BIULETYN PAŃSTWOWEGO INSTYTUTU GEOLOGICZNEGO 449: 119–130, 2012 R.

GEOLOGICAL AND PHYSICAL-CHEMICAL CHARACTERISTICS OF LOWER PALEOZOIC DEPOSITS OF VOLHYNO-PODILLYA, WESTERN UKRAINE

CHARAKTERYSTYKA GEOLOGICZNA I FIZYKOCHEMICZNA DOLNOPALEOZOICZNYCH OSADÓW WOŁYNIA I PODOLA (ZACHODNIA UKRAINA)

Ihor Kurovets[1], Danylo Drygant[2], Ihor Naumko[1], Serhiy Kurovets[3], Yuriy Koltun[1]

Abstract. The 340 to 1102 m thick multi-facies sequence was deposited during the Silurian at the Volhyno-Podillya margin of the East European Platform. The open shelf facies bordered from the west by a barrier formed by reefs, bioherms, crinoids, or by banks of detrital sediments (at the boundary of the lagoon and the open sea). Lagoonal deposits are represented by thin intercalations of sedimentary dolomites, sometimes with intercalations of organogenic limestones, marls, argillites, gypsum and anhydrite. Within the open shelf and slope facies, marls, lumpy clayey limestones and argillites are prevailing. A zone of reefal buildups has a rather complicated and insufficiently investigated structure. The exclusively terrigenous deposits of the submerged part of the continental slope form the entire Silurian sequence in the central part of the L'viv Depression and in the Carpathian Foredeep.

Open porosity of the Silurian argillites vary from 0.6 to 2.4% and they are almost impermeable (less than 0.001 $\mu m^2 \cdot 10^{-3}$). Volume weight ranges between 2.64 and 2.8 g/cm^3. Natural radioactivity of rocks varies from 9 to 18 mcR/hr, apparent electric resistance is 20–154 Ohmm, interval time of longitudinal waves spreading is 126–365 μcs/m. TOC content, determined in 21 samples using the thermal analysis, varies from 0.75 to 2.38%. The composition of volatiles of fluid inclusions and closed pores of argillites shows the predominance of methane (up to 100 vol. %). In deeper horizons, carbon dioxide, nitrogen and ethane (a few percent) appear.

Key words: geology, petrophysics, fluid inclusions, Lower Paleozoic, shale gas, Volhyno-Podillya.

Abstrakt. Zróżnicowane facjalnie utwory syluru, miąższości od 340 do 1102 m, były deponowane na wołyńsko-podolskiej krawędzi platformy wschodnioeuropejskiej. Bariera budowana przez rafy, biohermy i ławice materiału detrytycznego graniczyła na zachodzie z facjami otwartego szelfu. Na wschód od tej bariery, w lagunie, tworzyły się osady dolomitowe z przeławiceniami organogenicznych wapieni, margli, iłowców, gipsu i anhydrytu. Osady szelfu i skłonu są reprezentowane głównie przez margle i ilaste wapienie gruzełkowe oraz argility. Strefa bariery rafowej ma dość skomplikowaną i jeszcze niedostatecznie rozpoznaną budowę. Osady terygeniczne występują tylko w zanurzonym odcinku skłonu kontynentalnego w centralnej części depresji lwowskiej oraz w podłożu zapadliska przedkarpackiego.

Efektywna porowatość argilitów sylurskich wynosi od 0,6 do 2,4% i są one prawie nieprzepuszczalne (mniej niż 0,001 $\mu m^2 \cdot 10^{-3}$). Gęstość objętościowa waha się pomiędzy 2,64 i 2,8 g/cm^3. Promieniotwórczość naturalna skał sięga od 9 do 18 mcR/h, a pozorna oporność właściwa wynosi 20–154 Ohmm, czas interwałowy rozchodzenia się fal podłużnych – 126–365 μcs/m. Zawartość TOC, określona w 21 próbkach z wykorzystaniem analizy termicznej, waha się od 0,75 do 2,38%. Skład substancji lotnych z inkluzji fluidalnych i zamkniętych porów w argilitach wykazuje dominację metanu (do 100% obj.). W głębszych horyzontach pojawiają się dwutlenek węgla, azot i etan (kilka procent).

Słowa kluczowe: geologia, petrofizyka, inkluzje fluidalne, dolny paleozoik, gaz łupkowy, Wołyń, Podole.

---

[1] Institute of Geology and Geochemistry of Combustible Minerals of NAS of Ukraine, Naukova 3a, 79060 Lviv, Ukraine

[2] State Natural Museum of NAS of Ukraine, Teatralna 8, 79000 L'viv, Ukraine

[3] Ivano-Frankivs'k National Technical University of Oil and Gas, Ukraine, Karpatska 15, 76000 Ivano-Frankivs'k, Ukraine

INTRODUCTION

Early Paleozoic deposits of the south-western margin of the East European Platform are considered presently as one of the most prospective targets for shale gas exploration (Poprawa, 2010). In Ukraine, these are Silurian and Ordovician deep-marine sediments, which extend towards the SE from the Polish border to Romania (Drygant, 2010). Although these deposits are prospective for hydrocarbons (Kurovets *et al*., 2011), their structure, facies and sedimentological peculiarities are known only in general terms. The objective of this study is to specify the depositional and facies environments of these strata, which would be useful for understanding the possible shale gas occurrence in this territory, and to investigate the geochemical and petrophysical characteristics of black shales.

EXPERIMENTAL

Petrophysical investigations. Methods of petrophysical laboratory investigations of core samples includes a range of study methods of the rock matrix, diagnostics and estimates of physical-mechanical parameters of reservoir rocks, independently from the previous conclusions on the type and characteristics of the pore space of the rocks. Errors of measurements of the parameters are characterized by the following values: for integral time, the mean square error is 1.5–2%, for relative resistivity 2–2.5%, for saturation parameter 3–5%, for open porosity 5–7%, for permeability 10–15%.

Differential Thermal Analysis. TOC measurements in this study were made using the Differential Thermal Analysis. Thermogravimetric investigations were performed using the NETZSCH STA 449 F3 Jupiter instrument within the temperature range of 25–800°C, heating rate was 20°C/min in argon atmosphere. Sample weight ~300 mg. Precision of temperature measurements 1°C, mass change $1 \cdot 10^{-2}$ mg. At the temperature of up to 120°C, water is released from the sample, at 120–300°C – free hydrocarbons, at 300–390°C – bound hydrocarbons, at 390–550°C – CO_2 is formed during burning of kerogen (C >40).

Mass-spectrometry. Taking into account the specificity of shale gas, the methods, developed in the Department of Deep Fluids of IGGCM NAS of Ukraine (Naumko, 2006; Naumko *et al*., 2009), shall be involved in the determination of its concentrations and features of spatial distribution within the productive sequences of black shale formations. Their peculiarity is that the release of volatiles from fluid inclusions in minerals and from closed pores in rocks is made by mechanical crushing of rocks, which juxtaposes this process with the conditions of breakdown of rocks within the zone of artificial hydraulic fracturing.

Mineral-fluidological indexes: volatile content, relative gas saturation ΔP, Pa (pressure increase in the filling system of mass-spectrometer compared to the residual pressure in the order of $1 \cdot 10^{-3}$ Pa resulting from the release of volatiles) and relative water saturation C_{H_2O} (water vapour content in the total volume of the released volatiles; absorber – P_2O_5) were determined using the mass-spectrometric chemical method on time-of-flight mass-spectrometer MCX-3A (1–200 a.u.m.).

SEDIMENTARY ENVIRONMENTS

BASIN EVOLUTION

Nature and intensity of the processes, which had an impact on the formation of Silurian strata of the south-western margin of the East European Platform have been determined by the location of the region, which tectonically belonged to the zone of peri-cratonic subsidence, and was the floor of an epicontinental sea. The initial simple structure of this sequence was significantly complicated by the contrast and multi-directional tectonic movements during the long intervals of the continental evolution of the region at the end of Early Devonian and in the Late Carboniferous (Drygant, 2010). The Wenlock–Ludlow deposition was compensated by the more or less uniform subsidence, while in the Pridoli–Early Devonian, it was obviously excessive in its western part (Teisseyre-Tornquist Zone – TTZ). The continuous Silurian–Lower Devonian sequence (structural complex) shows almost a submeridional strike of the clearly defined facies zones and a significant increase of the thickness in the western direction (Fig. 1) (Drygant, 2000). It rests on the surface eroded during a long regression (caused by the Taconic orogeny). The surface is made up of Ordovician, Cambrian and Vendian rocks (Fig. 2).

The 340 to 1102 m thick multi-facies sequence was deposited during the Silurian at the Volhyno-Podillya margin of the East European Platform. The minimum thicknesses (340–385 m) are found in the eastern part of the region, where the shallow-water and lagoon facies prevail in the sequence. The maximum thicknesses (989–1102 m) are observed in the Carpathian Foredeep and central part of the L'viv Depression, where the slope and depressional facies (mainly graptolitic argillites) occur (Einasto *et al*., 1980).

Analysis of maps of isopachs distribution and facies occurrence shows that the open-shelf facies bordered from the west on the bottom of a barrier, formed by reefs, bioherms, crinoids or the banks of detrital sediments at the boundary of the lagoon and the open sea. In spite of the lateral migration

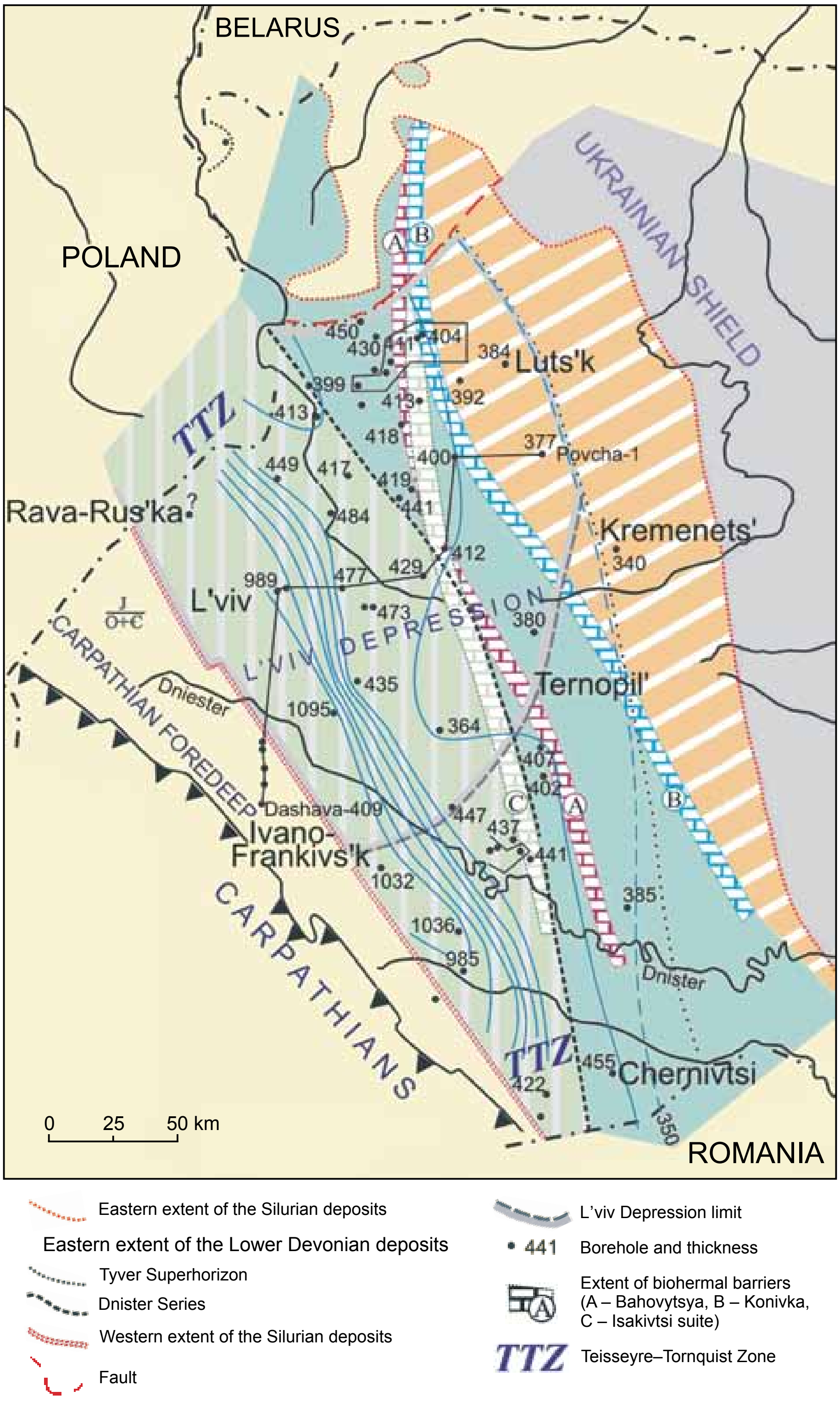

Fig. 1. Isopach map of the Silurian deposits

of the barrier and the facies zones, the structural plan did not change significantly during the entire Silurian. Growth of organogenic structures, because of their intense destruction and slow subsidence, only slightly advanced the rate of the coeval sedimentation in the pre-reef and back-reef zones, and therefore they did not form the bodies, which would exceed by thickness the enclosing rocks.

The most intense regressions developed in the Silurian at the beginning and before the end of Ludlow, when the Bahovytsya and Konivka reef structures formed. Transgression between them reached its peak in Malynivtsi time and caused the formation of a monotonous sequence (about 100 m) of clayey-carbonate sediments of the open-shelf and transition zones in almost the entire region.

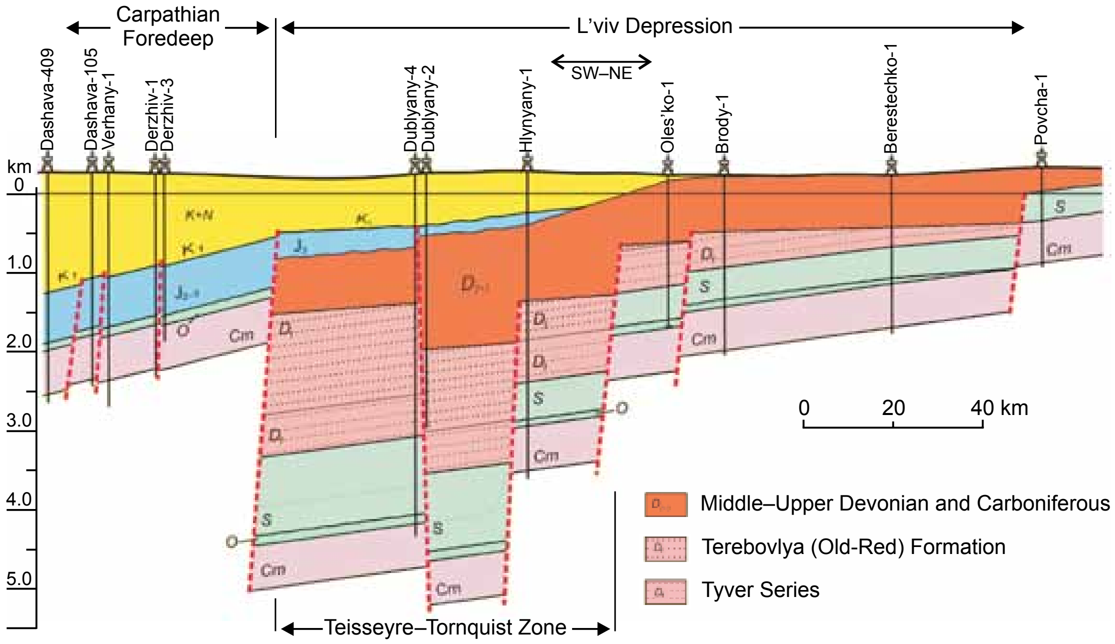

Fig. 2. Geological cross-section across the L'viv Depression and Carpathian Foredeep

FACIES ZONES

Stratigraphically, the Silurian sections in the southwest of the East European Platform are also made up of rather variable multi-facies sequences of lagoonal, shallow-water, open-shelf and slope sediments (Drygant, 2000). Facies similar by composition and origin form the zones of more or less submeridional strike. Their location and boundaries were changing with time and therefore the areas of occurrence of similar facies at different stratigraphic levels do not coincide. A regular shift of facies zones into one or another direction against the coastline, related to the changes of palaeogeographic environments, caused the cyclicity of the sequence structure on the whole. While the location and migration of facies zones were controlled by the palaeotectonic and palaeogeographic factors, the formation and composition of facies depended on the development of organisms, primarily the skeletal ones. The reef-forming organisms not only supplied the great amount of detrital material for the shallow-water facies, but also formed the entire structures like bioherm or reef massifs. Such structures separated a zone of lagoonal sedimentation (eastern part of the region) from the open basin, located westwards. A detailed facies-sedimentological model of the basin has been developed on the materials from its Baltic part (Nestor, Einasto, 1977; Einasto *et al.*, 1986).

Lagoonal deposits are represented by thin intercalations of sedimentary dolomites, sometimes with intercalations of organogenic limestones, marls, argillites, gypsum and anhydrite. Within the open-shelf and slope facies, marls, lumpy clayey limestones and argillites are dominant. Clay content in the rocks increases towards the open sea. A zone of reefal buildups has a rather complicated and not sufficiently investigated structure.

The typical feature of this zone is the presence of thick successions of secondary dolomites, dolomitized limestones with abundant remnants of reef-building and reef-related organisms. Back-reef facies are spread in somewhat wider band and are made up of massive organogenic-detrital limestones with interfingering clayey limestones and bioherms. Fore-reef facies are represented by dolomitized products of reef destruction, alternated with lagoonal deposits. Zones of reef constructions of different ages do not coincide in most part of the region. In the west, the early Skala (of Isakivtsi and Pryhorodok age) zone occurs. In the east, there is the early Malynivtsi zone. The Bahovytsya zone is approximately in the middle between them. The reef bodies are underlain mainly by massive organogenic-detrital limestones or dolomites. Their transitions to the adjacent facies are gradual, but occur within very narrow zones. In the Wenlock, which is represented over the entire territory by exclusively marine clayey-carbonate deposits (slope facies), facies zones cannot be distinguished. Other levels include lagoon, shallow-water (reef, back-reef and fore-reef) and open sea (open shelf) deposits. The most widespread sediments of the lagoon zone are laminated clayey dolomites and algal dolomites of the Ustiv formation. These dolomites are primary (syngenetic), because they were formed in the lagoon-coastal quiet-water environment, which occurred in a basin partly separated from the normal shelf sea with somewhat special sedimentary environment and clear cyclicity.

In close vicinity to the reef constructions (back-reef facies), brecciated dolomites are found, in which fine-grained or pelitomorphic dolomite debris is cemented with clayey matrix (reefogenic breccia).

The second facies zone is represented by deposits that formed within a relatively narrow shallow-water belt at the boundary between the lagoon and open shelf. Typical features of this zone are as follows: 1) primary calcareous composition of the rocks; 2) lack of terrigenous admixtures; 3) variety of structures and fabrics of the rocks; 4) predominance of remnants of reef-constructing and other sedentary organisms; 5) horizontal unevenness of layers and significant thickness variability. The most typical facies of this zone are reefs (bioherm constructions) and fore-reef detrital limestones.

Bioherm constructions are notable for their relatively small dimensions (height does not exceed 15 m, length 25 m), occurrence within homogeneous rocks, lack of significant secondary transformations (dolomitisation), lack or small dimensions of the apron. The Late Wenlockian bioherms cropping out on Podillya are lithologically rather homogeneous, however, biomorphic limestones prevail. They are bituminous, hard and massive.

In different periods of basin evolution, the barrier between the lagoon and the open shelf part may have been represented in different areas by a low reef, bioherm ridge, tangles of algae or crinoids, or banks. However, regardless of the type of the reef construction, fore-reef facies always formed near it from the open-sea side. They are made up of variously grained limestones with massive or (further from the construction) breccia-like fabric, without admixtures of clayey material and traces of dolomitisation, and with rather scarce faunal remnants.

Westwards from the shallow-water deposits, a significantly wider zone of open sea (open shelf) facies occurs in all the horizons. Their typical features are: 1) clayey-limy composition; 2) random clayey and grain components; 3) homogeneity of the sequence without visible lamination; 4) lumpy fabric of rocks; 5) some increase of thickness of deposits. In this zone, clayey and clayey-detrital limestones and marls with a typical lumpy fabric are observed. The zone of lumpy limestones is not tectonically separated and has no abrupt boundaries with the adjacent zones. Their transition to graptolitic argillites is gradual. The transitional rocks are represented by variously clayey marls, carbonate argillites and clays with lumpy or massive fabric.

The deposits of the submerged part of the continental slope occur in the fourth facies zone and form the entire Silurian sequence in the central part of the L'viv Depression and in the Carpathian Foredeep (in the Teisseyre-Tornquist Zone). They are characterized by exclusively terrigenous composition. These are dark-grey, almost black argillites, rarely slightly carbonaceous, with solitary graptolites. The thickness of the graptolitic argillites significantly exceeds the thickness of the coeval clayey-carbonate and carbonate deposits (Figs. 1, 2).

LITHOLOGICAL AND GEOCHEMICAL CHATRACTERISTICS OF ROCKS

SILURIAN ROCKS FROM THE LISCHYNA-1 WELL

A typical and complete sequence of deep-water terrigenous deposits with a core recovery sufficient for analysis has been penetrated by this well in the interval of 2278–3537 m (Fig. 3). This allowed performing detailed mineralogical-petrographic and petrophysical investigations. By the results of core investigations and well-log data, the Silurian sequence can be subdivided into three parts (Kurovets *et al*., 2010).

In the upper part of the sequence (interval of 2278–2804 m) occur grey argillites, in places with intercalations of siltstones (up to 0.5 cm) and clayey limestones. Argillites contain moderate amounts of pyrite. Solitary finds of fauna are represented by debris of shells of brachiopods and pelecypods, crinoid stems, and hieroglyphs. Argillites are micaceous, layered, and locally limy with transition into clayey marl. Authigenic quartz and sericite flakes are present. Core samples from a depth interval of 2755–2804 m contain a lot of sub-vertical fractures, filled with white calcite (Fig. 4A).

The middle part of the sequence (interval 2804–3020 m) is made up of dark-grey, massive, horizontally bedded, hydromicaceous argillites (Fig. 5C, D). Organic matter and pyritization is observed on bedding planes. Pyrite forms small grains or thin streaks. Besides, short (up to 1–1.5 mm) open micro-fractures are observed on bedding planes (Fig. 5D).

The lower part of the Silurian sequence in the well (interval 3020–3537 m) is composed of black, massive, horizontally thin thin-layered, hydromicaceous argillites, enriched with organic matter (Fig. 5E, F). The silt fraction is evenly dispersed in the rock.

Structural and fabric characteristics (cross bedding, change in the thickness of silt streaks, lumpiness) show that the sediments of the upper interval of the sequence were formed in a rather active-water environment, while the middle and lower parts in a quiet-water sedimentary environment as indicated by horizontal bedding and pelitic fabric.

PETROPHYSICAL PROPERTIES

According to petrophysical investigations, the open porosity of argillites changes within a range of 0.6–2.4% (Fig. 6, Tab. 1) and they are almost impermeable (less than 0.001 $\mu m^2 \cdot 10^{-3}$). The carbonate content reaches 20%. The lowest volume weight (2.64–2.70 g/cm^3) is characteristic for argillites containing organic matter, while the highest (2.75–2.8 g/cm^3) – for massive hydromicaceous argillites with pyrite inclusions. Well-log data show that the sequence is poorly differentiated, the natural radioactivity of rocks varies from 9 to 18 mcR/hr, apparent electric resistance is 20–154 Ohmm, interval time of longitudinal waves spreading is 126–365 µcs/m.

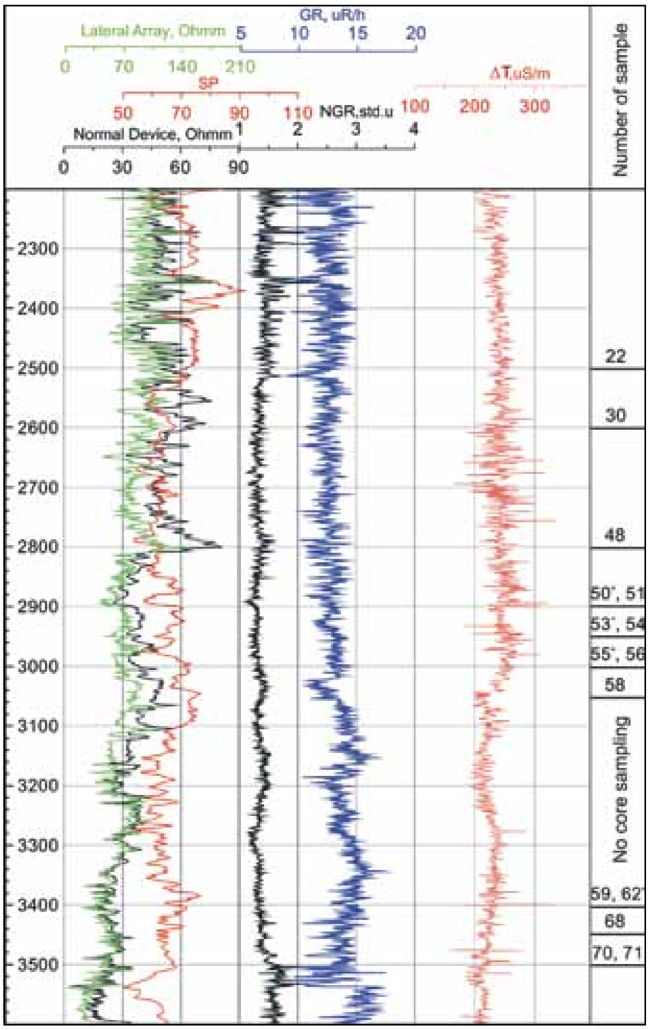

Fig. 3. Geophysical characteristics of Silurian deposits in the Lischyna-1 well

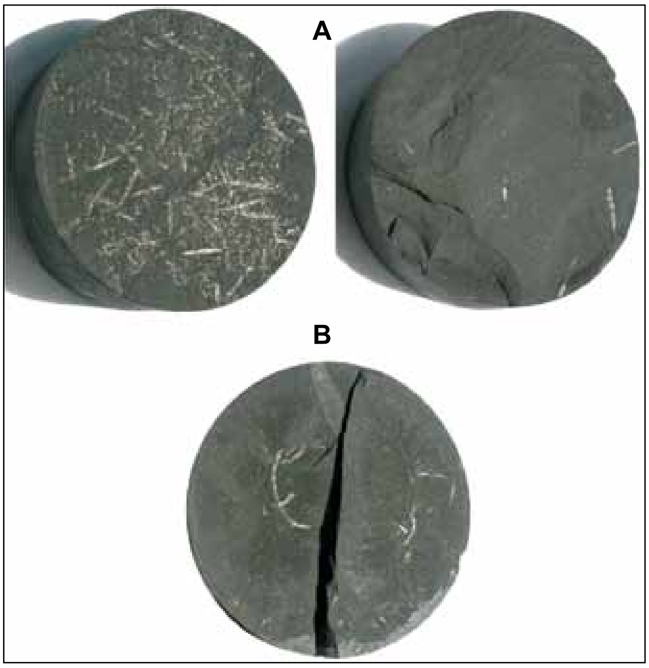

Fig. 4. Silurian graptolitic argillites from the Lischyna-1 well

A – sample 66, **B** – sample L-69

Table 1

Main statistic data of petrophysical parameters of Silurian argillite deposits in the Lischyna-1 well

Parameter	Quantity	Average	Minimum	Maximum	Dispersion	Standard deviation	Assimetry	Excess
Absolute porosity	45	0.0150	0.0021	0.0415	0.00008	0.0091	0.934	0.667
Specific gravity of rock, g/cm^3	42	2.7360	2.7000	2.7900	0.00043	0.0208	0.758	0.177

GEOCHEMICAL INVESTIGATIONS

Results of the chemical analysis (Tab. 2) show that the average silica content is 50% and does not depend on the depth of occurrence, which correlates with the data from Poland (Poprawa, 2010).

According to spectral analysis data (Tab. 3), a moderate content of almost all identified components is observed in the samples, which in general corresponds to the background content. Sample 41-Li is the best investigated one with all analyses made. In particular, according to the chemical analysis, it contains 2.27% of TOC and 13.2% of carbonates. Chemical and spectral analyses show that the carbonates are represented by magnesian limestones as well as by ferriferous varieties.

TOC content in this study was determined using the thermal analysis. In 21 samples, the TOC content varies from 0.75 to 2.38% (Tab. 4).

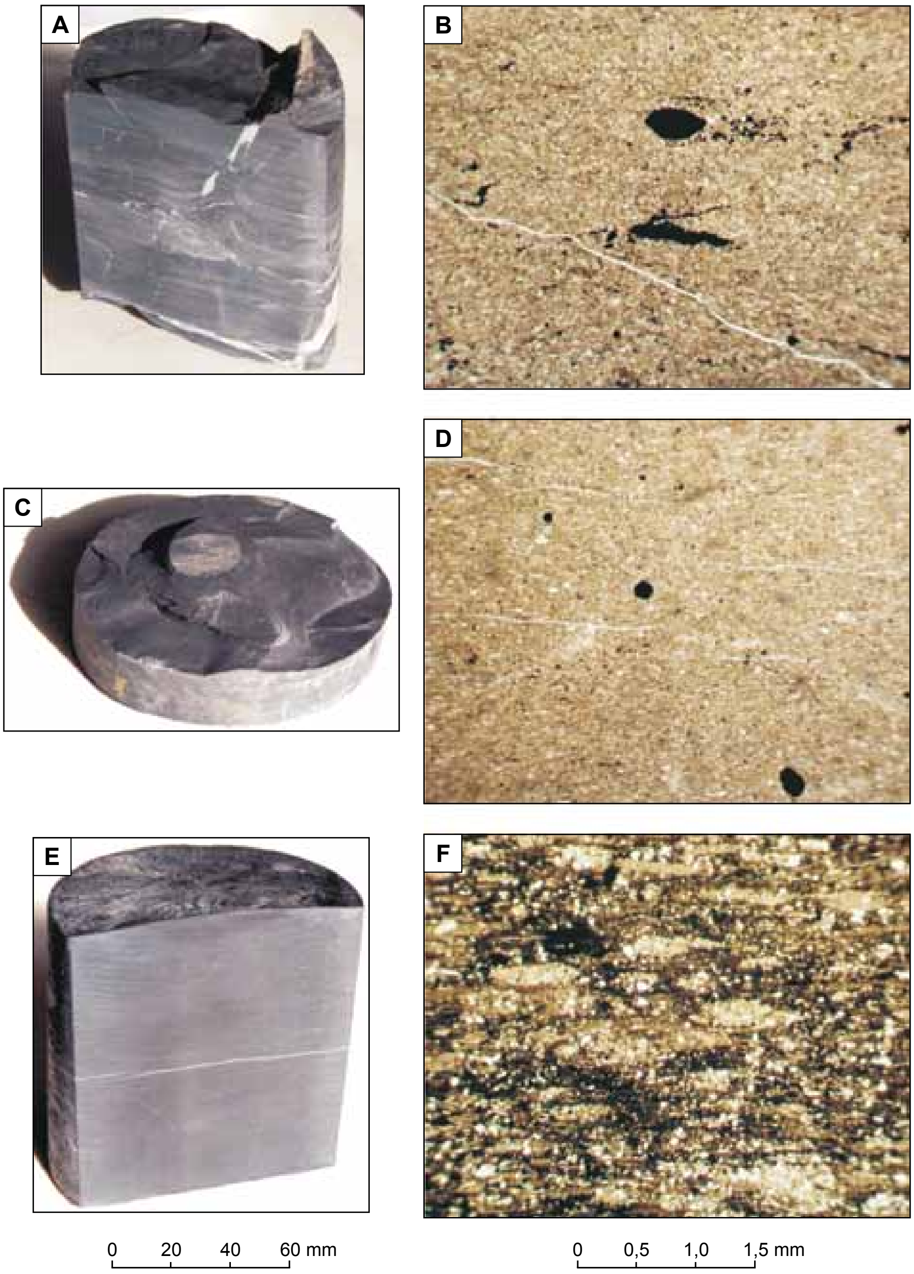

Fig. 5. Silurian rocks from the Lischyna-1 well

A – intercalation of hydromicaceous argillite with siltstone with a system of sub-vertical and horizontal fractures, filled with white calcite and quartz, depth interval 2755–2804 m, core ∅ 78 mm; **B** – fracture in hydromicaceous argillite, depth interval 2800–2804 m, nicols ||; **C** – grey, massive, hydromicaceous argillite with horizontal bedding, depth interval 2998–3003 m, core ∅ 78 mm; **D** – open micro-fractures in hydromicaceous argillite, depth interval 2998–3003 m, nikols ||; **E** – massive, black, hydromicaceous, organic-rich argillite with horizontal bedding, depth interval 3402–3406 m, core ∅ 78 mm; **F** – hydromicaceous organic-rich argillite, depth interval 3402–3406 m, nicols ||

Kerogen is overmature in the south-eastern part of the Ukrainian Carpathian Foredeep basement (Ispas-1 well) (Koltun, 2008).

Two Ordovician samples from the intervals of 3750–3753 and 3800–3803 m have been analysed. The rocks contain small amount of carbonate material, as their insoluble residue is 88–93%. The TOC content is 0.6–0.7%. The chloroform bitumen concentration in rocks is 0.013–0.015%, acid bitumen components are twice more common than the neutral ones. The bituminization extent of the organic matter is low, the reduced components content is only 1.4–2% in it. Taking into account the above-mentioned data and the great depths of occurrence, the conclusion can be made about the syngenetic nature of these bitumens and the residual character of the neutral bitumen.

Table 2

Results of chemical analysis of samples (Lischyna-1 well) (in %)

Sample No	SiO_2	$A1_2O_3$	FeO	Fe_2O_3	TiO_2	MnO	P_2O_5	CaO	MgO
39-Li	55.85	17.14	3.16	4.26	0.69	0.13	0.21	3.64	2.42
41-Li	42.15	13.98	5.75	0.88	0.63	0.21	0.09	11.06	3.75
55-Li	47.83	16.80	2.99	4.18	0.57	0.09	0.20	6.94	3.40
61-Li	48.81	15.23	2.13	4.17	0.50	0.04	0.12	7.17	3.86
69-Li	50.80	14.25	1.53	3.20	0.55	0.04	0.16	9.42	1.92
Sample No	**К$_2$O**	**Na_2O**	**SO_3**	**S_{pyr}**	**ВМП**	**Total**	**$CO_{2carb.}$**	**H_20^-**	**$C_{org.}$**
39-Li	3.53	1.05	0.11	0.73	6.56	99.58	–	0.37	–
41-Li	2.16	0.72	<0.1	0.58	17.77	99.51	13.2	0.20	2.27
55-Li	3.95	0.77	0.05	0.57	11.01	99.57	–	0.44	–
61-Li	3.98	0.97	0.21	1.16	11.55	99.56	–	0.10	–
69-Li	4.37	1.16	0.18	0.86	11.92	99.85	–	0.20	–

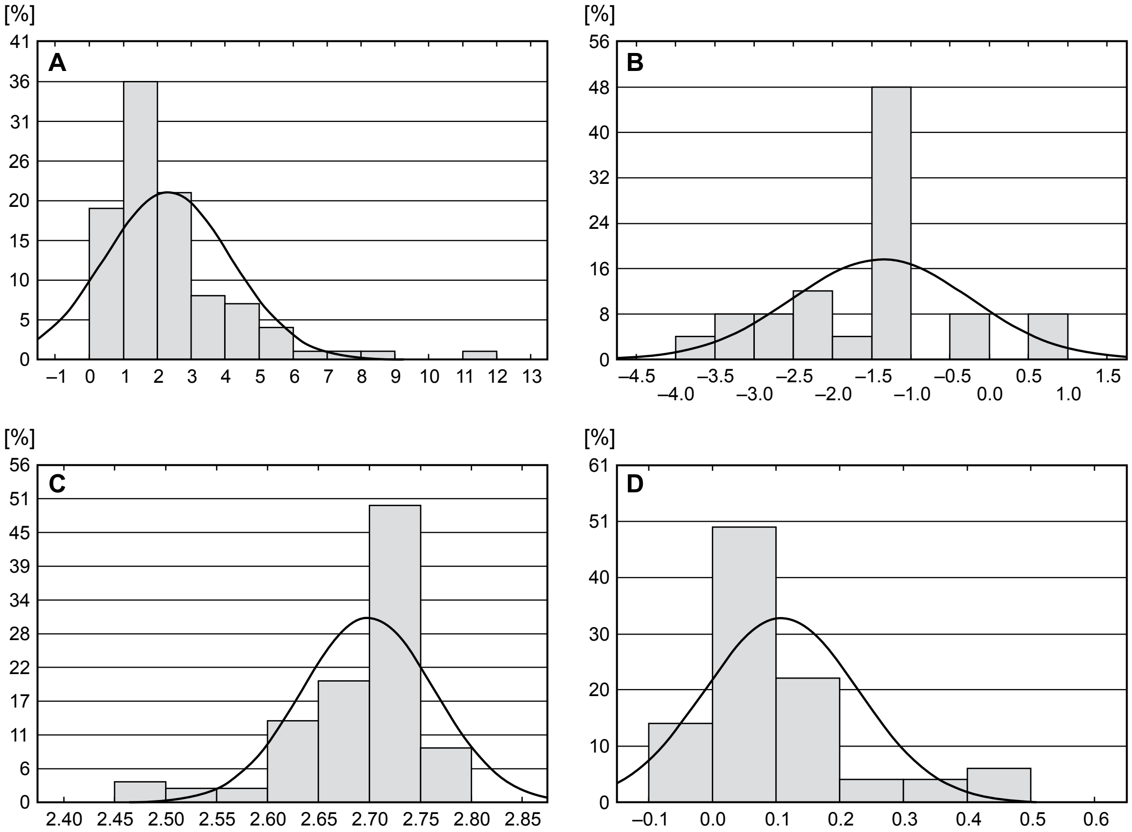

Fig. 6. Distribution of absolute porosity (A) and lg of permeability factor (B), specific gravity (C) and carbonate content (D) of Silurian argillite deposits in the Lischyna-1 well

Table 3

Microcomponents content in Silurian deposits of Volhyno-Podillya (core from well Lischyna-1) (in %)

Sample No	**Ba** [10^{-2}]	**Be** [10^{-4}]	**As** [10^{-2}]	**Te** [10^{-2}]	**Hg** [10^{-2}]	**Sc** [10^{-4}]	**P** [10^{-1}]	**Sb** [10^{-3}]	**Ge** [10^{-4}]	**Au** [10^{-4}]	**Pt** [10^{-3}]
39-Li	3	<5	<10	<1	<3	1	0.6	<3	<1	<2	<1
41-Li	4	<5	<10	<1	<3	0.6	<0,5	<3	<1	<2	<1
42-Li	3	<5	<10	<1	<3	1	0.6	<3	<1	<2	<1
43-Li	3	<5	<10	<1	<3	0.8	0.6	<3	<1	<2	<1
44-Li	3	<5	<10	<1	<3	0.6	0.5	<3	<1	<2	<1

Sample No	**Cr** [10^{-3}]	**Ta** [10^{-2}]	**TI** [10^{-2}]	**Pb** [10^{-3}]	**U** [10^{-2}]	**Th** [10^{-2}]	**Ti** [10^{-1}]	**Mn** [10^{-2}]	**W** [10^{-3}]	**Ga** [10^{-3}]	**Nb** [10^{-3}]	**Ni** [10^{-3}]
39-Li	6	<1	<0.5	2	<3	<1	2	4	<5	2	1	4
41-Li	6	<1	<0.5	2	<3	<1	1.5	5	<5	2	1	3
42-Li	8	<1	<0.5	2	<3	<1	2	3	<5	2	1.5	3
43-Li	6	<1	<0.5	2	<3	<1	2	3	<5	2	1.5	3
44-Li	6	<1	<0.5	2	<3	<1	2	2	<5	2	<1	4

Sample No	**Bi** [10^{-3}]	**Ce** [10^{-2}]	**La** [10^{-3}]	**Y** [10^{-3}]	**Yb** [10^{-4}]	**Hf** [10^{-2}]	**Mo** [10^{-4}]	**Sn** [10^{-4}]	**V** [10^{-3}]	**Li** [10^{-3}]	**Cd** [10^{-3}]	**Cu** [10^{-3}]
39-Li	0.1	<2	<5	1	1	<1	1	3	10	4	<1	3
41-Li	0.1	<2	<5	1	1	<1	1	2	8	3	<1	2
42-Li	0.1	<2	<5	1	1	<1	5	3	8	4	<1	3
43-Li	0.1	<2	<5	1	1.5	<1	6	3	10	4	<1	3
44-Li	0.1	<2	<5	1	1	<1	5	2	20	4	<1	3

Sample No	**Ag** [10^{-4}]	**Zn** [10^{-3}]	**Na** [%]	**Sr** [10^{-2}]	**Co** [10^{-3}]	**Zr** [10^{-3}]	**Si** [%]	**Al** [%]	**Mg** [%]	**Ca** [%]	**Fe** [%]	**In** [10^{-3}]
39-Li	<0.1	6	0.8	<3	3	10	15	5	0.8	4	4	<1
41-Li	<0.1	4	0.6	<3	2	8	10	5	1	6	4	<1
42-Li	<0.1	6	0.8	<3	2	10	20	5	1	5	4	<1
43-Li	0.1	6	0.8	<3	2	10	15	5	1	6	4	<1
44-Li	0.4	6	1	<3	2	10	15	5	1	6	4	<1

Table 4

Table of mass changes of samples (in %)

Sample No	<120°C	120–300°C	300–390°C	390–550°C	TOC [%]
Buch-3	0.3222	0.25328	0.06183	1.16962	1.80693
Buch-7	0.35807	0.34204	0.14047	1.54385	2.38443
Buch-10	0.31142	0.32816	0.08757	1.25861	1.98576
Buch-102	0.3908	0.51609	0.09311	1.26396	2.26396
5-Li	0.28881	0.19014	0.05382	0.92777	1.46054
32-Li	0.20336	0.13184	0.05726	1.00482	1.39728
37-Li	0.21568	0.18434	0.05857	0.94518	1.40377
38-Li	0.13659	0.1387	0.05387	0.96215	1.29131
39-Li	0.10508	0.11356	0.03955	0.80939	0.9625
40-Li	0.20553	0.13757	0.03446	0.73568	0.90771
41-Li	0.18909	0.11004	0.02887	0.61808	0.75699
42-Li	0.284	0.14877	0.04309	0.77413	0.96599
43-Li	0.28144	0.15914	0.05194	1.04027	1.53279
44-Li	0.04782	0.11693	0.05402	0.79788	0.96883
47-Li	0.25155	0.15393	0.05692	0.97901	1.44141
51-Li	0.16257	0.21515	0.0891	0.84177	1.30859
56-Li	0.14583	0.1932	0.05483	0.71788	1.11174
58-Li	0.29428	0.19494	0.05351	0.84413	1.38686
65-Li	0.06476	0.15209	0.14429	0.9513	1.31244
66-Li	0.16723	0.15545	0.05838	0.86958	1.25064
70-Li	0.02789	0.10137	0.05636	0.82978	1.0154

MASS-SPECTROMETRY

Unlike the conventional gas accumulations, where the reservoirs have high open porosity and the continuous gas phase, the shale gas occurs in dense low-permeable pelitomorphic sedimentary rocks with a high TOC content (≥1%, like in the fields of USA or Poland), formed within the black shale formations. In the shape of the discrete gas phase, sorbed and occluded by mineral and organic matter, it occurs in closed pores (cavities and fractures) of the rocks. Therefore, their total gas capacity must be higher than the normal total porosity of phaneromorphic rocks (sandstones, siltstones). Using appropriate technological means, it is possible to produce shale gas from them, which by its qualitative characteristics will in general not differ from the conventional gas, but will contain non-hydrocarbon gases (CO_2, N_2, H_2), as well as H_2S, mercaptanes and other harmful compounds.

Among volatiles of the fluid inclusions and closed pores of rocks (argillites) of all the investigated depth intervals from the Lischyna-1 well, methane is predominant (up to 100 vol. %). However, in deeper horizons there are also carbon dioxide and nitrogen as well as, which is important to emphasize, ethane (Tab. 5). Lack of vapour is observed, which may testify the “dryness” of the hydrocarbon-bearing systems in the argillite sequence. The low values of relative gas saturation can show that organic matter was the source of volatiles (first of all hydrocarbons). Its transformation did not occurr at low (mainly lithostatic) pressures. Influx of deep fluids through the postsedimentary fracture systems has been fixed in calcite of vein mineralization by the higher (by an order) relative water saturation and the presence of water in migration palaeo-systems.

The total weight concentration of components in the fluid is rather high (12.400–61.600)$\cdot 10^{-6}$ g/g sample (compared to the background values of 0.011$\cdot 10^{-6}$ g/g sample from the drill core of the non-productive well Dobromyl-Strilbychi-33 in the Carpathian Foredeep). In order to investigate it, a crushed sample was sieved through the 0.25 mm sieve and the results were related to the sieved part of the sample. A significant saturation of the studied samples with volatile is also indirectly indicated by the fact that the vacuumization of the samples occurred slower as compared to the other samples. The degassing in vacuum still continues after the analysis, and hence the determined concentration of volatiles is possibly higher. The sample after crushing was well sieved and this, together with the results of the chemical analyses (Tab. 6), testifies the predominance of the silica component over the clayey one, which is favourable for the hydraulic fracturing.

Hence, good conditions for shale gas generation by organic matter at the catagenesis stage existed within the natural complexes. Its quantitative proxies defined from data of the first research results of mass-spectrometric chemical analysis are rather significant, however need to be specified by further research. In summary, the composition of volatiles of fluid inclusions and closed pores of rocks (argillites) confirms the prospect for shale gas of the black shale sequence, for which the predominance of methane is characteristic (up to 100 vol. %), with carbon dioxide and nitrogen, and especially ethane (few %) (due to decrease of CH_4 content), appearing in deeper horizons.

Lack of the vapour may testify the "dryness" of the hydrocarbon-bearing systems, while the low values of relative gas saturation can show that the organic matter transformation, as a source of the volatile components (first of all hydrocarbon), occurred at low (mainly lithostatic) pressures. Simultaneously, an order higher relative gas saturation of the vein calcite, which fills the sub-vertical fractures in the argillite sequence, and the appearance of the water vapour indicate the possible influx through these fracture systems (or a huge system of connected fractures) of deep migration palaeofluids.

Table 5

Results of chemical analysis of rocks (argillites) in the sequence of the Lischyna-1 well (in %)

Components	Sample No			
	Li 1-39	Li 1-55	Li 1-61	Li 1-69
SiO_2	55.85	47.83	48.81	50.80
TiO_2	0.69	0.57	0.50	0.55
Al_2O_3	17.14	16.80	15.23	14.25
Fe_2O_3	4.26	4.18	4.17	3.20
FeO	3.16	2.99	2.13	1.53
CaO	3.64	6.94	7.17	9.42
MgO	2.42	3.40	3.86	1.92
MnO	0.13	0.09	0.04	0.04
K_2O	3.53	3.95	3.98	4.37
Na_2O	1.05	0.77	0.97	1.16
P_2O_5	0.21	0.20	0.12	0.16
SO_3	0.11	0.05	0.21	0.18
Spyr.	0.73	0.57	1.16	0.86
H_2O	0.37	0.44	0.10	0.20
Lah	6.56	11.01	11.55	11.92
Eq. S = 0	–0.27	–0.22	–0.44	–0.31
Total	99.58	99.57	99.56	99.85

Analysts: L.K. Bilyk, V.L. Kryzhevych (Institute of Geology and Geochemistry of Combustible Minerals of NAS of Ukraine, L'viv). Lah – weight loss after heating

Table 6

Volatile content of fluid inclusions and closed pores of rocks in the sequence of the Lischyna-1 well (according to data of mass-spectrometric chemical analysis[1])

Sample No	Depth interval [m]	Rock, mineral	Components[2]: volume content, per cent / weight concentrations, $n \cdot 10^{-6}$ g/g sample				Relative gas saturation ΔP, Pa[3]	Water saturation C_{H2O} vol. per cent[4]	Total weight concentration $n \cdot 10^{-6}$ g/g sample[5]
			CH_4	C_2H_6	CO_2	N_2			
Li 1-39	2750–2755	argillite	100.0 3.900	–	–	–	0.08	–	19.200
Li 1-46	2800–2804	argillite	100.0 61.600	–	–	–	0.27	–	61.600
Li 1-46	2800–2804	calcite	100.0 49.360	–	–	–	1.07	8.5	49.360
Li 1-56	2998–3003	argillite	100.0 15.400	–	–	–	0.07	–	15.400
Li 1-61	3402–3406	argillite	79.2 40.333	5.4 0.333	3.9 0.233	11.5 1.333	0.16	–	42.232
Li 1-69	3500–3504	argillite	62.1 9.000	–	12.0 0.800	25.9 2.600	0.10	–	12.400

Note:

[1] – analyst B.E. Sakhno (mass-spectrometer MCX-3A);

[2] – sample weight 200 mg, disintegrated by crushing in vacuum (until about $1 \cdot 10^{-3}$ Pa filling system) of mass-spectrometer;

[3] – ΔP – pressure increase in the filling system of mass-spectrometer with respect to the residual pressure of about $1 \cdot 10^{-3}$ Pa in it, which was created as a result of release of the volatile components from the inclusions while crushing the mineral (rock) sample, and may be a comparison value for the samples of the same weight;

[4] – C_{H2O} – percentage of water vapour in the total volume of the released volatile components;

[5] – to determine the weight concentration, crushed sample was sieved through the 0.25 mm sieve and the results were related to the sieved part of the sample.

CONCLUSIONS

Gradual lateral transitions between facies and minor thickness changes of the coeval deposits show that the Silurian basin shelf in most of the south-western margin of the East European Platform, during the Wenlock and most of the Ludlow (in pre-Skala time), was gently sloping (below 1–2°) and flat, without an abrupt ledge at the transition to the continental slope. Transverse geological cross-sections show that the continental slope of the basin was geomorphologically formed at the end of the Ludlow, when the trough of a graben related to the Teisseyre-Tornquist Zone originated and intense subsidence started in this area. At the beginning of the Devonian, uplift movements in the platform caused a gradual shallowing and regression of the basin, the eastern coastline of which moved in the Pragian to the TTZ. Simultaneously, the TTZ trough started to be filled exclusively with old-red facies.

The values of open porosity of argillites varies within a range of 0.6–2.4%. The permeability is below 0.001 $\mu m^2 \cdot 10^{-3}$, the carbonate content is up to 20%. According to spectral analysis data, the moderate content of almost all identified components is observed in the samples, which in general corresponds to the background content. The TOC content, determined in 21 samples using the thermal analysis, ranges from 0.75 to 1.53%.

Composition of volatiles of fluid inclusions and closed pores of rocks (argillites) confirms the prospect for shale gas of the studied black shale sequence, for which predominance of methane is characteristic (up to 100 vol. %). In deeper horizons, there are also carbon dioxide and nitrogen, and especially ethane (first %) (due to a decrease of CH_4 content).

Lack of the steam may testify the “dryness” of hydrocarbon-bearing systems, while low values of the relative gas saturation can show that the organic matter transformation, as a source of the volatile components (first of all hydrocarbon), occurred at low (mainly lithostatic) pressures. Simultaneously, an order higher relative gas saturation of the vein calcite, which fills the sub-vertical fractures in the argillite sequence and the appearance of the water indicate the possible influx through these fracture systems (or a huge system of connected fractures) of deep migration palaeofluids.

REFERENCES

DRYGANT D.M., 2000 — Lower and Middle Paleozoic of the Volyno-Podillia margin of the East-European Platform and Carpathian Foredeep. *Naukovi zapysky DPM NAS of Ukraine*, **15**: 24–129 [in Ukrainian with English abstract].

DRYGANT D.M., 2010 — Devonian conodonts of the south-western margin of the East-European Platform (Volyno-Podillia, Ukraine). Kyiv: 100 pp. [in Ukrainian with English abstract).

EINASTO R.E., KOTYK V.A., YUSHKEVICH V.I., 1980 — Formatsionnaya zonalnost siluriyskikh okrainnykh basseynov zapadnoy chasti Russkoy platformy. *In*: Types of sedimentary formations of the oil- and gas-bearing basins. Nauka, Moscow: 228–242 [in Russian].

EINASTO R., ABUSHIK A., KALJO D., KOREN T., MODZALEVSKAYA T., NESTOR H., 1986 — Silurian sedimentation and fauna of the East Baltic and Podolian marginal basins, a comparison. *In*: Theory and practice of ecostratigraphy (eds. D. Kaljo, E. Klaamann). Valgus, Tallinn: 65–72 [in Russian with English abstract].

KOLTUN Y., 2008 — Evolution of black shale deposits and generation of hydrocarbons within the ancient continental margin of Tethys (Ukrainian Carpathians and adjacent territories). Present-day problems of lithology and mineralogenesis of the sedimentary basins of Ukraine and adjacent territories. *Logos*, **36**: 87–92, Kyiv [in Ukrainian with English abstract].

KUROVETS I., NAUMKO I., PRYTULKA G., SHYRA A., SHUFLYAK Y., CHEPUSENKO P., 2010 — Litologo-petrofizychni i mineralogo-fluidologichni vlastyvosti syluriyskikh vidkladiy Lvivskogo paleozoyskogo progynu. Abstracts of the Conference, devoted to 65-years of the Geological Faculty of the Lviv National University “Conditions and prospects of the modern geological education and science”, Lviv, 13–15 October 2010, Printing center of LNU, Lviv: 115–117 [in Ukrainian].

KUROVETS I., DRYGANT D., CHEPIL P., CHEPUSENKO P., SHYRA A., 2010 — Geological-petrophysical characteristics of the basinal fine-grained Silurian rocks of the south-western margin of the East-European Platform. *Zb. Nauk. Prats Inst. Geol. Nauk NAS Ukraine,* **3**: 279–285 [in Ukrainian with English abstract].

KUROVETS I., PRYTULKA H., SHYRA A., SHUFLYAK YU., PERYT T.M., 2011 — Petrophysical properties of the Pre-Miocene rocks of the Outer zone of the Ukrainian Carpathian Foredeep. *Ann. Soc. Geol. Pol.*, **81**: 363–375.

NAUMKO I. M., 2006 — Fluid regime of mineral genesis of the rock-ore complexes of the Ukraine (based on inclusions in minerals of typical paragenesis): Thesis for a doctor’s degree in geology. Lviv: 52 pp. [in Ukrainian with English abstract].

NAUMKO I., KUROVETS I., SAKNO V., CHEPUSENKO P., 2009 — Complexing of the mineral-fluidological and petrophysical methods: an unconventional approach to investigation of hydrocarbon reservoir rocks (on example of the Lviv Paleozoic Depression). *Dopovidi Natsionalnoyi akademii nauk Ukrainy*. **1**: 106–113 [in Ukrainian with English abstract].

NESTOR H., EINASTO R., 1977 — Facies-sedimentary model of the Silurian Paleobaltic pericontinental basin. *In*: Facies and fauna of the Baltic Silurian (ed. D. Kaljo). Tallinn: 89–121 [in Russian with English abstract].

POPRAWA P., 2010 — Shale gas hydrocarbon system – North American experience and European potential. *Prz. Geol.*, **58**: 216–225 [in Polish with English summary].