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# GEOCHEMICAL CHARACTERISTICS AND THERMAL MATURITY OF THE UPPER DEVONIAN ROCKS (DNIEPER-DONETS BASIN) ACCORDING TO ROCK-EVAL PYROLYSIS DATA (EXPLORATION DRILLING)

*(Представлено членом редакційної колегії д-ром геол. наук, доц. О.В. Шабатурою)*

**Background.** *In the Dnieper-Donets Basin (DDB), Devonian deposits are a very interesting object of hydrocarbon system research – from the initial stage of hydrocarbon generation to the stage of formation of oil and gas deposits. The presence of sedimentary layers enriched with scattered organic matter determines the oil and gas generation potential of the deposits. The article presents the results of laboratory studies of Upper Devonian rocks performed on the Rock-Eval pyrolytic tool in order to assess their thermal maturity and degree of hydrocarbon generation.*

**Methods.** *Laboratory studies were carried out by the method of pyrolysis of rock samples (Rock-Eval) with the determination of a number of parameters that allow for the assessment of thermal maturity, the type of organic matter (kerogen) and the coefficient of organic matter transformation. Data processing was performed using the methods of mathematical statistics.*

**Results.** *An important result of the research is the established regularity that shales and limestones with an increased content of organic carbon (TOC) of the Famennian layer from between-salt strata in this part of the DDB are already in the active phase of oil generation and belong to oil-source rocks. Precisely in this part of the Dnieper-Donets depression the main explored reserves of liquid hydrocarbons in the Eastern region are concentrated.*

**Conclusions.** *Generalized conclusion based on the results of the above studies: most samples of shales (argillites) and limestones have quite high concentrations of organic carbon; the thermal maturity of the rocks for 63 % of the samples corresponds to the "oil window"; all four types of kerogen are present in the rocks; the best oil-generating properties are characteristic of shales from between-salt strata; also, these shales have the maximum degree of realization of the generating potential TRI – more than 0.3 at depths of 4,700 m. The results of the above studies indicate that the shales and limestones of the Frasnian and Famennian layers from the studied deposits can be considered as potential oil-source rocks.*

**Keywords:** *Devonian, kerogen, pyrolysis, sourse rock, hydrocarbons, Dnieper-Donetsk basin.*

## Background

The Dnieper-Donets avlakogen is known not only as a large reservoir of oil and gas fields, but also as a unique training ground for studying the formation processes of hydrocarbon deposits, and of all known types. This is exactly what was emphasized when writing this article. The material for the research was the results of laboratory analyzes of rock samples of predominantly clay composition, from the core obtained during the drilling of exploratory wells. The geography of the wells location covers a number of oil and gas producing areas of the Dnieper-Donets basin – from the northwest to its southern part. Materials – the results of laboratory analyzes that were the basis of this study are unique, new and therefore represent an undoubted interest for specialists dealing with issues of exploratory oil and gas geology. Core samples of the Upper Devonian, Famennian and Frasnian stages were taken from the sections of deep exploratory wells. The issue of selecting rocks from this stratigraphic interval is based on the well-known assumptions that rock strata were formed in the Devonian period, which later were regionally (all over the planet) one of the main "kitchens" where hydrocarbons were generated for many oil and gas deposits. A huge number of publications on this topic prompted the author's team to be engaged in specific research with the aim of assessing the oil and gas generation potential of mainly clayey rocks from certain areas of the DDB. The results of "fresh" laboratory studies performed on a modern Rock-Eval pyrolytic tool allowed an independent (unbiased) assessment of the generation potential of rocks from the Upper Devonian deposits.

Regarding the location (or vertical differentiation) of the Upper Devonian deposits, a working scheme was adopted in which the following main litho-stratigraphic complexes of the southern zone of the DDB are distinguished (Eisenberg, Berchenko, & Brazhnikova, 1988; Khomenko, 1986; Menning et al., 2006):

- the under salt-bearing complex is stratigraphically formed by the Givetian and Eifelian stratigraphic complexes ($D_2$ef-zv, 393,3–382,7 Ma) in the northwestern part of the basin, and within other areas by the Upper Frasnian Semilut horizon ($D_3fr_3$sm, 380, 2–375,5 Ma) and the Voronezh suite ($D_3fr_3$vr, 377,0–378,0 Ma);
- lower salt-bearing complex – stratigraphically formed by the Upper Frasnian, Lievean and Yevlanian horizons ($D_3fr_3$ev-lv, 378,8–375,0 Ma);
- between-salt complex ($D_3fm_1$zd-el, 372,0–367,0 Ma) formed by the Lower Famennian Zadonian and Jelets horizons;
- upper salt-bearing complex – formed by the Lower Famennian Yelets horizon and the Middle Famennian Lebedyan layer ($D_3fm_2$dn-lb, 367–365 Ma);
- over salt complex – formed by the Middle Famenian Dankovo-Lebedyan ($D_3fm_2$dn-lb) and Upper Famenian Ozersky-Khovansky ($D_3fm_2$oz-hv) horizons (360,0–359,5 Ma).

In the work (Karpenko, 2018), it is noted that seven oil fields have been discovered in the Devonian deposits in the northern pre-board zone: Yasenivske, Sukhivske, Zahidno-Koziivske, Koziivske, Bugruvativske, Golikyvske, Radianske. It is believed that the hydrocarbon deposits were formed by subhorizontal migration flows from the deeper part of the basin from the Devonian oil-source strata. They are associated with tectonically shielded deposits in over salt-bearing Upper Famennian deposits (West Koziivske, Yasenivske, Sukhivske deposits); lithologic-shielded deposit in breccia at the salt dome (Romenske); by fields of hydrocarbons in between-salt Devonian deposits (Bugruvativske, Holikivske); deposits in the Carboniferous and between-salt deposits of the hydrocarbons (Koziivske). At the same time, only one oil and gas condensate field (Lychkivske) and two gas-condensate fields (Bogatoyske and Ryaskivske) are known in Devonian deposits within the southern border zone. The Lychkivske gas condensate field is represented by 3 isolated deposits within the uplifted block surrounded by several subvertical tectonic faults. It is believed that the deposits were also formed by subhorizontal migration flows of hydrocarbons from the deeper part of the basin from the Devonian oil-source strata (Karpenko, 2018).

The idea of writing this article is to publish the obtained new results regarding the assessment of the generation possibilities of potential oil and gas source strata of the Upper Devonian in different sections of the DDB, taking into account their stratigraphic, structural and geographical location. The analysis of the results of core samples geochemical studies at the Rock-Eval pyrolytic tool has been renewed.

The main publications on the topic of the research, in which the results of study of the Devonian sediments of the Dnieper-Donets basin from the point of view of their oil and gas potential or as potential oil and gas source rocks, should be included (Ratnayake, Kularathne, & Sampei, 2018; Eisenberg, Berchenko, & Brazhnikova, 1988; Sachsenhofer et al., 2002; Sachsenhofer et al., 2010; Misch et al., 2015; Stryzhak, & Korzhnev, 2012; Karpenko, 2018). The detailed work on the history of the search for oil and gas accumulations in the Devonian deposits of the Dnieper-Donets depression, prospects for the discovery of hydrocarbon deposits belong to the authors (Stryzhak, & Korzhnev, 2012). It contains a detailed analysis of the negative results of search works over a long period of time. The significant contribution of many researchers to establishing the history of the formation and development of Devonian deposits in the DDB is also appreciated. Directions for further research and prospecting work are indicated. The conclusion of the authors of this work contains the following. To date, in the sedimentary complex of the Devonian deposits of the northwestern Dnieper-Donets avlakogen, industrial deposits of hydrocarbons have not been identified. The degree of discovery of the Devonian deposits of this area by parametric and exploratory drilling is relatively low. Obviously, the establishment of regularities of the distribution of explosive deposits in Devonian deposits will be facilitated by the gradual increase in drilling volumes and the receipt of relevant geological and geophysical information. Summarizing the conclusions of most researchers, we note that the main prospects of the territory of the northwest of the Dnieper-Donets avlakogen should be connected with the under-salt Zadonsko-Yeletsky strata. This is evidenced by the overwhelming number of oil and gas occurrences, favorable thermobaric, hydrogeological, shielding (lithological and tectonic) conditions for the formation and preservation of hydrocarbon deposits, the presence of biogenic carbonate and terrigenous reservoirs. The shielding capabilities of the lower (Lievean and Yevlanian) salt-bearing stratum leave certain prospects for the lower salt-bearing as well (Stryzhak, & Korzhnev, 2012). At the same time, it should be noted that the possibility of the existence of non-traditional hydrocarbon deposits in the Devonian sediments is not sufficiently appreciated, despite the fact that in the Devonian period there were favorable conditions for the accumulation and burial of huge masses of organic matter at the regional and planetary level. Which later served as raw material for the generation of hydrocarbons with the migration of the latter into the host strata and into structures of younger orders. Regarding the study of potential oil and gas source strata of the Devonian, it is worth noting the numerous works of Professor R. Sachsenhofer and his colleagues (Sachsenhofer et al., 2002; Sachsenhofer et al., 2010; Misch et al., 2015), Academician O.E. Lukin (Lukin, 2006), (Mykhailov et al., 2014), many other researchers. As a result of extremely heterogeneous genesis, mineral composition and spatial distribution of Devonian sediments (mainly terrigenous type), any additional new information regarding the geological and geochemical features of mudstone-like, organically enriched Devonian sediments (Karpenko, Bashkirov, & Karpenko, 2014), is an undoubted scientific and practical interest in terms of assessing the oil and gas potential of the entire Dnieper-Donetsk basin.

***Geological and geochemical features of the research objects.*** The studied core samples were taken from sections of 9 exploratory and parametric wells. In terms of location, the wells are divided into 2 groups: a) northern ones – tending to the northwestern part of the DDB, closer to the northern side, 7 wells; b) southern – to the central part of the southern board zone of the DDB, 2 wells. In terms of lithology, mainly shales (88 samples), siltstones (2 samples), sandstones (4 samples), interlayering of sandstones and shales (8 samples), limestones (16 samples), interlayering of shales and limestones (2 samples), metasomatites (2 samples). All samples belong to Upper Devonian deposits: – Frasnian layer ($D_3f_1$-$D_3f_2$) and Famennian layer ($D_3fm_1$, $D_3fm_2$, $D_3fm_3$). Regarding the main litho-stratigraphic complexes according to the classification (Eisenberg, Berchenko, & Brazhnikova, 1988; Khomenko, 1986; Menning et al., 2006): under-salt complex – 36 samples, lower-salt complex – 2 samples, between-salt complex – 70 samples, over-salt complex – 14 samples. The sampling depths differ significantly in the wells of the northern and southern groups: for the northern group of wells, the average values of depths are 3844 m (2559–5474 m), for the southern group the average values of depths are 2732 m (1695–4171 m).

The Tab. 1 shows the distribution of the main (representative) lithotypes of rocks depending on their location in the Upper Devonian salt-bearing layer of rocks and by stratigraphic affiliation. There are 2 main groups of rocks in the collection: shales (including a core with interlayering of shale and sandstone) and limestones (with a core where there is an interlayering of shale and limestone).

All the above-mentioned lithologic-stratigraphic features of the deposits, their spatial location are important factors that were taken into account during the analysis of the geochemical characteristics of the studied rocks.

**Methods**

All core samples from the above collection were subjected to a full set of laboratory tests on the Rock-Eval pyrolytic tool in the laboratory of the State Enterprise "Ukrnaukageocentre". Most of the selected mudstone samples (shales) are typical of Upper Devonian deposits. In some of them, during the macro description, the presence of plant remains was found, in some, a characteristic smell of hydrocarbons was observed.

*Table 1*

**Distribution of the main rocks lithotypes in the Upper Devonian salt-bearing layer of rocks ***

| Placement | D3f2 | D3fm1 | D3fm2 | D3fm3 |
|---|---|---|---|---|
| *Over salt* | | | 10(sh) | 2+2(sh-lm) |
| *Between salt* | | 58(sh)+8(sand+sh) | | |
| *Under salt* | 16(sh)+10(lm) | 6(lm) | | |

* sh – shale; lm – limestone; sh+lm – shale+limestone; sand+lm – sandstone+shale

The main parameters that were obtained during laboratory tests include:

$S_1$ is a measure of free hydrocarbons (HC), which evaporate from the rock without kerogen cracking (that is, up to a temperature of 280–300 °C). Peak $S_1$ corresponds to the explosives contained in the rock (mg of HC/g of rock); increases in relation to $S_2$ with increasing maturity of kerogen.

$S_2$ is the yield of heavy and light hydrocarbons during kerogen cracking (generated at higher temperatures – up to 550 °C), measured (mg of HC/g of rock). $S_2$ defines the potential of hydrocarbons generation by modern rock.

$S_1 + S_2$ is a measure of the genetic potential or the total amount of HC that could be generated by the rock (without taking into account the emigration of hydrocarbons from the rock that has already occurred).

$S_3$ – the amount of $CO_2$ released as a result of pyrolysis of dispersed organic matter in the temperature range of 300–390 °C; (measured as mg of substance/g of rock).

*Tmax* is the temperature of the maximum yield of hydrocarbons during kerogen cracking. *Tmax* is a function of the maximum peak temperature of $S_2$. The degree of catagenetic dosing of organic substances is estimated by the value of *Tmax*.

*TPI* or $S_1/(S_1+S_2)$, which is called the coefficient of transformation of organic substances; it indicates the amount of rock that has exhausted its generation potential.

*TOC* is the content of organic carbon in the rock, %.

*HI* or hydrogen index is the ratio $(S_2/TOC)$*100. High values of this parameter indicate the ability of the rock to generate hydrocarbons, mainly oil.

*OI* or oxygen index is the ratio $(S_3/TOC)$*100. The ratio of the hydrogen and oxygen indices of the appearance of the kerogen type (taking into account the degree of catagenetic changes that have occurred in the rock) is the Van Krevelen diagram (Tissot, & Welte,1984).

In order to obtain significant results and conclusions, in addition to the construction of "classical" diagrams and histograms of probability distributions of parameter values, methods of mathematical statistics were applied.

**Results**

The rather diverse composition of the studied samples in terms of their lateral and vertical placement in sedimentary strata, stratigraphic and lithological affiliation requires the introduction of certain restrictions regarding their further use in analytical studies. Thus, unrepresentative collections of individual lithological groups were excluded from the research. Data on all samples of lithotypes from the Upper Devonian deposits were given only on general diagrams (graphs). Tab. 2–3 show the statistical characteristics of the geochemical parameters of the main lithological types.

Fig. 1 shows the distribution of all samples from the collection on the diagram "oxygen-hydrogen indices" *OI-HI*, which is used to determine the transformation of organic matter (OM) or kerogen to one of the 4 generally accepted types. Dotted lines mark typical correlation dependences for individual types of kerogen. As can be seen, in the collection from Upper Devonian deposits there are representatives of all types of kerogen – from type I (marine-lacustrine sapropel OM) to type IV ("sedimentary").

*Table 2*

**Statistical characteristics of geochemical parameters of shales**

| Parameter | Valid N | Mean | Minimum | Maximum | Std.Dev. |
|---|---|---|---|---|---|
| *Depth, m* | 88 | 3644.8 | 1695.0 | 5474.0 | 1038.6 |
| $S_1$ | 88 | 0.4 | 0.0 | 4.4 | 0.8 |
| $S_2$ | 88 | 2.1 | 0.2 | 37.1 | 5.9 |
| $S_3$ ($CO_2$) | 88 | 0.3 | 0.0 | 2.6 | 0.4 |
| *Tmax, °C* | 88 | 435.2 | 417.0 | 463.0 | 10.8 |
| *HI* | 88 | 51.4 | 4.6 | 447.6 | 63.2 |
| *OI* | 88 | 17.4 | 0.7 | 138.0 | 24.2 |
| *TPI* | 88 | 0.2 | 0.0 | 0.6 | 0.1 |
| *TOC* | 88 | 2.7 | 0.8 | 17.2 | 2.5 |
| $S_1+S_2$ | 88 | 2.4 | 0.2 | 40.1 | 6.4 |
| $(S_1+S_2)/TOC$ | 88 | 64.4 | 6.1 | 611.3 | 85.7 |

*Table 3*

**Statistical characteristics of geochemical parameters of limestones**

| Parameter | Valid N | Mean | Minimum | Maximum | Std.Dev. |
|---|---|---|---|---|---|
| *Depth, m* | 16 | 4152.9 | 3794.0 | 4425.0 | 225.5 |
| $S_1$ | 16 | 0.26 | 0.02 | 1.65 | 0.40 |
| $S_2$ | 16 | 1.23 | 0.06 | 4.41 | 1.41 |
| $S_3$ ($CO_2$) | 16 | 0.37 | 0.05 | 0.89 | 0.33 |
| *Tmax, °C* | 16 | 431.9 | 406.0 | 442.0 | 8.2 |
| *HI* | 16 | 79.9 | 3.6 | 223.3 | 67.2 |
| *OI* | 16 | 41.9 | 1.8 | 246.9 | 60.1 |
| *TPI* | 16 | 0.2 | 0.1 | 0.4 | 0.1 |
| *TOC* | 16 | 1.5 | 0.3 | 3.4 | 0.9 |
| $S_1+S_2$ | 16 | 1.5 | 0.1 | 6.1 | 1.8 |
| $(S_1+S_2)/TOC$ | 16 | 96.0 | 5.1 | 256.2 | 77.3 |

*Table 4*

**Statistical characteristics of geochemical parameters of samples with layering of sandstones and mudstones**

| Parameter | Valid N | Mean | Minimum | Maximum | Std.Dev. |
|---|---|---|---|---|---|
| *Depth, m* | 8 | 2670.3 | 2640.0 | 2711.0 | 30.3 |
| *$S_1$* | 8 | 0.17 | 0.08 | 0.57 | 0.16 |
| *$S_2$* | 8 | 1.70 | 0.92 | 2.90 | 0.77 |
| *$S_3$ ($CO_2$)* | 8 | 0.70 | 0.05 | 1.46 | 0.61 |
| *Tmax, °C* | 8 | 423.8 | 414.0 | 433.0 | 6.4 |
| *HI* | 8 | 111.7 | 35.0 | 237.1 | 71.6 |
| *OI* | 8 | 42.0 | 3.2 | 91.1 | 36.7 |
| *TPI* | 8 | 0.1 | 0.0 | 0.2 | 0.0 |
| *TOC* | 8 | 1.8 | 1.2 | 2.9 | 0.7 |
| *$S_1$+$S_2$* | 8 | 1.9 | 1.0 | 3.5 | 0.9 |
| *($S_1$+$S_2$)/TOC* | 8 | 123.2 | 38.6 | 246.2 | 79.4 |

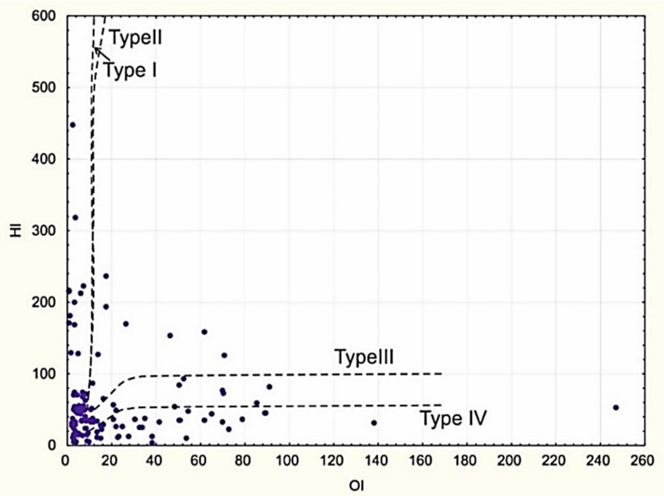


**Fig. 1. Classification of kerogen types of sediment core samples using oxygen and hydrogen indices from the studied wells. Modified Van Krevelen diagram (Tissot, & Welte,1984; Ratnayake, Kularathne, & Sampei, 2018)**

Traditionally, four types of kerogen are distinguished depending on the content of original organic matter (Tissot, & Welte,1984; Karpenko, Krochak, & Baisarovych, 2017).

***Liptinite (or alginite*) (type 1)** has a high ratio of hydrogen to carbon, but low – oxygen to carbon. It is mainly an oil-generating type, with a significant percentage of production (up to 80 %). It is formed primarily from algae, rich in lipids, which are formed in lagoon and lake environments. Liptinite fluoresces under ultraviolet radiation.

***Exinite (type 2)*** has average values of hydrogen/carbon and oxygen/carbon ratios. This type generates oil and gas, production is 40–50 %. The source of exinite formation is film remains of plants (spores, pollen, soft plant tissues), phytoplankton and bacterial marine microorganisms.

***Vitrinite (type 3)*** has low hydrogen and high – oxygen content, generates small volumes of hydrocarbons, mainly gas. The main source of vitrinite is the remains of higher plants found in coal or carbonaceous rocks. Vitrinite does not fluoresce under ultraviolet radiation, but has an extremely high reflectivity at higher stages of maturation, and therefore, it can be used as an indicator of the degree of maturity of the matter rock.

***Inertinite or fusinite (type 4)*** is a product of any of the above types of kerogen that does not fluoresce under ultraviolet radiation. It is characterized by high carbon content and low hydrogen content. Inertinite has no significant potential for generating oil and gas, which is why it was called "dead carbon".

Under the influence of temperature, large molecules of kerogen disintegrate into smaller molecules of liquid and gaseous hydrocarbons. Undoubtedly, there are many transitional forms (genetic types) of kerogen, which is clearly shown by the scatter of observation points – core measurements in Fig. 1. However, a significant number of rocks that gravitate to the I-II types of kerogen according to the distribution of *OI-HI* indices are distinguished (Fig. 1). It has been established that kerogens of these types are the main "producers" of oil and combustible gas in sedimentary rocks.

Fig. 2 shows the classic "*Tmax-HI*" diagram, which allows estimating the generation potential of kerogen, its genetic type, and establish the degree of catagenetic maturity of rocks.

Because of the uniqueness of this chart, it is possible to estimate the oil and gas generation capabilities of kerogen from a collection of researched samples based on the data of laboratory measurements on the Rock-Eval pyrolytic tool. Vertical lines in Fig. 2 show the conditional *Tmax* limits of the distribution of rocks by thermal maturity (all lithological types of rocks from the collection are given here). The value of *Tmax* correlates well with the vitrinite reflectance *Ro*, which is a recognized characteristic of the degree of maturity of rocks or catagenetic transformation of rocks and organic matter. Thus, the work (Waliczek et al., 2021) gives the equation of 3 regression dependences of the *Ro* coefficient on the *Tmax* value depending on the type of kerogen. For type II kerogen, the equation was calculated (Waliczek et al., 2021):

$$Ro = 0.0112 \cdot Tmax - 4.2072. \quad r = 0.84 \qquad (1)$$

Similar equations are found in other publications, and all of them are quite similar in coefficients, which allows the use of the *Tmax* parameter as a characteristic of the degree of genetic maturity of different types of kerogen. In Fig. 2 more than half of the rock samples belong to the "mature" category, the *Tmax* value of which, according to the Rock-Eval measurement results, is greater than 430 °C. Almost all samples of this group are within the "oil window". As will be shown later, these samples were mainly taken from the northern group of wells, from the northwestern part of the DDB. According to the value of the *HI* hydrogen index, most of the samples contain type III or even type IV kerogen. A smaller part gravitates towards transitional forms of II-III types. Single samples – with type II kerogen (Fig. 2).

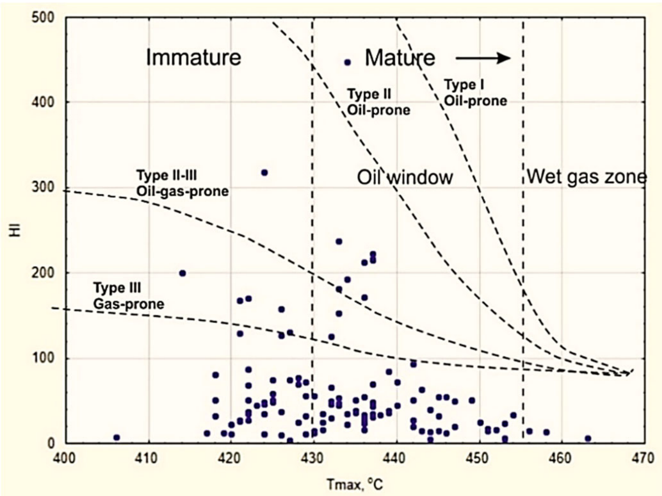


**Fig. 2. The distribution of *HI* relative to the *Tmax*, Rock–Eval coefficient, indicates the type of kerogen and the degree of maturity of the potential source rocks. Modified diagram lines by (Ratnayake, Kularathne, & Sampei, 2018)**

Fig. 3 shows the histograms of probability distributions of *Tmax* parameters and organic carbon content of *TOC* for the two main lithotypes of rocks in which the highest values of *TOC* content were observed - shales and limestones.

It is expected that the *TOC* organic carbon content in the limestone samples is significantly lower – it practically does not exceed 2 %. In shales, the peak *TOC* content is within 2–4 % (sometimes higher). This may indicate that mudstones here have a good probabilistic oil and gas generating potential (in general). The probability distribution of *Tmax* values indicates approximately the same level of catagenetic transformation of organic matter in limestones and shales. The approximate temperature range of maximum generation for the "oil window" of 430–457 °C (see Fig. 2) is typical for most samples of limestones and mudstones (Fig. 3). However, such conclusions are generalized; they do not take into account the features of the lateral and vertical distribution of carbonate and clay rocks in the studied area. A characteristic of the spatial position of the strata relative to the salt-bearing strata of the Upper Devonian should be added to the stratigraphic affiliation during a detailed analysis of the degree of catagenetic maturity and generational characteristics of the rocks. In Fig. 4 shows a cross-plot of the dependence of the *Tmax* parameter on the depth of mudstones beds, taking into account the position of the latter relative to salt-bearing strata. In the future, we will consider the geochemical features of clay rocks (shales) as the most likely sources of hydrocarbon generation from Upper Devonian deposits. This is also influenced by the fact that mudstones have the most representative sample in our collection compared to other lithological rock types. The lines of the regression equations in Fig. 4 are given for a visual representation of the "behavior" of the *Tmax* parameter with increasing depth and spatial placement of mudstones. Over-salt beds of Famennian shales $D_3fm_2$ and $D_3fm_3$ are characterized by slightly increased *Tmax* values at the depths of their occurrence compared to between-salt and under-salt counterparts at approximately the same depths (2000–4000 m).

However, at depths of more than 4,000 m, the degree of catagenetic maturity of rocks is highest in shales of between-salt deposits. The organic matter in all mudstone samples has a degree of maturity that corresponds to the "oil window" of hydrocarbon generation. Kerogen in some samples has a *Tmax* value already in the area of the "gas window" for wet gas (refers to between-salt deposits) (Fig. 4). In general, based on the results of laboratory analyzes of samples from the Upper Devonian sediments, the idea that terrigenous rocks (shales and mudstones with layers of sandstones) from between-salt strata have the greatest generating properties was formed.

The coefficient of transformation of organic matter *TPI*, as it was said, characterizes the degree to which the rock has exhausted its generation potential. In Fig. 5, a general regularity of the increase in the value of *TPI* with increasing depth of shale layers occurrence is observed, regardless of their position relative to salt-bearing strata.

A noticeable increase in this indicator begins at depths greater than 4,200 m. The analysis of the core selection show that all samples marked on the cross-plot deeper than 4,200 m refer to wells from the northwestern part of the DDB. Accordingly, shales with high TOC content of the Famennian layer from between-salt strata in this part of the DDB are already in the active phase of oil generation and belong to oil matter rocks. It is precisely in this part of the Dnieper-Donets depression that the main explored reserves of liquid hydrocarbons in the Eastern region are concentrated.

The results of the studies presented in the article with an assessment of the probable oil generation potential of the Upper Devonian deposits of two parts of the DDB show that the degree of thermal maturity of the kerogen of the rocks depends significantly not only on the depth of occurrence, but also on a number of other factors, such as the lateral placement of the deposits relative to the tectonic elements of the avlacogen, their position relative to salt-bearing strata, from the genetic type of organic matter. In addition, the degree of realization of the generating potential of *TPI* kerogen depends on its degree of maturity (parameter *Tmax*), this is a natural statement (see Fig 6). However, there is a peculiarity of the influence on such a dependence of the position relative to the saline strata: under-salt deposits of limestones and mudstones have increased values of *TPI* relative to over-salt deposits. This is clearly manifested in the *Tmax* range of 430–440 °C – in the left part of the "oil window" of hydrocarbon generation.

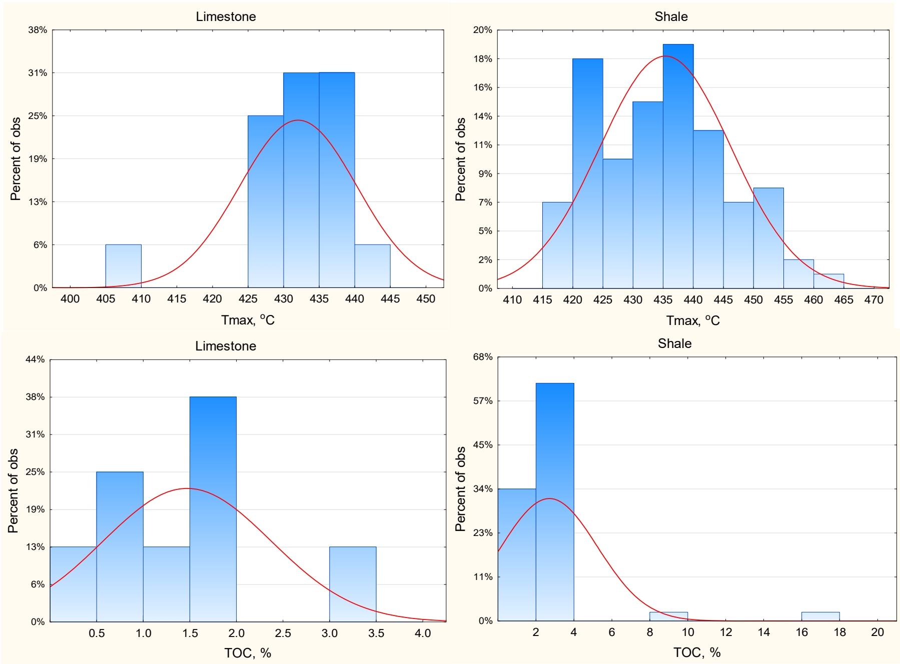


**Fig. 3. Probability distribution of *TOC* and *Tmax* values for limestones and shales from the collection. Upper Devonian, Frasnian and Famennian stages**

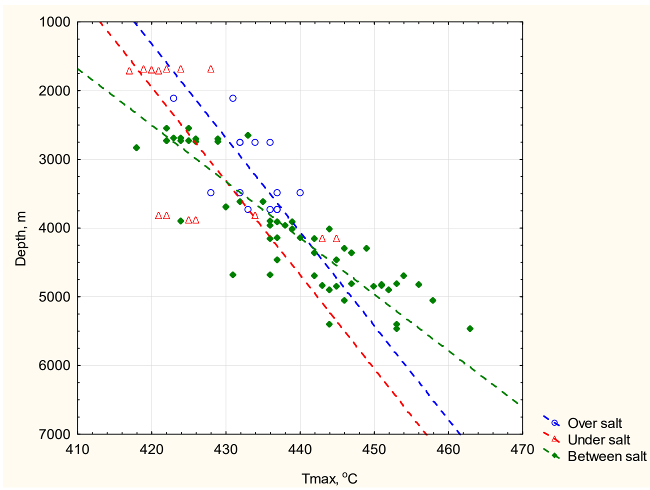


**Fig. 4. Dependence of the maximum hydrocarbon generation temperature parameter *Tmax* for shales on the depth of layers and their position relative to salt-bearing strata. Frasnian and Famennian stages**

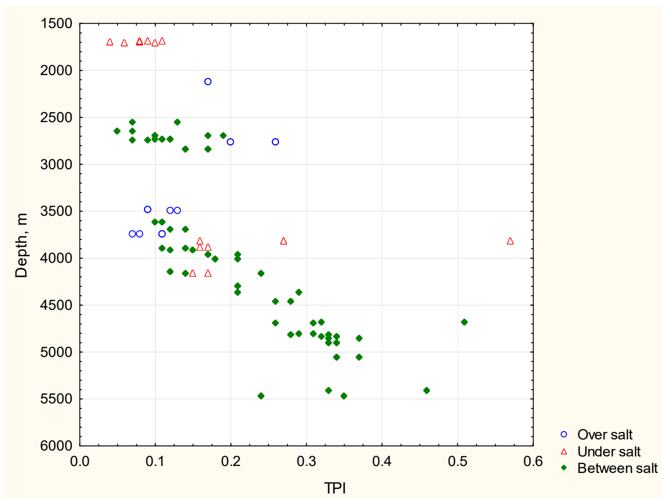


**Fig. 5. Dependence of the *TPI* parameter for shales on the depth of sediments and their position relative to salt-bearing strata. Frasnian and Famennian stages**

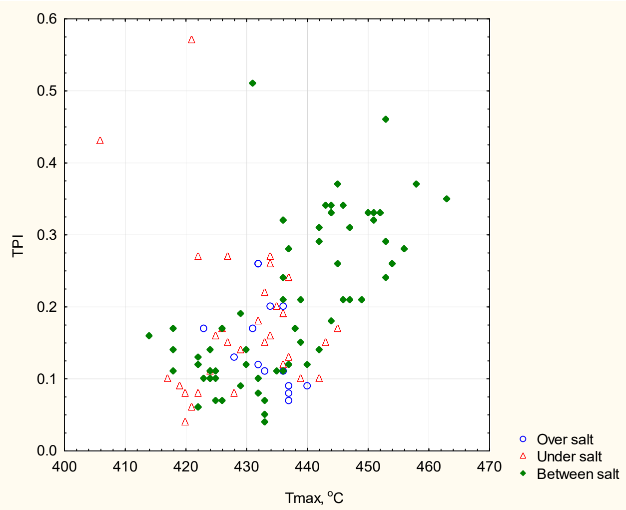


**Fig. 6. Dependence of the *TPI* parameter for shales and limestones on the maximum temperature of hydrocarbon generation *Tmax*, taking into account the position of the formations relative to salt-bearing strata. Frasnian and Famennian stages**

## Discussion and conclusions

The results of the performed geochemical studies of rock samples at the Rock-Eval pyrolytic tool from the Upper Devonian deposits of the northwestern and southern pre-border parts of the DDB made it possible to draw a number of important conclusions. Similar studies of rocks from the oil and gas regions of Ukraine are carried out in limited quantities. Data on the geochemical generation potential of probable oil-bearing strata have always been of increased interest to researchers and practicing geologists. In this collection, there are two main lithological groups of rocks – shales and limestones, in which an increased content of organic carbon *TOC* is observed: average values of *TOC* in shales are 2,7 %, in limestones – 1,5 % (for details, see Tab. 1, 2).

Cross-plots of *OI-HI* and *Tmax-HI* (Rock–Eval parameters) indicate the existence of all types of kerogen (I-IV) in the studied samples. The degree of thermal maturity of kerogen corresponds to the region of "immature" rocks – 35 % of the samples, the region of the "oil window" of hydrocarbon generation – 63 % of the samples.

The maximum generating property is characteristic of terrigenous rocks – shales and mudstones with layers of sandstones from between-salt strata ($D_3fm_1$). There is a natural trend of increasing thermal maturity of rocks with increasing depth of deposits. At depths of more than 4,000 m, the degree of catagenetic maturity of rocks is highest in shales from between-salt deposits. Also, with increasing depth, the degree of realization of the generating potential of *TPI* kerogen increases. This dependence is influenced by the position of the sediments relative to saline strata: under-salt deposits of limestones and shales have elevated values of *TPI* relative to over-salt deposits. This is clearly manifested in the *Tmax* range of 430–440 °C – in the left part of the "oil window" of hydrocarbon generation.

Generalized conclusion based on the results of the above studies: most samples of shales and limestones have rather high concentrations of organic carbon; the thermal maturity of the rocks for 63 % of the samples corresponds to the "oil window"; all four types of kerogen are present in the rocks; the best oil-generating properties are characteristic of shales from between-salt strata; also, these mudstones have the maximum degree of realization of the generating potential of *TPI* – more than 0,3 at depths of 4,700 m. The results of the above studies indicate that the shales and limestones of the Frasnian and Famennian stages from the studied deposits can be considered as potential oil source rocks.

**Authors' contributions:** Ivan Karpenko – conceptualization, methodology, formal analysis, writing (original draft); Ihor Ishchenko – data validation, writing (review and editing); Oleksii Karpenko – formal analysis, writing (review and editing).

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## ГЕОХІМІЧНІ ХАРАКТЕРИСТИКИ І ТЕРМАЛЬНА ЗРІЛІСТЬ ПОРІД ВЕРХНЬОГО ДЕВОНУ (ДНІПРОВСЬКО-ДОНЕЦЬКА ЗАПАДИНА) ЗА ДАНИМИ ПІРОЛІЗУ ROCK-EVAL (ПОШУКОВЕ БУРІННЯ)

**В с т у п .** ***У Дніпровсько-Донецькій западині девонські відклади є дуже цікавим об'єктом дослідження вуглеводневої системи – від початкового етапу генерації вуглеводнів до етапу формування покладів нафти і газу. Наявність осадових товщ, збагачених розсіяною органічною речовиною, визначає нафтогазогенераційний потенціал відкладів. У статті розглянуто результати лабораторних досліджень порід верхнього девону, виконаних на піролітичній установці Rock-Eval з метою оцінки їх термальної зрілості та ступеня вуглеводневої генерації.***

**М е т о д и .** ***Лабораторні дослідження виконано методом піролізу зразків гірських порід (Rock-Eval) з визначенням низки параметрів, які дають змогу оцінювати термальну зрілість, тип органічної речовини (керонгену) і коефіцієнта перетворення органічної речовини. Обробку даних виконано із застосуванням методів математичної статистики.***

**Р е з у л ь т а т и .** ***Важливим результатом досліджень є встановлено закономірність, що аргіліти з підвищеним вмістом органічного карбону (ТОС) фаменського ярусу з міжсольових товщ у цій частині ДДЗ вже перебувають в активній фазі нафтогенерації і належать до нафтоматеринських пород. Як раз у цій частині Дніпровсько-Донецької западини зосереджені основні розвідані запаси рідких вуглеводнів Східного регіону.***

**В и с н о в к и .** ***За результатами досліджень було встановлено: більшість зразків аргілітів і вапняків мають доволі високі концентрації органічного вуглецю; термальна зрілість порід для 63 % зразків відповідає "нафтовому вікну"; у породах присутні всі чотири типи керогену; найкращі нафтогенерувальні властивості притаманні аргілітам з міжсольових товщ, також ці аргіліти мають максимальний ступінь реалізації генераційного потенціалу TPI – більше 0,3 на глибинах від 4700 м. Результати наведених досліджень свідчать, що аргіліти і вапняки франського і фаменського ярусів з вивчених відкладів можуть розглядатись як потенційні нафтоматеринські породи.***

**К л ю ч о в і   с л о в а :** ***девон, кероген, піроліз, материнська порода, вуглеводні, Дніпровсько-Донецька западина.***

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