. Givetian stage of Middle Devonian complex. Promising intervals are represented by limestones and dolostones interbedded with shales, anhydrites, marls, and sometimes by sandstones. Biogenic packstones and wackestones as well as grainstones prevail. Dolostones are fine-grained and bituminous. TOC for limestones and shales vary from 0.2 to 3.5%. Kerogen type is of II-III type. The formation is characterized by average open porosity of 0.5% to 3.0% and permeability at 0.01÷0.1 mD. Thermal maturity of these rocks till the depth of 4500 m varies from 1.15% to 2.0%  $R_r$ . The thickness of prospective units is up to 10÷25 m and increasing in some cases to 25÷30 m. Average prospective interval depth ranges from 2200 to 4300 m. It is expected that tight carbonates of the Givetian stage will be favorable for unconventional dry gas.
3. Frasnian stage of Late Devonian complex. It is composed mainly of limestones and dolostones interbedded shales, marls, and occasionally by sandstones. The limestones are biogenic and fine-grained, re-crystallized and dolomitized. Primarily they are micro- to fine-grained and intensively sulphated dolostones dominating among other forms of dolomites. TOC for carbonate rocks is 0.2÷1.5%, and 0.8÷3.5% for shaly varieties. Kerogen is of II type. Open porosity changes from 0.5% to 4.5%, averaging to 2.3%. The permeability values are generally within the range of 0.01 to 0.05 mD. In some places the intra-formation fracturing is developed. Thermal maturity of this prospective interval till the depth of 4500 m is 0.95÷1.95%  $R_r$ . The thickness of prospective units is 35÷60 m. Average prospective interval depth ranges from 2800 to 4200 m. It is expected that tight carbonates of the Frasnian stage are mainly prospective for unconventional gas with high content of condensate, and light tight oil in some places.
4. Famennian stage of Late Devonian complex. Lithological composition of the Famennian prospective intervals is similar to ones of the Frasnian stage. TOC in the carbonate rocks is 0.2–1.0%, and 0.2–2.0% in shaly varieties. Kerogen is of I-II type. Thermal maturity of the Famennian rocks

till the depth of 4500 m is broad range 0.70÷1.55% *Rr*. Average open porosity is at 5.8% and average permeability is of 0.03÷0.08 mD. The thickness of prospective units is 25÷60 m. Average prospective interval depth ranges from 1600 to 4000 m. It is expected that tight carbonates of the Famennian stage are mainly prospective for unconventional gas with high content of condensate, and light tight oil.

## Volyn-Podillya basin

Upon the results of this study within this region two main stratigraphic levels of tight carbonate hydrocarbon-prone rocks development have been singled out.

1. Middle and upper parts of Ordovician system. Lithologically, these are composed of grainstones and biomicrite re-crystallized limestones alternating with shale and marl seams. TOC of shaly varieties reaches as much as 1.2%. It is assumed that kerogen type is II-III type (upon analogy with data from Polish part [3]. Open porosity is averaged to 3÷6% and permeability to 0.01÷0.05 mD. Expected

thermal maturity range is 1.10÷1.80% *Rr*. The thickness of prospective units is up to 40 m. Average prospective intervals depth varies from 2100 to 2800 m. It is expected that carbonates of the middle and upper parts of Ordovician sequence will be favorable for unconventional dry gas accumulations.

2. Silurian system complex. The prospective interval is composed of various biogenic grainstones alternated with shales. In some places biohermal limestones are developed to form shall patch reefs. TOC for pure carbonates is 0.1÷0.3% and up to 1.9% for shaly varieties. It is assumed that kerogen type is of II-III type [3]. Thermal maturity of the Silurian formations varies significantly from 0.60 to 3.7% *Rr*. Open porosity is averaged to 3–5% and permeability values to 0.05÷0.1 mD. The thickness of prospective units is up to 40÷50 m. Average prospective intervals depth varies from 1600 to 4300 m. It is expected that these Silurian carbonates will be favorable both for unconventional gas and oil.

## Conclusions

Based on the above listed criteria eleven lithostratigraphic complexes prospective for unconventional hydrocarbons in carbonate and shale carbonate rocks, including five in the Dnieper Donets basin, four in the Dobrogea foredeep basin, and two within the Volyn-Podillya basin have been identified. Top priority exploration plays for unconventional hydrocarbons are attributed to the Tournaisian and Lower Visean, as well as to Silurian and Famennian tight carbonates in the

Dnieper-Donets basin and Dobrogean foredeep, respectively. This study is the first step to elucidate unconventional hydrocarbons potential of the tight Paleozoic carbonates in Ukraine and to plan further detail researches and exploration activity. Such researches should certainly include extensive Rock-Eval pyrolytic measurements program, intra-formation fracturing evaluation, rock mechanics modeling and seismic attributive analysis for prospective carbonate intervals.

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Ph.D. Sergii G. VAKARCHUK  
Head of Petroleum Geology & Seismic Studies Centre  
SE Research Institute of Oil and Gas Industry  
NJSC Naftogaz of Ukraine  
8 Kyivska St., 08132 Vyshneve, Kyiv-Svyatoshyne Dist.  
Kyiv Oblast, Ukraine  
Email: [vakarchuk@naukanaftogaz.kiev.ua](mailto:vakarchuk@naukanaftogaz.kiev.ua)