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## DYNAMICS OF SEDIMENTO-LITHOGENESIS AND HYDROCARBON GENERATION IN DEVONIAN SEQUENCE OF THE LVIV DEPRESSION BASED ON THE RESULTS OF GEOCHEMICAL AND PALYNOLOGICAL STUDIES

The purpose of this work is to study depositional history and the dynamics of post-sedimentary transformations, in particular the thermal maturity of kerogen in the Middle-Upper Devonian rocks of the Lviv Paleozoic Depression. Methodology. This study utilized an integrated approach involving geochemical analyses, specifically focusing on parameters of Rock-Eval pyrolysis such as total organic carbon content, temperature  $T_{max}$ ,  $S_2$  oil potential, and palynological studies that included the color index of microfossils. Results. The results from the combined geochemical analysis (involving 20 core samples from 9 wells through Rock-Eval pyrolysis) and palynological analysis (44 core samples from 8 wells) allowed for determining the content, genetic type and generational properties of organic matter in the Middle and Upper Devonian rocks of the Lviv Paleozoic Depression. The rocks contain kerogen of both marine (type II) and terrestrial (type III) origin. Based on palynological studies, the kerogen was found to contain humic and sapropelic-liptinite components. The thermal maturity level of kerogen was determined using both Rock-Eval  $T_{max}$  parameter and the color index of microfossils. Within the Lviv Paleozoic Depression, three zones are identified according to the degree of thermal maturity of kerogen. Originality. As a result of this study, the sedimentary and post-sedimentary evolution of the Middle-Upper Devonian strata of the Lviv Paleozoic Depression was investigated. For the strata of this age range, the combined use of palynological and geochemical methods has been applied for the first time. This made it possible to estimate the thermal maturity of kerogen in organic-rich rocks in different parts of the Depression. Practical significance. The comprehensive geochemical and palynological studies allowed to establish the regularities of the processes of thermal maturation and hydrocarbon generation in the Middle-Upper Devonian rocks of the Lviv Paleozoic Depression. Based on these findings, we can determine their potential role in the formation of oil and gas accumulations.

**Keywords:** Lviv Depression; Devonian; kerogen type; temperature  $T_{max}$ ; color index of microfossils; hydrocarbon generation zones.

### Introduction

Within the western oil- and gas-bearing region of Ukraine, the Lviv Paleozoic Depression is of particular interest from the point of view of petroleum exploration. Numerous geological and geophysical studies have been carried out within this territory, yet it remains largely underexplored with significant oil and gas potential that is often underestimated [Krupsky et al., 2020]. Currently, the primary focus of research is on Middle Devonian deposits, which include two discovered gas fields: Lokachi and Velyki Mosty. Additionally, the Middle and Upper Devonian strata within the adjacent territory of the Lublin Depression of Poland are known to be oil and gas-bearing, with three gas and one oil field identified: Ciecierzyn,

Melgiew, Komarów and Glinnik [Helcel-Weil, Dzięgielowski, 2003]. Devonian strata were formed within the single sedimentary basin of the southwestern slope of the East European Platform. As a result of large-scale post-Variscan erosion, they were preserved only in such geological structures as the Lublin and Lviv Depressions as well as in the Dobrogean Foredeep. Devonian sequence is the thickest within the Paleozoic sedimentary succession.

The sediments of this age have a global distribution and are typical deposits of the carbonate platform [Kiessling et al., 2003; Shevchuk et al., 2024]. The Devonian sequence of the Lviv Depression includes both organic-rich rocks capable of generating hydrocarbons and thick terrigenous-carbonate beds with high reservoir properties, as well as sulfate-

carbonate rocks that serve as seals. This provides favorable geological conditions for the formation and preservation of hydrocarbons [Radkovets et al., 2017].

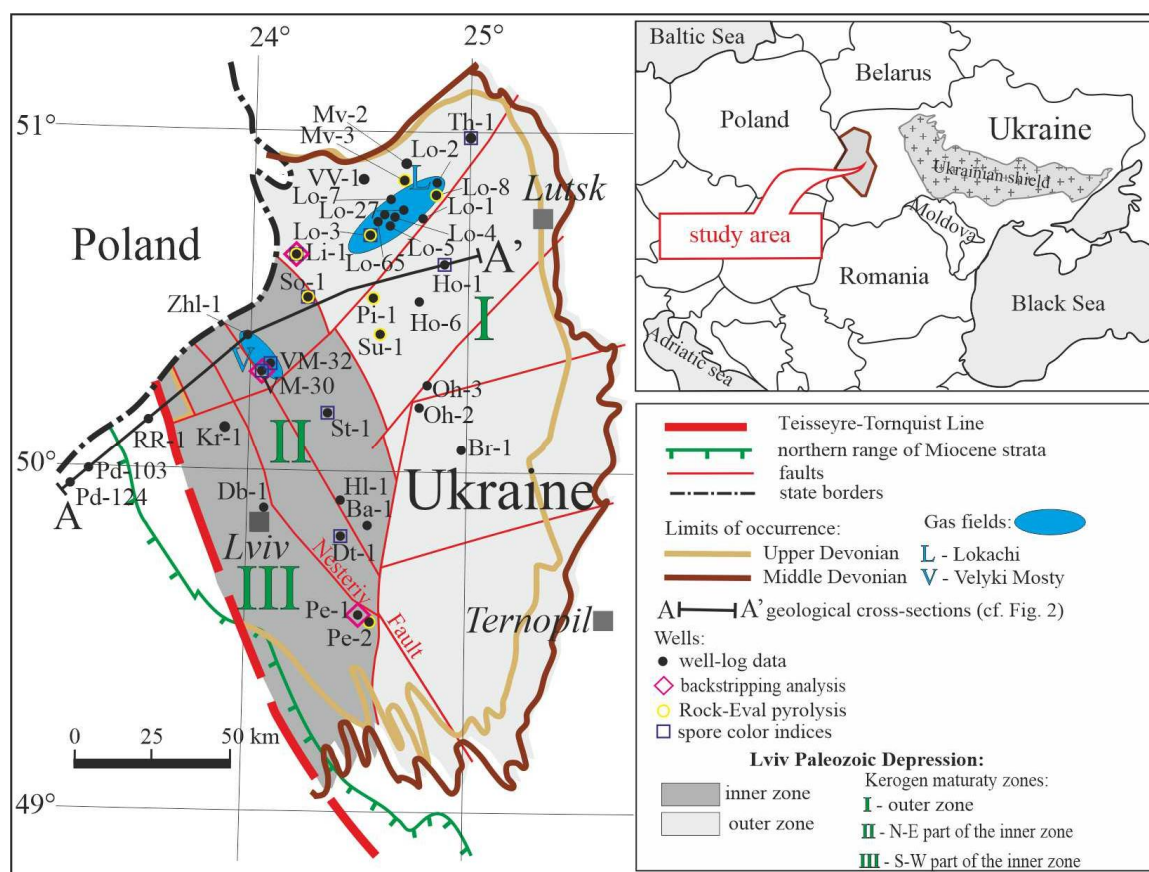
An important component for elucidating the patterns of hydrocarbon accumulations distribution in the Paleozoic sequence of the Lviv Paleozoic Depression is the study of hydrocarbon generation processes, in particular the thermal maturity of organic-rich rocks. For this purpose, a complex of palynological and geochemical investigations was used in this study, which allowed assessing the postsedimentary transformations of the Devonian oil and gas-bearing sedimentary sequence. Reconstruction of the history of tectonic subsidence and sedimentation rate using 1-D modeling became the basis for elucidating the patterns of the sedimentary

basin evolution and postsedimentary transformations of Paleozoic sediments within the studied region.

## Geological structure

### Tectonic structure of the Lviv Paleozoic Depression

According to the tectonic scheme [Fedyshyn, 1998; Krupsky, 2020; Anikeyev & Maksymchuk, 2025], Hercynian tectonic movements in the region led to the emergence of such a structure as the Lviv Paleozoic Depression. From the north and west, the Lviv Depression is limited by tectonic dislocations: the Volodymyr-Volyn and Rava-Ruska faults. The southern and southeastern boundaries are traced along the wedging line of Middle Devonian deposits. The Lviv Depression is divided into two zones, inner and outer (Fig. 1).



Wells: Ba – Baluchyn; Br – Brody; VV – Volodymyr-Volynskyi; VM – Velyki Mosty; Db – Dublyany; Dt – Dobrotvir; Hl – Hlynyany; Ho – Horokhiv; Kr – Krekhiv; Li – Litovyzh; Lo – Lokachi; Mv – Mynkiv; Oh – Ohlyadiv; Pe – Peremyshlyany; Pi – Pidberezzya; So – Sokal; Su – Sushne; St – Stremin; Pd – Pidluby; RR – Rava Ruska; Th – Tykhotyn; Zhl – Zhuzhelyany.

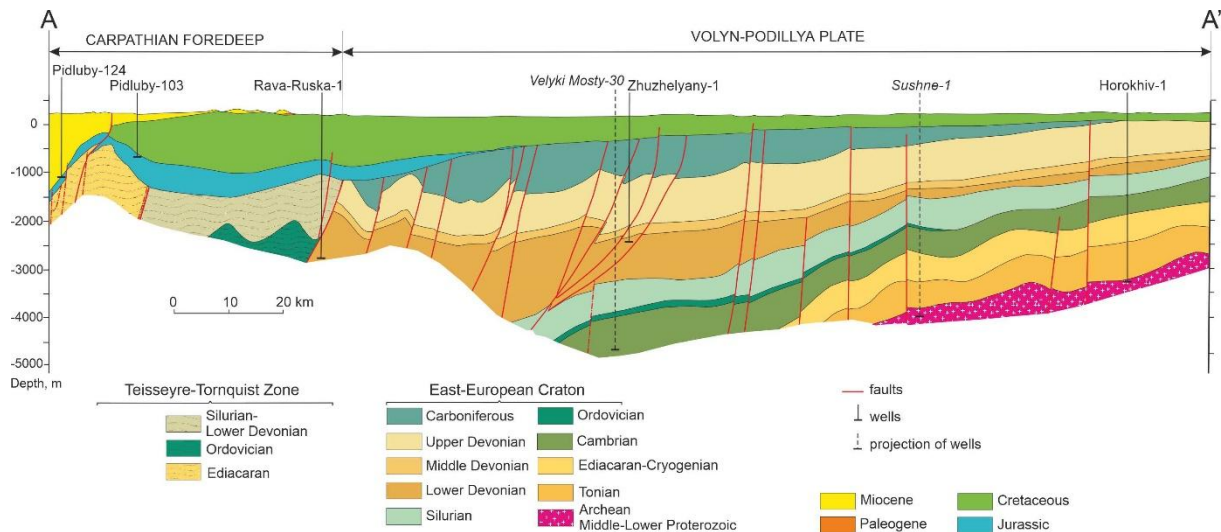
The boundary between the outer and inner zones goes along the Ustyluh-Rohatyn fault. The outer zone gently dips in the west and southwest direction to depths of 3–3.5 km. The basement of the Depression is overlain by a platform cover, which lies monoclinaly (Fig. 2). The cover comprises differently oriented and separated plicative dislocations and low-amplitude faults. The inner zone differs significantly in its structure from the outer one. The surface of the crystalline basement here dips quite sharply to the southwest to a depth of over 8 km.

### ***Lithological and stratigraphic characteristics of Middle and Upper Devonian rocks***

The Middle Devonian sequence within the Lviv Depression is represented by both Eifelian and Givetian stages [Gozhyk, 2013]. Their maximum thickness is 300 m. Middle Devonian strata are composed of carbonate rocks with layers of sulphate-carbonate

and clastic rocks. The thicknesses of each stage almost coincide, with only minor differences, irrespective of the depth at which the Middle Devonian deposits are found. This indicates denudation processes that occurred in Middle Devonian time, leading to the “leveling” of the pre-Upper Devonian surface. Clayey-carbonate (marls) and clayey (mudstones) rocks are also common in the sequence of this age [Krupsky, 2020; Radkovets et al., 2017, 2022].

The Upper Devonian formations are represented by the Frasnian and Famennian stages [Gozhyk, 2013] and have almost the same distribution area as the Middle Devonian (see Fig. 1). The sediments of this age are composed of carbonate and terrigenous-carbonate rocks. Their thickness varies from 50 m to 1,150 m, increasing from east to west. The Upper Devonian sediments are characterized by a rather uniform lithological composition throughout their distribution area.



**Fig. 2.** Geological cross-section along the line A – A' through the Carpathian Foredeep and the Volyn-Podillya plate [Vashchenko et al., 2007].

### **Purpose**

The purpose of this work is to study depositional history and the dynamics of post-sedimentary transformations, in particular the thermal maturity of kerogen in the Middle-Upper Devonian rocks of the Lviv Paleozoic Depression, their generation properties, and spatial patterns of the development of hydrocarbon generation processes.

### **Methodology**

The study utilized an integrated application of geochemical methods, specifically focusing on Rock-Eval pyrolysis parameters, including total organic carbon content, temperature  $T_{max}$ , hydrocarbon

potential  $S_2$ , and palynological analysis, in particular the color index of microfossils. Rock-Eval pyrolysis method is described in detail in [Espitalié et al., 1985]. The method of optical determination of the type of organic matter and the level of its catagenetic transformation by the composition of the organomacerate, the preservation and color of microphytofossils is described in [Staplin, 1977; Batten, 1996]. The composition, ratio of components, degree of maturity and stage of transformation of organic matter are determined on the basis of traditional palynological studies without additional costs for special equipment and technical processing of samples. Backstripping analysis of sedimentary history based on 1-D modeling was used to analyze the tectonic subsidence of

the paleobasin [Sclater, Christie, 1980]. Using the 1-D modeling, the history of tectonic subsidence and sedimentation rate of the Volyn-Podillya Basin was reconstructed. The Rock-Eval pyrolysis was conducted at AGH University, Krakow, Poland.

## Results

### Depositional history

Sedimentation in the Volyn-Podillya Basin lasted from the Ediacaran to the Carboniferous. As a result of post-Variscan erosion [Poprawa et al., 2018], the area of distribution of Ediacaran-Paleozoic sediments gradually decreases in the direction of the dipping of

the East European Platform. Thus, the Middle-Upper Devonian and Carboniferous strata occur only within the Lviv Paleozoic Depression (Fig. 3). Backstripping analysis has been made for 3 wells (Litovyzh-1, Velyki Mosty-30, Peremyshlyany-1) for a stratigraphic section from the Ediacaran to the Paleozoic (Fig. 4). For analysis, wells were selected in three tectonic blocks of the Lviv Paleozoic Depression, which penetrated the most complete section of the Ediacaran-Paleozoic (see Fig. 1). The blocks include: I - the outer zone of the Lviv Depression, II - the northeastern part of the inner zone of the Lviv Depression, III - the southwestern part of the inner zone of the Lviv Depression.



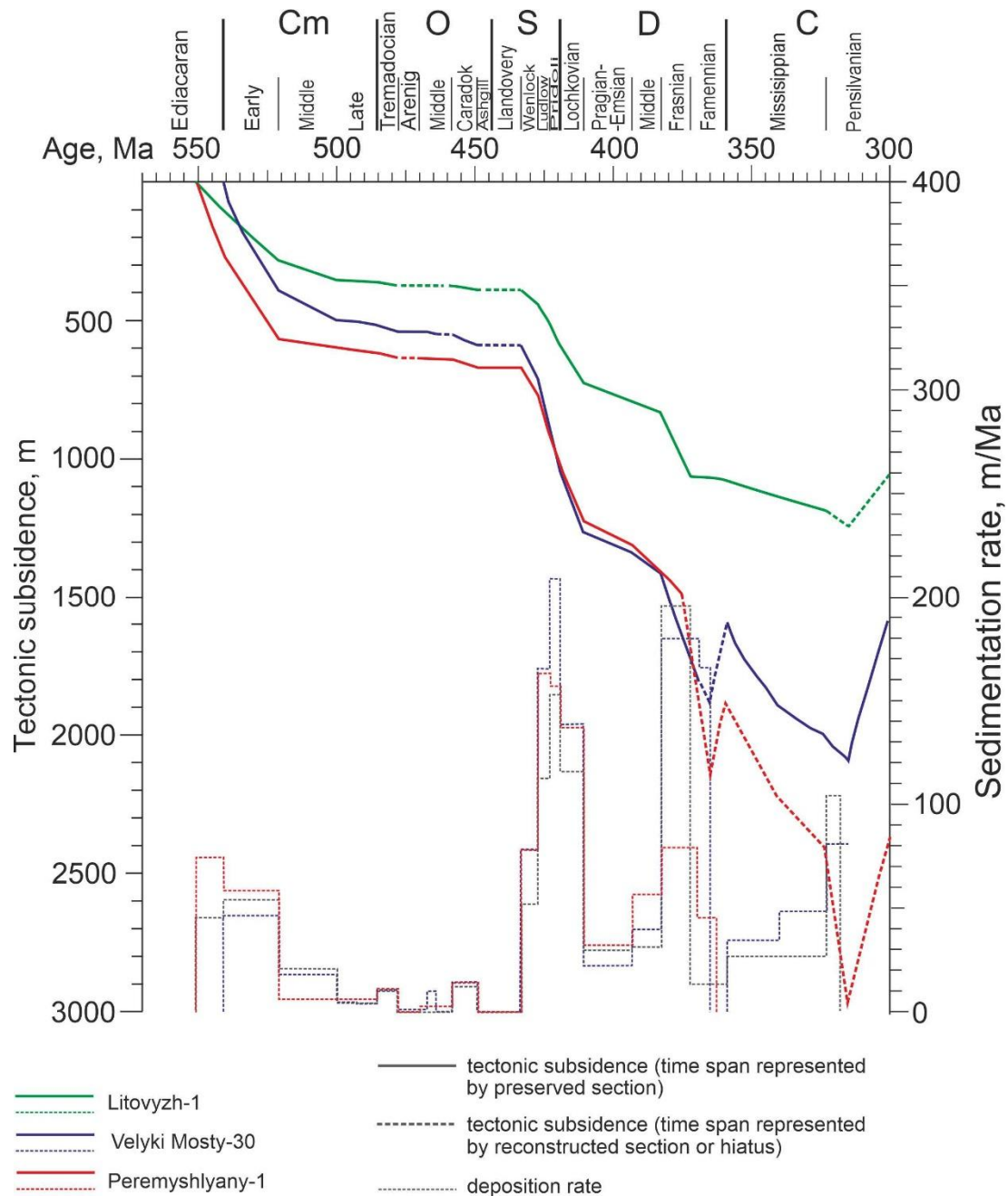
**Fig. 3.** Geological map of the pre-Mesozoic surface of the southwestern slope of the East European Platform. Compiled according to [Krupskiy, 2020; Radkovets, 2015].

As shown in our previous study [Poprawa et al., 2018], during the Middle-Upper Devonian period, the Lviv Paleozoic Depression experienced ongoing tectonic subsidence of the basin, marked by local phases of pronounced acceleration during the Frasnian and/or Famennian ages. This is evidenced by findings from such wells as Litovyzh-1 and Velyki Mosty-30. Such short-term phases of rapid subsidence in small depocenters can be considered as a possible manifestation

of the tectonic extensional regime. The thickness of the Middle Devonian section increases towards the west and southwest of the paleobasin and reaches its maximum values in the Peremyshlyany-1 well. The sedimentation rate of the Middle Devonian section is in the range of 20–40 m/million years. The Upper Devonian section is also characterized by a lateral increase in thickness in the western direction and reaches a maximum value of 1,300 m in the area of

Peremyshlyany (see Fig. 4). The sedimentation rate of the Upper Devonian section varies significantly laterally (Frasnian: 20–105 m/Ma; Famennian: 10–75 m/Ma), reflecting tectonic-induced lateral changes in the localization of sediment accumulation associated with the extensional tectonic regime model. The accumulation of a thick coal-bearing Carboniferous sequence caused rapid subsidence of Devonian deposits. In the area of the Velyki Mosty, the thickness of the existing Lower Carboniferous section is 371 m. Taking into account the

large-scale post-Variscan erosion, we assume that the initial thickness of the Lower and Upper Carboniferous sections was about 1,500 m. Considering that the area of Peremyshlyany was located in the more subsided part of the paleobasin, we assume that the thickness of the Carboniferous deposits, which were cut by post-Variscan erosion here, was at least 2,000 m. Such subsidence history had a decisive influence on the thermal maturation of Paleozoic deposits, particularly those of the Middle-Upper Devonian period.



**Fig. 4.** Results of backstripping analysis of depositional history based on 1-D modeling: tectonic subsidence curves and sedimentation rate diagrams for the Lviv Paleozoic Depression.

Modified after [Poprawa et al., 2018].

Cm – Cambrian; O – Ordovician; S – Silurian; D – Devonian; C – Carboniferous.

**Palynological studies of the genetic type of kerogen**

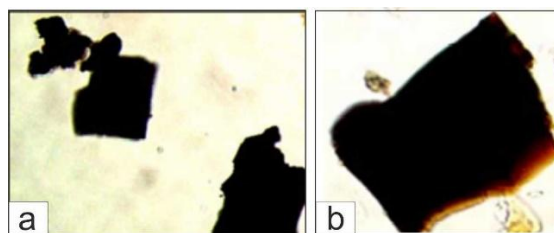
The study of microcomponents of kerogen of Middle and Upper Devonian strata using palynological methods confirms the results of geochemical research on the genetic type of kerogen (Tables 1, 2). The kerogen composition of the studied rocks in the Lviv Trough reveals two main types of components: humic (including inertinite and vitrinite of various sizes) (see Fig. 5) and sapropelic-liptinitic (comprising spores, fragments of plant tissues, acritarchs, etc.) (see Fig. 6). The content and ratios of these components indicate three genetic types of kerogen:

1. Humic type (see Fig. 7). This type is characterized by a dominance of condensed aromatic hydrocarbons that are depleted in hydrogen, primarily consisting of inertinite and vitrinite.

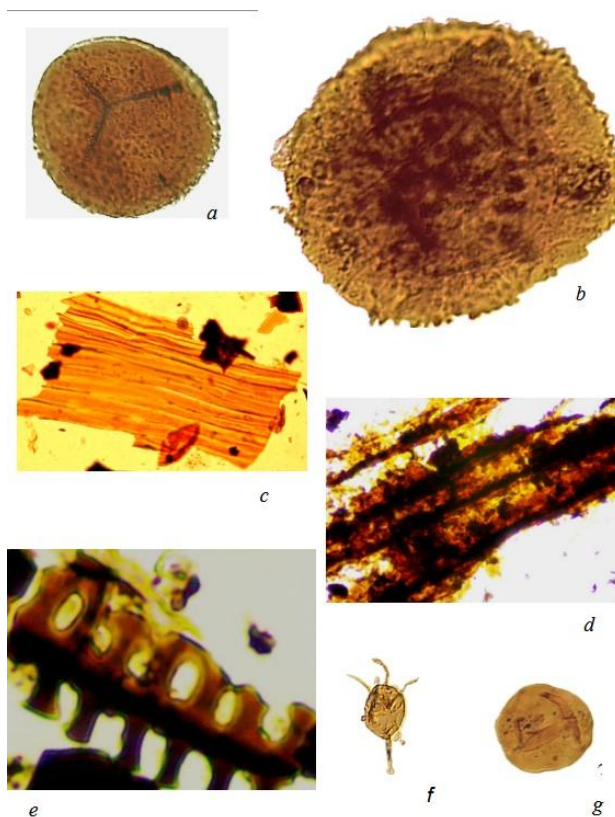
2. Sapropelic-liptinitic type. This type is enriched with hydrogen and consists of aliphatic and alicyclic compounds. It is predominantly made up of collo-morphic forms, including spores, plant tissue fragments, acritarchs and amorphous substances, with a marine origin.

3. Mixed type (humic-sapropelic) (see Fig. 8). This type contains humic and sapropelic-liptinitic components in approximately equal proportions.

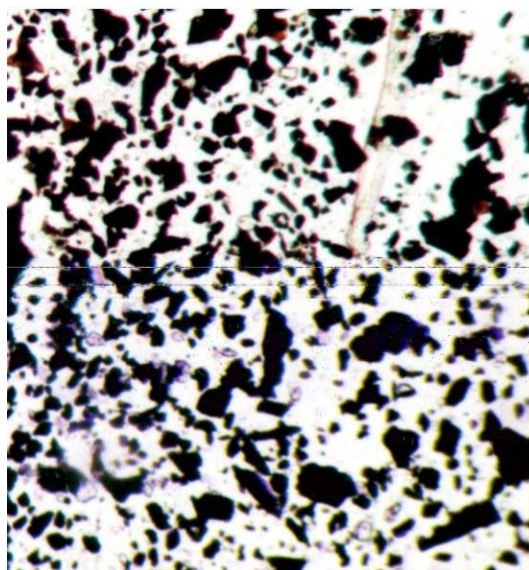
Humic components of kerogen are widespread, represented mainly by inertinite in the form of small fragments; they predominate and sometimes are the only components in humic kerogen in well sections of the inner part of the Lviv Depression. Among the lip-tinitic components of kerogen, the most important are myospores. The content and composition of myospores are controlled by several factors, including the degree of evolutionary development and prevalence of parent plants, taphonomic fossilization conditions, and the level of host rock catagenetic transformation.



**Fig. 5.** Humic components of kerogen of the Middle-Upper Devonian sediments of the Lviv Paleozoic Depression: a – inertinite; b – vitrinite. Magnification  $\times 600$

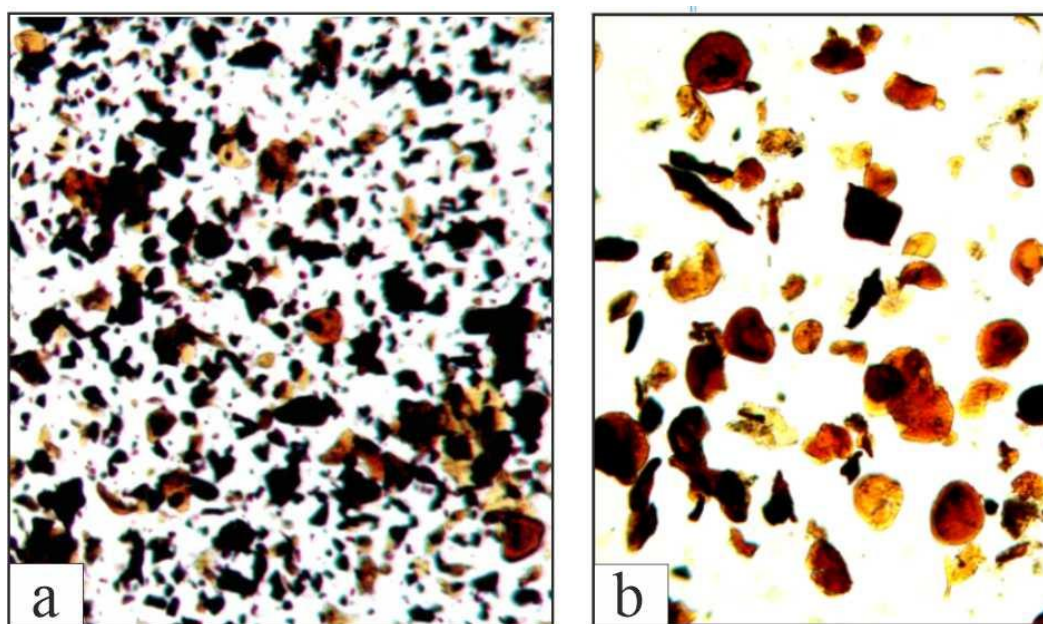


**Fig. 6.** Sapropelic-liptinitic components of kerogen of the Middle-Upper Devonian deposits of the Lviv Paleozoic Depression: a, b – spores; c, d – fragments of plant integumentary tissues; e – fragment of plant conductive tissue; f – acritarchs; g – algae. Magnification  $\times 600$ .



**Fig. 7.** Humic type of kerogen of the Middle-Upper Devonian strata of the Lviv Paleozoic Depression. Magnification  $\times 200$

In the Devonian section of the Lviv Depression, palynological material is extremely massive and polytaxonomic. The number of taxa in the spectra ranges from 11 to 62. Spores with a strong and medium degree of saturation were isolated from almost all samples of the Middle-Upper Devonian of the Lviv Depression. In the sections of the extreme western part of the Depression's inner zone, liptinitic elements and, in particular, myospores were not detected. Plant tissues are fragments of integumentary and connective tissues of plants, noted only in the spectra of the Middle and Upper Devonian of the outer zone of the Lviv Depression. Sapropel elements are represented by the remains of aquatic organisms: algae – unicellular representatives of lower plants; problematic remains – acritarchs, scolecodonts (occur only in marine facies), and amorphous matter. They occur in insignificant quantities in the spectra of the outer zone of the Lviv Depression. Liptinitic matter dominates in the sections of the Middle and Upper Devonian.



**Fig. 8.** Types of kerogen of the Middle-Upper Devonian deposits of the Lviv Paleozoic Depression: a – sapropelic-liptinitic; b – humic-sapropelic. Magnification  $\times 200$

#### **Geochemical studies of the content, genetic type, and generation properties of organic matter**

Both terrigenous (Fig. 9) and carbonate (Fig. 10) organic-rich rocks occur in the section of the Middle and Upper Devonian of the Lviv Paleozoic Depression. Table 1 shows the results of Rock-Eval pyrolysis for the Middle and Upper Devonian rocks. The total organic carbon (TOC) content in the Middle Devonian rocks is

in the range from 0.03 to 2.35 vol. %, and in the Upper Devonian – from 0.07 to 1.43 vol. %. A significant part of the samples contains more than 0.5 vol. % of TOC, which allows us to consider them as potentially hydrocarbon-generating rocks.

The content of free hydrocarbons ( $S_1$ ) in the Middle and Upper Devonian rocks is from 0.01 to 0.46 mg hydrocarbons/g of rock. The petroleum potential ( $S_2$ ) ranges from poor to medium, varying from 0.02 to

3.61 mg hydrocarbons/g rock. Both parameters confirm the ability of the rocks to generate hydrocarbons. The hydrogen index reaches 252 mg hydrocarbons/g TOC. This indicates the existence of an effective oil and gas-generating strata. For the Middle and Upper Devonian samples, the mineral carbon content has a wide range from 0.06 to >12, indicating the presence of both clay-terrigenous and clay-carbonate rocks, as well as organogenic limestones, in the Middle and Upper Devonian

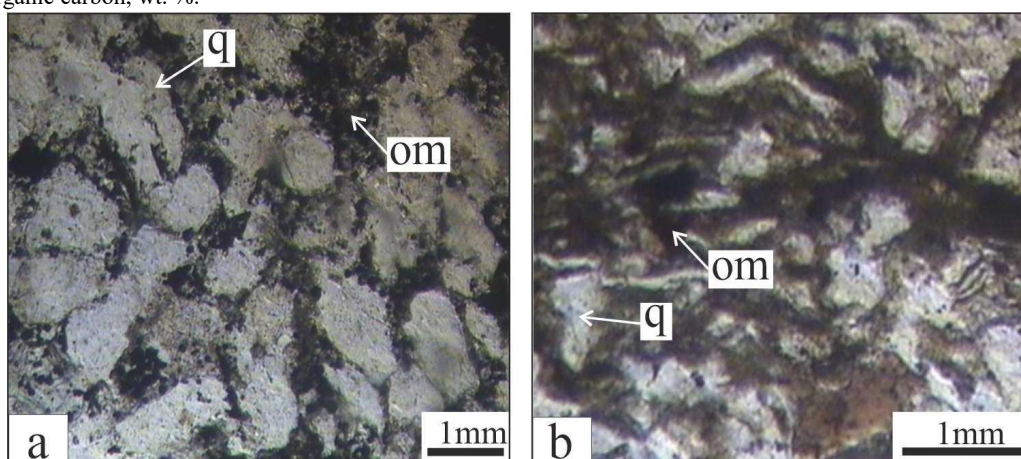
sequence. Kerogen of both marine (type II) and terrestrial (type III) origin was indicated in the studied Middle and Upper Devonian rocks (Fig. 11). The dominance of type III kerogen in the graph is possibly related to primary oxidation during deposition and/or secondary hydrothermal oxidation of dispersed organic matter during dolomitization, and therefore indicates the possible prevalence of type II marine kerogen [Kotarba et al., 2011].

Table 1

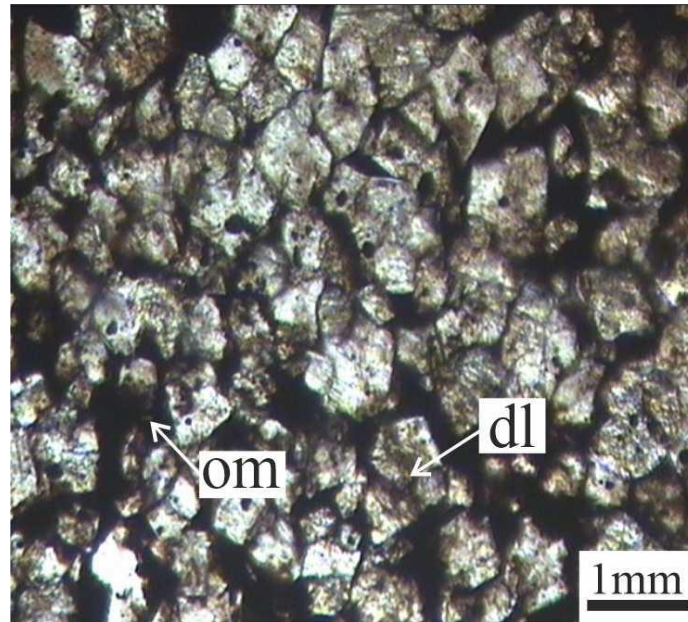
## Rock-Eval pyrolysis results for the Devonian rocks of the Lviv Paleozoic Depression

| Wells                  |      | Depth, m      | Stages    | TOC  | $T_{\max}$ | $S_1$ | $S_2$ | PI   | HI  | OI  | TIC   |
|------------------------|------|---------------|-----------|------|------------|-------|-------|------|-----|-----|-------|
| <i>Middle Devonian</i> |      |               |           |      |            |       |       |      |     |     |       |
| Litovyzh-1             | Li-1 | 1,796–1,806   | Eifelian  | 0.10 | 428        | 0.03  | 0.09  | 0.21 | 90  | 90  | 0.49  |
| Mynkiv-3               | Mn-3 | 1,220–1,226   | Eifelian  | 0.11 | 434        | 0.00  | 0.06  | 0.07 | 55  | 0   | 2.17  |
| Pidberezzya-1          | Pi-1 | 1,458–1,462   | Eifelian  | 0.64 | 428        | 0.08  | 0.97  | 0.07 | 152 | 353 | 3.78  |
| Sokal-1                | So-1 | 1,902–1,914   | Eifelian  | 0.21 | 440        | 0.02  | 0.25  | 0.07 | 119 | 0   | 0.13  |
| Sokal-1                | So-1 | 1,914–1,927   | Eifelian  | 0.03 | 441        | 0.00  | 0.03  | 0.11 | 100 | 100 | 2.96  |
| Lokachi-3              | Lo-3 | 920–924       | Givetian  | 0.19 | 416        | 0.01  | 0.04  | 0.20 | 21  | 0   | 0.06  |
| Lokachi-3              | Lo-3 | 921.7–928.2   | Givetian  | 0.08 | 427        | 0.02  | 0.04  | 0.33 | 50  | 12  | 1.09  |
| Lokachi-3              | Lo-3 | 938–942       | Givetian  | 0.46 | 429        | 0.04  | 0.97  | 0.04 | 211 | 13  | 2.56  |
| Lokachi-3              | Lo-3 | 948–952       | Givetian  | 0.17 | 431        | 0.03  | 0.2   | 0.12 | 118 | 94  | > 12  |
| Lokachi-3              | Lo-3 | 952–962       | Givetian  | 0.19 | 427        | 0.03  | 0.19  | 0.13 | 100 | 153 | 9.49  |
| Lokachi-8              | Lo-8 | 930–939.3     | Givetian  | 1.89 | 429        | 0.41  | 1.06  | 0.28 | 56  | 49  | 0.53  |
| Lokachi-8              | Lo-8 | 932.3–948     | Givetian  | 2.35 | 424        | 0.16  | 0.52  | 0.24 | 22  | 41  | 0.91  |
| Mynkiv-3               | Mn-3 | 118–1,191     | Givetian  | 0.24 | 430        | 0.01  | 0.16  | 0.06 | 67  | 17  | 0.10  |
| Peremyslyany-2         | Pe-2 | 968–974       | Givetian  | 0.38 | 527        | 0.02  | 0.02  | 0.39 | 5   | 18  | > 12  |
| Peremyslyany-2         | Pe-2 | 991–997       | Givetian  | 0.57 | 518        | 0.02  | 0.07  | 0.24 | 12  | 7   | 9.44  |
| <i>Upper Devonian</i>  |      |               |           |      |            |       |       |      |     |     |       |
| Litovyzh-1             | Li-1 | 1,139.8–1,143 | Famennian | 0.07 | 431        | 0.01  | 0.02  | 0.20 | 29  | 29  | 11.03 |
| Litovyzh-1             | Li-1 | 1,207.3–1,213 | Famennian | 0.10 | 435        | 0.02  | 0.16  | 0.09 | 160 | 20  | 7.54  |
| Mynkiv-2               | Mn-2 | 928–933       | Frasnian  | 0.37 | 428        | 0.01  | 0.11  | 0.07 | 30  | 19  | 0.07  |
| Sushne-1               | Su-1 | 1,250–1,258   | Frasnian  | 1.43 | 428        | 0.46  | 3.61  | 0.11 | 252 | 3   | > 12  |

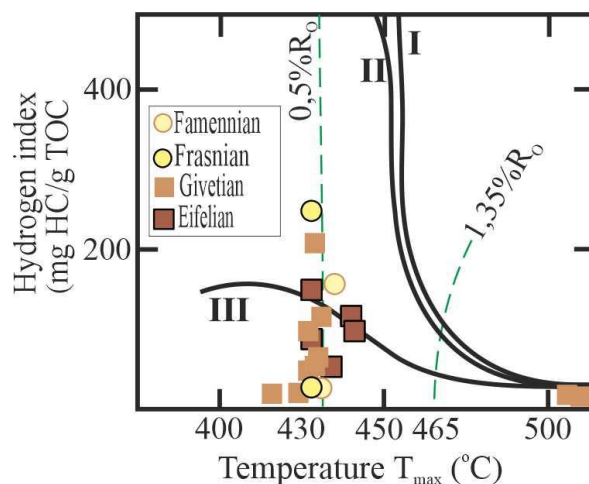
TOC – total organic carbon content, wt. %;  $T_{\max}$  – temperature of pyrolysis at maximum yield of kerogen cracking products, °C;  $S_1$  – free hydrocarbons content, mg hydrocarbons / g rock;  $S_2$  – residual hydrocarbons potential, mg hydrocarbons / g rock; PI – production index; HI – mg hydrogen index, mg hydrocarbons / g TOC; OI – oxygen index, mg CO<sub>2</sub> / g TOC; TIC – total inorganic carbon, wt. %.



**Fig. 9.** Photomicrographs of organic-rich Middle Devonian terrigenous rocks from the Lokachi-27 well: a – medium-grained sandstone with clay matrix, depth 847–851 m; b – coarse-grained siltstone with clay matrix, depth 863–868 m: q – quartz, om – organic matter



**Fig. 10.** Photomicrograph of organic-rich fine-medium-grained Middle Devonian dolomite from the Krekhiv-1 well, depth 1775–1780 m: dl – dolomite grains, om – organic matter



**Fig. 11.** Diagram of the Temperature of pyrolysis at maximum yield of kerogen cracking products ( $T_{\max}$ ) vs Hydrogen Index for the Middle and Upper Devonian rocks of the Lviv Paleozoic Depression. Modified after [Radkovets et al., 2017]. Kerogen genetic type curves and thermal maturity fields after [Espitalié et al., 1985].

#### Geochemical and palynological studies of the thermal maturity of kerogen

Determining the color index of myospores is an informative feature to define catagenetic kerogen transformation (Table 2). Color of microfossils was analyzed, and several panchronous myospores with a moderately thick exine were selected as indicators for determining the degree of catagenetic transformations. These myo-

spores exhibit significant stratigraphic and lateral distribution and possess a clear morphological structure, which makes them easily diagnosable in palynological preparations. They are also found in substantial quantities. Notable transit genera among the myospores include *Retusotriletes*, *Granulatisporites*, *Lophotriletes*, *Acanthotriletes*, *Microreticulatisporites*, and *Stenozonotriletes*. For Middle-Upper Devonian sections, color change is easily diagnosed in representatives of the genus *Geminospora* (Fig. 12). The color of the myospores ranges from light brown (color index 4) to dark brown (color index 6 on a seven-point scale) [Staplin, 1977].

In the western direction, the color of myospores changes from light brown and brown (index 4) in the outer part of the Lviv Depression to dark brown (index 5–6) in its inner part (see Table 2). The study of the kerogen maturation level in the Middle and Upper Devonian strata of the Lviv Paleozoic Depression utilized a combination of palynological and geochemical data. This approach enabled us to evaluate the thermal maturation patterns of these deposits, both with depth and across different parts of this geological structure. Fig. 13 demonstrates certain patterns, as it compares the Rock-Eval pyrolysis data and the color index of microfossils for the studied deposits from different wells and at various depths. In order to combine the data of these two inherently different methods, their results were normalized to the corresponding values of the vitrinite reflectance. The scale [Waliczek, 2021] was used to normalize the  $T_{\max}$  parameter of Rock-Eval pyrolysis, and the scale [Staplin, 1977; Ivanina, 2003, 2016] was used to normalize the color of microfossils with the vitrinite reflectance.

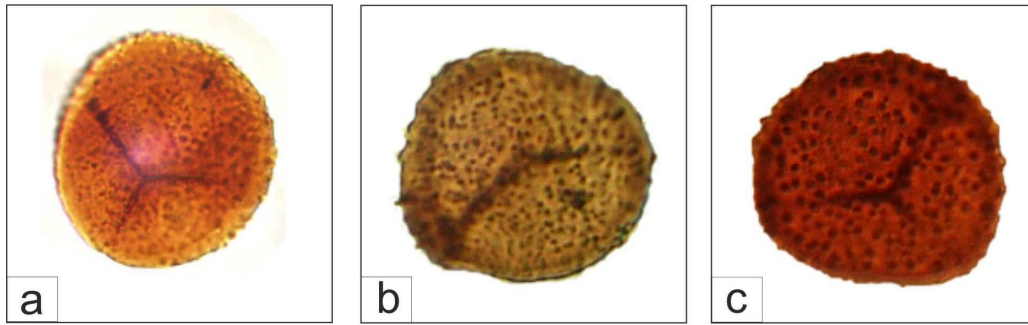
Table 2

**Kerogen types, spore color indices, and vitrinite reflectance  
of the Middle and Upper Devonian strata of the Lviv Paleozoic Depression**

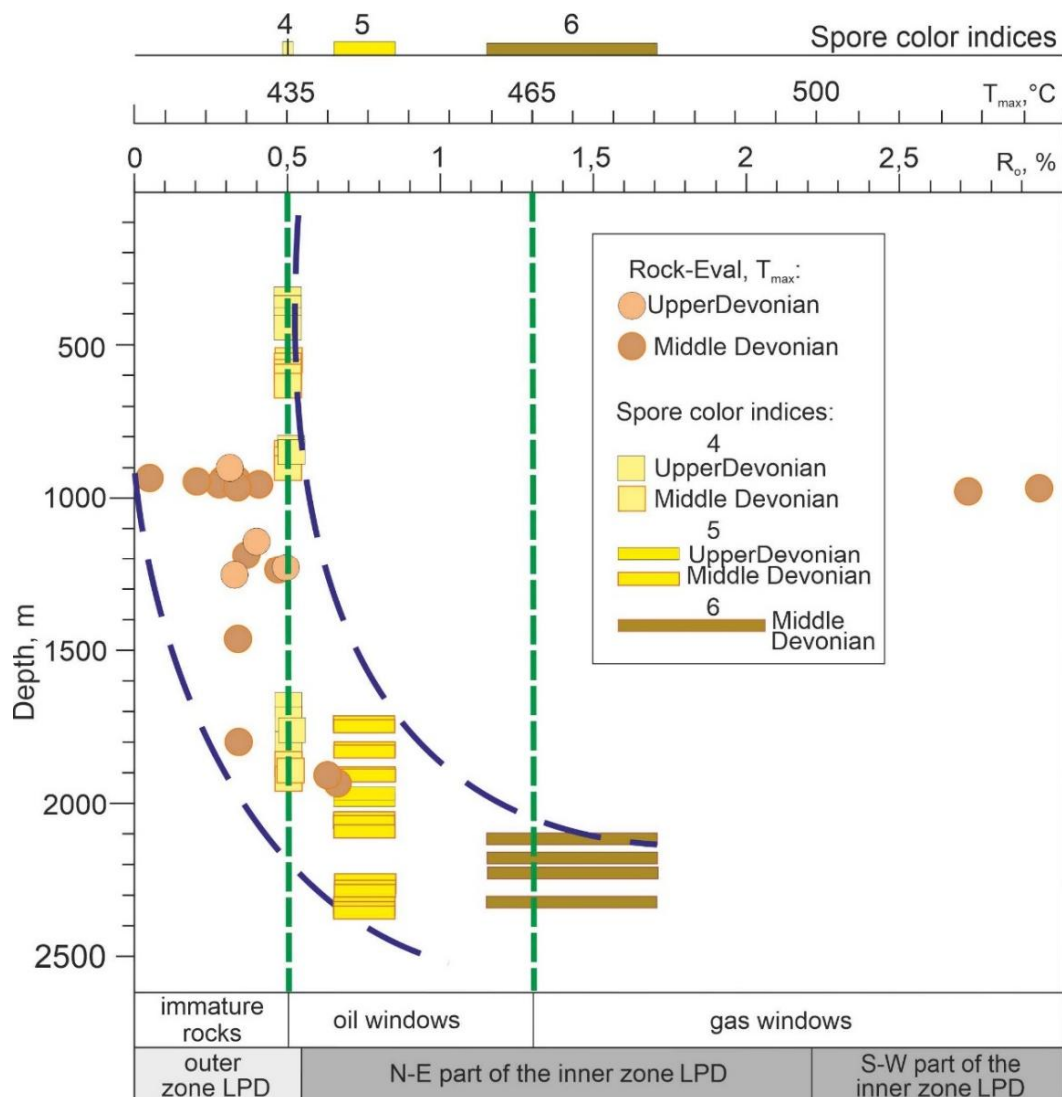
| Wells             | Depth, m                                                                               | Age   | Kerogen type | Spore color index | Vitrinite reflectance, Ro, % |
|-------------------|----------------------------------------------------------------------------------------|-------|--------------|-------------------|------------------------------|
| Velyki Mosty – 30 | 2,190–2,193<br>2,215–2,218<br>2,311–2,316                                              | $D_2$ | H–S          | 6                 | 1.15–1.71                    |
| Velyki Mosty – 32 | 2,250–2,256<br>2,256–2,270<br>2,270–2,286<br>2,316–2,324<br>2,324–2,332<br>2,332–2,340 | $D_2$ | H            | 5                 | 0.65–0.85                    |
| Dobrotvir – 1     | 1,725–1,729<br>1,729–1,735<br>1,814–1,823<br>1,823–1,831<br>1,892–1,900<br>1,900–1,906 | $D_2$ | H            | 5                 | 0.65–0.85                    |
|                   | 1,313–1,318<br>1,321–1,328                                                             |       | H–S          |                   |                              |
| Stremin – 1       | 1,968–1,978,                                                                           | $D_3$ | H–S          | 5                 | 0.65–0.85                    |
|                   | 1,978–1,988                                                                            |       | H            | 5                 |                              |
|                   | 2,040–2,048<br>2,048–2,056                                                             | $D_2$ | S–L          | 5                 |                              |
|                   | 2,089–2,100                                                                            |       | H            | 6                 | 1.15–1.71                    |
| Tykhotyn – 1      | 540–550<br>580–590<br>590–596<br>596–601<br>625–630<br>636–642                         | $D_2$ | S–L          | 4                 | 0.5                          |
| Horokhiv – 1      | 370–373<br>393–395<br>417–422<br>430–432                                               | $D_3$ | S–L          | 4                 | 0.5                          |
|                   | 853–857<br>857–863<br>897–900                                                          | $D_2$ |              |                   |                              |
| Sokal – 1         | 1,800–1,802<br>1,874–1,882<br>1,902–1,914                                              | $D_2$ | S–L          | 4                 | 0.5                          |
| Litovyzh – 1      | 831–835<br>850–854                                                                     | $D_3$ | H            | 4                 | 0.5                          |
|                   | 1,679–1,684                                                                            | $D_2$ | S–L          |                   |                              |
|                   | 1,723–1,724<br>1,778–1,782                                                             |       | H–S          |                   |                              |
|                   | 1,803–1,805                                                                            |       | S–L          |                   |                              |

$D_2$  – Middle Devonian,  $D_3$  – Upper Devonian.

Kerogen types: H – humic; H–S – humic–sapropelic; S–L – sapropelic–liptinitic



**Fig. 12.** Spore color index on the example of *Geminospora extensa* (Naumova) Gao, Middle Devonian: a – index 4 – light brown, Horokhiv–1 well, depth 857–863 m; b – index 5 – brown, Stremin–1 well, depth 2,040–2,048 m; c – index 6 – dark brown, Velyki Mosty–30 well, depth 2,190–2,193 m. Magnification  $\times 600$



**Fig. 13.** Diagram of thermal maturity of kerogen vs depth for the Middle and Upper Devonian rocks of the Lviv Paleozoic Depression according to the data of the  $T_{max}$  temperature of Rock-Eval pyrolysis and the spore color index, normalized to the values of vitrinite reflectance ( $R_o$ ).

Green dashed lines are the boundaries of the oil window according to [Espitalié et al., 1985].

Blue dashed lines are added to outline the depth-related trend of the kerogen thermal maturity.

LPD – Lviv Paleozoic Depression

A clear relationship is observed between the maturation level of the rocks and their depth in the outer zone and the northeastern part of the inner zone of the Lviv Paleozoic Depression. In contrast, the southwestern part of the inner zone demonstrates a different pattern (see Fig. 13). Within the depth interval from 370 to 1,914 m, the rocks in the outer zone of the Lviv Paleozoic Depression (found in wells, such as Horokhiv-1, Lokachi-3, -8; Lityzh-1, Mynkiv-2, -3, and Tikhodyn-1) occur in the zone of thermally immature rocks and around the upper boundary of the oil generation zone. In the northeastern part of the inner zone of the Lviv Depression, extending to the Nesteriv fault and at depths ranging from 1,725 to 2,316 m, there is a change in the maturation level of the kerogen. This change transitions from the middle part of the oil window in the wells Velyki Mosty-30, Dobrotvir-1 and Stremin-1 to the lower part of the oil window – and the upper part of the gas window in well Velyki Mosty-32. The diagram (see Fig. 13) illustrates that the strata in the outer zone of the Depression, as well as the northeastern section of its inner zone, exhibit a consistent trend in the thermal maturity of the rock changes with depth. Given that the kerogen of the Devonian deposits is largely composed of organic matter of terrestrial origin (type III kerogen), as demonstrated by both geochemical (Rock-Eval pyrolysis) (see Fig. 11) and palynological studies, which show in detail the composition of kerogen components (see Fig. 5–8, see Table 2), it can be assumed that the Devonian rocks participated in the gas generation process of the Lokachi and Velyki Mosty fields, since type III kerogen is predominantly gas-generating at all stages of kerogen maturation. However, this does not deny the possible participation of the underlying Silurian strata in the formation of this and possibly other gas accumulations. At the same time, in the southwestern part of the inner zone of the Lviv Depression, behind the Nesteriv fault, a significant increase of the maturation level of kerogen is observed (see Fig. 13). Parameter  $T_{\max}$  of rocks from the Peremyshlyany-2 well already at depths of 968–997 m shows the values from 518 to 527 °C, indicating that these rocks occur within the zone of dry gas generation. The above data allow us to state that the sediments of the northeastern and southwestern parts of the inner zone of the Lviv Depression had significantly different burial and maturation history. It can be assumed that the Devonian strata of the southwestern part of the Depression's inner zone underwent quite deep subsidence in Carboniferous time, and then were uplifted as a result of post-Variscan erosion of the Carboniferous sequence of this part of the Lviv Depression. Evidently, the Carboni-

ferous coal basin extended far to the southeast compared to its modern occurrence (see Fig. 3). This is evidenced, in particular, by numerous finds of Carboniferous coal debris in the Carpathian flysch. As a result of deep erosion of the central part of the Carpathian Foredeep basement, Carboniferous strata were eroded and redeposited into the Carpathian flysch basin.

### Originality

As a result of this study, the sedimentary and post-sedimentary evolution of the Middle-Upper Devonian strata of the Lviv Paleozoic Depression was investigated. For the strata of this age range, the combined use of palynological and geochemical methods has been applied for the first time. This approach made it possible to estimate the thermal maturity of kerogen in organic-rich rocks in different parts of the Depression.

### Practical significance

The applied complex of geochemical and palynological studies allowed for establishing the regularities of the processes of thermal maturation and hydrocarbon generation by the Middle-Upper Devonian rocks of the Lviv Paleozoic Depression and, on this basis, to determine their potential participation in the formation of oil and gas accumulations.

### Conclusions

1. The combination of the results of palynological and geochemical research methods for assessing the thermal maturity of kerogen in organic-rich rocks within a wide depth interval demonstrates its effectiveness.
2. The results of the combined geochemical and palynological investigations allowed distinguishing three separate tectonic zones with different dynamics of the processes of thermal maturation of kerogen.
3. Within the outer zone of the Lviv Depression, the Middle-Upper Devonian rocks are thermally immature or are at the beginning of the oil window.
4. In the northeastern part of the Depression's inner zone extending to the Nesteriv fault, the maturation level of kerogen changes from the middle part of the oil window to the lower part of the oil and upper part of the gas window.
5. In the southwestern part of the inner zone of the Lviv depression behind the Nesteriv fault, the rocks are in the zone of dry gas generation.
6. Different trends of thermal evolution within the inner zone of the Lviv Depression clearly demonstrate the heterogeneity of tectonic processes. Despite the fact that the southwestern part of the inner zone of the

Depression is elevated compared to its northeastern part, the kerogen maturation level of the former is significantly higher. This was a result of large-scale erosion of the Carboniferous strata due to the Late Carboniferous tectonic inversion and the uplift of this part of the Lviv Depression.

7. The organic-rich Middle-Upper Devonian strata, of both the outer and inner zones of the Lviv Paleozoic Depression, according to their geochemical indicators, can be considered as potentially oil- and gas-generating and, together with the underlying Silurian strata, could participate in the formation of hydrocarbon accumulations in the Paleozoic sequence.

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## ДИНАМІКА СЕДИМЕНТО-ЛІТОГЕНЕЗУ ТА ГЕНЕРАЦІЇ ВУГЛЕВОДНІВ У ВІДКЛАДАХ ДЕВОНУ ЛЬВІВСЬКОГО ПРОГИНУ ЗА РЕЗУЛЬТАТАМИ ГЕОХІМІЧНИХ ТА ПАЛІНОЛОГІЧНИХ ДОСЛІДЖЕНЬ

Метою даної роботи є вивчення історії седиментації та динаміки постседиментаційних перетворень, зокрема термальної зрілості керогену порід середнього-верхнього девону Львівського палеозойського прогину. Методологія. Комплексне застосування геохімічних досліджень, зокрема таких параметрів програмованого піролізу Rock-Eval, як вміст загального органічного вуглецю, температура  $T_{\max}$ , нафтовий потенціал  $S_2$  та палінологічних досліджень, а саме, індекс кольору мікрофосилій. Результати. На основі аналізу комплексу одержаних результатів геохімічних (аналіз 20 зразків керну із 9 свердловин методом піролізу Rock-Eval) та палінологічних (аналіз 44 зразків керну із 8 свердловин) досліджень встановлені вміст, генетичний тип та генераційні властивості органічної речовини порід середнього та верхнього девону Львівського палеозойського прогину. Породи вміщують кероген, як морського (тип II), так і наземного (тип III) походження. На основі палінологічних досліджень у складі керогену визначені гумусові та сапропелево-ліптинітові компоненти. Ступінь термальної зрілості керогену визначався на основі комбінованого застосування параметру  $T_{\max}$  піролізу Rock-Eval та індексу кольору мікрофосилій. В межах Львівського палеозойського прогину, за ступенем термальної зрілості керогену встановлені три зони. Наукова новизна. В результаті проведених досліджень була вивчена седиментаційна та постседиментаційна еволюція нашарувань середнього-верхнього девону Львівського палеозойського прогину. Для відкладів цього вікового інтервалу вперше сумісно використано палінологічних та геохімічних методів, що дозволило дати оцінку термальної зрілості керогену порід, збагачених органічною речовиною у різних частинах прогину. Практична значимість. Застосований комплекс геохімічних та палінологічних досліджень дозволив встановити закономірності процесів термального дозрівання та генерації вуглеводнів породами середнього-верхнього девону Львівського палеозойського прогину й на цій основі визначити їх потенційну участь у формуванні покладів вуглеводнів.

*Ключові слова:* Львівський прогин; девон; тип керогену; температура  $T_{\max}$ ; індекс кольору мікрофосилій; зони генерації вуглеводнів