

зованы електронно-мікроскопічні дослідження. Були проведені дослідження впливу шунгитових добавок на прочнісні антикорозійні властивості цементного каменя за рахунок впливу шунгитового порошку на його щільність.

**Результати.** Шунгитові концентрати, отримані з шунгита Бакырчикського родовища, є перспективними для використання як заповнювачі цементних бетонів і шунгитового сировини золотосульфідних родовищ (Бакырчик) відкриває нові економічні перспективи одночасної обробки золота і значительні, але не використовувані запаси шунгита в межах відомих золоторудних полів Східного Казахстану.

**Наукова новизна.** Було доведено, що шунгитовий порошок є як пігмент і заповнювач

покращує антикорозійні властивості лаків і лакофарбових матеріалів.

**Практична значимість.** Дані дослідження дозволять значно скоротити кількість техногенних шунгитосодержащих відходів, нерідко містять забруднюючі речовини, які викликають забруднення повітря, ґрунту і ґрунтових вод в районах техногенного впливу розробки родовищ золота. Важливість досліджень підтверджується гострою нехваткою нових будівельних матеріалів з антикорозійними властивостями. Ці дослідження дозволять створити абсолютно нові матеріали з заданими властивостями для будівельної промисловості Казахстану.

**Ключові слова:** шунгит, бетон, корозійна стійкість, золотосульфідні родовища

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## STRATIGRAPHIC LEVELS OF VENDIAN (EDIACARAN) BLACK SHALES OF THE TRANSDNIESTRIAN PODILLIA

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## СТРАТИГРАФІЧНІ РІВНІ ЧОРНОСЛАНЦЕВИХ УТВОРЕНЬ ВЕНДУ ПРИДНІСТРОВСЬКОГО ПОДІЛЛЯ

**Purpose.** It is based on investigation of regularities of distribution patterns of black shales in space and time in sections of the Late Proterozoic of the Transdnistria for further investigating by lithological, mineralogical, petrographical and geochemical analysis.

**Methodology.** It consists of field working in outcrops of the Vendian section and their detailed lithological description, facies analysis, petrographical and lithology-geochemical investigations.

**Findings.** A revision of the Late Proterozoic sediment section of the Transdnistrian Podillia was done; conditions of stratification and under- and overburden contacts of layers were updated; textural, structural and other features of stratigraphic layers which indicate genetic and facial aspects of their formation were determined. In the deposits of Mohyliv-Podilskiy range of the Vendian five stratigraphic levels which contain black shale were allocated: lomozivski, liadavski, bronnytski, zinkivski and kaliuski layers. Also new strata of the Ediacaran biota which will be described in detail in the following publications were found.

**Originality.** For the first time, for Mohyliv-Podilskiy range of the Transdnistria five stratigraphic grades of black shale accumulation were distinguished. Black shales precipitated in uncompensated depressions of an epicontinental basin and were concentrated with a lot of organic matter. They could be considered as petroleum source rocks of the Precambrian and Early Paleozoic sedimentary formations of the Volyn-Podillia.

**Practical value.** It is based on using the data for predicting works within the Volyn-Podillia plate related to the petroleum potential areas.

**Keywords:** *black shale, stratigraphic layers, Precambrian, Vendian, non-skeletal biota, sedimentation conditions*

**Introduction, analysis of the recent research and objectives of the article.** Black shales (Eng.) are pelitomorphic, fissile, schistose, from dark gray to black formations which feature clayey, siliceous-clayey and siliceous-carbonate-clayey composition. One of the main features of these rocks is high content of organic matter. Black shales (BS) were called “domanikoyids” by litologists of the Soviet Union. Therefore, these terms are often used as synonyms in articles [1].

BS formed mainly of uncompensated marine sedimentary basins. They are associated with deposits of some ore and rare elements, in particular Cu, Zn, V, P, Mo, Re, Se, Hg, U, etc.; oil shales and solid bitumens.

Recently BS have been considered as petroleum source rocks and a potential unconventional reservoir of oil and gas. Consequently, they are the object of study by petroleum geologists.

In the general section of the sedimentary cover BS are defined at all stratigraphic levels ranging from the Archean to the Neogene inclusive. Their Phanerozoic and Precambrian occurrences are regulated by sedimentary and geotectonic cycles.

Phanerozoic BS are observed the most extensively. The reliable correlation between BS and petroleum formations has been determined in the USA petroleum basins (Green River formation), Tajikistan basins (Suzakski shale), the Volga-Ural oil and gas bearing province (OGBP), the Prypiat, Carpathian, Peredobruzhzhia and Dnipro-Donets basin etc.

According to recent studies by S. O. Machulina (2016), 26 levels of BS formation are distinguished in the Phanerozoic eon. Their extension was due to planetary and subplanetary transgressions and tectogenetic facilities.

Precambrian BS have been investigated in the least [2]. According to estimations of S.A. Sydorenko they make about 10 % of all sedimentary-metamorphic Precambrian complexes. BS spread both locally and regionally on all continents and their thickness exceeds one hundred meters.

Most of Precambrian carbon formations were metamorphosed and their organic matter has been converted into graphite and schungite shales, solid bitumens. Nowadays, there is not direct relation between oil and gas fields and the Precambrian BS. But it can be assumed that they are determinative in the occurrence of petroleum Lower Phanerozoic formations.

In the Precambrian there are three megacycle of BS accumulation at intervals of 600, 300 and 100 million years: Archaean, Lower and Upper Proterozoic. They include the time interval of accumulation from Paleoarchean carbonaceous shales to Vendian BS. The total tendency for Precambrian deposits is to increase BS capacity in the general section from the Early to the Late Precambrian which is associated with increasing amount of biota on the Earth.

Archaean carbon graphite shales have been determined in deposits of the Baltic, Aldan, Guiana, Guinea

shields, the Stanovoy Range (Far East, Russia) etc. Proterozoic carbon formations spread on the Baltic shield (Karelian formations), Siberian platform (spropel shales of Ust-ilimsk horizon, Riphean shales of Tunguska oil and gas bearing region (OGBR), China (Xin'an basin), North America (Michigan basin, Natsach shales), Australia (uranium shales), East European platform (EEP) (Vendian BS) etc.

The Vendian period (Ediacaran period) is a transition stage from the Proterozoic to the Paleozoic, which lasted from 600 to 535 million years and has features of biota evolution. At the beginning of the Cambrian spineless biota was getting skeletons and in the marine basins clastic sedimentation was supplemented by carbonate precipitation.

On the territory of Ukraine Vendian deposits crop out in the Podillia Transdnestrian and have been sufficiently described by geologists [3]. Investigations were mostly focused on stratifying and allocating the strata and describing the Ediacaran biota [4].

According to the researchers of the Neoproterozoic, Vendian (Ediacaran) outcrops in the Ukrainian Transdnestria are one of the most complete. There are a lot of non-skeleton fossils which feature diversity and belong to various species. At the present time, material composition and genesis of these deposits are less investigated in Vendian outcrops.

Collaborative research studies between Taras Shevchenko National University of Kyiv, State Higher Education Institution “National Mining University” and University of Poitiers (France) in the Podillia Transdnestrian were implemented in 2015–2016. They provided investigating a lot of Vendian outcrops and sampling for further complex lithological and mineralogical laboratory investigations. Stratigraphic units and features of spatial extension of BS were also determined.

**Presentation of the main research.** The research area spans outcrops of the Dniester valley and its tributaries between Mohyliv-Podilskyi and Novodnistrovsk cities. In these parts Vendian deposits form almost continuous sections beginning from their contact with the basement rocks to the transition zone of Baltic series of the Lower Cambrian.

In outcrops conditions of bedding, contacts of lithotypes with under- and overlying rocks, textural and structural features etc. were studied in detail. These characteristics can point to genetic and facial formation aspects of these deposits. Points of detailed observations and sampling for further laboratory research are illustrated in Fig. 1.

As is known, in the general Vendian section clastic formations absolutely dominate. However, in some areas they are enriched by pyroclastic material. Therefore, we focused on carbonate rocks, layers which are enriched by organic matter, fossils and phosphate mineralization that could indicate sedimentary modifications.



Fig. 1. Schematic geological map of Precambrian and Paleozoic deposits of the Transdnjestria [6] with points (P.1–6) of detailed observations and sampling:

1 – bedrock; Precambrian formations: 2 – mohylivska; 3 – yaryshivska; 4 – nahorianska; 5 – kanylivska; 6 – Paleozoic (Ordovician and Silurian) system

Based on the comprehensive analysis of published data and our own field research of Upper Vendian outcrops of the Transdnjestria five stratigraphic levels which contain black shale were allocated. For different layers BS capacity ranges from 10 (bronnytski) to 45 m (kalyuski) (Fig. 2). Summary of strata which contain BS is represented below.

**BS of the lomozivski layers.** In the Vendian section they are located at the lower level. These deposits consist of silty and micaceous argillites which rhythmically alternate with fine-grained sandstones and siltstones. Capacity of some argillaceous rhythm varies from 1 to 3 m and their total capacity is about 15 m. BS are thinly laminated, carbonate-free, intensely dislocated, dark gray rocks with a greenish tinge. Also they are transformed into thin-platelet gruss and their color is changed to brown by weathering. Lamination of argillites is caused by the presence of silty and micaceous materials

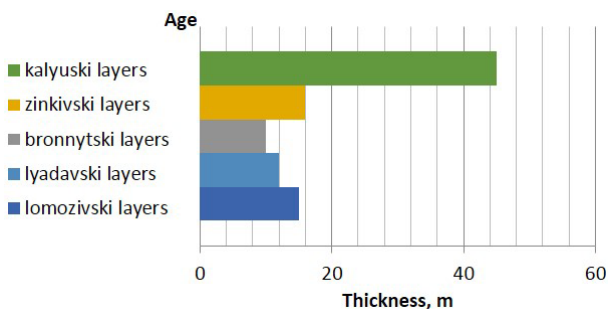


Fig. 2. Comparison chart of capacity of Vendian BS of the Volyn-Podillia

on bedding planes. In the upper part of the section of the lomozivski layers there are marcasite concretions.

These layers contain different types of Metazoa which is the largest among all Vendian strata. The main accumulations of organic remains are located in the bottom of the section – contact with the olchedaiivski layers or the basement, and are characterized by the argillaceous or silty argillaceous substrate prevalence in composition.

Occasionally, the presence of numerous biota influences changing color of the bedding planes which become darker to black.

The best outcrops of the lomozivski layers with BS are located in coastal ledges of the Liadova and Zhvan rivers. Their stratotype is placed in outcrops of the Liadova river between Vinozh and Nyzhchy Olchedaiiv villages where they are located on the olchedaiivski layers or the basement and are overlaid by yampilski sandstones.

We studied in detail new outcrop of BS of the lomozivski layers near to Popeliuhy village (right tributary of the Liadova river). There is stratum of BS argillites (to 3 m) with two small (10 cm) interlayers of silty sandstones which are overlaid unconformably by sandstones of the yampilski layers (Fig. 3).

In the lomozivski layers there are flow traces and a lot of biota remains. Fossil samples are represented in Fig. 4.

**BS of the liadavski layers.** These deposits consist of argillites and lenticular low-power interlayers of fine-grained sandstone. Argillites account for 60 % of the stratum section and, in general, in the liadavski layers their capacity is 12 m. Argillites are carbonate-free, thinly laminated of variegated color (from dark gray, gray-green to brown with different shades) and split into thin-platelet gruss. Cleavage planes are enriched by silty and micaceous materials. Possibly the color changing of argillites is due to varying degrees of pyroclastic material oxidation. Sandy deposits of the liadavski layers are mainly in the lower part of the section which is located conformably, gradually and without visible traces of interruptions on yampilski sandstones. In outcrops yampilski sandstones are more solid and light (yellow), liadavski sandstones are more brittle and darker (gray) with platy jointing. The upper transition boundary between liadavski and bernashivski layers is detected distinctly – argillaceous stratum are sharply overlaid by sandstones and gritstones.

At the bottom of the argillaceous stratum there are iron disulfide concretions which form several levels.

Biota remains in the liadavski layers are sporadic and represented mainly by bacterial structures of various types. Stratotype outcrops of these deposits are described on the Liadova river near Nyzhchy Olchedaiiv and Zhrebylivka villages, also the Murafa, Derlo, Zhvan rivers (Bukatynka, Borshchiv Yar, Murovani Kurylivtsi villages). But today, this section is better revealed by the quarry near the dam of the Dniester HES-1. Here the liadavski layers are directly located on yampilski sandstones and their capacity is about 4 m (Fig. 5).



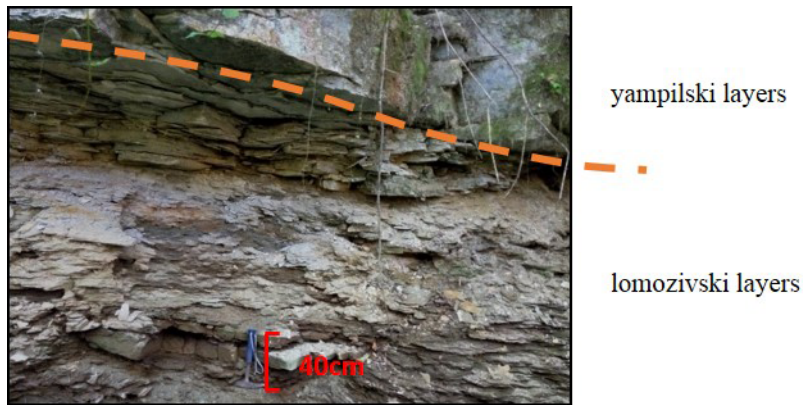


Fig. 3. Outcrop of the lomozivski and yampilski layers, the eastern edge of the Popeliuhy village, right tributary of the Liadova river (Popeliuhy ranive)

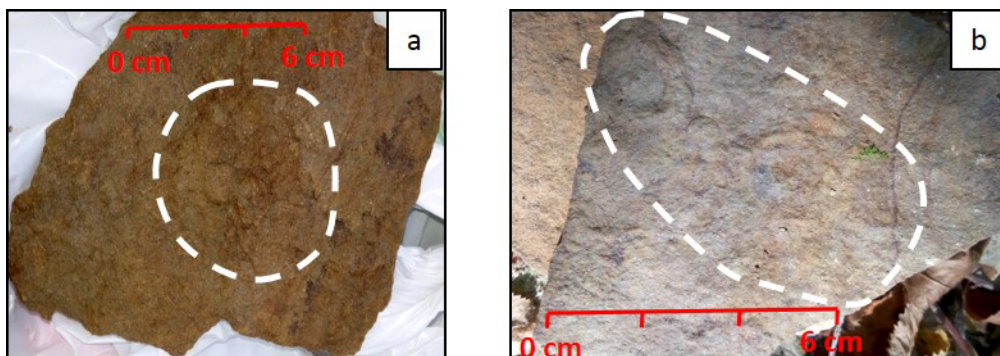


Fig. 4. Fossils in argillites of the lomozivski layers (Popeliuhy ranive):  
a – discoidal imprints; b – discoidal and tube-like imprints



Fig. 5. Outcrop of the yampilski and liadavski layers in the quarry near the dam of the Dniester HES-1

**BS of the bronnytski layers.** They are the composition of carbonate-free tufaceous argillites and argillites. Their general capacity is about 20 m. BS have two layers structure which is well observed visually by structural and textural features and nature of disintegration. The lower layer is more solid, coarse-grained, coarse-laminated and composed of variegated color (brown, greenish-brown) tufaceous argillites, tufaceous siltstones and their combinations. Their capacity is 7–8 m. The upper

layer is more fine-grained and thinly laminated and contains variegated color tufaceous argillites, argillites and silty argillites. Rocks are poorly-consolidated and split into thin-platelet gruss due to weathering. Their capacity is 10–13 m. The color diversity of the bronnytski layers is associated with varying degrees of oxidation of volcanic material in the section.

Stratotype outcrops of these deposits are located in the valley of the Bronnytsya river. Today section of the

bronnytski layers is better revealed in the Borshchiv Yar. There is all lithological diversity of the lower layer of these deposits. Their capacity is to 2 m. They consist of platy, light green, dark purple and red argillites of different weathering degree which is directly located on sandstones of the bernashivski layers (Fig. 6).

In the bronnytski layers there are detected well-preserved numerous prints of non-skeleton biota which are mainly located in the bottom of the section, in contact with the bernashivski layers. Then in the top of the section their quantity significantly reduced and fossils are sporadically founded.

**BS of the zinkivski layers.** These deposits consist of gray, dark gray, sometimes with a bluish tinge, varying degrees silty argillites and thin layers and lenses of the same color of small- and medium-grained sandstones. Argillites account for 2/3 of the stratum section and, in general, in the zinkivski layers their capacity is 13–15 m. Their main feature is the presence of several texture types in section – concentric shucks cleavage and the presence of different directions of coarse and fine lamination. Small lenses of phosphorite silts and single phosphorite concretions of pebble dimension are sporadically detected in the lower part of the section.

Outcrops of parts of the zinkivski layers can be observed in valleys of the Liadova (mouth), Zhvan (near Skazyntsi and Halaikivtsi villages), Kalius (Nova Ushytsia and Hlybivka villages), Ushytsia rivers (from Verbka-Murovana and Zinkova to Mynkivtsi villages). In the investigated outcrops, the zinkivski layers are located on the bronnytski layers. Contact between them, which is detected by the presence of thin kaolinite interlayer in the base of the zinkivski layers, is gradual. Unfortunately, this layer is not continuous and then this border on some sections is several conditional. The upper contact of the zinkivski layers is more perceptible which is due to changes in lithology – appearance of arkose sandstones. The last already belong to the dzhurzhivski layers. Capacity of the zinkivski layers is changeable and in different outcrops varies from 5 to 27 m.

**BS of the kaliuski layers.** These deposits almost consist of monotonous, from dark gray to black, thinly lam-

inated argillites. They split into thin-platelet gruss and their color is changed to brown by weathering. These layers complete the section of Mohyliv-Podilskyi range of Upper Vendian.

The kaliuski layers are directly located on the dzhurzhivski layers in the most studied outcrops. Their contact is detected by an abrupt change of lithology. The upper part of the dzhurzhivski layers consists of fine-grained, greenish-gray sandstones with a high content of carbonate component. The upper part of the kaliuski layers in the most outcrops has eroded surface on which deposited sediments of the kanylivska range of Vendian, Paleozoic, Mesozoic and Cenozoic.

General capacity of the kaliuski layers varies from several to 45 m.

The main feature of the kaliuski layers is the presence of phosphorite concretions. The latter are located on the central and upper parts in the most outcrops where particular horizons form. To 12–14 concretionary horizons are detected in the most complete sections of the kaliuski layers.

Concretions are located conformably towards enclosing rocks. Argillites plastically envelop them without visible cleavage (Fig. 7).

The morphology of concretions is very various but spherical and oval shapes dominate. Sometimes there are aggregates of several concretions (Fig. 8). The size of concretions is from a few millimeters to 15 centimeters or more.

There are concretions with and without carbonates or sulfides rudimentary centers. Many concretions contain desiccation cracks and are empty, but there are those that are filled with secondary minerals.

In the medium and preferably in the upper parts of section of the kaliuski layers there are «cone-in-cone» structures. At these levels, we observe significant carbonate content in argillites.

Outcrops of BS of the kaliuski layers with concretions could be observed from the left and right banks of the Dnister river near Lypchany and Voloshkove villages (Fig. 9) and in the valley of the Ushytsia river (near



Fig. 6. Outcrop of the bernashivski and bronnytski layers (Borshchiv Yar, edge of the Mohyliv-Podilskyi cities)



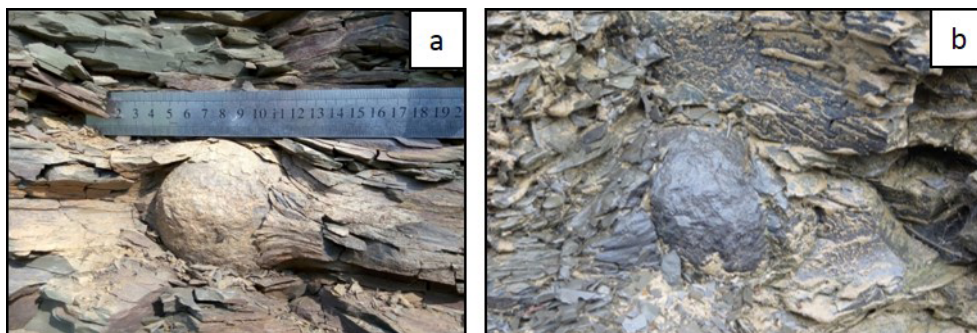


Fig. 7. Examples of bedding of phosphorite concretions in the kaliuski layers (the Dniester River, near Lypchany and Voloshkove villages):

a – contact of phosphorite concretions with host rocks; b – draping structure of host layers

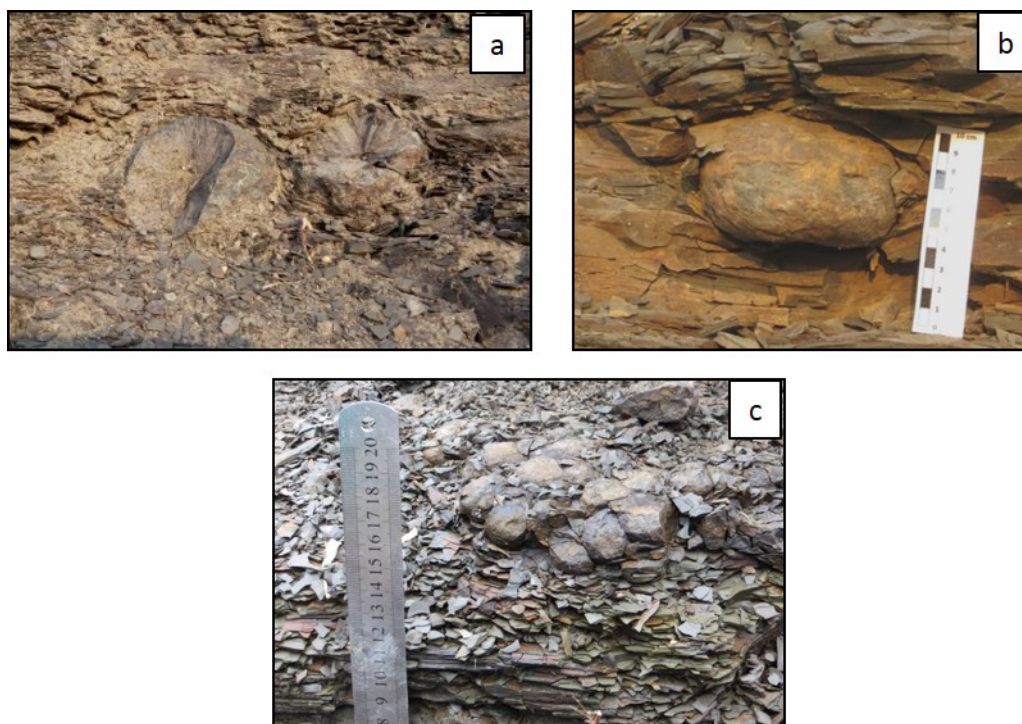


Fig. 8. Examples of phosphorite concretions in the kaliuski layers (the Dniester river, near Lypchany and Voloshkove villages):

a – internal structure of concretion; b – elliptic-like concretion; c – example of coalescent concretion

Tynkivtsi village). Unfortunately, one of the best outcrops of the kaliuski layers in Antoniv Yar (Mynkivtsi village), which for a long time has been considered classic, at the present time is completely matted with bushes and vegetation.

The numerous prints of bacterial structures and other Ediacaran biota non-skeleton remains were detected during our research in the kaliuski layers of the upper and lower parts of the section.

**Explanation of scientific results.** Podilsk structural facial zone, which associate with Podolsk ledge of the Ukrainian Shield, is a specific area of the Late Vendian lithogenesis. In general, the sedimentation depended on tectonics, seabed terrain, climate and rock composition of the continental part. The most common rocks in section of Mohyliv-Podilskyi series are psephites and psammites among which gritstones, hard- and coarse-

grained sandstones dominate. To a lesser extent fine-grained sandstones, siltstones and argillites are laying. The latter, as noted above, is about 10 % in the general section of this series.

All these data indicate that the Upper Vendian lithogenesis occurred in relatively shallow basin, the nature of composition and sorting of clastic material denote a near transportation.

Glauconite, which is present in all facial groups of Vendian sediments, is an indicator of epicontinental basin with alkalescent water dynamics. However, seabed terrain was divided. There were more deepwater areas where fine-grained material accumulated. As seen from the general section, these areas occurred at different age levels. Some depressions had uncompensated nature and there are accumulation only of disperse material. And in others there were anoxic conditions as

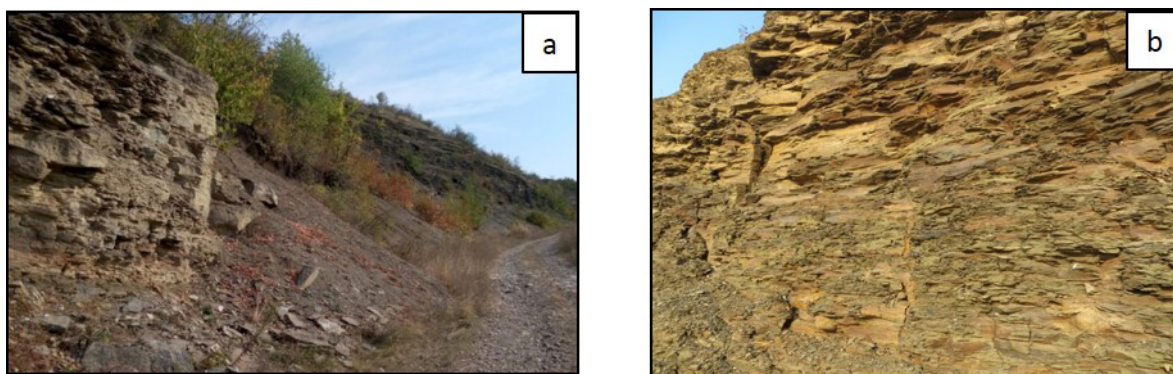


Fig. 9. Outcrop of the kaliuski layers (the Dniester river, Lypchany village):  
a – general view of outcrops; b – horizontal occurrence of kaliuski layers

indicated the present of iron disulfide concretions in sections.

In this period of time with varying intensity the evolution of primitive non-skeleton organisms (bacteria, algae, medusoids, worms and corals-like) occurred. This biota enriched the Vendian section with organic matter which is located in the most dispersed types of sediments. Though, the Vendian fossils are better preserved at the interbedding border of clayey and silty formations. Therefore, in the kaliuski layers, which consist of only clayey rocks, we define fewer amounts of organic remains than in other layers. However, the evolution of the biota was the largest at that time.

The Total Organic Carbon (TOC) in BS of Mohyliv-Podilskyi series vary from 1 to 4 %.

Deposits of Mohyliv-Podilskyi series of the Transdnestria are characterized by low post-sedimentation changes. The mineral composition of argillites, locating within the marcasite, pyrite, phosphorite concretions and authigenic mineralization indicate diagenetic changes.

#### Conclusions.

1. Vendian sedimentation in the Middle Transdnestria is occurred in epicontinental marine basin with an alkaline solution and active tectonic processes. This contributed lithogenesis of clastic rocks in the basin shelf which had poor sorting of output material.

2. Divided topography of the seabed caused occurrence of area where fine material (pelitic dimension) accumulated. Those were mainly areas with non-offset sedimentation. Within clayey silts accumulated, which later turned into argillites.

3. In the deposits of Mohyliv-Podilskyi series of the Vendian five stratigraphic levels which contain BS were allocated. They are thinly layered, from dark gray to black argillites which are rich in organic matter varying degrees.

4. Numerous non-skeleton biota remains (Ediacaran type) were recorded in all stratigraphic levels of Mohyliv-Podilskyi series.

5. The apogee of BS accumulation in the Transdnestria is kaliuski age when exemplary deposits formed.

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**Мета.** Визначення просторово-часових закономірностей поширення чорносланцевих товщ у розрізах пізнього протерозою на території Придністров'я для подальших їх літолого-мінералогічних, петрографічних і геохімічних досліджень.

**Методика.** Польові спостереження відслонень вендського розрізу та їх детальний літологічний опис, фаціальний аналіз, петрографічні й літолого-геохімічні дослідження.

**Результати.** Проведено ревізію відслонень пізньодокембрійського розрізу території Подільського Придністров'я, уточнено умови залягання, контакти літотипів із підстеляючими й перекриваючими породами, встановлено текстурно-структурні та інші особливості стратиграфічних таксонів, що вказують на генетичні й фаціальні аспекти їх формування. У відкладах могилів-подільської серії венду виділено п'ять стратиграфічних рівнів, що вміщують чорносланцеві породи: ломозівські, лядавські, бронницькі, зінківські й калюські верстви. Також встановлені нові таксони едіакарської фауни, що детально будуть описані в подальших публікаціях.

**Наукова новизна.** Уперше для могилів-подільської серії Придністров'я виділено п'ять стратиграфічних рівнів розвитку чорносланцевих порід. Останні накопичувались у некомпенсованих прогинах епіконтинентального басейну й були збагачені органічною речовиною. Вони можуть розглядатись як материнські породи вуглеводнів докемб-

рійських і ранньопалеозойських осадових формацій Волино-Поділля.

**Практична значимість.** Полягає у використанні даних для прогнозування в межах Волино-Подільської плити робіт, пов'язаних із вивченням нафтогазності територій.

**Ключові слова:** *чорносланцеві породи, стратиграфічні рівні, докембрій, венд, безскелетна фауна, умови осадконакопичення*

**Цель.** Выявление пространственно-временных закономерностей распространения черносланцевых толщ в разрезах позднего протерозоя на территории Приднестровья для дальнейших их литолого-минералогических, петрографических и геохимических изучений.

**Методика.** Полевые наблюдения отложений вендского разреза и их детальное литологическое описание, фациальный анализ, петрографические и литолого-геохимические исследования.

**Результаты.** Проведена ревизия отложений позднепротерозойского разреза территории Подольского Приднестровья, уточнены условия залегания, контакты литотипов с подстилающими и перекрывающими породами, установлены текстурно-структурные и другие особенности стратиграфических таксонов, что указывают на генетиче-

ские и фациальные аспекты их формирования. В отложениях могилев-подольской серии венда выделено пять стратиграфических уровней, которые содержат черносланцевые породы: ламозовские, лядавские, бронницкие, зиньковские и калюские слои. Также установлены новые таксоны эдикарской фауны, которые детально будут описаны в дальнейших публикациях.

**Научная новизна.** Впервые для могилев-подольской серии Приднестровья выделено пять стратиграфических уровней развития черносланцевых пород. Последние отлагались в некомпенсационных прогибах эпиконтинентального бассейна и были обогащены органическим веществом. Они могут рассматриваться как материнские породы углеводородов докембрійских и раннепалеозойских осадочных формаций Волино-Подолья.

**Практическая значимость.** Состоит в использовании данных для прогнозирования в пределах Волино-Подольской плиты работ, связанных с изучением нефтегазоносности территорий.

**Ключевые слова:** *чорносланцеві породи, стратиграфічні рівні, докембрій, венд, бесскелетна фауна, умовия осадконакоплення*

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