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THERMAL MATURITY OF DEVONIAN ROCKS IN TERMS OF THEIR LITHOLOGICAL-FACIES AND AGE AFFILIATION. NORTHERN AND SOUTHERN SIDES OF THE DNIPRO-DONETS BASIN

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

Background. *The production of hydrocarbons (HC) in open fields is decreasing, and the fields that were discovered in recent years, as a rule, are small in terms of reserves and can no longer provide a resource base for its expansion. An analysis of the experience of leading oil and gas companies shows that a significant expansion of the resource base and the discovery of significant reserves of hydrocarbon deposits can be obtained through the use of modern exploration technologies, which actively use in their arsenal the modeling of hydrocarbon systems in the studied territories. Carboniferous and Upper Devonian deposits remain the most promising stratigraphic complexes for the search for new deposits of explosives within the Eastern region of Ukraine.*

Methods. *Mathematical statistics methods were used to create model constructions that allowed meaningful analysis of the original geological and geochemical information. The initial data were the results of laboratory studies by the pyrolysis method (Rock-Eval) of rock samples from search and exploration wells of the southern and northern sides of the Dnipro-Donets basin (DDB). In terms of lithology, the core samples were argillites (shales) – the vast majority, siltstones, sandstones, and limestones.*

Results. *An important result of this study is that the feature of the spatial distribution of the main parameters of kerogen organic matter has been established, depending on the depth of the Devonian oil and gas source rocks, their age, as well as the location of the wells from which the core was taken, on the Northern or Southern sides of the DDB. Using the methods of mathematical statistics on the basis of cluster analysis, the classification of rock samples with a clay composition relative to the prevailing type of organic matter was performed based on the data of laboratory studies on the Rock-Eval apparatus.*

Conclusions. *Quite high concentrations of organic matter in a significant number of studied samples (mainly in shales and limestones) were found at different depths, which are primarily corrected by the age of the Upper Devonian deposits. The regularities of changes in Tmax – the temperature of the maximum yield of hydrocarbons during kerogen cracking, depending on the depth of the location of rocks, which are distinct on the Southern and Northern sides of the DDB, have been established. This indicates different paleotectonic activity of the specified structural-tectonic elements in the post-Devonian period. On the South side, clay formations with a high kerogen content and high Tmax values are hypsometrically higher than on the Northern side of the Dnipro-Donets depression.*

Keywords: *Devonian, kerogen, pyrolysis, cluster analysis, hydrocarbons, Dnipro-Donets basin.*

Background

The study of the kerogen distribution in the Upper Devonian stratum of the Dnipro-Donets basin is important for understanding the geological structure and evolution of the sedimentary basin in the context of the reproduction of the hydrocarbon system, as well as for assessing their oil and gas potential. Kerogen, as the main source of hydrocarbons, is an important object in the process of basin analysis. The study of its quantitative and qualitative composition, as well as the features of its spatial distribution, makes it possible to increase the reliability of forecasts regarding the prospects of individual zones within the Dnipro-Donets basin. This is especially relevant for the onshore slope parts of the Dnipro-Donets depression, which for a long time has been one of the key areas of oil and gas exploration, including directly in Devonian deposits.

Highlighting previously unresolved parts of the overall problem

If we consider this article as a source of information with certain meaningful conclusions, then the research results below can be considered to be a certain addition to those already existing published data regarding the study of Upper Devonian deposits of the Dnipro-Donets basin, as a geological environment with existing oil and gas petroleum source rock. Due to the small number of prospecting and exploratory wells that revealed Devonian deposits, all representative collections of core material from such sections are extremely interesting in various geological aspects.

In the period 1980–2000, *interest in research on Devonian sediments* in oil and gas prospects within the Dnipro-Donets basin was *disengaged*. This was due to the negative results of drilling and testing, which did not meet the initial expectations for oil and gas deposits in the Devonian layers. However, poor oil and gas deposits were found in several areas, such as Yadutivska and Kinashivska. Therefore, the ultimate futility of Devonian deposits was not proven, and scientific research continued, albeit on a smaller scale.

Scientists Arsiriy and Kabyshev analyzed the difference of oil and gas potential between the Devonian deposits in the DDB and the Pripyat Trough. They concluded that the conditions for the formation and accumulation of oil and gas in these regions are different, and the prospects in the northwest of the DDB are worse. However, this does not indicate that this segment is completely hopeless. Researchers continue to consider Famennian as promising intersalt deposits, and Frasnian subsalt – less important. From a structural point of view, more attention is paid to the peripheral zones of large depressions and the slopes of the basement protrusions, while the basement uplifts are considered less promising (Stryzhak, & Korzhnev, 2012).

To evaluate the prospects of Devonian deposits, it is necessary to comprehensively assess the condition of all components of the hydrocarbon system. As you know, even the absence of one component or the conditionality of its parameters is enough to give up further studies regarding the assessment of oil and gas capacity and the presence of significant accumulations of hydrocarbons.

Many researchers were engaged in the study of the oil and gas source component system in the Dnipro-Donets basin. Rocks with a high content of organic matter were studied in detail. This mainly concerned the Carboniferous deposits, to a much lesser extent – the Devonian deposits of the depression (Lukin, 2006; Menning[1] et al., 2006; Menning[2] et al., 2006; Sachsenhofer et al., 2018; Stryzhak, & Korzhnev, 2012).

The most characterized by the core and the most studied is the upper part of the Devonian deposits within the Dnipro-Donets basin. However, the geochemical study of the deposits in relation to the oil and gas generation potential is insufficient and fragmented in the literature. For example, we can cite the monograph (Mykhailov et al., 2014), in which the structural and stratigraphic features of Devonian deposits are described in particular, as well as data on estimates of the thermal maturity of rocks (by the reflectivity of vitrinite), the content of organic carbon from mainly clayey parts of well sections in individual areas and deposits are given.

Therefore, additional new geochemical data on other areas from Devonian terrigenous sections are extremely important in terms of studying oil and gas formation with the aim of searching for new oil and gas deposits in the region.

Geological and geochemical features of the research objects

Special feature of the studied Upper Devonian deposits is primarily the presence of layers with a high or increased content of organic matter, which will potentially serve as a source of hydrocarbon generation. This fact is sufficiently described in the special literature, and we have every right to use the main theses and provisions regarding Devonian deposits, thanks to which the formation of deposits in the Devonian and post-Devonian times took place in the past.

Regarding the stratigraphic and spatial position of individual layers, strata and horizons of the Famennian and Frasnian layers of the Upper Devonian, one can refer to their concise description from the monograph (Mykhailov et al., 2014): "..Devonian deposits, as a rule, do not go beyond the edge faults, being located within the graben. In their composition, subsalt, lower salt, intersalt, upper salt and suprasalt complexes are often distinguished." The subsalt complex of the Frasnian layer is composed mainly of terrigenous rocks, in the upper part of the section they are replaced by limestones, dolomites and shales. It is noted that in the northwestern part of the depression, the Semyluk deposits of the Frasnian layers are composed of dark gray bituminous limestones, dolomites with interlayers of shales, bearing marks *of Domanicoid* sedimentation. It should be noted that volcanogenic conglomerates and tuff sandstones are sometimes found everywhere. The lower salt complex is represented by the Yevlanivsky and Livensky horizons. They lie transgressively on the sediments of the Voronezh horizon. Their lower part is composed of layering of rock salt, limestones, marls, anhydrites, sandstones, siltstones and tuffites. The upper one is completely composed of saline deposits (Mykhailov et al., 2014). The intersalt complex of the Famennian layer is the Zadonsky and Yeletsky horizons. They lie unconformably on the Evlanivsky-Livensky sediments. Composed of gray-colored rocks – shales, siltstones, sandstones with subordinate lenses of limestones, effusives and pyroclastic formations. Mudstones and siltstones predominate in the central parts of the depression, and sandstones dominate in the coastal areas (Mykhailov et al., 2014; Mykhailov, & Karpenko, 2020). The suprasalt complex of the Famennian stage corresponds to the upper part of the Dankovo-Lebedyan Formation. It is composed in the lower part of gray sandstones, siltstones and shales.

Within the northwestern part of the Dnipro-Donets basin, only three small deposits of heavy oil have been discovered in the Devonian sediments – Bakhmatske, Kholmske and Tvanske. Also, recoverable oil potential has been established on Yadutivske (Northern pre-board zone), and recoverable gas potential – on Petrovska Square (Southern pre-board zone) (Mykhailov et al., 2014).

Rock samples from the deposits of the Famennian and Frasnian levels were taken from wells, which can be divided into two groups according to their geographical location: belonging to the Northern and Southern subzones. Tab. 1–3 characterize the general distribution of samples by lithology, stratigraphic affiliation and location of wells. Statistical characteristics refer to the total organic carbon content (TOC) in rocks.

Table 1

Statistics characteristics of the total organic carbon content (TOC, %) in the rocks of the main lithotypes

Lithology	Valid N	Mean	Minimum	Maximum	Std.Dev.
Shale	90	2,65	0,81	17,18	2,51
Limestone	16	1,46	0,31	3,39	0,90
Siltstone	2	1,58	1,58	1,58	0
Shale+limestone	2	2,77	2,77	2,77	0
Metasomatitis	2	1,05	1,05	1,05	0
Sandstone+shale	8	1,77	1,17	2,9	0,7
Sandstone	4	8,18	1,92	14,44	7,2

Table 2

Statistics characteristics of the total organic carbon content (TOC, %) in the rocks of the Devonian stratigraphic subdivisions

Stratigraphy	Valid N	Mean	Minimum	Maximum	Std.Dev.
D_3fm_2	10	5,97	1,02	17,18	6,58
D_3f_2	28	2,81	0,67	14,44	3,41
D_3fm_1	70	2,20	1,02	3,96	0,73
D_3fm_3	6	2,70	2,47	2,87	0,19
D_3f_3	2	1,05	1,05	1,05	0,00
D_3f_1	8	1,12	0,31	1,69	0,63

Table 3

Statistics characteristics of the total organic carbon content (TOC, %) in Devonian rocks depending on the location of the investigated layers of rocks

Placement	Geography	Valid N	Mean	Minimum	Maximum	Std.Dev.
Over salt	Northwestern board zone	6	9,24	2,1	17,18	6,77
Under salt	Northwestern board zone	18	1,60	0,31	3,39	0,89
Between salt	Northwestern board zone	70	2,20	1,02	3,96	0,73
Over salt	Southern board zone	10	2,05	1,02	2,87	0,86
Under salt	Southern board zone	18	3,27	0,67	14,44	4,17

Fig. 1 shows an example of a typical shale from a collection of rock samples from the Famennian layer of the studied deposits. It should be noted that all clay rocks contain transformed organic material of varying degrees of preservation. Lithology of the sample: siltstone's shale. The structure is silt-pelitic, the texture is disordered. The rock is composed of hydromica, muscovite, biotite, admixture of the silt fraction is 10 %, paleontological fossils occupy 10 %, replaced by calcite, sometimes by silica. The fossils are represented by algal detritus and undiagnosed remains. The rock is sprinkled with pyrite, an interlayer enriched with pyrite secretions is observed.

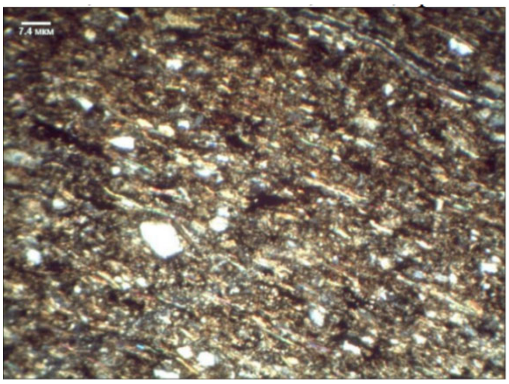

Fig. 1. Photomicrograph of siltstone's shale from a depth of 5319-5324 m. The Famennian layer, the northern board zone of the Dnipro-Donets basin

Methods

Express methods for assessing the maturity of organic matter in sedimentary rocks often use physical and chemical indicators, which allows you to quickly and efficiently determine the stage of maturity of rocks and organic matter (OM). The main methods include (Hunt, 1979; Mack, & Engel, 1993; Peters, Walters, & Moldowan, 2005; Lupoi et al., 2017):

Rock-Eval pyrolysis (Rock-Eval): this is one of the most common methods that allows you to assess the thermal maturity of OM by pyrolysis. Indicators S_1, S_2 and *Tmax* are determined, which indicate the amount of hydrocarbons that have already formed or may be formed when the rock is heated. The parameter *Tmax* (temperature of maximum release of hydrocarbons) serves as the main indicator of thermal maturity.

Vitrinite reflectance (imprint analysis): this is a method of measuring the level of vitrinite reflectance in a rock, which is also an indicator of maturity. A vitrinite reflectance under a microscope gives an idea of the maximum temperature the rock has experienced, which correlates with the maturity of the OM.

Fluorescence of organic components: a method that uses fluorescence to determine changes in the structure of organic matter. Over time, OM loses its ability to fluoresce, which can be an indicator of maturity.

IR spectroscopy: infrared spectroscopy helps to detect changes in the functional groups of OM that depend on the degree of maturity. In particular, absorption analysis in areas characteristic of methylene groups, aromatic structures, etc. When it is carried out, the sample is irradiated with infrared light, and certain functional groups in the molecules absorb light at their characteristic wavelengths. This makes it possible to analyze which groups are present in the sample and how their concentrations change with the growth of OM maturity.

The main aspects of the method:

Absorption at different wavelengths: Changes in methylene ($–CH_2–$) and methyl ($–CH_3$) groups, as well as aromatic and oxygen-containing groups (carbonyl, carboxyl) are important for the maturity of organic matter.

Intensity of methylene and methyl band groups: an increase in intensity in the 2850–2950 cm^{-1} window, characteristic of aliphatic hydrocarbons, often indicates increased maturity.

Changes in aromatic groups: in the range of 1600 cm^{-1} the intensity of the band may indicate an increase in the content of aromatic structures, which is characteristic of more mature OM.

Ratio of band intensities: the ratio of the intensities of aromatic and aliphatic bands (for example, the ratio of intensities in the 1600 cm^{-1} and 2850 cm^{-1} windows) allows one to estimate how thermally the material has been exposed.

Gas chromatography and gas chromatographic mass spectrometric analysis: these methods allow analyzing the chemical composition of organic components, revealing hydrocarbon fractions and the ratio of biomarkers, which are indicators of OM maturity.

Gas chromatographic mass spectrometric analysis is widely used to analyze hydrocarbon fractions, especially biomarkers, which are organic molecules with a clear correlation with OM maturity. It combines gas chromatography (GChr) to separate the components of a mixture and mass spectrometry (MS) to identify and determine the structure of individual molecules.

The main aspects of the method:

Biomarker analysis: biomarkers are complex organic molecules that can store information about the chemical environment and maturation stage of the OM.

Steroids and triterpenoids: with increasing temperature and pressure, steroid and triterpenoid molecules are converted into more stable forms. The ratio of steranes to triterpenes (eg, sterane/hopane) can indicate the stage of maturity.

Isomers of hopanes and steranes: the ratio of different structural isomers, such as αβ- to ββ-hopanes, shows the degree to which organic molecules are transformed under the influence of temperature.

Distribution of n-alkanes: long-chain n-alkanes gradually disappear, and short-chain ones become dominant in the late stages of maturity. This makes it possible to estimate maturity by the distribution of hydrocarbons.

Gas chromatographic mass spectrometric analysis makes it possible to determine the stages of OM catagenesis, especially when other methods, such as Rock-Eval pyrolysis, are no longer accurate.

Each of the above methods has its advantages and limitations, and is often used in combination with others to obtain a more accurate picture of the maturity of organic matter in sedimentary rocks.

Nevertheless, pyrolysis on the device Rock-Eval is one of the most effective methods for estimating the amount and maturity of organic matter in sedimentary rocks used in geochemistry to determine hydrocarbon generation potential. This method is fast, does not require complex sample preparation, and provides valuable information on the carbon composition and thermal history of the OM.

During the analysis, the sample is gradually heated to different temperatures in two main stages:

Pyrolysis: the first stage of heating without access to air, during which organic matter is decomposed into volatile compounds, which can be hydrocarbons, CO_2 and other gases.

Oxidation: after pyrolysis, the sample residue is oxidized to measure the amount of residual organic carbon.

Detect the thermal maturity: *Tmax* parameter is a fairly reliable indicator of thermal maturity, which allows you to assess whether the rock has reached the necessary temperature to generate oil or gas.

Assessment of the generation potential: indicators S_1 and S_2 allow assessing whether the rock is promising for hydrocarbon generation, and also indicating the stage of catagenesis.

Division of types of OM: in addition to the indices *HI* and *OI*, one can determine the type of OM, for example, humus, sapropelitic or mixed origin, which is important for predicting the characteristics of possible hydrocarbons.

Evaluation of thermal history: the method allows getting an idea of the thermal history of rocks and the stage of catagenesis, which is important for the exploration of deposits.

Limitations of the Rock-Eval method. Limitations for highly mature rocks: for highly mature rocks, the method becomes less effective because the OM has undergone maximum changes and further heating does not release sufficient hydrocarbons for accurate measurements.

Difficulty in interpretation: results can be difficult to interpret in complex systems with multiple OM types or mixed thermal histories.

Due to its advantages, Rock-Eval remains the main tool in the study of thermal maturity and hydrocarbon generation potential of sedimentary rocks, allowing reliable rapid analysis of OM in the early stages of exploration.

This article is based on the results of laboratory studies of rocks from the Devonian deposits of the Northern and Southern sides of the Dnipro-Donets basin.

Results

A significant number of the figures below allow visualizing the peculiarities of the distribution of organic matter (more precisely, its indicator – TOC), parameters of OM depending on the stratigraphic affiliation and geographical location of the wells from which the rock material was taken for analysis. Only shale samples were selected for the study, which, among other lithological types of rocks, can be potential oil and gas source rocks for this type of section of the Dnipro-Donets basin.

The content of organic carbon TOC in Devonian rocks almost everywhere, regardless of age, is mostly more than 1 %, on average 2,65 % (Tab. 2, Fig. 2). That is, Devonian shales can potentially serve under certain thermal conditions as part of the hydrocarbon system – the parent rock. Anomalous values of two samples D_3fm_1 age (TOC > 8 %) correspond to black shale rocks, which are potentially (again under certain other conditions) oil- or gas shale layers, in the future – separately hydrocarbon deposits.

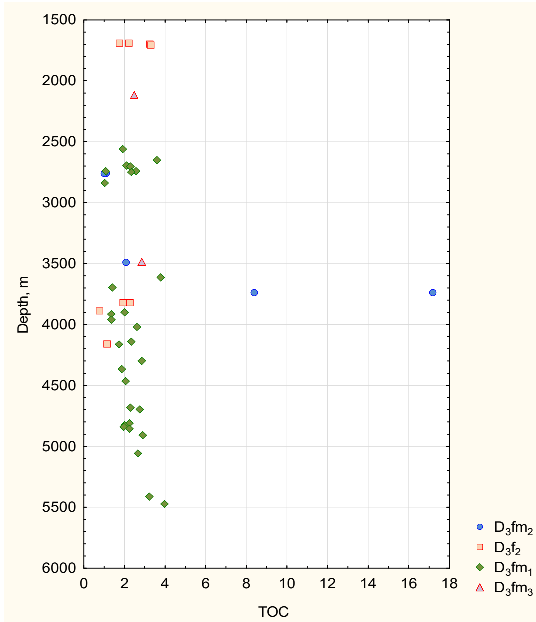

Fig. 2. Dependence of the *TOC* parameter for shales on the depth of sediments relative to Frasnian and Famennian stages

Distribution of TOC practically does not change for shales, remaining within 1–4 %.

Fig. 3 indicates the regularity of the distribution of depths of Devonian shale strata for the Southern and Northern sides of the DDB. On the Northern side, the Devonian sediments dip significantly in the well sections – in the range of 2550–5500 m, on average – 3900 m. In the South side, in the well sections, the Devonian is much higher: shales are found at depths of 1700–4200 m, on average – 2800 m. However, the distribution of the values of the indicator (*S1+S2)/TOC* almost does not change: from very low values to 80–90. 8 samples of shales of the North side have abnormally high values of generation potential – 200 or more (*S1+S2)/TOC*. The Rock-Eval studies carried out in the laboratory of the State Enterprise "Ukrnaukageotsentr" (Poltava) and their meaningful interpretation indicate the absence of mature hydrocarbons in a significant number of mudstone samples. At the same time, a group of clay rocks in the amount of 8 samples shows that the Devonian deposits are currently thermally mature, which indicates their generative potential to contribute to the formation of hydrocarbon deposits.

The considered distributions of individual parameters of shales depending on the depth of the sediments indicate fairly uniform characteristics of the rocks inherent in the Southern and Northern sides of the Dnipro-Donets basin. However, not everything is so clear-cut regarding the trends of changes in the thermal maturity of organic matter in these zones. In Fig. 4, significantly different gradients of changes in the value of *Tmax* are observed from the depth of deposits.

Constructed orthogonal regression lines clearly indicate different gradients of *Tmax* change: a significantly larger angle of inclination for the Northern part of the DDB and a smaller one in the Southern part (zone).

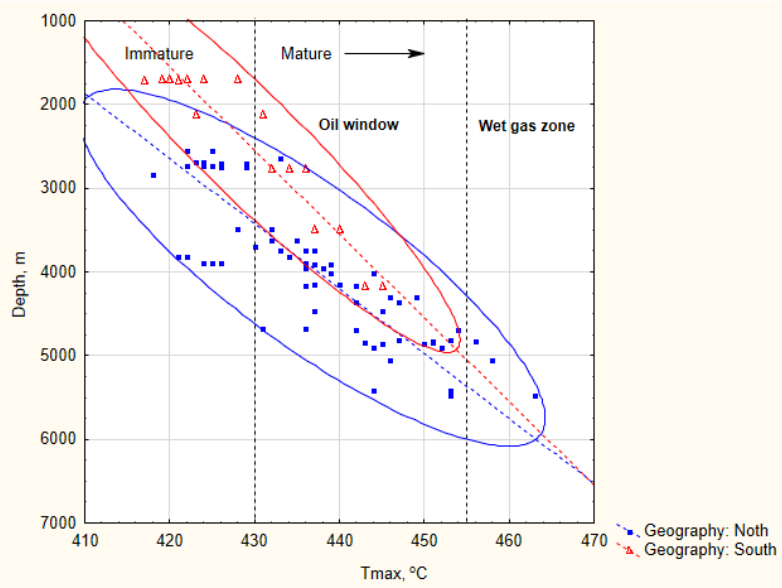

Fig. 3. Dependence of the *Tmax* parameter for shales on the depth of sediments relative to the Northern and Southern sides of the Dnipro-Donets depression

There may be several reasons for such differences:

Structure and mineral composition of rocks. Although the studied rocks are of the same age and lithological affiliation, their mineral composition may be different. Accordingly, the influence of chemically active components of the solid part (matrix) of rocks can also be different. However, this is a rather weak argument regarding the significant differences in *Tmax* values found, especially at depths less than 3500 m.

Temperature gradients. Paleotemperature gradients could vary significantly in different parts of the depression. The Southern part may have experienced more intense geothermal flow, leading to faster thermal maturity of the kerogen.

Tectonic processes in the past. Tectonic activity could affect the distribution of pressures and temperatures, which changed the conditions for maturity (Karpenko, & Tynik, 2018). For example, more significant tectonic events could have occurred in the Southern part, which created conditions for increased maturity. Here it should be noted that, most likely, tectonic processes affected the significant uplift of the territory in the post-Devonian period within the Southern Coastal Zone, which caused the removal of mudstones with sufficiently mature organic matter – kerogen to shallower depths already after their thermal heating in the Devonian period.

Also, an important factor could be *the time* during which the organic matter was under the influence of heat and pressure, which affected its maturity.

Composition and type of kerogen. Different types (composition) of the original organic material could react differently to the same paleoconditions of kerogen maturation.

Hydrogeological conditions. Mineralization and the composition of chemical compounds in formation water could affect the processes of thermal maturity.

The listed factors deserve a detailed study regarding their influence on the degree of thermal maturation of kerogen. However, it is already possible to make some assumptions based on the results of the analysis of published studies. In the paper (Ivanova, & Gavryltsev, 2021), the data of paleogeothermal reconstructions performed at the Institute of Geological Sciences of the National Academy of Sciences are given. The authors of this work determined paleogeothermal gradients, paleodepths of maximum paleotemperatures, and amplitudes of vertical movements of rock massifs over a significant part of the Dnipro-Donets depression. The analysis of cartographic constructions in the work (Ivanova, & Gavryltsev, 2021) allows us to draw conclusions about the main factors that led to significant differences between the thermal maturity of rocks at the same depths of occurrence in the Southern and Northern sides of the DDB. The value of the geothermal gradient in the late Paleozoic time was 3,3–3,5 ˚C/100m within the Northern zone of wells and 2,9–3,3 ˚C/100m within the Southern zone of wells. That is, more significant temperatures may have been in the Northern zone. However, there is a significant difference in the amplitudes of vertical movements, which are determined on the map of vertical movements of tectonic and salt dome structures in the Permian period in the article (Ivanova, & Gavryltsev, 2021). In the Northern zone, amplitudes of vertical movements corresponding to a layer of eroded rocks of less than 0,5 km have been established. At the same time, in the Southern zone within the studied wells, the thickness of eroded rocks is 1–1,5 km according to the map.

Actually, these vertical movements in the post-Devonian (mainly Permian) time caused the erosion of sedimentary deposits, which is significantly different in the Northern and Southern side zones. Therefore, a different degree of maturity of rocks and organic matter is observed at the same depths in different side zones. At a depth of approximately 3000 m (Fig. 3) in the Northern zone, organic matter has not yet reached the maturity of active generation of hydrocarbons. And at this depth in the Southern zone, the kerogen in mudstones has already reached maturity, which corresponds to the "oil window" of generation (*Tmax* more than 430 ˚C). At modern sediment depths of 4,000–5,000 m in mudstones of Late Devonian age, the kerogen is sufficiently mature and in terms of *Tmax* is in the "oil window" zone, regardless of the geographical location of the wells for both zones. At the same time, at such depths, the trend of higher values of thermal maturity of organic matter in the sections of wells of the South zone still persists. At the same values of

Tmax, the depth difference in the "oil window" zone between the two zones is approximately 0,5 km. This corresponds to the difference in the values of the amplitudes of vertical movements in the Northern and Southern zones of the Dnipro-Donets basin in the areas where the wells are located.

The unclear question remains regarding the type of organic matter (kerogen) and its ability to generate a significant amount of hydrocarbons under all favorable conditions (temperature, time, pressure, hydrogeological regime, etc.). There are standard approaches that allow for the characteristics of studies obtained on Rock-Eval using Van Krevelen diagrams to obtain the most likely type of organic matter and its thermal maturity (Hunt, 1979). We made an attempt to estimate the type of organic matter in the Upper Devonian mudstones using the cluster analysis method, which refers to "classification without learning" technologies. The main parameters obtained during pyrolysis of shale samples using the Rock-Eval method were used as initial data (Tab. 4).

The optimal 4 groups (clusters) of shale rocks, which differ significantly in the complex of geochemical parameters, were chosen (Tab. 4). The highest values of the hydrogen index *are HI* and, at the same time, the lowest are the values of the oxygen index *OI* – in shales of the first group. This clearly indicates the genetic origin of organic matter, which according to the Van Krevelen diagram corresponds to kerogen types I–II (Fig. 4).

Table 4

Statistics characteristics (mean) of the geochemical parameters of the Upper Devonian mudstones organic matter for each cluster (according to the results of the cluster analysis)

Parameters	Cluster no. 1	Cluster no. 2	Cluster no. 3	Cluster no. 4
Tmax, °C	431,0	432,5	436,8	429,0
HI	208,6	60,9	21,9	52,4
OI	9,68	11,3	14,4	91,6
TPI	0,179	0,13 5	0,229	0,146
S_3/TOC	9,57	11,37	14,51	91, 8
(S_1+S_2)/TOC	262,5	70,2	28,0	60,9

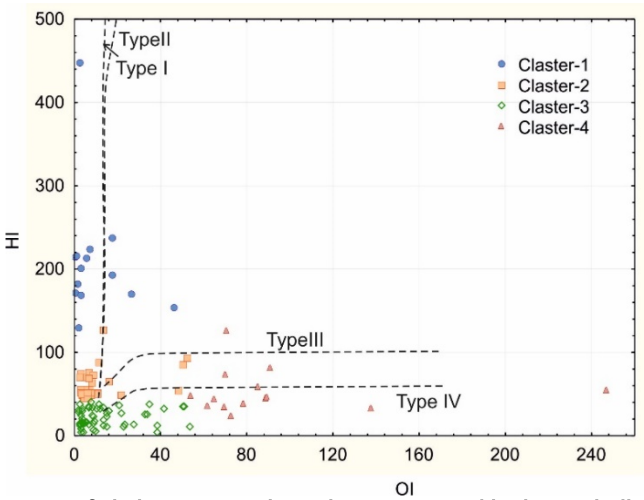

Fig. 4. Classification of kerogen types of shale core samples using oxygen and hydrogen indices from the studied wells taking into account cluster analysis grouping. Modified Van Krevelen diagram (Ratnayake, Kularathne, & Sampei, 2018)

It should be noted that the average values of the *Tmax* parameter in the clusters do not differ significantly, which indicates the classification of shales according to the data of the cluster analysis according to other parameters, which are largely related to the type of organic matter and the phase of hydrocarbon generation. The parameter *$(S_1+S_2)/TOC$* indicates the genetic potential or the total amount of HC that could be generated by the rock (without taking into account the migration of hydrocarbons from the rock that has already occurred). The combination of S_1+S_2 is advisable here, because differentiation by the type of hydrocarbons (liquid or gaseous) capable of generating kerogen will lead to an increase in the number of predefined classes in cluster analysis, which is inappropriate with a relatively small sample size. A significant number of shale rocks in statistical sample have a degree of thermal maturity within the "oil window" (Fig. 3) and only 3 samples in value of *Tmax* are in the wet-gas zone. The organic matter of samples belonging to clusters 3 and 4 has the lowest generation potential. This is confirmed by low values of the *$(S_1+S_2)/TOC$* parameter and high values of the S_3 */TOC* parameter. In the Rock-Eval method, the S_3 parameter analysis helps estimate the amount of oxygen-containing organic components in the core sample. During the analysis, S_3 displays the amount of carbon dioxide (CO_2) released when the organic substance is heated in an inert gas atmosphere. High values *of* S_3 can indicate such characteristics of the organic matter as the type of organic matter, the high degree of oxidation of the organic matter, as well as the low potential ability to generate hydrocarbons. Type of organic matter: high values of S_3 are usually associated with humic or carbonaceous organic matter (types III and IV kerogen), rich in oxygen, which is characteristic of terrestrial vegetation, peat deposits, coal, and highly oxidized samples. A high content of oxygen-containing groups in organic matter can be a sign of oxidation or decomposition of organic matter, which is also observed in samples with kerogen types III or IV. Samples with high *S_3/TOC* generally have less oil and gas generation capacity because the oxygen-containing groups contribute to the formation of CO_2 during thermal decomposition, rather than liquid or gaseous hydrocarbons. The organic matter in the samples of cluster 2 most likely belongs to types II–III, but its potential for generating hydrocarbons is not high. The general conclusion about the kerogen of samples in cluster 2 based on the complex of geochemical features (see Tab. 4) is as follows. Kerogen has a low residual generation potential, may be represented by type III kerogen, with limited potential for oil generation, or type II in the phase of reduced generation capacity. It is at the late stage of the oil window, or has already partially exhausted its potential for the generation of liquid hydrocarbons. This kerogen is already mature and has low residual hydrocarbon content, which limits its prospects as a source of liquid hydrocarbons.

Based on the results of the analysis, it can be stated that only a small number of samples (which belong to cluster 1) have a high potential for the generation of liquid and gaseous hydrocarbons. All others, although their generation cannot be denied, have limited opportunities to generate oil (mostly) or gas in significant volumes even at thermal maturity.

Discussion and conclusions

Analysis of pyrolysis results of 114 core samples (shales, sandy shales, calcareous shales) from the Upper Devonian deposits (Famenan and Frasnian layers) of the Northern and Southern side zones of the Dnipro-Donets Basin was performed**.** Laboratory studies were performed on pyrolytic equipment Rock-Eval. The geochemical characteristics of the rocks made it possible to draw several important conclusions.

1. Most of the core samples have already reached the thermal stage of the "oil window", but some are still in the state of "immaturity", especially at depths below 3000–2500 m.

2. A different degree of organic matter maturity of shales at the same depths in different side zones was established. At a depth of approximately 3000 m in the Northern zone, the organic matter has not yet reached the maturity of active generation of hydrocarbons (Fig. 3). And at this depth in the Southern zone, the kerogen in mudstones has already reached maturity, which corresponds to the "oil window" of generation (*Tmax* more than 430 ˚C).

3. The difference in the depth of sediments, where the boundary of kerogen maturity passes in the Southern and Northern zones of the Dnipro-Donets depression, is explained by different tectonic activity mainly in Permian time. In the Northern zone, the amplitudes of vertical movements corresponding to a thickness of eroded rocks of less than 0,5 km were calculated. At the same time, in the Southern zone within the studied wells, the thickness of eroded rocks is 1–1,5 km according to the map data (Ivanova, Gavryltsev , 2021).

4. At sediment depths of 4,000–5,000 m in mudstones of the Famennian and Fransian levels, the kerogen is sufficiently mature and in terms of *Tmax* is in the "oil window" zone, regardless of the geographical location of the wells for both zones (Fig. 3).

5. The results of the cluster analysis of geochemical parameters allowed to distinguish 4 classes of shales. Only a small number of samples 12,2 % (Class 1) host kerogen with high hydrocarbon generation capacity at this time, are thermally mature and have high hydrogen index at very low oxygen. They correspond to the 1st type of organic matter. Such a percentage is explained by the variety of facies conditions of the formation of the Upper Devonian deposits, respectively, by the different types of organic matter preserved in them.

The final conclusion regarding the potential of hydrocarbon generation, even with a limited volume of shale core sampling, can be made with a more detailed analysis of all sample parameters at Rock-Eval, lithological and petrographic studies. It is also possible to significantly expand the research on the generation potential of Devonian argillites using the results of well logging using the Q. Passey method for determining the content of organic carbon.

Authors' contribution: Ivan Karpenko – conceptualization, methodology, formal analysis, writing (original draft); Anastasiia Chupryna – data validation, writing (review and editing); Oleksii Karpenko – formal analysis, writing (review and editing).

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ТЕРМІЧНА ЗРІЛІСТЬ ПОРІД ДЕВОНУ В АСПЕКТІ ЇХ ЛІТОЛОГО-ФАЦІАЛЬНОЇ І ВІКОВОЇ НАЛЕЖНОСТІ. ПІВНІЧНИЙ І ПІВДЕННИЙ БОРТИ ДНІПРОВСЬКО-ДОНЕЦЬКОЇ ЗАПАДИНИ

Вступ. ***Видобуток вуглеводнів (ВВ) у відкритих родовищах скорочується, а родовища, відкриті останніми роками, зазвичай невеликі за запасами і вже не можуть забезпечити ресурсну базу для його нарощування. Аналіз досвіду провідних нафтогазових компаній показує, що суттєве нарощування ресурсної бази та відкриття значних за запасами родовищ ВВ можливо отримати за рахунок використання сучасних технологій пошуків, які активно використовують у своєму арсеналі моделювання вуглеводневих систем на територіях, що вивчають. Найперспективнішими стратиграфічними комплексами для пошуку нових родовищ ВВ в межах Східного регіону України залишаються кам'яновугільні та верхньодевонські відклади.***

Методи. ***Використовувались методи математичної статистики для створення модельних побудов, які дали змогу провести змістовний аналіз вихідної геологічної і геохімічної інформації. Вихідними даними були результати лабораторних досліджень методом піролізу (Rock-Eval) зразків гірських порід з пошукових і розвідувальних свердловин південного і північного бортів Дніпровсько-Донецької западини (ДДЗ). У літологічному плані зразки керну являли собою аргіліти (переважна більшість), алевроліти, пісковики, вапняки.***

Результати. ***Важливим результатом дослідження є те, що встановлено особливість просторового розподілу основних параметрів керогену органічної речовини залежно від глибини залягання перспективних нафтогазоматеринських порід девону, їх віку, а також – від розташування свердловин, з яких відбирався керн, – на Північному чи Південному бортах ДДЗ. Методами математичної статистики на основі кластерного аналізу виконано класифікацію зразків порід глинистого складу відносно переважального типу органічної речовини на основі даних лабораторних досліджень на апаратурі Rock-Eval.***

Висновки. ***Доволі високі концентрації органічної речовини у значній кількості досліджених зразків (переважно в аргілітах і вапняках) виявлено на різних глибинах, які передусім корегуються віковою належністю відкладів верхнього девону. Встановлено закономірності зміни T_{max} – температури максимального виходу вуглеводнів при крекінгу керогену залежно від глибини розташування гірських порід, які є відмінними на Південному і Північному бортах ДДЗ. Це свідчить про різну палеотектонічну активність вказаних структурно-тектонічних елементів у післядевонський час. На Південному борту переважно глинисті утворення з високим вмістом керогену і високими значеннями T_{max} зосереджені гіпсометрично вище, ніж на Північному борті Дніпровсько-Донецької западини.***

Ключові слова: ***девон, кероген, піроліз, кластерний аналіз, вуглеводні, Дніпровсько-Донецька западина.***

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